

TEM crack tip investigations of SCC

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I. Abstract

TEM crack tip investigations of SCC

Thesis submitted for D.Phil from the Materials Science Department, Oxford University by Sergio Lozano-Perez in Michaelmas term 2002.

Over the last few years, TEM has become a powerful technique to study cracks and specially crack tips. However, the number of publications including TEM results has not grown as it was expected. The main reason for this might be difficulties in the sample preparation. In this work we present a novel FIB sample preparation technique which has proved to be an ideal tool for preparing cross sectional samples containing crack tips. The morphology of intergranular stress corrosion cracking (IGSCC) has been investigated in Alloy 600 subjected to constant load and slow strain rate tests in simulated primary circuit pressurized water reactor conditions. Cracks were observed to nucleate at high-angle grain boundaries and propagate to depths of a few tens of micrometer along such boundaries, still in the initiation stage.

Electron diffraction, energy dispersive x-ray (EDX) and electron energy loss spectroscopy (EELS) have been used to identify the different corrosion products and precipitates. Elemental mapping was employed to reveal changes in composition in the crack tip area. Major observations at cracks and grain boundaries include: the presence of different oxides in different locations, differences in grain boundary oxides and open crack/free surface oxides. These observations suggest that IGSCC involves oxygen diffusion through a porous oxide region along grain boundaries to the bare metal. This is a novel concept that offers an alternative to previous mechanisms proposed in the literature e.g. H embrittlement, slip-dissolution, etc., for which no supporting evidence has been found.

II. Preface

This thesis is an account of the work carried out by the author in the Department of Materials, University of Oxford, under the supervision of Prof. J.M. Titchmarsh and Dr. M.L. Jenkins.

No part of this thesis has been previously submitted for a degree at this or any other university. The work of other authors has been freely drawn upon and is duly acknowledged in the text. A list of cited references is given at the end of each chapter.

Some of the work described in the thesis has been presented in the following publications and conferences:

Huang, Y. Z., S. Lozano-Perez, et al. (2001). Microstructural characterisation of intergranular stress corrosion cracking of 300 series stainless steels in PWR conditions. EMAG 2001, Dundee, Institute of Physics Publishing, Bristol and Philadelphia: 203 .

Lozano-Perez, S., Y. Z. Huang, et al. (2001). Preparation of TEM specimens containing stress corrosion cracks in austenitic alloys using FIB. EMAG 2001, Dundee, Institute of Physics Publishing, Bristol and Philadelphia: 191.

Langford, R. M., Y. Z. Huang, et al. (2001). "Preparation of site specific transmission electron microscopy plan-view specimens using a focused ion beam system." Journal-of-Vacuum-Science-&-Technology-B **19**, no.3: 755-8.

Huang, Y. Z., S. Lozano Perez, et al. (2002). "Preparation of TEM cross-section specimens of crack tips using focused ion beam milling." Journal of Microscopy **207**: 129-136.

Lozano-Perez, S. and Titchmarsh, J. M. (2002). International symposium on the mechanisms of materials degradation and non-destructive evaluation in LWR. INSS publishing (Japan): S3 (**in press**)

Lozano-Perez, S., J. M. Titchmarsh, et al. (2002). Characterisation of stress corrosion cracks in Alloy. ICEM 15, Durban, South Africa: 787. (**in press**)

Lozano-Perez, S., Y.Z. Huang, et al. (2002). TEM investigations of Intergranular Stress Corrosion Cracking in austenitic alloys in PWR environmental conditions. Microscopy of oxidation 5, Limmerick, Ireland. (**in press**)

This thesis will try to clarify some aspects of Stress Corrosion Cracking (SCC) of Alloy 600 and SS304 (to a lesser extent). In order to achieve this, a new approach to the problem has been used. While traditionally, “macroscopic” techniques have been widely to study SCC, it has not been until the last decade when Transmission Electron Microscopy (TEM) has become a powerful tool to study cracks. In this project, TEM has been used to characterize stress corrosion cracks and, based upon direct observations, to try to clarify the mechanisms operating under Pressurized Water Reactor (PWR) primary side water.

In the first chapter the characteristics of Alloy 600 are presented. Although this alloy is used in many different applications, this project has focused on the nuclear industry, specifically on Steam Generators in PWRs, as will be shown later in the same chapter.

After a brief introduction to the oxidation and corrosion theory and how they apply to Alloy 600, the major problem of SCC is described in Chapter 2. A list of all the proposed models and its implications has been also included.

The experimental and sample preparation techniques (Chapters 3 and 4) have had a great relevance in this project, as they have allowed the characterization of a new range of samples prepared with novel techniques. In Chapter 5, the traditional testing methods to simulate SCC in the lab will be described, with a special interest on those used for this project.

The results obtained during the course of this project will be shown in Chapters 6, 7, 8 and 9. They will basically consist of a characterization of the most relevant samples using all the different techniques described in Chapter 3. A discussion of these results can be found in Chapter 10, together with a proposal for a “new” SCC mechanism.

III. Acknowledgements

This thesis project would have not been possible without the priceless help of many people. I would specially like to thank Prof. John M. Titchmarsh and Dr. Mike L. Jenkins for their help, supervision and guidance through the course of this thesis. It has been an incredible pleasure and honour to be able to work with them during this thesis project and for the next three years. The help from INSS (Japan) and specially Dr. K. Fujii is greatly appreciated. Their interest in this project was really encouraging.

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Chapter 1:

Alloy 600

1.1. Introduction

Nickel is a corrosion resistant metal with a high melting temperature (1453°C) and because of its face-centered cubic (fcc) structure it exhibits good ductility. Nickel can be easily alloyed with other metallic elements to form a wide range of commercial alloys. The major nickel-base alloying systems are nickel-copper, nickel-iron, nickel-chromium, nickel-molybdenum and nickel-iron-chromium.

Nickel-iron-chromium-base alloys comprise a large number of industrially important materials. Most of these alloys, as shown in Fig. 1.1, are in the broad austenitic, γ -phase area of the ternary Ni-Fe-Cr phase diagram and they are known for good high-temperature strength, good workability, and resistance to corrosion and oxidation. Many of these alloys serve equally well in a wide range of both high-temperature and aqueous corrosion environments. The high nickel content provides metallurgical stability and corrosion resistance in reducing environments, while the chromium addition contributes to strength, oxidation resistance, and corrosion resistance in oxidizing environments^{7; 6}.

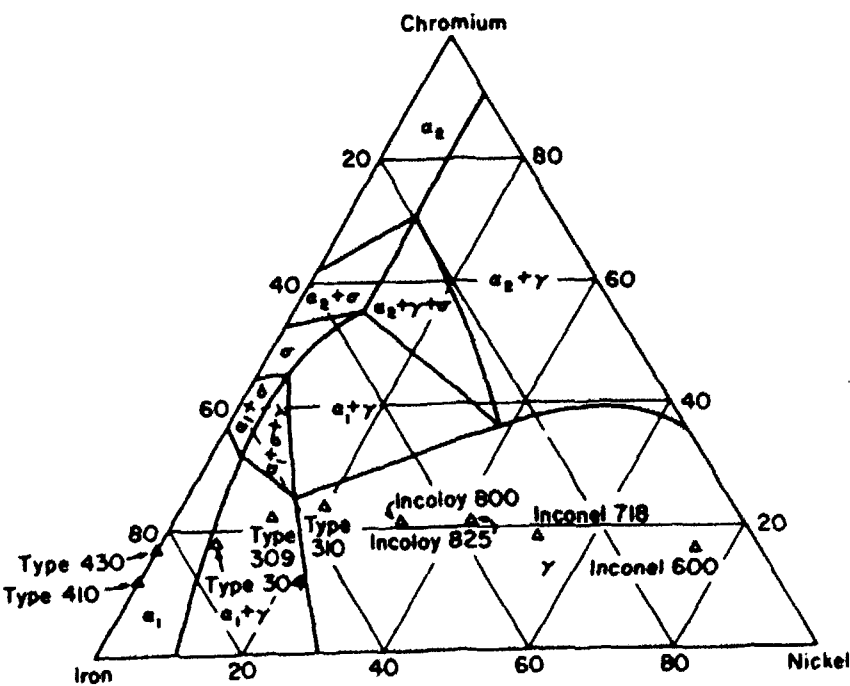


Fig 1.1. Fe-Ni-Cr ternary diagram at 400°C.³⁴

The numbering and identification of a nickel alloy is initially defined by the individual producers and users of the alloy. The Special Metals Corporation sells products under the trademarks ALLOY, INCOLOY, MONEL, among others.

1.1.1 Alloy 600

Alloy 600 (75 wt.% Ni, 15 wt.% Cr, 8 wt.% Fe) was developed in 1931. It is a nickel-base, solid-solution alloy that is easily fabricated and joined. Its main characteristics are a good strength and toughness from very low to very high temperatures and good corrosion and oxidation resistance in many media.

Most of the nickel alloys are based on the nickel-chromium system, with alloy 600 being the prototype, as is described in Fig. 1.2.

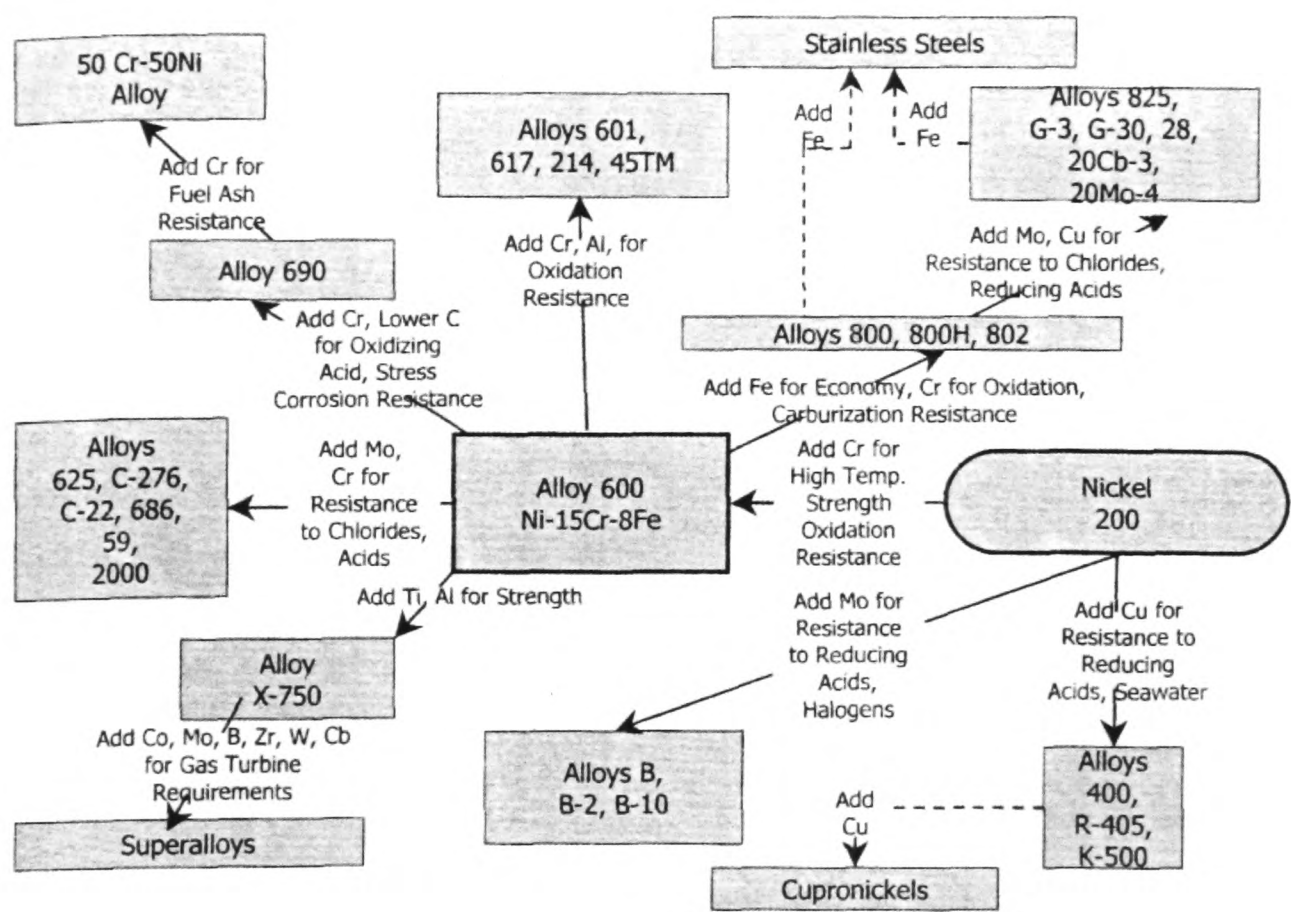


Fig 1.2. Compositional and property linkages for nickel alloys ¹³

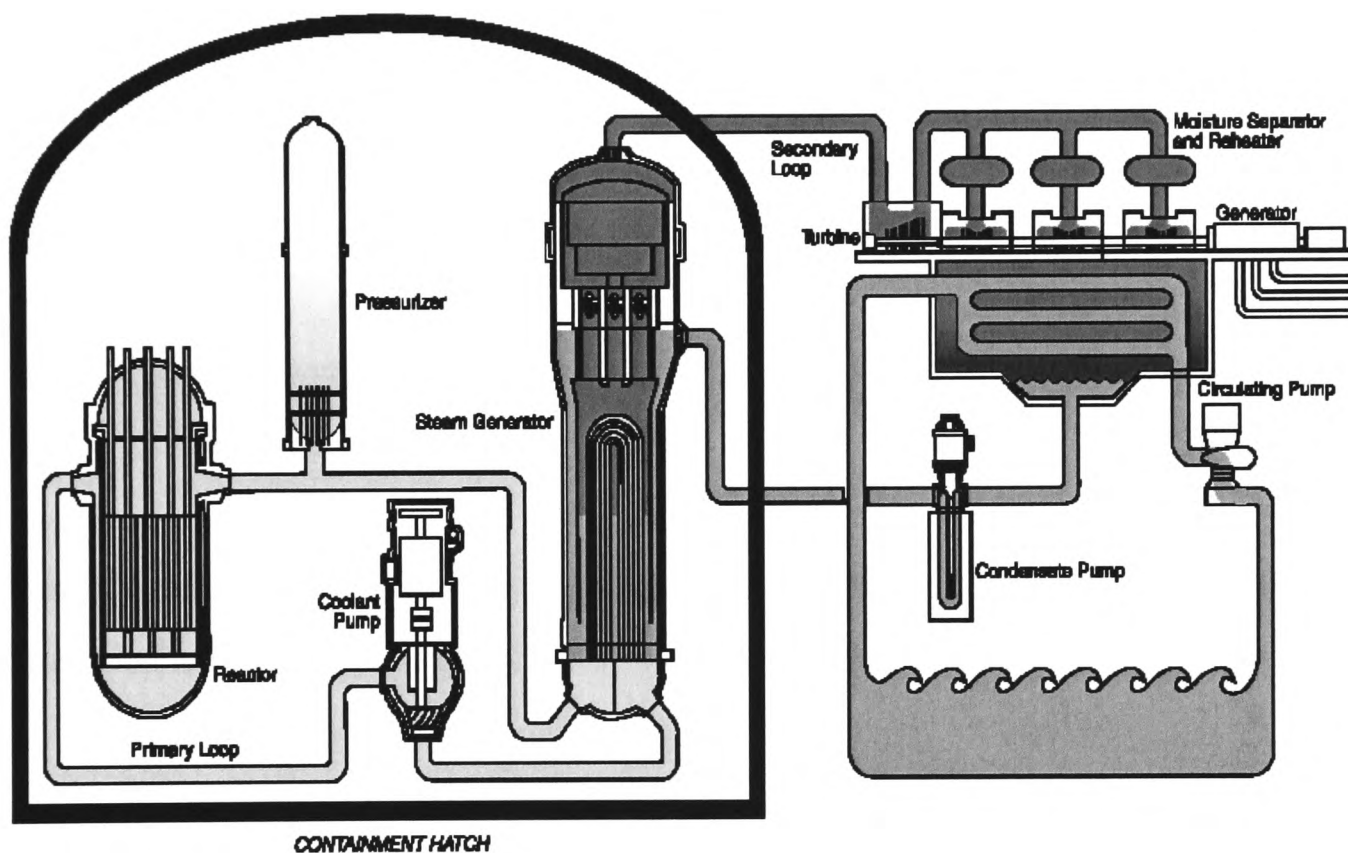
Alloy 600 is a commonly used material in the nuclear energy industry, especially in pressurized water reactors (PWRs). It is found mainly in the steam generator tubes or in control rod drive mechanisms (CRDMs).

1.2. Pressurized Water Reactors (PWRs)

At present the water-cooled reactors are mainly designated as light water reactor (LWRs), representing more than 80% worldwide of the operating reactors

(about 430 in 32 countries). The LWRs are built as two different types: the pressurized water reactor (PWR) and the boiling water reactor (BWR). The PWR design is used today for most nuclear power plants.

The basic principles of operation are similar for all PWRs but the design details of the various manufacturers differ. The main features of the heat transfer system are shown in Fig. 1.3.



Source: Westinghouse Corporation.

Fig. 1.3: Schematic diagram of a PWR.

The heat from the core in the reactor pressure vessel is transferred to the primary water loop. The water is circulated by coolant pumps under high pressure (158 bar). In the reactor core it is heated to a temperature in the range 292°C to 326°C. In the steam generator the heat is transferred to the secondary water loop, where steam of 68 bar and 285°C is generated. The steam drives the turbine and the generator. The steam exhausted by the turbine is precipitated in the condensate pump. Then the condensed water is pumped back into the steam generator. Waste heat delivered to the condenser is discharged into the environment by different routes (cooling tower, river, sea water)¹⁶.

1.2.1 Water chemistry

The water in LWRs has to fulfill the functional requirements in the heat transfer systems and has to operate as the moderator in the core region. The materials used in the system have to be compatible with the water chemistry, especially the structural materials. To avoid compatibility problems, the water in the primary system of PWRs is optimized to:

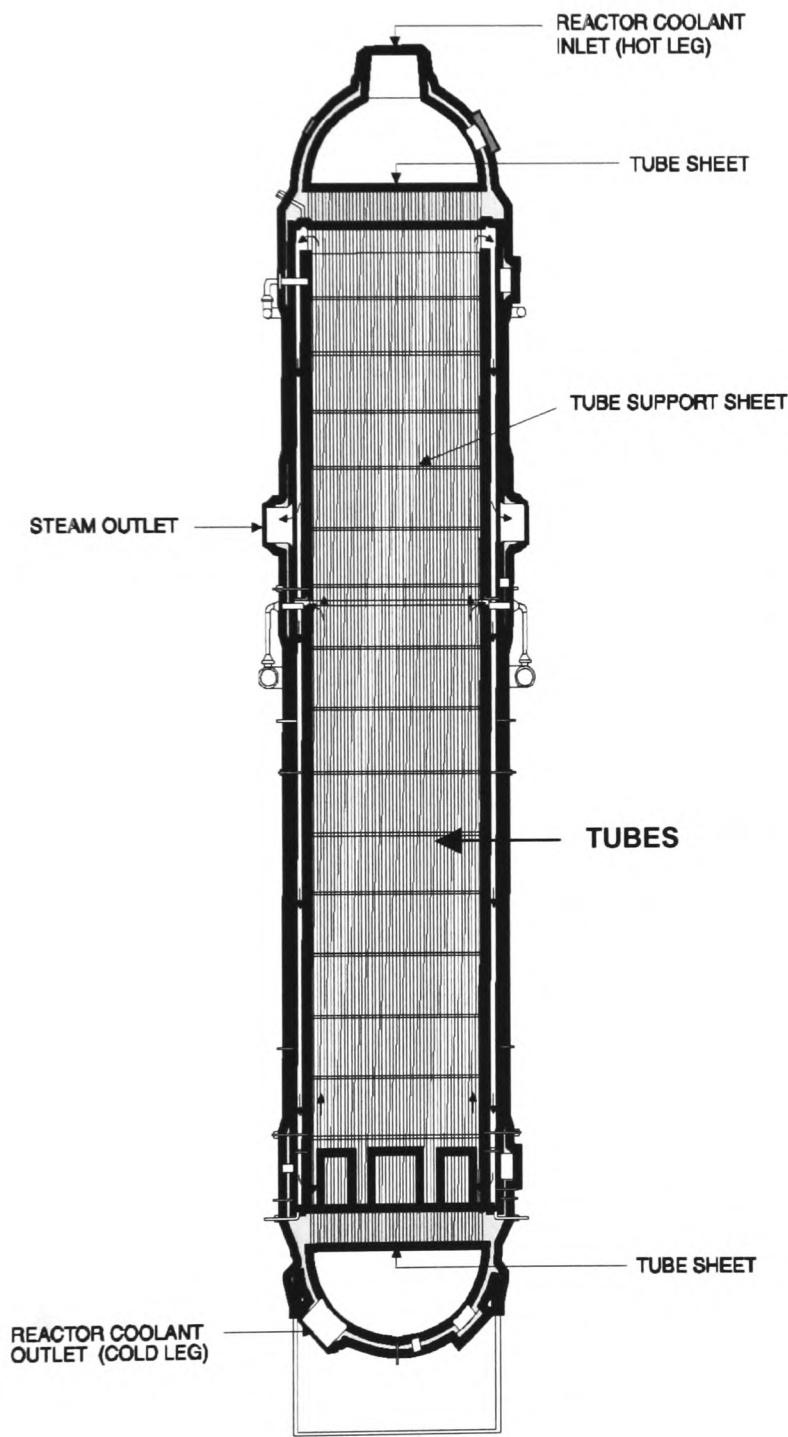
- Minimize metal release rates of materials
- Suppress localized or selective corrosion, including stress corrosion cracking and intergranular attack
- Minimize the contamination of the primary system (as a result of transport and deposition of corrosion products)
- Prevent as far as possible the deposition of corrosion products on heat transfer surfaces, particularly on fuel pins

In PWRs, the primary side water is basically deaerated pure water with very low concentrations of oxygen (5ppb). The pH of the coolant is adjusted to 6.5 ± 0.2 at room temperature by the addition of lithium, potassium or ammonium hydroxide. The quantity of Li hydroxide is adjusted to the boric acid quantity. Boric acid (≤ 200 mg/kg) is used as a neutron absorber for reactivity control during fuel burnup. Reduced metal loss is observed with increasing pH. This is explained by a reduced solubility of iron and nickel oxides with increasing pH.

Hydrogen is necessary for the control of the oxygen content. Oxygen is produced by radiolytic decomposition of the primary coolant by the reaction $2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$. Some other elements are specified as impurities, and the maximum size of entrained particles is also specified to prevent deposition on fuel rods^{18; 44}.

1.2.2 Alloy 600 in PWRs

Alloy 600 can be mainly found in the U-type tubes of the steam generators or in penetration nozzles in control rod drive mechanisms.



Source: Babcock & Wilcox Company.

1.2.2.1 Steam generators

PWR's have two, three, or four steam generators and hence are called two-loop, three-loop, or four-loop units, respectively. Generally, the plants with larger capacities have more loops in order to accommodate a larger total heat transfer surface area while limiting the size of each steam generator. The capacity, shape, and features of a steam generator depend mostly on the manufacturer. In a once-through design, for instance, the primary-side water enters the steam generator at the top, flows through the generator in unbent tubes, and exits at the bottom (Fig. 1.4).

Fig. 1.4: Sketch of a steam generator section (once through design).

In the U-bend design, the primary-side water enters at the bottom of the steam generator, flows through tubes that bend in an inverted “U” approximately in the middle of the steam generator, and returns to exit at the bottom of the steam generator.

The number of tubes in the steam generator varies by manufacturer, unit capacity, and type of design. Westinghouse units contain about 3,200 to 5,600 tubes per steam generator, Combustion Engineering uses 5,000 to 11,000 tubes per steam generator, and Babcock & Wilcox uses 15,500 tubes in each of its steam generators. E.g., a Siemens 1300 MW PWR steam generator has a heat transfer surface of the tubes of 5400 m².

The Babcock & Wilcox steam generators require more tubes than the Westinghouse or Combustion Engineering units because the once-through design with straight tubing provides less surface area per tube for a given tube shell length than does the U-bend design. The diameter of each tube ranges from 19 to 25 millimeters. The cooling tubes are sealed in a base plate to form a loop which carries the primary water. Carbon steel tube sheets or tube plates are used to hold these several thousand tubes as a rigid assembly. Water from the reactor pressure vessel enters the steam generator through the “hot leg” pipe, circulates under pressure through the tubes, and exits through the “cold leg” pipe. A typical steam generator weighs 250 to 400 metric tons and exceeds 15 meters in length and 6 meters in diameter^{18; 44}.

1.2.2.2 Control Rod Drive Mechanisms

Control rod drive mechanisms (CRDMs) are used to position the movable neutron-absorbing control rods (rod cluster control assemblies) within the core, thereby controlling the reactivity.

The CRDM is an electromechanical device which operates on the magnetic jack principle. In an emergency shutdown, the control rods are inserted in to the core by gravity when the power is switched off. This mechanism is highly reliable and does not require any maintenance or inspection during its lifetime

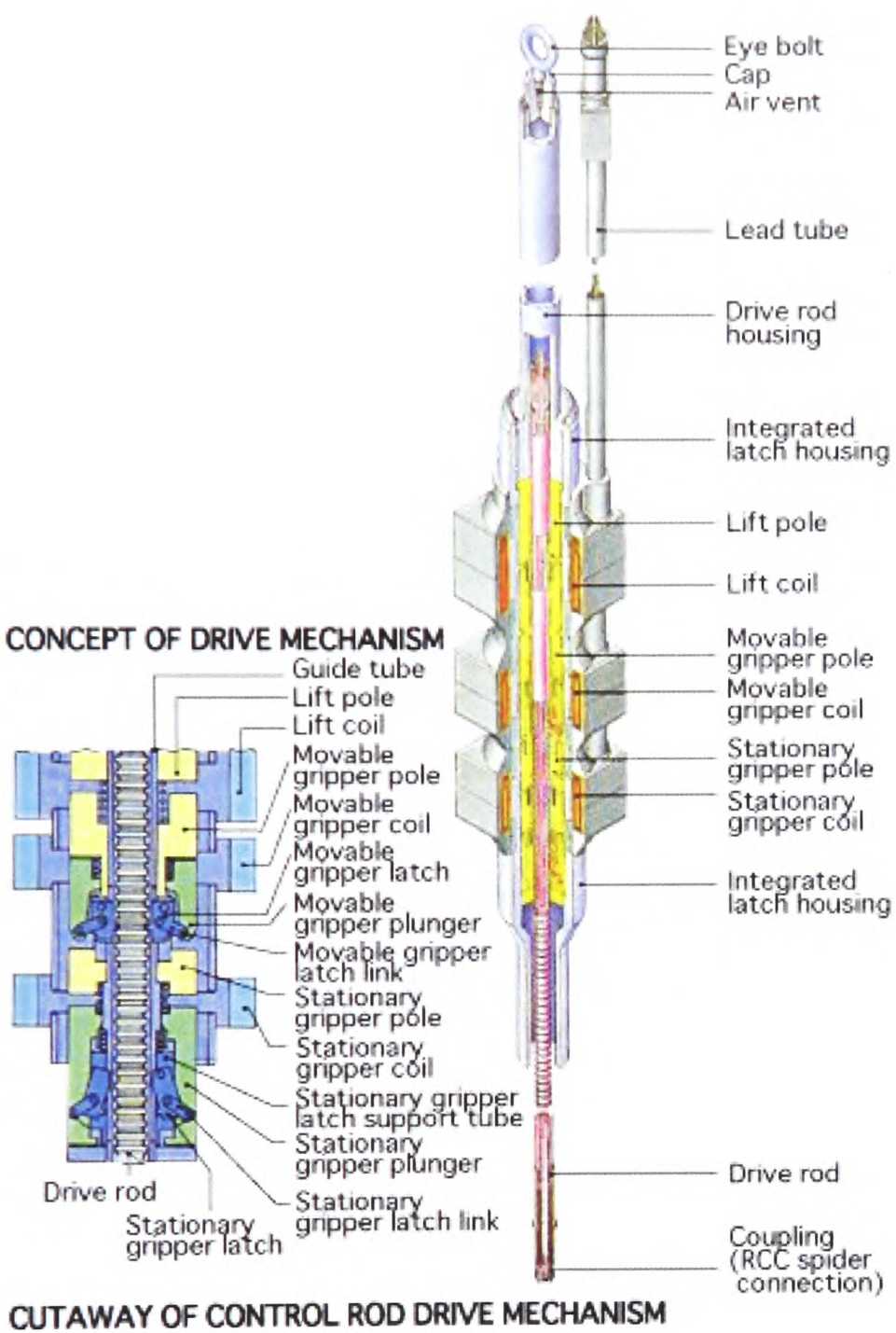


Fig. 1.5: Control rod drive mechanism (Courtesy of Mitsubishi Heavy Industries).

The nozzles are in a critical position. Control rod drive shafts pass through penetration nozzles that sit at the top of a reactor vessel head. There can be anywhere from 40 to 100 nozzles per reactor, depending upon its size and design. These nozzles are fabricated from Alloy 600 material. One function of the nozzles is to maintain the reactor coolant system pressure boundary. Cracking of the CRDM nozzles represents a degradation of the primary reactor coolant system boundary, and hence, is therefore a safety issue of great importance³¹.

1.3. Types of failure and degradation issues

The water environment will be responsible of most of the corrosion phenomena which have to be considered. The main observations are summarized in the following list:

Intergranular attack (IGA)

Intergranular stress corrosion cracking (IGSCC)

Strain-induced corrosion cracking

Stress corrosion cracking (SCC)

Transgranular stress corrosion cracking (TGSCC)

Uniform corrosion

Some of them will be commented on in detail later.

The experience accumulated in materials performance and environment effects now amounts to more than 5500 reactor years. The observed problems have been solved (or attempts made to solve them) by, e.g., optimizing the environmental conditions (chemistry, control of electrochemical potential), improving component design, reducing stresses and fabricating better materials.

A survey of types of material degradation observed in PWR plants is given in Table 1.1.

Components			Degradation mechanisms	Inspection methods
Internal structures; and valves	RPV screws	Guide tube pins	Corrosion (IASCC)	UT
		High-strength screws	HISCC(?)	UT
Pressure vessels and primary circuits		Valves and pipes	Corrosion	Visual radiography
			Fatigue	
		Vessels	Irradiation embrittlement	UT
		Elbows (cast material)	Aging	Radiography
Exchangers				Surveillance program
				Radiography
		SG tubes (Alloy 600)	Corrosion	Hardness
			Wear	EC
			Fatigue	UT
		Condenser tubes (Cu alloys)	Corrosion	EC
Balance of plant			Abrasion	
			Erosion	
		Secondary circuits (plain ferritics)	Wear	
			Fatigue	
		Turbine blades and disks (high strength materials)	Corrosion-erosion	UT
			Corrosion	UT
			Fatigue	MPT

Table 1.1: Types of material degradation presently observed in PWR plant, where EC: Eddy current testing, MPT: magnetic particle testing and UT: ultrasonic testing

1.3.1 Steam generator tubing degradation

The issues associated with steam generator degradation have had a significant impact on nuclear power plant operation. As a result, utilities with degrading steam generators must make a tradeoff between either continued operation with high operation and maintenance costs, high worker radiation exposures, increased risks of forced outage from tube ruptures or replacement.

Currently, the most common form of failure is intergranular attack/stress corrosion cracking, although it is not the only one. In table 1.2, a brief description of the other problems is described:

Type of Degradation	Definition
Denting	The physical deformation of the Alloy 600 tubes as they pass through the support plate. Caused by a buildup of corrosive material in the space between the tube and the plate.

Fatigue cracking	Caused by tube vibration.
Fretting	The wearing of tubes in their supports due to flow induced vibration.
Intergranular attack/stress-corrosion cracking	Caused when tube material is attacked by chemical impurities from the (outside diameter) secondary-loop water. It occurs primarily within tube sheet crevices and other areas where impurities concentrate.
Pitting	The result of local breakdown in the protective film on the tube. Active corrosion occurs at the site of breakdown.
Stress-corrosion cracking (inside diameter)	Cracking of steam generator tubes occurring at the tangent point and apex of U-bend tubes, and in tube dents. It occurs when Alloy 600 tubing is exposed to primary-loop water.
Tube wear	A thinning of tubes caused by contact with support structures either as the tubes vibrate or as feedwater entering the vessel impinges on the tube bundle at that location.
Wastage	A general corrosion caused by chemical attack from acid phosphate residues in areas of low water flow, such as crevices.

Table 1.2: Steam Generator Degradation Definition

Intergranular attack/stress-corrosion cracking accounts for 60 to 80% of all tube defects requiring tube plugging. Fretting and pitting combine to account for another 15 to 20% of all tube defects ⁴⁴.

Attention will be focused on the primary water stress corrosion cracking, as this was the condition simulated and studied in the present experiments. The cracks are normally situated in the U-bends of the tubes, in the tube/tube-sheet transition zone or at dented tube support plate intersections. The cracks are intergranular in the axial direction, but circumferential cracks on dented tubes have also been observed ^{30; 21; 17}.

Initially, the problems were thought to be isolated incidents resulting mainly from defects in manufacturing, poor operation, poor water chemistry, etc. However, these failures were found to follow similar patterns, and common factors and common failure models were suggested. The physical factors most often responsible for these failures and the typical corrective actions are:

- **Tube alloys**—The most common factor in tube defects has been the tube alloy most widely used in original steam generators throughout the world, Alloy 600 mill-annealed, a thin nickel alloy material that has proven susceptible to many forms of cracking, pitting, denting, and other types of degradation. Replacement steam generators manufactured by Westinghouse, Babcock & Wilcox, Framatome and Mitsubishi now use thermally treated Alloy 690. The Alloy 690 thermally treated tube has proven to be 9 to 10 times more resistant to secondary-loop cracking than Alloy 600 mill-annealed^{10; 11; 5}.
- **Tube sheet design and alloys**—The tube bundles connect to a tube sheet on each end of the tubes. The tube sheet separates the primary-loop water from the secondary-loop water. Both the tube sheet connection and the exterior of the tubes at the connection tend to accumulate sludge, crack from vibration, and show excessive fatigue cracking. Replacement tubes in more modern steam generators use different tube sheet designs, tube sheet materials, and tube/tube sheet attachments to reduce these problems.
- **Tube support plate designs and alloys**—The tube bundles are supported above the tube sheet by tube support plates and antivibration bars. Tube support connections tend to accumulate corrosive sludge, crack, and fret. Improved designs and materials that permit better venting of steam around the tube supports and minimize formation of corrosive sludge in crevices have improved steam generator performance.
- **Small-radius U-bends**—In “U-bend” steam generators, the tubes nearest the center of the tube bundle have the smallest radius U-bends. During manufacture and operation, small-radius U-bends are subject to greater stress than large-radius U-bends or the unbent portion of the tubes. Recent designs enlarge the small-radius U-bends and rely on improved or additional antivibration bars.

It was also found that if Alloy 600 with reduced carbon content ($C \leq 0.03\%$) was thermally treated (TT) at $715 (\pm 15)^\circ\text{C}$ for a minimum of 12 h, the tube fabrication residual stress was relaxed and a more corrosion-resistant structure was provided⁸. A plot of minimum failure times as a function of temperature in an

analysis of laboratory-type experiments, shows a lower curve for the most SCC susceptible mill annealed (MA) material (Fig. 1.6). The slope of this curve determines the activation energy and is around $40 \text{ kcal mol}^{-1} \text{ K}^{-1}$, a value that is close to the activation energy of bulk diffusion of C in Ni-base alloys³⁵.

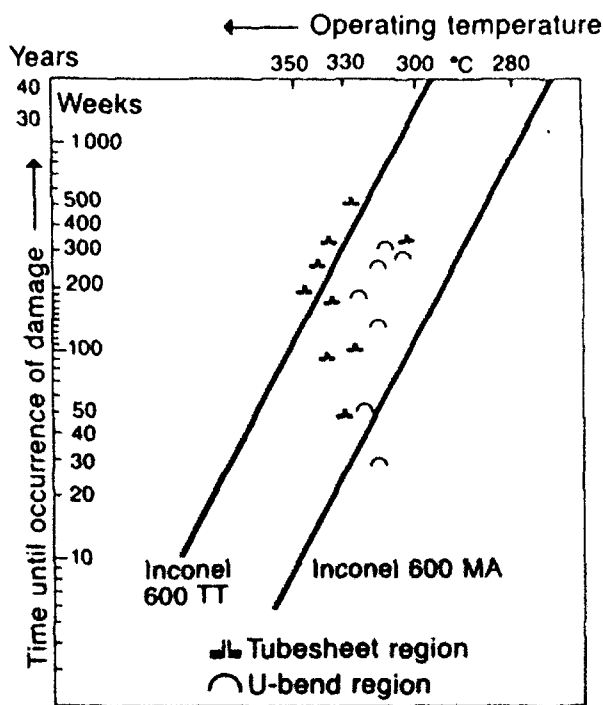


Fig. 1.6: Time until occurrence of primary water stress corrosion cracking versus temperature for Alloy 600³⁵

The plot also shows that thermal treatment improves the SCC performance over that of mill-annealed material by a factor of 2.5. However, the heat treatment does not make the material completely immune to SCC.

Despite all the effort in recent decades, the sensitivity of Alloy 600 to Primary Water SCC (PWSCC) is not fully understood. For example, increasing the Cr content of the alloy from about 16 wt. % to 19 wt. % improves the resistance to PWSCC, although such experimental alloys had a microstructure similar to sensitive materials. This leads to the conclusion that electrochemical properties of the surface (passive films) could be more important than the microstructure, for example, sensitization and presence of carbides¹⁶.

1.4. Alloy 600 Microstructure

The microstructure of Alloy 600 is austenitic with some chromium carbide present. In some of the samples studied TiN was detected, as well as SiO and other inclusions. The main variables relating to microstructure are the grain size, the carbide distribution and the grain boundary character. All these variables are basically dependent on the previous heat treatments experienced by the sample.

1.4.1 Heat treatments

Nickel and the nickel alloys are, in some ways, easier to heat treat than many of the iron-base alloys that depend on carbon-related microstructural changes to achieve desired properties. Nickel is an austenite former, and in the nickel and high-nickel family of alloys, no allotropic phase transformations occur—the alloys are austenitic from the melting temperature down to absolute zero. While some precipitates may form, such as carbides and the χ' hardening phase, these do not change the basic austenitic-type structure of the matrix.

Nickel is found in nature as nickel sulphide and nickel oxide ores, showing that it has a natural tendency to combine with sulphur and/or oxygen. The solubility for carbon in the solid state is relatively low and nickel does not readily carburize. For this reason the nickel-chromium alloys, most notably Alloy 600, are used as fixtures in carburizing furnaces. Almost all heat treatment methods used with nickel and the nickel alloys are employed either to soften them, such as annealing, or to increase their strength, such as age hardening.

1.4.1.1 Types of Heat Treatment

Nickel and the nickel alloys may be subjected to one or more of six principal types of heat treatment, depending on chemical composition, fabrication requirements, and intended service. These methods include: annealing, solution annealing, stress relieving, stress equalizing, solution treating and age hardening.

As we will see later, all the Alloy 600 samples used for this research have been annealed in one or other form. We will focus our attention in the different annealing processes.

1.4.1.1.1 Annealing

The annealing of nickel and nickel alloys consists of heating the metal at a predetermined temperature for a definite time and then slowly or rapidly cooling it to produce a change in mechanical properties, usually a complete softening, as the result of recrystallization. Nickel and nickel alloys that have been hardened by cold-working operations, such as rolling, deep drawing, spinning, or severe bending, require softening before cold working can be continued. The thermal treatment that does this is known as annealing, or soft annealing.

The differences in chemical composition among nickel and nickel alloys necessitate modifications in annealing temperatures and furnace atmospheres. The precipitation-hardening alloys must be cooled rapidly after annealing if maximum softness is desired ⁶.

Today, none of the steam generator manufacturers use tubing given the same thermal treatment. E.g., Combustion Engineering uses mill-annealed tubing, while Westinghouse subjects the tubing to an overaging thermal treatment, and Babcock & Wilcox operates its steam generators with stress-relieved tubing.

Three important processes occur during aging of Alloy 600 at temperatures between 500 and 800 °C. Chromium carbides of the form $M_{23}C_6$ or M_7C_3 precipitate at grain boundaries and are accompanied by chromium depletion in the surrounding matrix. In addition to carbide precipitation and chromium depletion, trace elements such as P, S, B, Ti and others, may segregate to the grain boundary ⁴⁷.

-Mill Annealing temperature

The solubility of carbon in alloy 600 as a function of temperature has been assessed by metallographic examination of variously heat treated then rapidly quenched specimens ³², producing data as shown in figure 1.7.

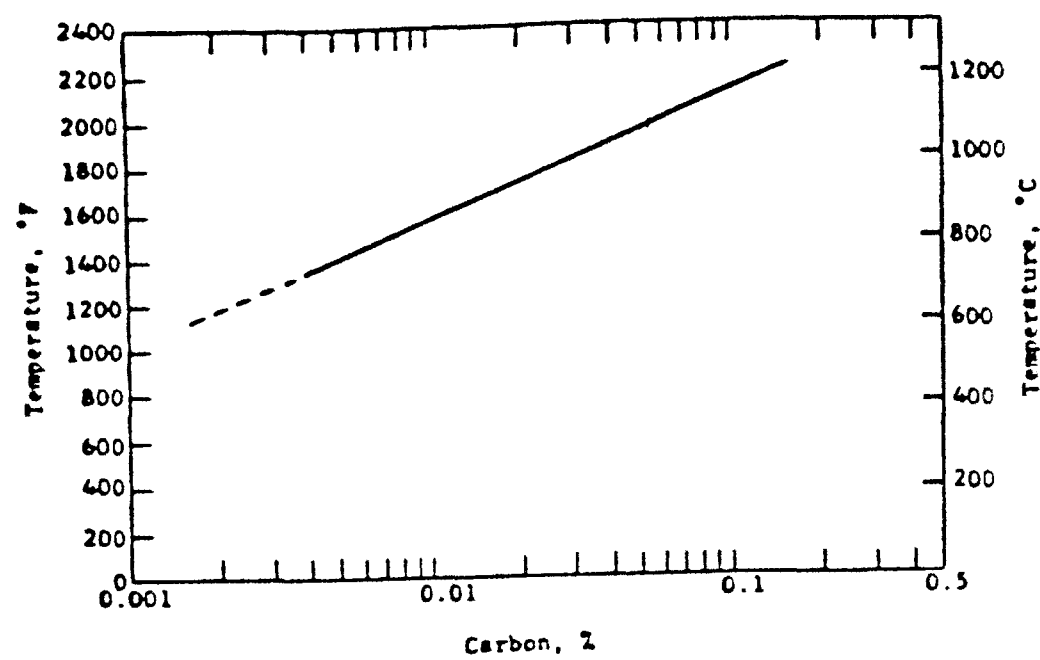


Fig. 1.7: Solubility of carbon in Alloy 600 ⁴⁷.

This shows that for an alloy with 0.15%C , a temperature of ~1200°C would be required to dissolve all of the carbide. Mill annealing temperatures are usually of the order of 1000°C so that alloys with less than 0.03%C will have all the carbon taken into solution at this temperature and if the subsequent quenching is rapid enough, no precipitation will occur during cooling. The solubility of carbon in alloy 600 is only about 0.001% at the lower temperature and of the order of 0.01% at ~900°C , so there is an adequate driving force for precipitation during subsequent thermal treatment. If a low mill annealing temperature is used, some carbide may remain undissolved and there will be less carbon in solution for subsequent precipitation. A low mill annealing temperature is also likely to result in a finer grain size than a high mill annealing temperature, and a correspondingly higher yield strength ⁴⁷.

Sui and Titchmarsh ³⁷ performed reversed U-bend tests on Alloy 600 and Alloy 690 in a 380°C hydrogen/steam environment. They found that Alloy 600 was

susceptible to intergranular cracking when mill annealed at 925°C. Mill annealed at 965°C Alloy 690 also exhibited intergranular cracking but with a longer incubation time. All the samples that cracked had little grain boundary decoration, whereas the ones that did not crack were heavily decorated. No correlation between cracking and chromium depletion was found.

In 1997, a semi-empirical model was reported by Mayo²⁹ to predict the minimum Cr concentration at grain boundaries as a function of thermal treatment time and temperature. Based upon computed Temperature-Time-Composition (TTC) diagrams, two new heat treatment ranges were proposed at 550-600°C/1 h and 725-750°C/8-15 h that should avoid the high IGSCC/IGA sensitivity region. The confirmation of these proposals could not be found in the literature.

1.4.2 Carbide precipitation and sensitisation

Chromium carbides precipitate initially at grain boundaries. The diffusivity of carbon, which diffuses as an interstitial, is much higher than that of chromium which must diffuse substitutionally. This difference in diffusivities permits the formation of chromium carbides which then produces a chromium depleted region surrounding the grain boundary. The extent of depletion is dependent upon such variables as temperature, time, and carbon content. The effects of these variables on the precipitation reaction can be illustrated in a time-temperature-transformation (TTT) diagram as shown in the schematic in Fig. 1.8¹⁸.

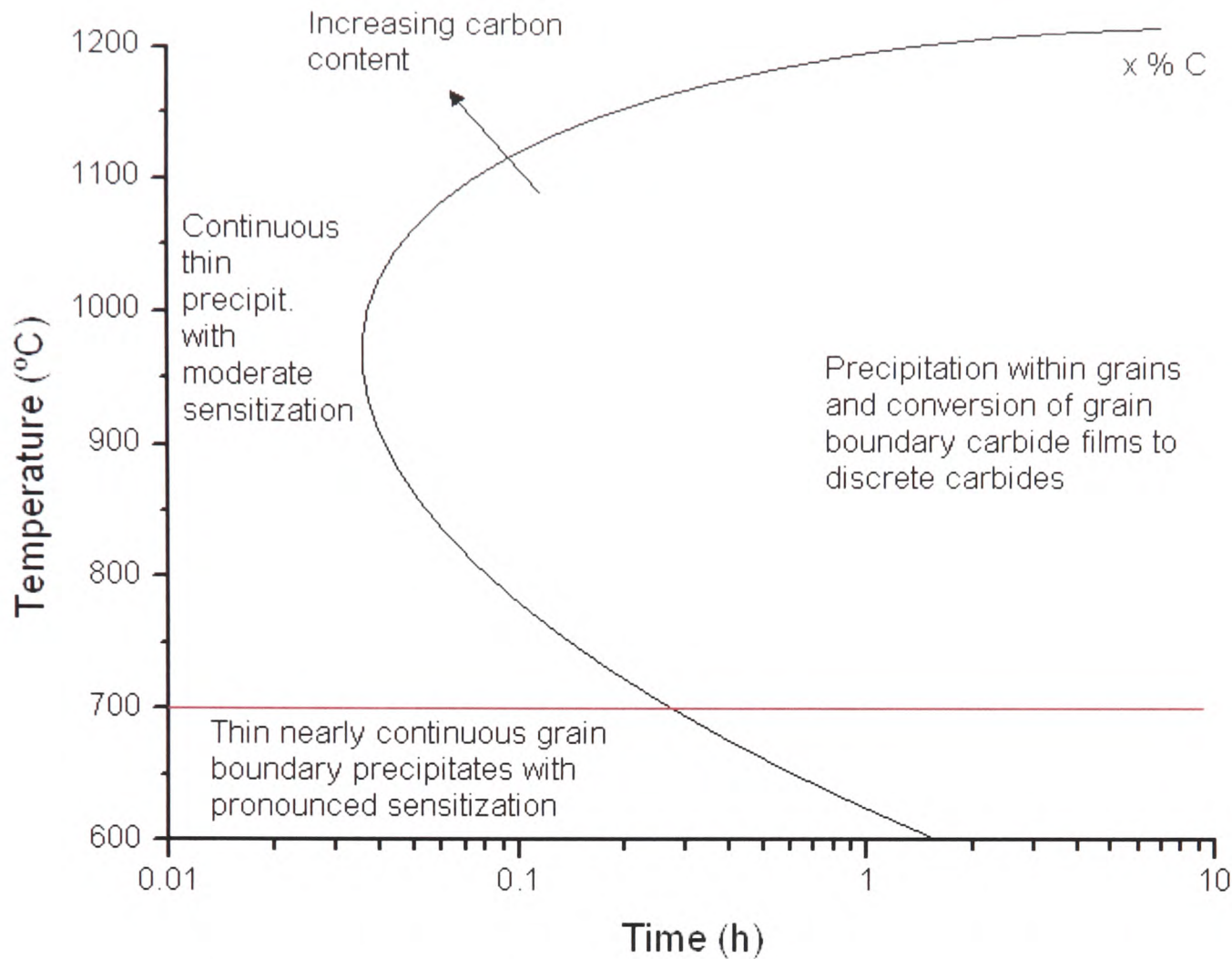


Fig. 1.8: Schematic of a carbide precipitation (TTT) diagram for Alloy 600

Carbide distributions can vary from predominately intergranular to predominately intra-granular and from high to low densities. These variations result from heat-to-heat differences in bulk composition (primarily carbon content) and thermochemical history during processing and fabrication. The final processing temperature has a critical effect on the amount of carbon that is taken back into solution and the amount of carbide precipitation that occurs during cooling. A high temperature anneal ($>1000^{\circ}\text{C}$) tends to put more carbon into solution, produces a higher density of intergranular precipitates and be more resistant to SCC. However, better understanding of the role of bulk composition, prior thermomechanical history and cooling rate is required to control microstructural development.

The ability to produce a good microstructure depends on the carbon remaining in the solution available to precipitate. A low temperature final anneal and a slow cooling rate may result in a high density of intragranular precipitates and an insufficient supply of carbon for subsequent intergranular precipitation. Maximum

improvement in SCC resistance was correlated with the presence of a semi-continuous array of carbides ¹².

The precipitation of chromium-rich carbides at grain boundaries in Alloy 600 also promotes the formation of a chromium-depleted region under certain time-temperature conditions. Because of the lower solubility of carbon and faster diffusion of chromium, this depletion occurs much more rapidly (i.e., at shorter times at temperatures between 500 and 750°C and at faster cooling rates from higher temperatures) in Alloy 600 than in unstabilized austenitic stainless steels.

Even in mill anneal microstructures showing few intergranular carbides, some local chromium depletion can be present. However, this depletion is often not continuous along the grain boundaries, being most significant adjacent to the carbides. The relatively high diffusivity of chromium in Alloy 600 enables the chromium content to be replenished at the boundaries during heat treatments at temperatures greater than 650°C. As a result, thermal treatment can produce a "healed" microstructure (i.e., semi-continuous carbide precipitation without chromium depletion). The exact time-temperature dependence of chromium depletion and healing will again be dependent on the material bulk composition and prior thermo-mechanical history ^{3;2}.

Although chromium depletion can be present in mill anneal tubing and may be increased during long exposures at steam generator operating temperatures, it is not a controlling factor in the SCC of Alloy 600 in deaerated water or caustic environments ¹². Chromium depletion does appear to accelerate cracking in oxygenated tests, but the opposite is more consistent with the data for deaerated water tests. Since it is difficult to produce significant chromium depletion without semicontinuous carbide precipitation, the effect of chromium depletion on SCC resistance has not been isolated. If chromium depletion is detrimental, its effect appears to be minor compared to the beneficial effect of the presence of intergranular carbides ¹².

In 1980, Airey ¹ proved that it was possible to introduce a wide range of grain boundary microstructures by a thermal treatment. He classified the grain boundary precipitates as fine-discrete, semi-continuous, coarse semi-continuous and large-

discrete. He also mentioned the presence of a chromium-depleted layer and grain boundary phosphorous segregation for some thermal treatments. According to him, the maximum SCC caustic resistance is associated with the presence of a semi-continuous grain boundary precipitate, with or without an associated Cr depleted layer. In 1981, he added that the critical chromium content below which there is susceptibility to cracking in polythionic acid is 9.8-11.7 wt. %, using Huey, reactivation polarization and eddy current test techniques to measure Cr levels³.

Was⁴⁷ used STEM to measure shape and depth of Cr depleted zones and concluded that it was a function of the thermal treatment time and Cr level. The sensitised area reached a maximum after 10 h at 700°C. Preferential corrosion at grain boundaries was found to happen when the Cr level fell below 9 wt.%. This value is also the self-healing level of Cr for Alloy 600.

Bruemmer¹² considered the grain boundary carbides as low energy dislocation sources, producing more homogenous plastic deformation and modifying the local strain rate. The presence of a semi-continuous array of carbides might continuously blunt the crack tip and reduce SCC crack propagation. He could not find any evidence that proved that impurity segregation promotes IGSCC of Alloy 600 in high temperature primary water. A model was proposed assuming that the primary component affecting cracking is microdeformation which characteristics result from the intergranular carbide precipitate distribution.

In 1988, Kai and Tsai^{24; 25} found that the constant load test in sodium thiosulfate was sensitive to the depleted depth of Cr in the grain boundary, and insensitive to the width or shape of the depletion profile. The critical Cr concentration was found to be 8 wt. %.

In 1991, Alloy 690 was proven to be not as ideal as it was supposed. While its chemical properties are much improved, its mechanical properties have always been inferior to Alloy 600. The accident due to an Alloy 690 steam generator tube rupture at Mihama-2 of Kansai Electric Power in February 1991 just confirmed this, and was found to be related to fatigue failure. Besides, the low thermal conductivity of Alloy 690 requires an increment in the total length of tubes of about 10%.

Yamanaka ⁴⁸, tried to find out why the IGA (IGC+IGSCC) resistance of Alloy 600 is improved by the precipitation of chromium carbides at the grain boundaries. The samples were previously annealed at 950°C for 20 min and the U-bend tested in a caustic environment. He found that the main chemical contribution factor of grain boundary chromium carbides to the IGA resistance was related to the cleansing of the grain boundary due to the incorporation of grain boundary segregated elements such as C, B, P into the Cr carbides. However, he found that the insolubility of the Cr carbide, the formation of a Cr-depleted zone and grain boundary strengthening due to alternative coherent carbide precipitation did not contribute to the IGA resistance.

In 1995, Hertzberg and Was ²³ showed that after CERTs and Constant Load tests (CLTs) in 360°C primary water conditions, controlled purity Ni-16Cr-9Fe-xC alloys containing carbon in solid solution exhibit increased strength and ductility compared to carbon-free alloys. They also noted that alloys containing grain boundary carbides experienced reductions in both strength and ductility relative to those maintaining all carbon in solution, while maintaining a high degree of resistance to IG cracking on the fracture surface.

Hertzberg et al. ²³ used CERT tests, in 360°C primary water, to determine the effect of carbon distribution on IGSCC. Again, the presence of grain boundary carbides was found to increase the IGSCC resistance of Alloy 600 and similar alloys with different carbon concentrations. As a new observation, the grain boundary carbide density was found to play a more important role than the amount of carbon in solution in the cracking resistance. Besides, the importance of the beneficial effect of grain boundary carbides was found to be a function of hydrogen overpressure, so the effect of hydrogen on the operative cracking mechanism has to be determined by the carbon distribution.

Stiller ³⁶ did an extensive study on how different parameters affected IGSCC resistance. She analyzed MA and TT variants of Alloy 600 and 690 with different C and B concentrations after performing U-bend tests in high-purity water at 365°C. She found that both carbon and boron segregate to grain boundaries in Alloy 600 and 690 and that most of the intergranular precipitates were Cr-rich carbides with small B additions (if B was present in the alloy). According to her study, the most important

factor improving the resistance to IGSCC is a high Cr content in the material. In Alloy 600, a high concentration of C in solution has beneficial effects on corrosion properties. These effects were explained mechanistically as an improvement of creep resistance. Also denser intergranular carbide precipitates, seem to make the alloy stronger than dissolved carbon. She concluded that internal oxidation might be responsible for IGSCC of Alloy 600.

Symmons et al.³⁹ studied the SCC response of Alloy 600 as a function of microstructure in a hydrogenated doped-steam environment. They controlled the initial microstructure by annealing the samples or applying cold-work, finding that heat treated materials were more resistant to SCC than the others. Through cold work, the yield strength is increased, and a decrease in the SCC resistance was observed. The presence of dendritic M_7C_3 carbides and the reduction of dislocations in the heat treated structures were related to an improvement in the SCC resistance. Cold-work was found to enhance SCC in the doped steam tests, probably by the creation of grain boundary voids (no evidence shown).

In 1997, Fish et al.²⁰ performed some TEM study of the SCC cracks in Alloy 600. Primary water conditions were simulated using Constant Load Precracked Compact Tension tests and Constant Displacement tests, conducted at 338°C and 360°C. The oxides in the crack tip were analyzed by Analytical Electron Microscopy (AEM). With this new detailed information, some mechanisms could be contrasted. They found that SCC cracks normally follow grain boundaries free of carbides and, when an IG carbide was reached, the crack was not blunted. As a consequence, no beneficial mechanical role of carbides was found. However, IG carbides may improve passivity at the crack tip by reducing the amount of carbon segregated along grain boundaries. No evidence of microvoids was found, as previously suggested by Shewmon³³ and no increase in oxygen concentration ahead of the crack tip was detected (using EDX spectroscopy with a probe size of 5nm).

Thomas and Bruemmer⁴⁰ tested some U-bend Alloy 600 (0.3% C, MA 927°C) samples in 330°C PWR primary water and characterized them using AEM. They found locally oxidized structures ahead of the SCC crack tips and deep attacks along grain boundaries that intersected the crack. In this attack, selective oxidation of Cr

was observed, together with the presence of nanopores within the grain boundary plane and Cr_2O_3 formation.

1.4.3 Grain boundary segregation

Considerable data exist in the literature documenting the segregation of impurities to surfaces and grain boundaries of Alloy 600 during thermal treating^{12; 45; 15; 46}. The first suggestion that impurities act as hydrogen recombination poison was made by Latanision and Oppenhauser^{27; 28}. The exact mechanism by which these impurities aid hydrogen embrittlement is not known yet.

Was⁴⁵ and Caceras¹⁴, among others, have shown that phosphorous and silicon can enhance intergranular corrosion in Alloy 600 and austenitic stainless steels. Although phosphorous is the primary impurity segregant to grain boundaries in Alloy 600, the thermal treatments used in the samples investigated in this project prevented any segregation to grain boundaries, as will be shown in the following sections.

Several other impurities have been identified at the grain boundaries according to the literature, including boron, sulphur, nitrogen and titanium. Grain boundary segregation of boron and sulfur has been observed in nickel and iron alloys, even when bulk contents are only several parts per million. Blanchet et al noted that precipitates rich in sulfur species occurred on the intergranular fracture surfaces of Alloy 600 tested in 350°C water⁹. Van Rooyan suggested that the main trace element segregation to grain boundaries took place during the service life of the steam generator⁴³. Boron may be particularly important since it is often observed at grain boundaries of MA specimens. Contrary to the effects of sulfur or phosphorous, boron segregation does not directly induce intergranular corrosion or stress corrosion¹².

The actual detrimental or innocuous effect of the segregation of these trace elements is still a subject of debate, as is difficult to separate the effects of segregation and carbide formation, so the full role of these segregations is still far from being established. A few systematic experiments have been performed. The most relevant results will be summarized next:

Caceras¹⁵ studied the segregation of phosphorous, boron and silicon to grain boundaries, concluding that the addition of B increased the ductility of the alloy but did not increase grain boundary segregation. However, additions of silicon had no significant effect on the ductility of Alloy 600.

In 1989, Sung and Was³⁸ showed that high purity Ni-16Cr-9Fe alloys showed inherent intergranular (IG) cracking susceptibility at 360°C in high purity water and in Ar atmosphere. They suggested that creep played an important role in IG cracking in high purity water. In similar experiments, alloy impurities (C, B and P) retarded IG cracking relative to the high purity alloys. Low grain-boundary diffusivity of metal due to impurity segregation was suggested to be responsible for that. They also found that impurity segregation, chromium depletion and intergranular carbides did not promote IG cracking and that IG cracking was dominant in small grain size samples.

Thuvander et al. contributed to the understanding of grain boundary segregation of C in Alloy 600 with an Atom Probe Field Microscope (APFM) and TEM study^{42; 41}. They showed that during heat treatment of Alloy 600 at 600°C, the highest amount of carbon segregation to the grain boundaries occurred after 1h. The amount of segregation is, consequently, related to the chromium carbide precipitation.

1.4.4 Grain boundary engineering

Grain boundary engineering is a relatively new field within materials science in which some material properties are improved through modifications to grain boundary networks. Normally, grain boundaries are categorized as “special” or random with reference to the coincident site lattice (CSL) model, whereas the grain boundary network is characterized by the grain boundary character distribution (GBCD) and triple junction distribution (TJD). The CSL model describes the degree of coincidence of lattice sites from the adjacent grains, and hence is a rough measure of the grain boundary energy. Sequential thermomechanical processing (deformation followed by annealing) has been shown to produce significant improvements in material properties such as corrosion resistance, SCC, creep, etc^{4; 22}. One of the first

materials which it was tried to improve was Alloy 600. It was proven that through thermomechanical processing it was possible to increase the fraction of special boundaries²⁶. Experiments designed to investigate IGSCC in Alloy 600 revealed that low-angle grain boundaries ($\leq 15^\circ$) did not crack. CSL boundaries were not completely immune to cracking, but in general they were more resistant than normal boundaries¹⁹. A general conclusion from all reports consulted is that only twin boundaries ($\Sigma 3$) have been found to be crack-resistant. The intersection of a twin with a random boundary is suggested to act as a barrier to crack advance²².

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Chapter 2:

Oxidation and SCC of Alloy 600

2.1. Oxidation of Alloy 600

2.1.1 Introduction

“The oxidation of metals and alloys in high temperature water systems, will normally result in the formation of adherent films, non-protective oxide layers, soluble components, and colloidal matter. The overall corrosion mechanism will depend on a complex sequence of electrochemical processes involving the transport of electrons and ions through both solid and liquid phases”⁷⁰.

The total chemical reaction for the reaction of a metal M and oxygen gas O₂ to form oxide M_aO_b is:



The reaction path and the oxidation behaviour may depend on many factors. The reaction mechanisms are also proven to be complex. If the process is simplified, it could be imagined as:

- The oxygen gas is absorbed on the clean surface of the metal
- The oxygen may dissolve in the metal and oxide is formed on the surface
- Adsorption and oxide formation are functions of surface orientation, crystal defects, surface preparation, etc.

The surface oxide separates the metal from the gas. When a continuous film covers the surface, the reaction can proceed only through the solid-state diffusion of the reactants through the film. For thin films, the driving force for the transport of the reactants may be electric fields in or across the film, implying a potential gradient. For thick films (or scales) it is determined by the chemical potential gradient across the scale, although it is still uncertain what happens down a crack in the metal⁹.

2.1.2 Thermodynamical approach

The overall driving energy of metal-oxygen reactions is the free energy change associated with the formation of the oxide from the reactants. Thermodynamically, the oxide will be formed only if the ambient oxygen pressure is larger than the dissociation pressure of the oxide in equilibrium with the metal. The formation of the oxide M_aO_b , for which $\Delta G^\circ (M_aO_b)$ represents the standard free energy change of the reaction at the temperature under consideration, will be controlled by the partial oxygen pressure³⁶. The metal M can then only be oxidized to the oxide M_aO_b if:

$$p_{O_2} \geq e^{\frac{2\Delta G^\circ (M_aO_b)}{bRT}} \quad \text{Eq. 2.2}$$

According to the Ellingham/Richardson diagrams, the most stable oxides have the largest negative values of ΔG° . At 360°C, the stability of the oxides of the mayor alloying elements in Alloy 600, ΔG° , increases in the following order:

$$|\Delta G^\circ| (Fe_2O_3) > |\Delta G^\circ| (NiO) > |\Delta G^\circ| (Fe_3O_4) > |\Delta G^\circ| (Cr_2O_3)$$

Under PWR conditions, the most stable oxide will be Cr_2O_3 and only one of the iron oxides will form: Fe_3O_4 .

Hence, it is thermodynamically possible to predict which alloy will oxidize first in a specific pressure of O_2 . The same applies to the carbides, where the order is:

$$|\Delta G^\circ| (Fe_3C) > |\Delta G^\circ| (Cr_7C_3) > |\Delta G^\circ| (Cr_{23}C_6) > |\Delta G^\circ| (TiC)$$

However, at the relatively low temperatures of PWR operation, the establishment of thermodynamic equilibrium might take a very long time (i.e. tens of years). Kinetics and metastable equilibrium states are likely to be relevant⁸. $\Delta G^\circ (Cr_7C_3)$ and $\Delta G^\circ (Cr_{23}C_6)$ values might be affected by the composition of the carbides, as they usually include Fe.

2.1.3 Some diffusion aspects

Many chemical reactions or microstructural changes can take place through solid-state diffusion, e.g.: the movement and transport of atoms in solid phases. This diffusion takes place because of the presence of defects in the solid. Vacancies or interstitials ions are responsible for lattice diffusion. Diffusion can also take place along line and surface defects which include grain boundaries, dislocations, etc. This diffusion will be faster than in the lattice as these mechanisms have smaller activation energy. Grain boundary diffusion will be dependent on the grain size of the oxide. It will be particularly relevant at low temperatures. Diffusion can be also enhanced by stress, as described by Rauh^{63; 65; 64}. The particular stress conditions of a crack tip might enhance the selective diffusion of some alloy components to the flanks, to the boundary ahead of the crack tip, or to slip bands propagating from the crack tip.

2.1.4 Multilayered scales

When a metal can form different oxide phases with different compositions, depending upon the oxygen pressure, a sequence of oxide layers may be formed. The most metal-rich oxide will form next to the metal and the most oxygen-rich will form next to the gas phase^{8; 9}.

If only a primary film is present, its formation can be explained in terms of “redox” reactions but, as corrosion continues, this primary layer will progressively thicken and the oxygen potential at the metal/oxide interface will decrease. Under hydrothermal conditions, a secondary film of a less highly oxidized phase will begin to grow in this oxygen deficient region and continue to grow into a non-uniform thick layer. This second layer will act as a barrier to metal ion transport via diffusion and the growth mechanism of the primary layer will be affected^{77; 8; 9}. This behaviour was not observed in the oxidation of Alloy 600, as Cr_2O_3 has more oxygen than NiO and it is formed next to the metal. The solid state diffusion model described by Robertson described the location of the different oxide phases in a more successful way⁶⁷.

2.1.5 Stress development and relief in oxide films

Growth stresses in scales may have several causes. Starting from the situation when oxygen diffuses inward through the scale, the oxide is then formed at the metal/oxide interface. If the volume of the oxide is larger than that of the metal from which the oxide is formed, compressive stresses build up in the scale⁷⁷. This stress in the oxide may be related to the Pilling-Bedworth ratio:

$$PBR = V \text{ (per metal ion in oxide)} / V \text{ (per metal ion in metal)}$$

(V is the atomic volume)

Eq. 2.3

If $PBR > 1$, the oxide is expected to be in compression
If $PBR < 1$, the oxide is expected to be in tension

Normally, if $PBR < 1$, the protective oxide film cannot be maintained. Here, we show some typical values⁷⁷. Note that all the values for iron oxides are referred to oxides in α -Fe.

Oxide	PBR
NiO	1.65
FeO	1.68
Cr ₂ O ₃	2.07
Fe ₃ O ₄	2.10
Fe ₂ O ₃	2.14

If oxide growth takes place by outward migration of metal ions, the new oxide is formed at the scale/metal interface in a supposedly stress-free manner. But as metal diffuses outwards and the volume of the metal core decreases, growth stress will still arise due to the tendency of the oxide to adhere to the metal.

Epitaxial stresses should be also taken into account, as nucleation considerations may dictate that the first oxide to form will have an epitaxial relationship with the substrate. As the scale thickens, the epitaxial stresses in the oxide are reduced. As an example: At 400°C and 1 atm of O₂, the rate of oxidation of different faces in pure Ni decreases in the order {110} > {100} > {111} > {311}. The {110} faces will oxidize 10 times faster than the {311} face⁹.

If the growth stresses cannot be sufficiently alleviated through plastic deformation of the oxide scales or plastic deformation of the metal, the scale will crack and detachment at/or near the scale/metal interface (spallation) can occur.

2.1.6 Internal oxidation

The components of the alloys have different affinities for oxygen and the reacting atoms do not diffuse at the same rates either in the oxide or in the alloy phases. As a result, the oxide scales on alloys will not contain the same relative amount of the alloy constituents as does the alloy phase. The composition and structure of the oxide scales on the alloys will often change as the oxidation proceeds.

When oxygen dissolves and diffuses into the alloy phase during oxidation, the less noble alloy component may react to form oxide particles within the metal. This is called internal oxidation ^{8; 36}.

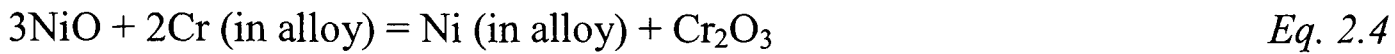
2.1.6.1 Transition from internal to external oxidation

When the concentration of the less noble alloy component is increased, a critical concentration will be reached above which the oxidation leads to the formation of a surface scale of the less noble metal, and the alloy no longer oxidizes internally. When the rate of growth of the external scale is slow compared with the internal oxidation, then the oxidation rate drops from a relatively fast dissolution of oxygen in the alloy phase below the critical concentration to a slower protective oxidation where the diffusion of oxygen inwards or metal ion outwards through the surface scale is rate-determining at higher concentrations. That is called: “Passivation” ⁹.

2.1.7 Gettering effect in multicomponents alloys

Most high temperature alloys are multicomponent alloys, such as stainless steels and nickel-base alloys, where more than one of the less noble alloying additions may in principle be internally oxidized or form external protective scales. In such cases one

alloy component may aid another to be selectively oxidized^{77; 8}. In a Ni-Cr alloy, during the very initial oxidation, oxides of all components may form: NiO, Cr₂O₃, etc. However, if sufficient Cr is present in the alloy, the NiO formed initially will be reduced by Cr through the reaction:



So a continuous layer of Cr₂O₃ is formed in the alloy.

2.1.8 Alloy 600

The oxide scales found in Alloy in PWR conditions are usually Cr₂O₃ and an outer layer of NiO and NiFe₂O₄^{15; 45; 84}. Several studies have been undertaken to try to understand which oxides grow inside cracks and under which conditions. The similarities between the oxides formed in PWR primary water and during high-temperature oxidation of Ni-Cr alloys in O₂ will be an important argument against a hydrogen-induced SCC mechanism^{66; 28; 27}.

Robertson⁶⁷ suggested that the corrosion of Alloy 600 follows the solid state diffusion model. This model proposes that the alloy oxidizes non-selectively to form a duplex layer oxide, with the inner layer growing by the ingress of water along oxide micropores and the outer layer growing by the outward diffusion of metal ions along oxide grain boundaries. Whether an alloy constituent is present in the outer or inner layer would be determined by its diffusion coefficient in cubic oxides: Mn>Fe>Co>Ni>>Cr, and then the faster diffusing elements would diffuse to the outer layer. For the composition of Alloy 600 (74% Ni, 16% Cr, 9% Fe), an inner layer oxide containing 32% Cr and 68% Ni and an outer oxide layer of 18% Fe and 82% Ni is expected according to the model. Due to their fixed valences, Ni and Cr can only form one spinel: NiCr₂O₄. Thus, the inner layer would consist of 48% NiCr₂O₄ and 52% NiO and the outer layer would consist of 27% NiFe₂O₄ and 73% NiO. The presence of NiO in both layers allows the oxidation rate to be controlled by the faster growth rate of NiO, rather than the slower rates of the spinels. This model predicts that Cr will not lower the oxidation rate of the alloy until its content reaches 33%,

which is in agreement with the good SCC resistance of Alloy 690 (60% Ni, 30% Cr, 9% Fe).

Combrade showed that the stability and the solubility of metal and oxides change with the pH of the water. According to his study, the surface films are different in neutral and caustic environments (without and with external NiO layer) ¹⁵. A protective oxide film mainly made of two layers was predicted ²⁰: a Cr rich inner layer of spinel type and an outer layer of precipitated oxide crystals. He accepted that the inner layer is compact and protective and grows by a solid state diffusion mechanism. For the outer layer, he suggested that it grows by precipitation of cation diffusion through the inner layer, being Fe rich and containing NiO if the corrosion potential is high enough. Combrade expected the composition of the oxide film to change rapidly with applied potential in the range of the Ni/NiO equilibrium, because Ni may increasingly enter the oxide with increasing potential. As the variation of the film repair kinetics did not correlate with the cracking sensitivity, he suggested that other transport properties of the oxygen anions towards the matrix should be considered (pores or stress-induced).

McIntyre, in 1994, showed that some acid exposures resulted in films which were less protective than those formed under PWR chemistry ⁴⁴.

2.2. Stress Corrosion Cracking

2.2.1 Introduction

Stress corrosion cracking (SCC) is one of the most expensive modes of materials failure. Despite this, it is still difficult to apply the science of SCC to life prediction of engineering components and structures. In metal alloys, it can have a devastating impact on the safety and reliability of all types of structures, mechanisms, and high-pressure gaseous systems. Many times, this type of failure is unexpected and occurs at the worst possible moment in a schedule of critical operation of a system ⁴⁷;

SCC is, basically, a progressive fracture mechanism in metals that is caused by the simultaneous interaction of a corrodent and a sustained tensile stress. Structural failure due to SCC is often sudden and unpredictable, occurring sometimes after only a few hours of exposure, or after months or even years of satisfactory service. It is frequently encountered in the absence of any other obvious kinds of corrosive attack. Virtually all alloy systems are susceptible to SCC by a specific corrodent under a specific set of conditions. It affects many alloys in many components, e.g. conventional power generator plants, nuclear reactor components, offshore rigs, aircraft landing gears, etc.

Predicting SCC is not an easy task. To date, no one has been able to put forward a theory that can satisfactorily explain all the observed cases of SCC and their characteristics. Without a single "unified" theory to predict SCC, the only way to be sure that any particular alloy is not susceptible to SCC in any particular environment is to obtain actual experimental data.

In the last decade, significant advances have been made in understanding, quantitatively, the cracking mechanism pertinent to a particular alloy/environment system, and this offers the design operating engineer the capability of validating the empirically derived remedial actions of operating specifications, developing realistic life-predictions methodologies for specific plant conditions. To develop quantitative, mechanistically based methodologies, it has been necessary to do the following:

- Define a working hypothesis for the cracking mechanism. Such a mechanism must account for the full spectrum of loading conditions expected in practice.
- Independently evaluate the relevant parameters in that mechanism.
- Validate the theoretical predictions of the cracking response by comparison with as wide a spectrum of observed databases as possible^{47; 72}.

In order for SCC to occur three factors must be present at the same time. The alloy must be 'susceptible'. It must be under stress. It must be in a corrosive environment. Thus, it is useful to represent the SCC phenomenon as the interaction of these three factors (Fig. 2.1):

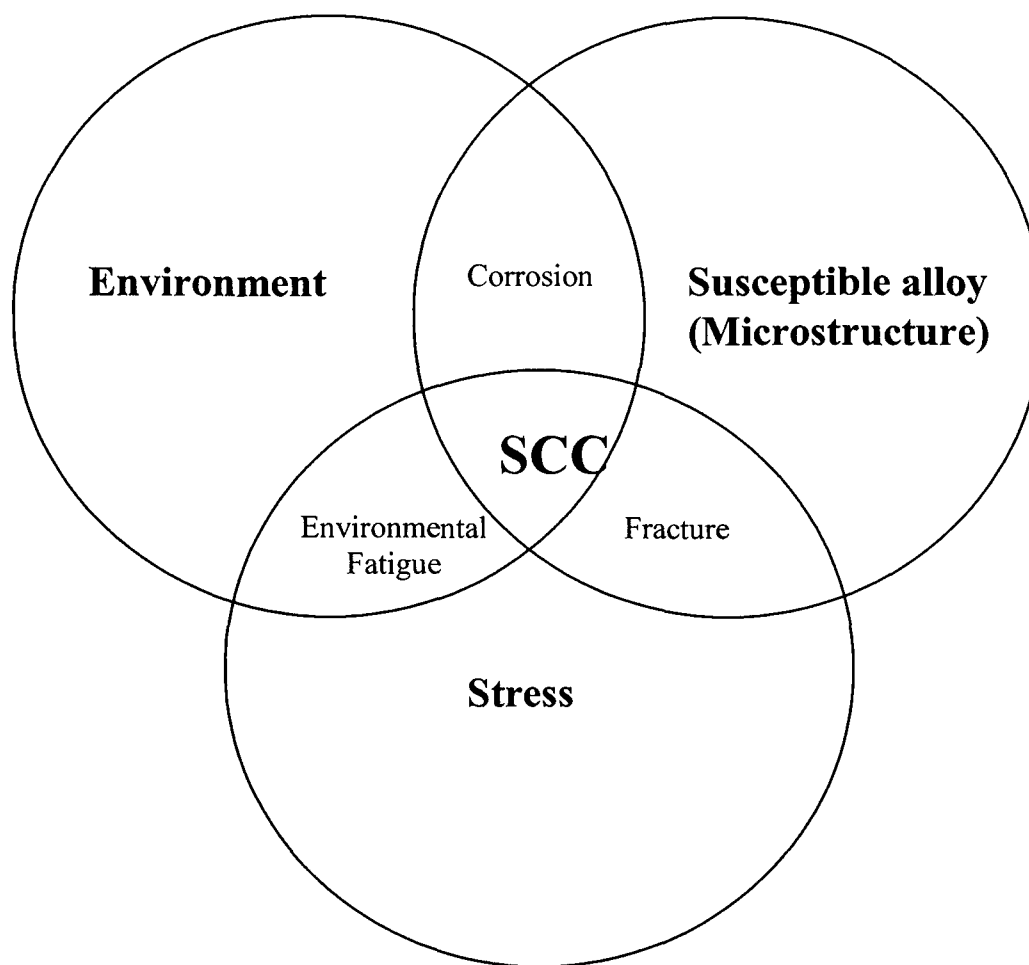


Fig. 2.1. Sketch representing the three interactions required to have SCC.

If any of these factors is not present, SCC will not occur although other failure mechanisms might operate that require only one or two of the factors. The aim of this project has been to try to clarify SCC of Alloy 600 (mainly) and Austenitic Stainless Steel (SS304) in Steam Generators of Nuclear Power Plants. So, in our case, the environment will be the Primary Side Water in the Steam Generator; the susceptible alloy will be Alloy 600 or SS304 and stress will be present because a tensile stress is developed under conditions of high pressure and temperature.

The kinetics of the crack growth rate process can be characterized by monitoring the rate of crack advance da/dt as a function of the instantaneous stress intensity level. Three different crack growth regimes have been identified^{43,55}. In Region I, da/dt is found to depend strongly on the prevailing stress intensity level, in opposition to Region II, which is more dependent on temperature, pressure and environment. Region III reflects a second regime where da/dt varies strongly with K . This can be seen schematically in Fig. 2.2.

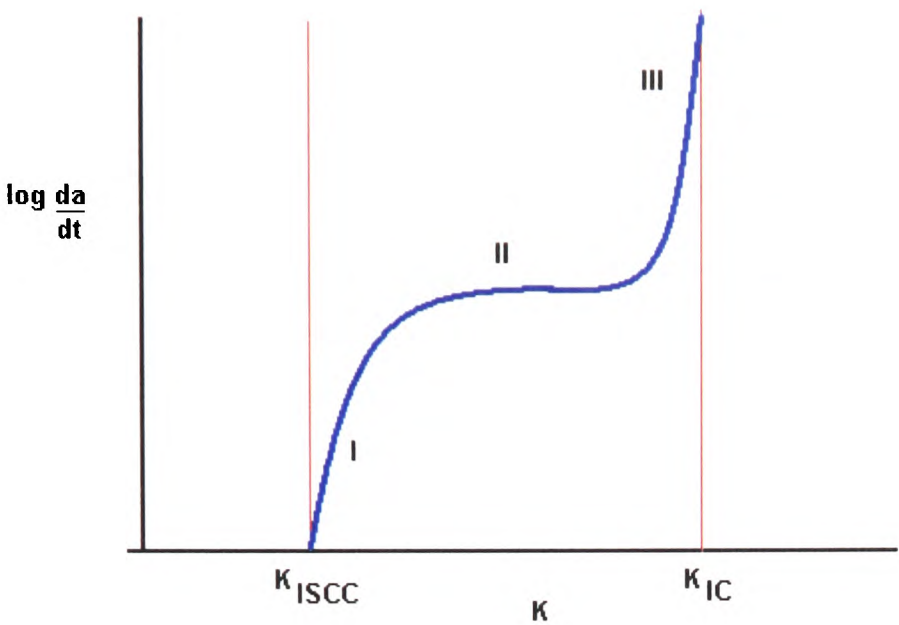


Fig. 2.2. Diagram showing the three stages of SCC.

2.2.2 Stress Corrosion Cracking Mechanisms

An SCC mechanism is the combination of mechanical, physical, and chemical processes (Fig. 2.1) that accomplishes the separation of bonds at the crack tip, thereby advancing the crack. Normally, the rate of SCC will be controlled by the rate of a process that is a prelude to the actual bond breaking, like adsorption or mass transport. This way, kinetic measurements may only permit a restricted test of the mechanism^{81; 47}.

The usual energy balance approach to fracture, by equating the strain energy released to the energy consumed in creating new surface and in achieving plastic deformation³⁰, needs further modifications where corrosion processes are involved to take account of the chemical energy released, and it is the latter that distinguishes stress corrosion from other modes of fracture not involving environmental interaction:

$$\begin{aligned} \text{Surface energy change} + \text{Plastic work} &= \text{Change in initial stored energy} \\ &+ \text{Electrochemical energy released} \quad \text{Eq. 2.4} \end{aligned}$$

Since the surface energy term will usually be negligible by comparison with the plastic work term in the stress corrosion of ductile materials, it may be neglected. The remaining terms may be derived from fracture mechanics and conventional

electrochemical considerations and, for the various boundary conditions indicated by West⁹², result in:

$$\gamma_p = K_I^2 \frac{1-\nu^2}{E} + \frac{zF\rho\delta}{M} \eta \quad \text{Eq. 2.5}$$

where γ_p is an appropriate plastic work term, K_I is the stress intensity, ν is Poisson's ratio, E is Young's modulus, z is the valence of the solvated ions, F is Faraday's constant, ρ is the density, δ is the height of the advancing crack front, M is the molecular mass of the metal and η is the anodic overpotential. In the absence of corrosion effects, only the first term of Eq. 2.5 is required. At the threshold stress intensity K_{ISCC} , i.e. the minimum value of K_I for SCC is:

$$K_{ISCC} = \sqrt{\frac{E}{1-\nu^2} \left(\gamma_p - \frac{zF\rho\delta\eta}{M} \right)_{\min}} \quad \text{Eq. 2.6}$$

Then, we can see that the variables that may influence K_{ISCC} , and hence the susceptibility to SCC, are γ_p and η :

$$K_{ISCC} = \sqrt{k_1 (\gamma_p - k_2 \eta)_{\min}} \quad \text{Eq. 2.7}$$

Lowering of the plastic work term γ_p will result from an increase in the effective yield stress or an increase in the work hardening rate in the crack tip region, either of which, for constant η , will lower K_{ISCC} and hence increase the susceptibility to stress corrosion. An increase in the anodic overpotential η_a (the potential in the metal is made more positive) relative to the plastic work term is also predicted to increase susceptibility to stress corrosion; η_a will be some function of the electrochemical conditions within the crack that control the active to passive transition which determines whether or not cracking occurs (i.e. it will be some function of pH, anion activity, metal composition and electrode potential). The interdependence of all of these terms upon structure, composition, electrochemical conditions, etc, make the quantification of the argument very difficult, and its relation to the detailed

mechanisms of crack propagation virtually impossible, as West indicates. However, just the recognition of the need for a critical balance between a number of variables if stress corrosion is to occur, is important⁷⁷. This project has permitted, using direct observations of crack tip chemistry and corrosion products, a better informed modelling.

2.2.3 Classification of SCC mechanisms

Any successful working hypothesis for explaining the SCC phenomena should account for the following facts⁸¹:

- High specificity of environment required for SCC of many metals and the lack of any general relation to their intensity as corrosive agents.
- General resistance or immunity of pure metals or, similarly, the effect of trace impurities or larger amounts of alloying elements to either inhibit or enhance SCC.
- Usually beneficial effect of cathodic polarization.
- Inhibiting effect of extraneous anions.
- Effect of structure (e.g. ferritic vs. austenitic steel) and grain size (increasing tendency to failure with increasing grain size).

The basic premise for all the proposed cracking mechanisms in aqueous solutions is that the crack tip must propagate faster than the corrosion rate on the unstrained crack sides, or the crack will degrade into a blunt notch. We can group all the different proposed mechanisms into the 3 following groups.

2.2.3.1 Pre-existing active path mechanisms

These relate the cracking susceptibility to the chemical activity of the grain boundary. The localized intergranular attack could be due to inherently high activity of the disordered grain boundary structure or to the presence of chemically active grain boundary impurities, precipitates, etc. If the alloy has some structural features like a segregate or precipitate at the grain boundary, a local galvanic cell can be established, as Dix¹⁷ originally proposed. The precipitate or segregate may act as the anode in the local cell or, by acting as an efficient cathode, may cause the dissolution to be localised upon the immediately adjacent matrix (Fig. 2.3).

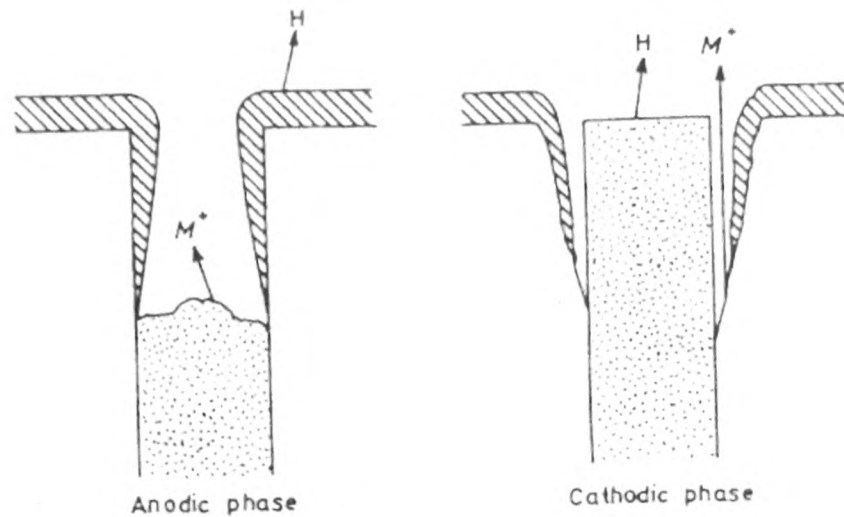


Fig. 2.3. Pre-existing active path mechanisms, in which H represents cathodic Hydrogen⁷⁷

It has been argued that pre-existing active path mechanisms cannot work unless corrosion is directional, e.g. along a grain boundary²⁵.

2.2.3.2 Strain-Assisted active path mechanisms

These mechanisms relate crack propagation to dissolution at the crack tip and the stress/strain condition in that region^{19; 79; 78}.

2.2.3.3 Adsorption related phenomena (stress sorption cracking)

There are alternative mechanisms also proposed to explain subcritical crack propagation. They rely on the decrease in mechanical integrity at the crack tip due to adsorption of species from the environment followed by possible absorption into the underlying matrix^{93; 61; 49; 31; 68}.

However, Parkins⁵⁶ pointed out that the controlling factors in the active path, strain-assisted active path and adsorption-related mechanisms form a **spectrum** of interrelated effects. Although under a particular testing condition one mechanism may be valid, an alteration of the system variables could lead to operation of a different mechanism. There could also be situations where two or more mechanisms may be operating simultaneously.

A comprehensive review of the extensive literature reports on SCC shows that we still do not have a model or a theory capable of explaining stress corrosion

cracking phenomena in anything other than specific materials under a specific environment. Notable is the absence of a realistic model for Fe-Ni-Cr alloys (Alloy 600, SS304, SS316), basically due to the lack of controlled experiment data.

2.2.4 Main proposed SCC models and mechanisms

2.2.4.1 Slip-Dissolution Model

This model ^{83; 58; 55; 25} considers that crack growth occurs by extremely localized anodic dissolution. The sides of the crack are protected by a film, usually an oxide, which is fractured as a result of plastic strain in the metal at the crack tip. Crack growth develops as a cyclic process of film rupture, dissolution, and film repair ⁴³. This model has been associated with the names of Vermilyea, Scully, Staehle, Parkins, Ford and Galvele. It was the focus of most SCC research in the 70s and early 80s ²⁵. A key development, made by Vermilyea ⁸³ was the demonstration that SCC under static load is explicable if the film formation-dissolution process promotes further creep type deformation at the crack tip, although it is also very likely to be influenced by temperature.

Another fact that supports the model is the good general correlation between the average oxidation current density on a straining surface and the crack propagation rate for a number of systems ^{57; 58}. We can see a schematic representation of this model in Fig. 2.4.

It has been argued by Sieradzki that pre-existing active path mechanisms cannot work unless corrosion is directional, e.g. along a grain boundary ²⁵.

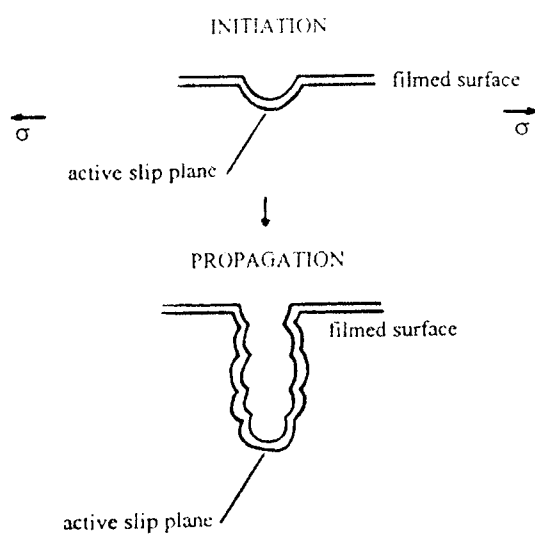


Fig. 2.4. Schematic representation of the Slip-dissolution model ⁴³.

2.2.4.2 Film-Induced Cleavage Model

This model offers an alternative when pre-existing active paths are non-existent or inoperative. It was originally proposed for explaining the fact that superficial dezincification of α -brass in ammonia solution could trigger a brittle fracture through several micrometers of the unattacked substrate. It was even proved, using an optical microscope, that a crack-jumping phenomenon existed¹⁹. Nowadays, this model does not require a special property of the fcc substrate through which the cracks jump. It is the film itself which is able to trigger a crack with a fast enough velocity^{79; 78; 25}.

The plastic strain in the underlying metal may bring about the disruption of the protective film whereby active metal is exposed, in the manner shown schematically in the Fig. 2.5:

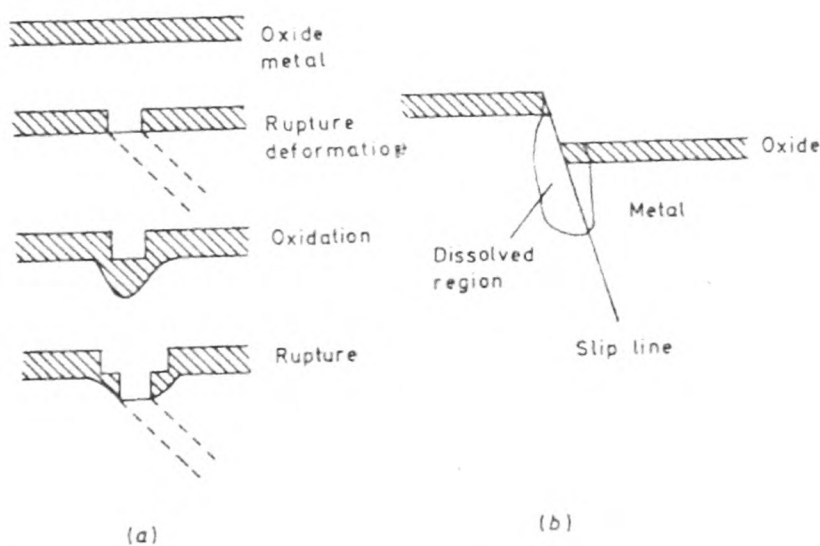


Fig 2.5. a) Film rupture model film
b) Slip step dissolution model⁷⁷

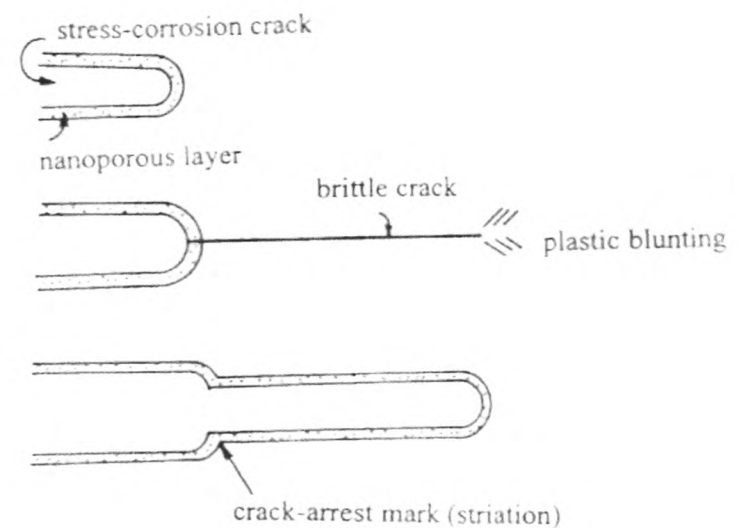


Fig 2.6. Crack growth by induced cleavage in an fcc alloy⁴³

The active path along which the crack propagates is cyclically generated as disruptive strain and film build-up alternate with one another, or propagation is related to the slip characteristics of the underlying metal (Fig. 2.6). This strain-generated active path mechanism would be expected to result in transgranular cracks⁷⁷.

This model, which relied on the chemical activity of a strained region at the crack tip (through plasticity arguments) or on the effect of dissolution on the mechanical integrity of the crack tip, were absorbed by theories⁹¹ that relied on the

rupture of a protective film at the crack tip. It was realized that for a high aspect ratio crack to exist, the sides of the crack must be protected. That happens even when the crack tip was in a chemically active condition due to the mechanical rupture of the protective film followed by metal penetration by bare surface dissolution and/or film growth. Here is when slip dissolution and brittle film⁸⁰ were proposed.

Different types of protective film were proposed varying from oxide, through mixed oxides and salts⁸⁰ to noble metals⁸¹ left on the surface after selective dissolution of a more active component in an alloy. These theories were supported by observing that high stress corrosion susceptibility was encountered under some pH/potential conditions where a protective film was thermodynamically stable. If this film was broken, bare-surface dissolution was thermodynamically possible. What gave the definitive support to these theories was the observation that the crack propagation rates for many systems were in direct proportion to the experimentally determined dissolution rates under the mechanical and the chemical conditions expected at the crack tip, as seen in Fig. 2.7⁵⁷. This assumes that the potential at the tip of the tight crack is the same as the potential at the sample surface.

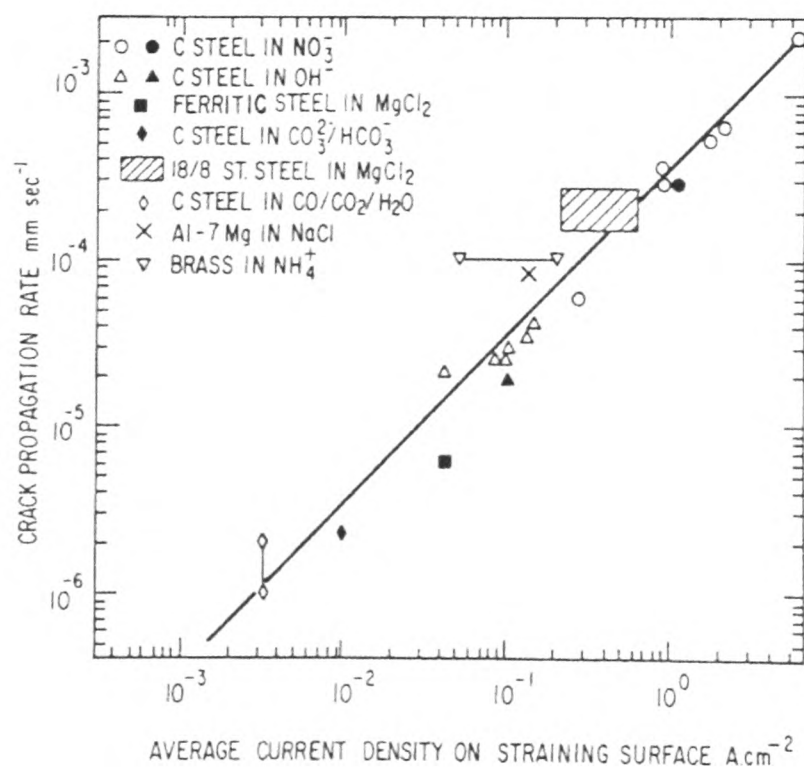


Fig. 2.7. Crack propagation rate versus average current density on straining surface

2.2.4.3 Hydrogen embrittlement model

Inspection of the energy balance described by Eq. 2.3 shows that, with negligible contribution from dissolution, crack extension will be facilitated by a reduction in the surface energy required to form crack faces or a reduction in the plastic work term by embrittlement of the metal in the crack tip region. If the environment can provide species that are adsorbed at the crack tip to reduce the effective bond strength, then the surface energy would be effectively lowered. Alternatively, the species may diffuse into the metal forming a brittle phase, like hydride, at the crack tip where the stress and strain conditions are particularly appropriate for the nucleation of a crack. The cracking of zirconium alloys by hydride formation at a crack tip has been well documented. It has been a major problem in nuclear fuel cladding, e.g. in the Canadian CANDU reactors^{94; 61; 49; 31; 68}.

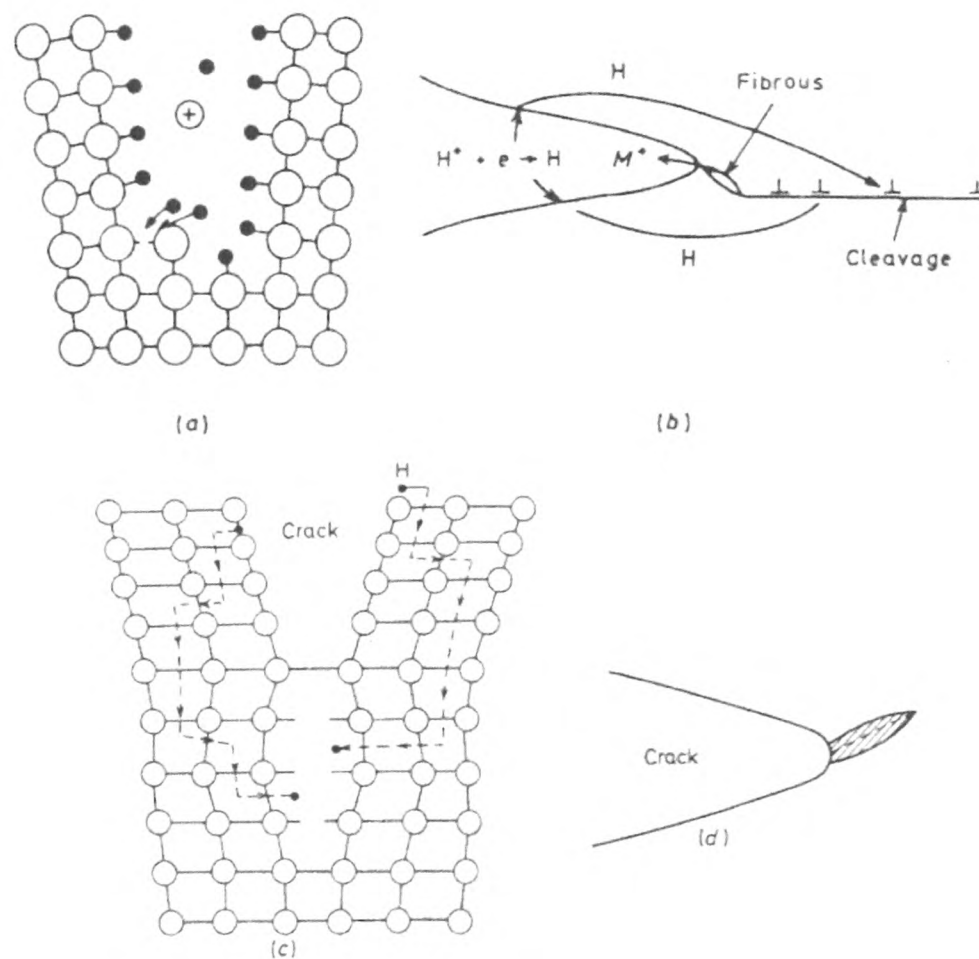


Fig. 2.8. Mechanisms involving embrittlement of the metal: a) Crack tip adsorption, b) Hydrogen adsorption, c) decoherence by hydrogen influx to dilated lattice and d) crack extension due to brittle hydride particle forming at crack tip⁷⁷.

That is what happens with H, the only specie that can diffuse with sufficient speed to account for observed crack propagation rates. Hydrogen adsorption is well

established as responsible for SCC of high-strength steels in aqueous environments⁸³. But the role of H in fcc systems still remains controversial, especially in austenitic stainless steels and Ni alloys²⁵. Hydrogen discharge and absorption occur easily when there is acidification of the local environment by cation hydrolysis²⁵, especially if this acidification damages or destroys a passive film in the crack (Fig. 2.8). Although this model is very attractive, a number of objections have been suggested by Staehle and Latanision⁸³:

- Cathodic charging is a severe experimental condition and it is unlikely that such an intense situation exists at the tip of the crack, especially in view of the relatively high concentration of positive ions being produced as the crack advances.
- The thermodynamic argument pointed out by Hoar³³, while apparently not explaining the hydrogen evolution of Barnartt and van Rooyen⁸⁹, clearly suggests that high pH solutions would not cause cracking owing to the reduction of available H^+ ions. Furthermore, at neutral pH and above, it has been clearly demonstrated that oxygen is required for crack propagation⁸³.

Both authors consider that from the present evidence, hydrogen absorption may not be a determining factor in cracking but, in low pH, may exert a secondary influence.

The Decohesion model was proposed specifically for hydrogen embrittlement and temper embrittlement (Fig. 2.8c), where subsurface atom-atom rupture is facilitated by local concentrations of hydrogen or temper-embrittling elements which modify the electron d-band structure or expand the lattice. This applies to the first series of transition metals, e.g. steels and Ni-based alloys^{80; 51; 59; 52; 53; 54}. It cannot be considered strictly an “environmental cracking” phenomenon.

2.2.4.4 Surface energy reduction models

These models^{62; 32; 22} rely on surface chemisorption of an environmental species on the crack tip, which reduces the surface energy term, γ_s , in the equilibrium

Griffith relationship ³⁰ and thereby the local fracture stress of the metal lattice. Such an argument has been used for hydrogen embrittlement and liquid metal embrittlement ⁵⁰. It has been demonstrated ⁸¹ that certain environmental species adsorb in preference to others. Associated with such adsorptions must be varying degrees of surface energy lowering, as was proposed by Uhlig ⁸⁸. The essence of this proposal involves the interaction of the critical environment species with the stressed metal bonds at the crack tip, causing bond breaking and consequent advance of the crack. This idea, however, fails in the following respects when trying to explain cracking in austenitic steels or Inconel alloys:

- Yielding with associated or attendant step emergence is clearly operating at the base of cracks in ductile alloys. Any scheme of bond breaking would require an infinitely sharp crack which does not exist.
- Greater energy lowering will come from dissolution than adsorption. Thus, dissolution processes would be favoured.
- Crack advance is clearly an electrochemical dissolution process. The experimental reports of dissolution are too numerous to disregard ⁸¹.

The main conceptual difference between these last models is that in the surface-energy models rupture occurs at the crack tip surface whereas, in the decohesion models, subcritical crack propagation relies on the diffusion of the aggressive atom to some point beneath the surface where the rupture occurs. This crack propagation is specific to hydrogen because of the high mobility of the atom.

2.3. SCC in Alloy 600

Intergranular stress corrosion cracking (IGSCC) of Alloy 600 has been encountered on both the primary and secondary sides of pressurized water reactor (PWR) recirculating steam generator tubing.

The service performance of alloy 600 tubes in primary side water has generally been excellent ²⁹. Of the thousands of tubes in use, there have only been cracking in a very small number of them, but even if one fails, it can cause shut down of a nuclear plant, which is a very serious and expensive problem ⁸⁹.

The first reported failure of a steam generator tube by IGSCC was in 1959 by Coriou¹⁶. That awoke the interest of many researchers to SCC of Alloy 600 in PWR. Most of the reported failures nucleate from the secondary side, although Garud²⁶ has reported that in recent years at least twenty PWR have also suffered primary side IGSCC of alloy 600 steam generator cooling tubes.

In the late 60's⁹⁰ it was shown that the stress corrosion cracking experience reported by Coriou in PWR reactors can be reproduced in the laboratory. Since then, many investigations have been made to clarify the various aspects of stress corrosion cracking of alloy 600 in PWR steam generator tubes from the primary⁶⁰ and secondary side⁷. It is generally acknowledged that IGSCC of alloy 600 in secondary water is a result of alkalinity caused by agglomeration of residual salts in feedwater. The mechanism of IGSCC in primary water is less well understood and is still the subject of numerous studies.

Reviews by van Rooyen⁸⁹ showed that the cracking severity in PWR primary water increases with increasing temperature (up to 365 centigrade degrees) and with hydrogen additions to the water, although it has been recently proven that high additions of H to water containing O₂ reduces IGSCC⁸². Carbide precipitation on the grain boundaries, with or without chromium depletion, seems to prevent the cracking for practical purposes, and "thermally treated" (carbide-precipitated) material is now to be used in some new PWR steam generators. This observation demonstrates the complexity of SCC because the reverse situation is believed to operate in 300 series stainless steels, i.e. grain boundary carbide precipitation causes sensitisation and enhances SCC by dissolution of the Cr-depleted matrix adjacent to the carbides¹⁰.

Until recently, it was widely assumed that some form of anodic SCC mechanism was operating in the type 600 failures, but the effect of potential (as influenced by hydrogen overpressure) has forced a re-evaluation of the problem⁴⁷.

Primary PWR coolant is a near neutral deaerated environment containing boric acid, lithium hydroxide and dissolved hydrogen. Some experimental data from Magnin⁴⁰ proved that Alloy 600 suffers intergranular cracking only in a limited range

of partial pressures of dissolved hydrogen. In terms of redox potential, these cracking conditions correspond to a relatively narrow range of potentials almost centered around the Ni/NiO equilibrium (Fig. 2.9).

The following figure (Fig. 2.9) shows Ni-NiO, Ni-NiCr₂O₄ and FeCr₂O₄ thermodynamic stability plots⁹⁵. Each plot is independent from the others. Upper and lower plot show Ni-NiO and Ni-NiCr₂O₄ stability regions, respectively. FeCr₂O₄ is stable under all plotted condition. The values come from theoretical calculations. In addition, some experimental XDS data were used to check the validity of the calculations. The vertical line between CrOOH and Cr₂O₃ shows the boundary of stability between these two species. The experimental conditions used for the samples analysed in this project are $T = 360^{\circ}\text{C}$ and $H_2 \text{ in liquid} = 30 \text{ cc/kg}$, which, although outside the region shown in the plot, are in the NiO and NiCr₂O₄ stable region. This condition is valid for the surface oxidation, but not necessarily for any intergranular oxides formed.

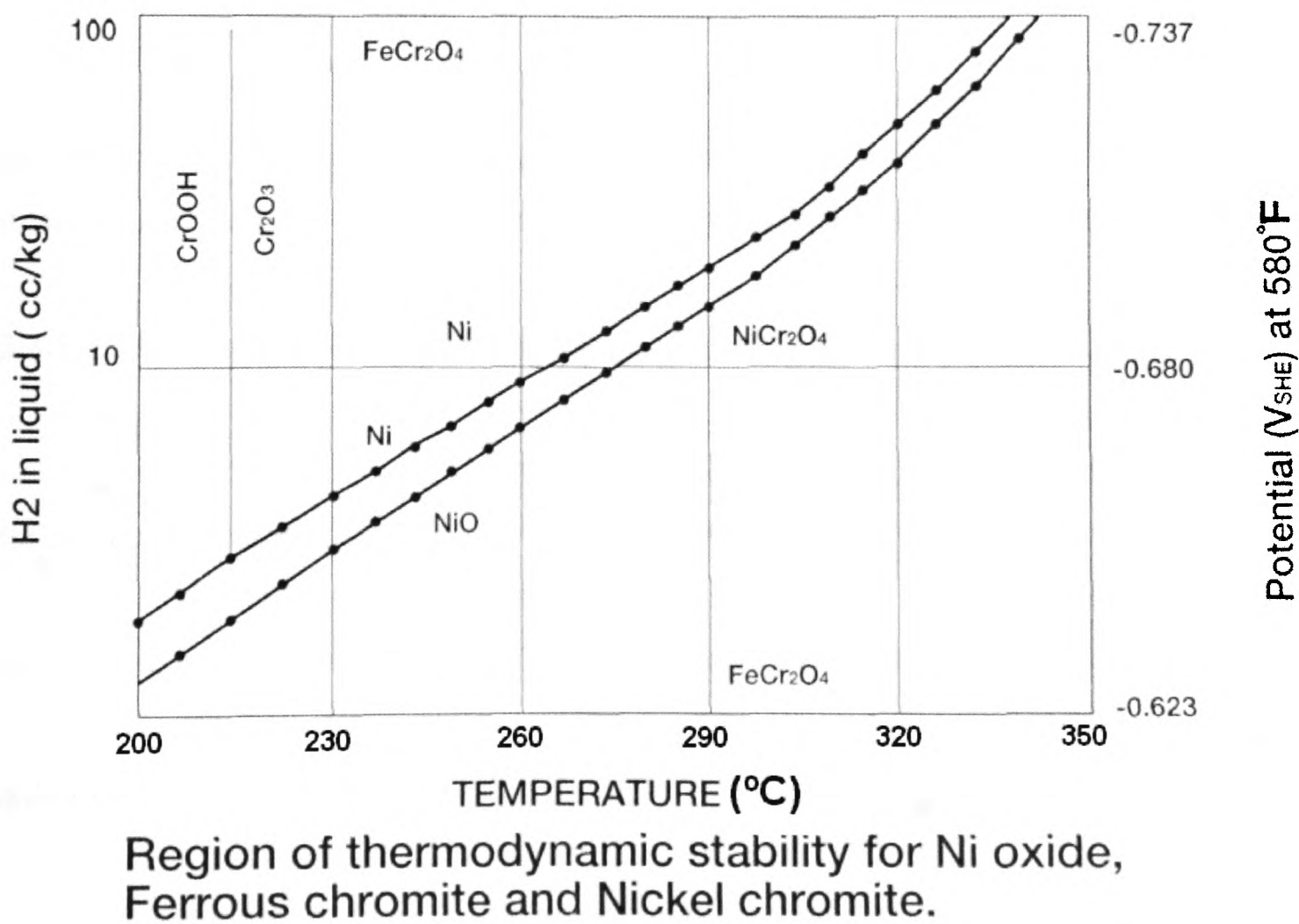


Fig 2.9. K. Fujii, INSS (unpublished data)

The embrittlement of Alloy 600 continues in hydrogenated steam¹⁸. Thermal treatment to give grain-boundary carbides continues to be effective in this environment, and there is no reason to believe that the mechanism of cracking is different from that in water²⁵. This is relevant because steam, rather than water, might occur in the crack tip region, if local overheating were to occur.

Parameters influencing the performance of Alloy 600 in primary and secondary waters can be divided into two groups:

- Related to the tubing material: composition, carbon content, microstructure, stresses, surface films,...)
- Related to the environment: pH, temperature, electrochemical potential, hydrogen concentration, additives,...)

2.3.1 SCC mechanisms and models proposed for Alloy 600

In the last years, many review papers have appeared in the literature collecting and reviewing the mechanisms proposed to explain SCC of Alloy 600^{48; 66; 72; 82}. The main proposed mechanisms for Alloy 600 are considered to be:

2.3.1.1 The slip dissolution/film rupture mechanism of Ford and Andresen

The crack advance is related to the oxidation reactions that occur at the crack tip as the protective film is ruptured by increasing strain in the underlying matrix. Ford and Andresen stated that there is a high degree of independence of the mechanical and chemical contributions to the crack growth rate (CGR)^{2; 4; 5}.

Advantages:

- The model predicts the crack growth rate well in region I (up to $K_{I1}=30\text{Mpa}/\sqrt{\text{m}}$, still in the elastic region)⁶⁶.
- It is a practical model and combines a theoretical approach with data fitting.

Disadvantages:

- Neither the region II ($K_I > 30 \text{ Mpa}/\sqrt{\text{m}}$, entering in the plastic deformation region) nor the transition between region I and II is well predicted ⁶⁶.
- The final formulation does not explain the role of the temperature, pH, carbides at the grain boundaries, cold work, etc.
- The model does not explain how crack nucleation occurs.
- It has been proven that detrimental effect of hydrogen overpressure on SCC was not due to an increase in dissolution via a destabilization of the film ⁴⁸.
- A dissolution model cannot explain the detrimental effect of the cathodic potentials. It was proven that dissolution did not increase when working in the range of cathodic potentials ⁴⁸.

2.3.1.2 The enhanced surface mobility theory of Galvele

This model has the peculiarity of being the first to predict cases of environmental sensitive cracking before they occurred. According to Galvele ^{22; 24; 75; 23}, an atom at the crack tip is transported by surface diffusion from its highly stressed location to a new site at the less stressed crack sides, thereby advancing the crack by one atom spacing for each such movement. A similar mechanism, but using bulk diffusion instead of surface diffusion was proposed by Rauh and Bullough ^{63; 65; 64} in order to explain sulfur embrittlement in stainless steels. The crack propagation results from the capture of vacancies by the stressed lattice at the tip of the crack. According to the magnitude of the surface diffusion coefficient (D_s , see ²²), Galvele classified the compounds of different elements as innocuous, unsafe and dangerous. The compounds that Alloy 600 can form in high temperature water are Fe_3O_4 , NiO and Cr_2O_3 . In Table 2.1 some values of D_s for different temperatures are listed. T_m is the melting point of the oxide.

Oxide	T_m (°C)	Temperature		
		290°C	330°C	350°C
NiO	1990	5.24×10^{-18}	3.00×10^{-17}	6.60×10^{-17}

Fe ₃ O ₄	1597	5.11 x 10 ⁻¹⁶	2.16 x 10 ⁻¹⁵	4.14 x 10 ⁻¹⁵
Cr ₂ O ₃	2435	2.97 x 10 ⁻²⁰	2.39 x 10 ⁻¹⁹	6.15 x 10 ⁻¹⁹

Table 2.1. Values of D_S for different temperatures and oxides.

Advantages:

- Predicts correctly the crack growth rate at 330°C in the region II ⁶⁶.
- Predicts correctly that the formation of NiO is a necessary condition for IG cracking to occur. When NiO does not form either because p_{H_2} is high or the temperature is too low (<250°C), cracking does not occur. At temperatures below the equilibrium of NiO formation ($T < 250^\circ\text{C}$), only Cr₂O₃ and Fe₃O₄ form on the metal surfaces. If NiO does not form, chromium oxide will form the inner protective layer and chromia will control the susceptibility of Alloy 600 to SCC.
- Predicts correctly the value of the activation energy (Q) for SCC in the 290-350°C range ($Q = 118 \text{ J/mol}$ at $K_I = 20 \text{ Mpa}/\sqrt{\text{m}}$) and that Q decreases slightly as K_I increases.
- The beneficial effects of the carbides at the grain boundaries is obtained because on the surface carbides only form Cr₂O₃, which has a very low D_S . As we could see in the previous table, if the crack growth rate is governed by the formation of Cr₂O₃ instead of NiO the value of D_S would be 2 orders of magnitude lower (and so the crack growth rate).

Disadvantages

- The model does not predict the transition in the crack growth rate between region I and region II ⁶⁶.
- The predicted CGR values for region I are one order of magnitude higher than the measured ones ⁶⁶.
- The model does not account the effects of the pH, cold work or heat treatment
- It does not explain why, when Alloy 600 is exposed to high temperature water, there is a long induction time for crack nucleation.

2.3.1.3 The internal oxidation mechanism

This mechanism was proposed by Scott and Le Calvar in 1993^{73; 71} and tried to give an explanation for IG embrittlement of Alloy 600 based on the diffusion of oxygen into the metal lattice. This embrittlement could be caused by a layer of oxygen atoms at the grain boundary, by the formation of internal Cr_2O_3 or by the formation of gas bubbles (CO , CO_2).

Advantages

- This model gives a fair prediction of CGR in region II.
- Oxygen diffuses in grain boundaries at similar rates to those of SC crack advance⁸².
- Good agreement on activation energies of O diffusion⁸².
- Grain boundary embrittlement due to the formation of internal oxides in the range of 10 μm have been produced at 360°C on unstrained alloy 600 in primary water^{28; 27}.
- AEM work has shown the presence of reactions near the crack tip that would suggest reactions with oxygen in the solid state⁸⁵.
- The good SCC resistance of Alloy 690 suggests that chromium acts to slow the diffusion of oxygen along grain boundaries^{48; 82}.

Disadvantages

- Much higher prediction of CGR in region I than observed experimentally⁶⁶.
- No evidence of grain boundary gas bubble formation ahead of the crack tip has been found.
- It is not supported by the results of CERTs at cathodic potentials. According to this mechanism, cracking should only occur on a narrow range of potential near the Ni/NiO equilibrium. It predicts a decrease in the CGR below the corrosion potential, as the oxygen activity decreases strongly, and not an increase as observed by Noel⁴⁸.
- The grain boundary diffusion coefficients of O in Ni (extrapolated to PWR temperatures from high-T data¹¹) are two orders of magnitude lower than those predicted by Scott to support model⁸².

2.3.1.4 Hydrogen-induced cracking model

In this model, as a consequence of corrosion or polarization, atomic hydrogen can be dissolved into the alloy. Experimental evidence in the literature support this model but the embrittling action of hydrogen is not known⁸⁷, although the classical decohesion theory may offer an explanation.

Advantages

- The increase of SCC at cathodic potentials can be related to an active role of hydrogen⁶⁶.
- Alloy 600 is much less susceptible to high temperature water SCC in the absence of hydrogen^{1;6}.
- The protective character of the oxide film cannot be only explained by the oxide properties. A hydrogen related mechanism should operate¹².

Disadvantages

- SCC has been found independent of the hydrogen fugacity and the hydrogen permeation rate by Andresen³.
- Hydrogen embrittlement of Alloy 600 has been demonstrated at low temperatures but never at 360°C⁶⁹.
- Failure to explain why SCC gets worse with increasing temperature⁷².

2.3.1.5 Cavity formation model of Bricknell and Woodford

Although this model was proposed to explain the high temperature oxidation of Ni (at temperatures of ~1000°C), it is interesting to mention, as it focused its attention to the existence of grain boundary voids in metals after oxidation¹¹. Three possible explanations are suggested to explain this:

- The outward diffusion of cations which form the outer Ni-rich oxide layer must be counterbalanced by an inward flux of metal vacancies. These vacancies would migrate to the grain boundaries and precipitate there as voids.
- Due to internal oxidation of carbon segregated to grain boundaries, CO or CO₂ bubbles are produced, although little evidence of these exists.
- The oxide growth stresses due to volume change between metal and oxide cause deformation of the underlying metal and voids grow by the Hull-Rimmer mechanism of creep cavitation³⁴.

As cavitation in Ni under conditions where no external oxide was formed was observed, the mechanism involving internal gas formation by the diffusion of oxygen down grain boundaries was supported. It was also observed that a reduction in the carbon level in the Ni alloy reduced or eliminated the cavitation.

This model cannot directly explain SCC in Alloy 600 at PWR primary water temperature, as no big cavities have been observed, but could contribute to clarify the origin of the nanopores^{85; 39}.

2.3.1.6 Recently proposed models

-Magnin proposed in 1996 the **Corrosion Enhanced Plasticity Model**^{41; 42}, which was subsequently reviewed by Chateau in 2002^{13; 14}. This model tried to explain some zigzag-type intragranular micro-fracture along alternating {111} slip planes. It is based on a localized softening effect at the extreme tip of crack, due to corrosion. In this model, fracture occurs because of the enhanced plasticity along one slip-plane, inducing the formation of a pile-up and a local decrease of the cohesion energy due to the presence of hydrogen. It was also found that hydrogen effects are only possible when critical surface defects are formed, either by localized dissolution (pits, localized dissolution in slips bands, etc) or mechanically (microcracks during fatigue). If such formation of defects is delayed, SCC resistance can be improved. This model was developed for austenitic steel monocrystals in Cl⁻ solutions, so its application to Alloy 600 is not obvious. This model specifically includes the effects of dissolution and hydrogen interaction and is compatible with the effect of cathodic potentials, but these effects are not explained.

- Lagerström et al.³⁷ proposed a **model for environmentally assisted cracking of Alloy 600** in PWR primary water based on an assumption that the crack tip environment consist of steam+hydrogen bubbles. The CGR would be dependent then on the H diffusion into the material ahead of the crack tip along the grain boundary. According to the model, the most important factor governing the incorporation of H is whether a gas phase has developed along the crack front or not. A high hydrogen partial pressure may increase the adsorption of hydrogen and decrease the oxidation of the crack surface. Once the H has diffused into the metal, it could react with C and form CH₄, resulting in cracking, as suggested by Shen and Shewmon⁷⁶. Again, the main problem is that the predicted bubbles have not been observed convincingly.

2.4 Summary

Any successful model of IGSCC in Alloy 600 must predict the following experimental features of primary water IGSCC of Alloy 600⁷¹:

- Initiation times in PWR plants of up to 25 years.
- Huge heat to heat variability in service, with factors of 50 between the best and the worst heats
- Influence of hydrogen partial pressure (or corrosion potential) and observation of a worst case centred on corrosion potentials near the nickel-nickel oxide (Ni/NiO) equilibrium. Hydrogen is added to the primary coolant to eliminate any net water radiolysis and, as a consequence, the electrochemical corrosion potential is close to the Ni/NiO equilibrium⁷⁴.
- Apparently continuous mechanism of failure between 300°C subcooled water and 400°C superheated steam
- High and variable activation energy typically 180 kJ/mole but with a scatter band of 80 kJ/mole to 220 kJ/mole, suggesting solid state diffusion.
- Influence of carbon content and microstructure, particularly the favourable influence of grain boundary carbides and undesirable effect of cold work.
- High-stress exponent of ~ 4 for lifetime-to-failure, which seems to be similar to that found for dislocation creep.

The dependence of IGSCC of Alloy 600 on the redox potential (hydrogen partial pressure) and the higher susceptibility occurring around the NiO/Ni equilibrium suggest that oxygen might be playing an important role, as at these potentials the protective oxide film is specially weak, permitting the diffusion of oxygen along the boundary.

A hydrogen embrittlement model seems to be unlikely as there are some observations that cannot be satisfactorily explained: Grain boundary carbides enhance IGSCC resistance in primary water when the opposite is expected according to a hydrogen embrittlement model. Besides, the expected hydrogen fugacities reported by some authors imply transient cathodic potentials and current densities during crack advance that are considered by others as physically impossible to sustain ⁴⁶.

The latest TEM observations of SC cracks ^{86; 85; 38; 21; 39} indicate the presence of Cr-oxides at the crack tip and beyond, along the attacked grain boundary. These observations are difficult to reconcile to a slip-dissolution model, that predicts the contact of the bare metal with the environment after the rupture.

Thus, an oxidation-embrittlement mechanism seems to be “a priori” the most plausible to give an explanation to all the observed experimental features.

However, it is very important to separate the early stages of growth (nucleation/initiation) from the macroscopic crack growth (da/dt). It has been shown that many parameters could play an important role in the initiation but not in the macroscopic growth or vice versa. Cracks remain in the initiation region for most of their “lives”. The microstructure in the sample will affect short cracks ($< 20 \mu\text{m}$) and long cracks in a very different way. Kamaya showed that crack growth prediction for short cracks should be studied separately, including parameters such as grain boundary orientation with respect to the loading direction and crack kinking ³⁵. The role of the impurities, inclusions and intergranular precipitates could be more important on short cracks for which the stress intensity factor is very sensitive to the parameters mentioned before: grain boundary orientation and crack kink, being up to 3 times smaller at the earlier stages than that predicted macroscopically. This could

explain the long initiation times observed. If not separated carefully, the experimentally calculated da/dt will have contributions from both the initiation and the macroscopic growth phases. This fact must be taken into account in any realistic attempt to predict the crack growth. Observations such as the large heat to heat variability remain a big problem. It might be due to the presence of elements such as B or N that are sometimes overlooked in analysis and that might precipitate at boundaries. The variability of the microstructure found by the crack in the initiation stage (advancing along the first 2 or 3 grain boundaries) might also be an important factor for the initiation mechanism that transfers into one or two dominant cracks.

All the cracks in Alloy 600 studied for this project can be considered “short” cracks, as they were shorter than 20 μm . None of them propagated beyond a 3rd triple point and the grain boundary orientation and intergranular precipitates were found to play a crucial role, as will be shown in Chapters 8 and 9.

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Chapter 3:

Experimental techniques

3.1. Introduction

This project has required a wide range of techniques to be developed, from sample preparation to analytical techniques. The goal has always been to characterize the crack and crack tip microstructure and composition. The starting point was always a bulk piece of material with dimensions of millimetres to generally end with an electron transparent area with a thickness smaller than 100 nm and an area of microns in both lateral dimensions in which the crack is contained.

3.2. TEM Sample preparation

3.2.1 Electropolishing

Electropolishing has been used when the position of the electron transparent area was not crucial, e.g. to characterize the microstructure of the matrix. The samples were thinned in a Struers Tenupol. The control unit was a model 5 and the polishing unit a model 3. The operation is very simple. The specimen is placed between two immersed jets, while a pump sends a flow of electrolyte through the jets against the specimen. An electric circuit is established with a DC-power supply, with a platinum cathode placed in the electrolyte and the specimen acting as the anode. When the electric circuit is closed, material will be removed electrolytically from the specimen. The result is the formation of a small hole in the middle of the specimen if the parameters have been adjusted properly. The edge of the specimen should be as thin and wide as possible, in order to allow further structural examinations. The Tenupol 3 is equipped with an infrared detector system, which automatically cuts off the process when the hole appears²⁰.

The polishing conditions should be optimised in order to obtain high quality samples. The parameters that we control are:

-the type of electrolyte: For Alloy 600 and Stainless steels, a 5% Perchloric-95% Methanol solution was used. The solution should not be used more than a few times. Normally, the best indicator is the colour: when it turns too yellow, it means that a new solution has to be prepared.

-the flow rate of the electrolyte: The flow rate determines first of all whether a viscous anodic layer can be maintained during polishing. Jet polishing tends to remove the layer. The proper choice of flow rate is therefore mostly determined by the material to be polished and by the electrolyte. The best flow rate differs much from case to case and it is not possible to give general rules. A flow intense enough to keep both jets almost horizontal and hitting the centre of the specimen was found to be optimum.

-the temperature: In some cases a lower temperature will give better results. A lower temperature slows down the polishing and provides less etching and oxidation. For Alloy 600, the optimum temperature was found to be around -40°C . The temperature in the solution bath was controlled by addition of liquid nitrogen and monitored with a digital thermometer part of the Tenupol 5 system.

-the electrical conditions: The electrical conditions determined whether acceptable polishing was obtained. The right conditions will only be present within a certain range of current densities. If a current versus voltage curve is drawn the best polishing conditions will be found where the current is approximately constant within a range of voltages. With the Tenupol 5 control unit, this curve is plotted automatically, so the determination of the “plateau” is trivial. For the 304SS samples, a voltage of 50V was used, giving a current of 260 mA for a 3 mm diameter disc. For the Alloy 600, the voltage used was 22V, giving a current of 110 mA.

-the composition of the sample: The thinning rate depends on the sample composition. The alloys used for this project contained chromium carbides which have a better corrosion resistance than the matrix, so they generally remain thicker in the transparent regions. However, these carbides were relatively common, and usually several per sample had the right thickness to be characterized.

3.2.2 Ion beam thinning

Ion milling involves bombarding a thin TEM specimen with energetic ions or neutral atoms and sputtering material from the film until it is thin enough to be studied

in the TEM. A schematic diagram is shown in Figure 10.8. The variables which can be controlled include the voltage, the nature of the ion, and the geometry (the angle of incidence).

An accelerating voltage of 4-6 keV is usually used. The ion beam will always penetrate the specimen to some extent, so this was minimized by inclining the incident ion beam²⁸.

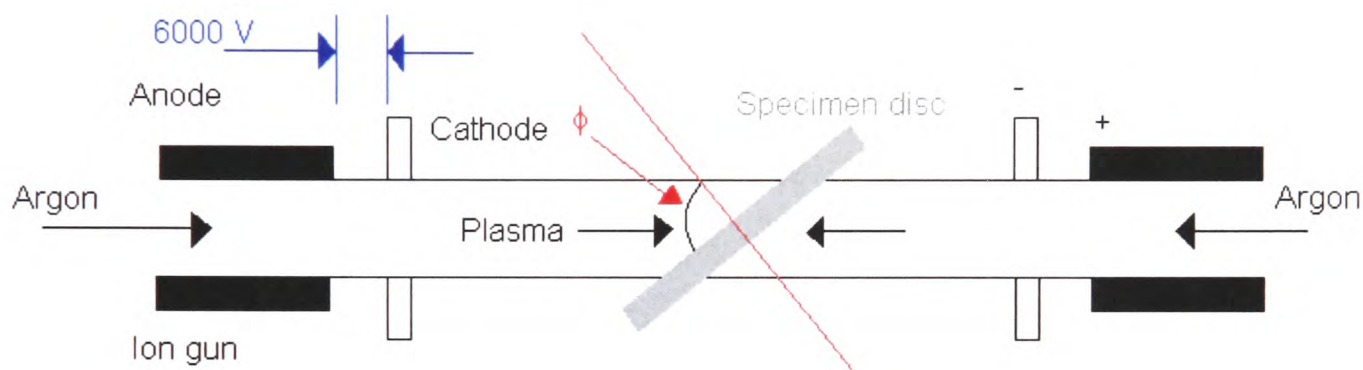


Fig. 3.1. Schematic diagram of an ion-beam thinning device: Ar gas bleeds into an ionization chamber where a potential up to 6 keV creates a beam of Ar ions that impinge on a rotating specimen.

Initial thinning is done at 25° incidence. However, the best specimens are obtained from a traditional ion beam thinner when the final stage of thinning is done at an angle of incidence of ~5° and at the lower end of the energy range (Fig. 3.1). This minimises the depth of the ion induced damage, the topography induced and the differential thinning caused by different sputtering rates.

A significant advance came with the development of systems capable of thinning at very low angles of incidence following the work of Barna and Alani & Swann². This type of equipment is now available commercially (E.g. Gatan PIPS). The high efficiency ion guns mean that the thinning rate is fast even at the low angles of incidence.

With all ion beam systems there is a problem of re-deposition which means that either both sides have to be thinned simultaneously, or the side that is not being thinned has to be covered by a protective layer.

The ion beam miller used was a Gatan 691 Precision Ion Polishing System (PIPSTM). Several reasons recommended the use of a PIPS over a conventional Ion Beam Miller ¹¹:

- The PIPS has two independent guns which have the ability to accurately centre the beam onto the specimen at any angle within $\pm 10^\circ$.
- Specimen contamination is minimized because of the special ion optics of the gun, oil-free vacuum system and the Gatan DuoPost specimen holder.

Although not a crucial advantage, the milling rate of the PIPS can be up to 20 times higher than in conventional ion beam miller. A typical value is 14 $\mu\text{m/hr}$ / gun pair at 4° using 2 ion guns operating at 5.0 keV with a gun current of 25 μA , and specimen rotation off. However, unless the sample is rotated, significant topography builds up along certain crystallographic directions ⁵, so realistic thinning rates are then reduced to a few $\mu\text{m/hr}$.

Disadvantages:

- Previous grinding and cutting of the sample can introduce undesired artefacts.
- Beam induced oxides, as reported by Thomas ²¹.
- Formation of grooved sample along cracks during low angle (4° to 6°) ion milling ²¹.
- Sputtering of material inside the cracks and redeposition on the surface of the sample.
- Removal of crack oxides due to preferential milling of soft materials.
- Difficulty to correlate the position of the observed crack to the macroscopic orientation of the sample, as well as the path followed by the observed crack through the grain boundaries.
- When thinning quickly it is easier to remove completely features of interest.

3.2.3 FIB

With the advent of bright liquid Ga ion sources, it is possible to generate an image with a resolution of ~ 10 nm using ions with an energy ~ 30 keV. An instrument called a Focussed Ion Beam (FIB) system that has functions very similar to those of an SEM is used. Such a system can be used to prepare TEM specimens in many different ways^{12; 15; 14}. FIB systems can be used for the preparation of Transmission Electron Microscopy cross-section specimens of a wide range of materials. A major potential advantage of using a FIB system over established preparation techniques such as broad ion beam milling (BIB), including PIPS, is that a specimen can be prepared to within 50 nm of a specific point. This capability makes FIB an ideal tool for the preparation of TEM specimens through cracks in metal alloys such as steels. However, such use of FIB is not well documented. In the sample preparation section, some novel techniques will be described, that have been developed during the course of this project.

The FIB used for this research is a FEI 200, which can be used for site-specific ion milling, ion implantation and ion lithography. This instrument also has some extra facilities available including in-situ deposition of platinum.

It can operate within an ion accelerating range of 5-30 keV and the current of the beam can be set within the range 10-20000 nA.

The advantages and disadvantages of this instrument will be widely discussed in Chapter 4, although it is important to mention that when using old carbon grids an extra disadvantage arises. If the carbon grid is too old or it is not stored in a dry atmosphere, it will oxidize and special attention has to be paid when studying the composition of the sample, as oxygen could appear as an artefact. Some carbon grids also showed a high silicon content. The way of overcoming this problem was ensuring that the position of the holey grid was previously known. When the TEM sample was too thick to let us see the carbon grid over the sample, the BS detector located over the specimen in the CM20 was used to clearly identify the location of the carbon. Before, the grid had to be loaded so that the carbon was between the detector and the FIB sample.

3.3. Sample examination

The sample examination techniques used in this project are divided into four categories: Optical microscopy, SEM, TEM and STEM.

3.3.1 Optical microscopy

An Olympus BX60M optical microscope was used to examine optically the surface of the sample and determine the grain size as well as the lengths of the cracks at a first approach. It was also particularly useful to determine the degree of the attack (Fig. 3.2), as some samples did not show any SCC at all. When the original surface of the sample did not contain any visible cracks, cross-sections were examined. The magnification was calibrated using a magnification standard graticule.

The relatively poor quality of plan-view surface optical micrographs was due to the surface corrosion and earlier surface polishing.

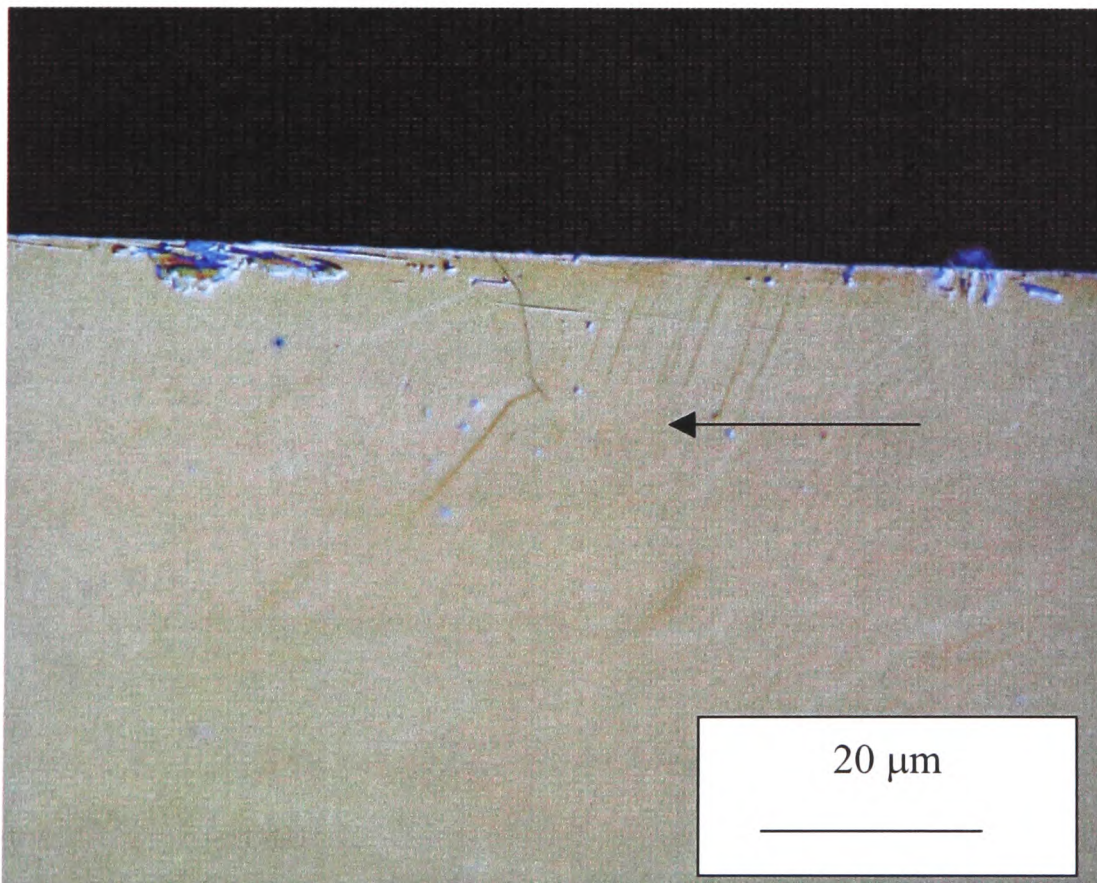


Fig. 3.2. Cross-section optical micrograph of an etched Alloy 600 sample showing intergranular cracking.

3.3.2 SEM

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope.

The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. When the electron beam hits the sample, electrons and x-rays can be emitted, as can be seen in Fig. 3.3.

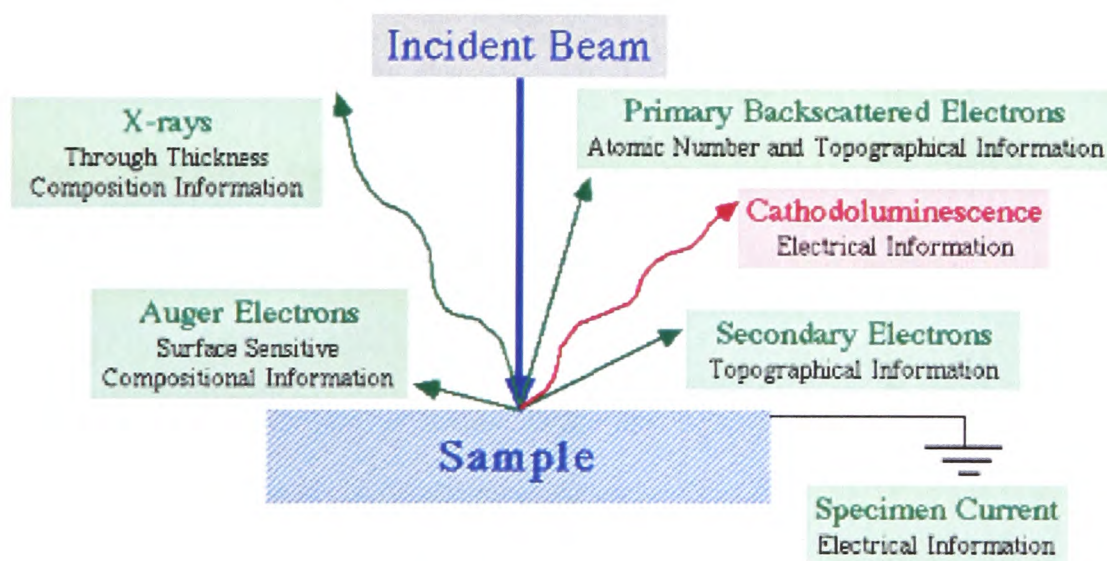


Fig. 3.3 Diagram showing all the signals generated by the incident beam in the SEM.

While all these signals are present in the SEM, not all of them are detected and used for information. The signals most commonly used in this project were the Secondary Electrons (SE) and the Backscattered Electrons (BSE). x-rays were only used to characterize some inclusions revealed after x-sectioning and polishing. These inclusions were found frequently on the surface and had the same nature as those mentioned in the Chapter 8.

3.3.2.1 Secondary electrons (SE)

Secondary electrons are specimen electrons that obtain energy by inelastic collisions with beam electrons. They are defined as electrons emitted from the specimen with energy less than 50 eV. Secondary electrons (SE) are predominantly produced by the interactions between energetic beam electrons and weakly bonded conduction-band electrons in metals or the valence electrons of insulators and semiconductors. SE and BSE give different types of signal. SE yields are usually much higher than BSE. SE are used to reveal the topography of the sample and their images have better signal to noise ratio. BSE give information dependent on atomic number and are useful for chemical and phase contrast and crystallographic contrast (EBSD). An electron detector is used with the SEM to convert the radiation of interest into an electrical signal for manipulation and display by signal processing electronics. SE have been used for high-quality imaging, as the efficiency of SE is much higher than those of BSE.

In Fig. 3.4, a typical SE image of an stress corrosion crack in Alloy 600 can be observed.

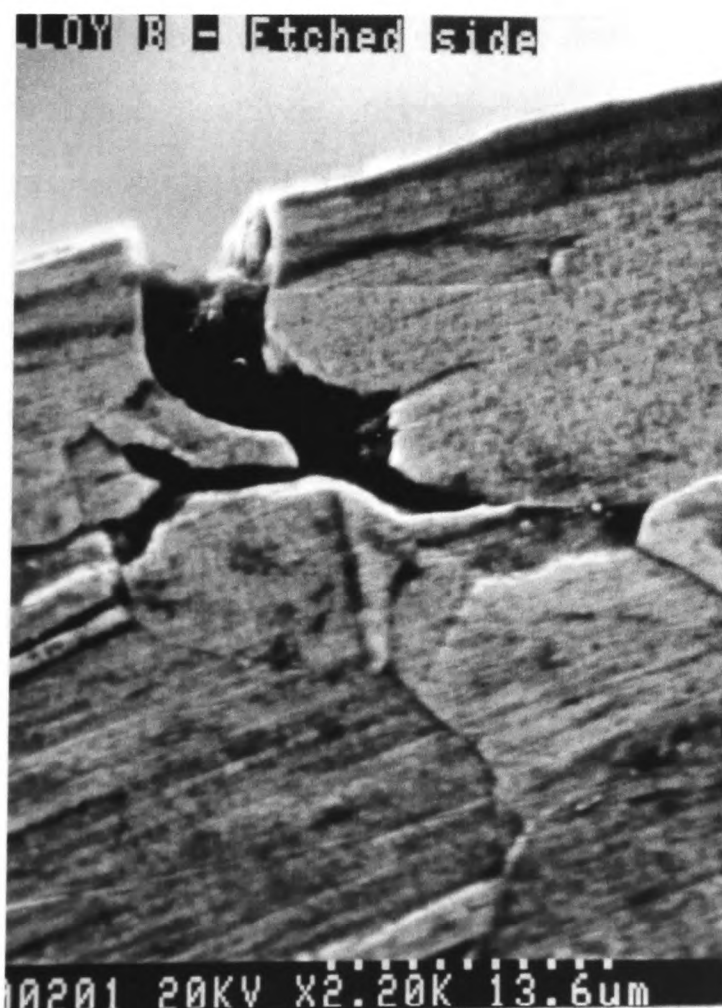


Fig. 3.4. SEM SE micrograph of a stress corrosion crack in Alloy 600 (acquired with the Hitachi S520).

3.3.2.2 Backscattered electrons (BSE)

The incident electrons that are sent into the sample are scattered in different ways. There are two broad categories to describe electron scattering, namely, elastic and inelastic.

-Elastic Scattering of Primary Electrons: As the name implies, elastic scattering results in little ($<1\text{ eV}$) or no change in energy of the scattered electron, although there is a change in momentum. Since momentum, $p=mv$, and m does not change, the direction of the velocity vector must change. The angle of scattering can range from 0-180 degrees, with a typical value being about 5 degrees. Elastic scattering occurs between the negative electron and the positive nucleus. This is essentially Rutherford scattering. Sometimes the angle is such that the electron comes back out of the sample, i.e. scattering angle $> 90^\circ$. These are backscattered electrons.

-Inelastic Scattering: During inelastic scattering, energy is transferred to the electrons surrounding the atoms and the kinetic energy of the energetic electron involved decreases. A single inelastic event can transfer a various amount of energy from the beam electron ranging from a fraction to many kiloelectron volts. The main processes include phonon excitation, plasmon excitation, secondary electron excitation, continuum x-ray generation, and ionization of inner shells. In all processes of inelastic scattering, energy is lost, though different processes lose energy at varying rates.

In Fig. 3.5, a typical BSE image acquired from a polished x-sectional surface in Alloy 600 can be observed. This image was acquired to reveal the grain structure of the sample without etching.



Fig. 3.5. SEM BS picture of a polished x-section of Alloy 600 (acquired in the JSM 6300 in Topo mode).

3.3.2.3 EBSD

The collection of an electron backscatter diffraction pattern (EBSP) in the SEM has become a standard process due to the use of computer-controlled systems. A polished sample must be tilted to a relatively high angle (typically 70°) inside the SEM. The electron beam is then stopped at the point of interest on the sample surface: initial elastic scattering of the incident beam causes the electrons to diverge from a point just below the sample surface and to impinge upon crystal planes in all directions. Wherever the Bragg condition for diffraction is satisfied by a family of atomic lattice planes in the crystal, 2 cones of diffracted electrons are produced. These cones are produced for each family of lattice planes (Fig. 3.6).

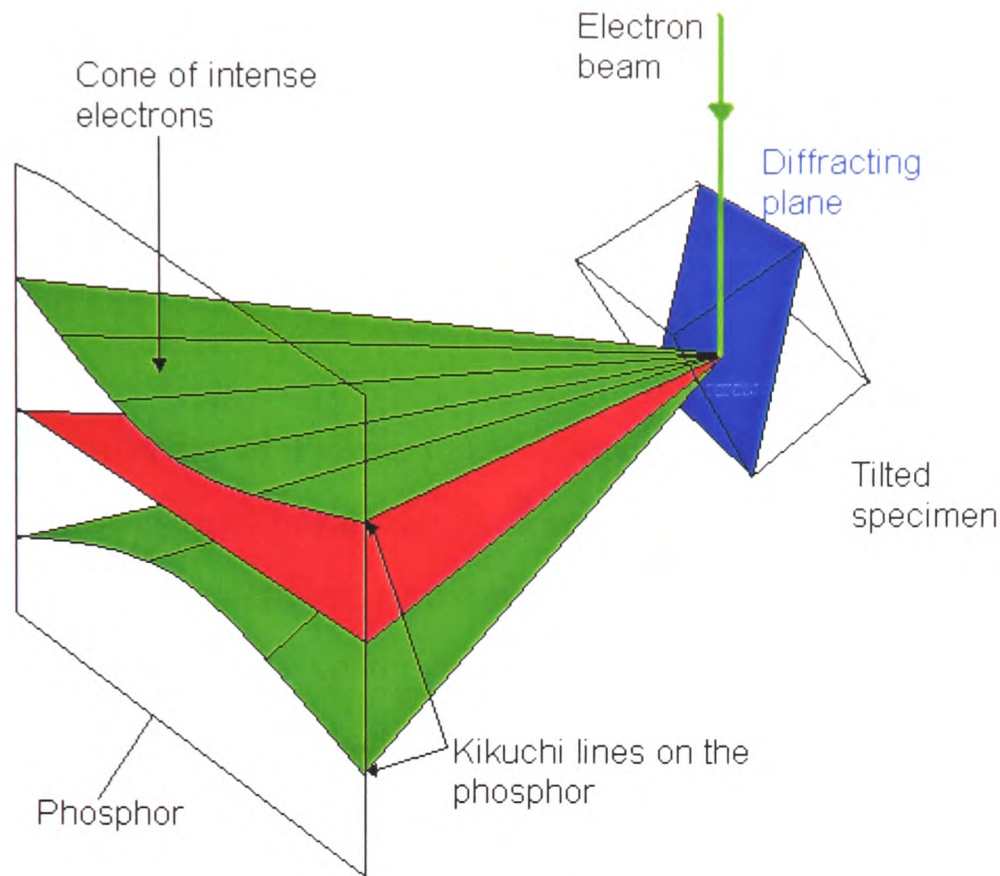


Fig. 3.6. Geometry of the EBSD electron generation.

These cones of electrons can be imaged using a phosphor screen attached to a sensitive camera. The camera is usually positioned horizontally, so that the phosphor screen is close to the sample in order to capture a wide angle of the diffraction patterns. Where the cones of electrons intersect with the phosphor screen, they appear as thin bands. These are called "Kikuchi bands", and each one corresponds to a family of crystal lattice planes. The resulting EBSP is made up of many Kikuchi bands (as observed in Fig. 7) ^{18; 19; 3; 6; 24; 25; 16}.

EBSD software (Oxford Instruments Opal, replaced by Oxford Instruments INCA Crystal in May 2002) automatically locates the positions of individual Kikuchi bands, compares these to theoretical data about the relevant phase and automatically calculates the 3-D crystallographic orientation ⁷.

This method has been used for the determination of grain misorientation measurements reported in chapter 6, as can be seen in Fig. 3.8.

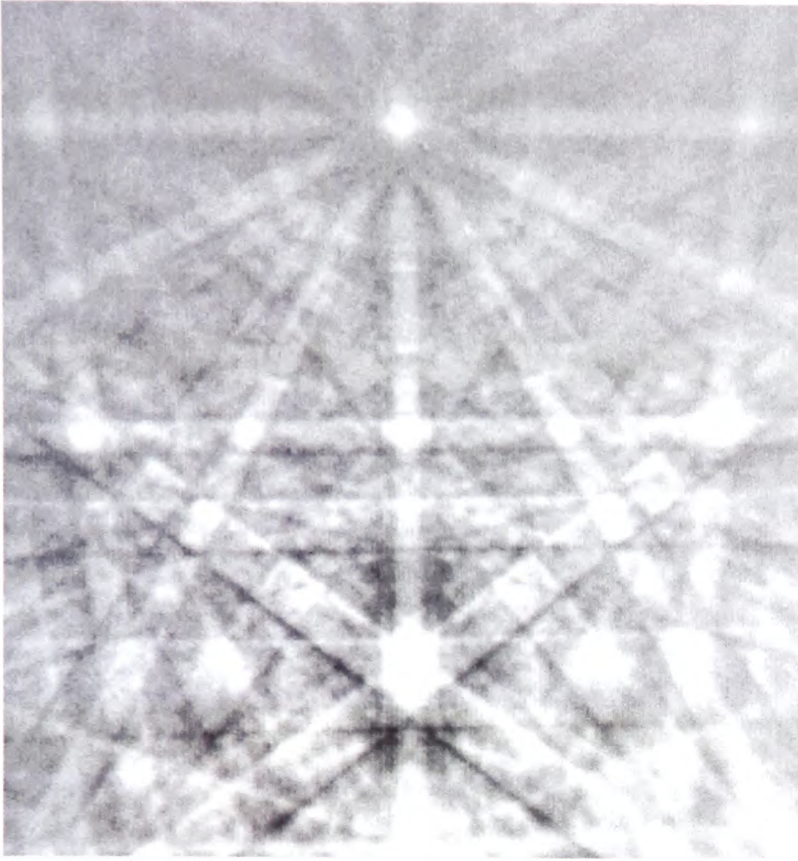


Fig. 3.7. EBSD pattern of fcc Alloy 600.

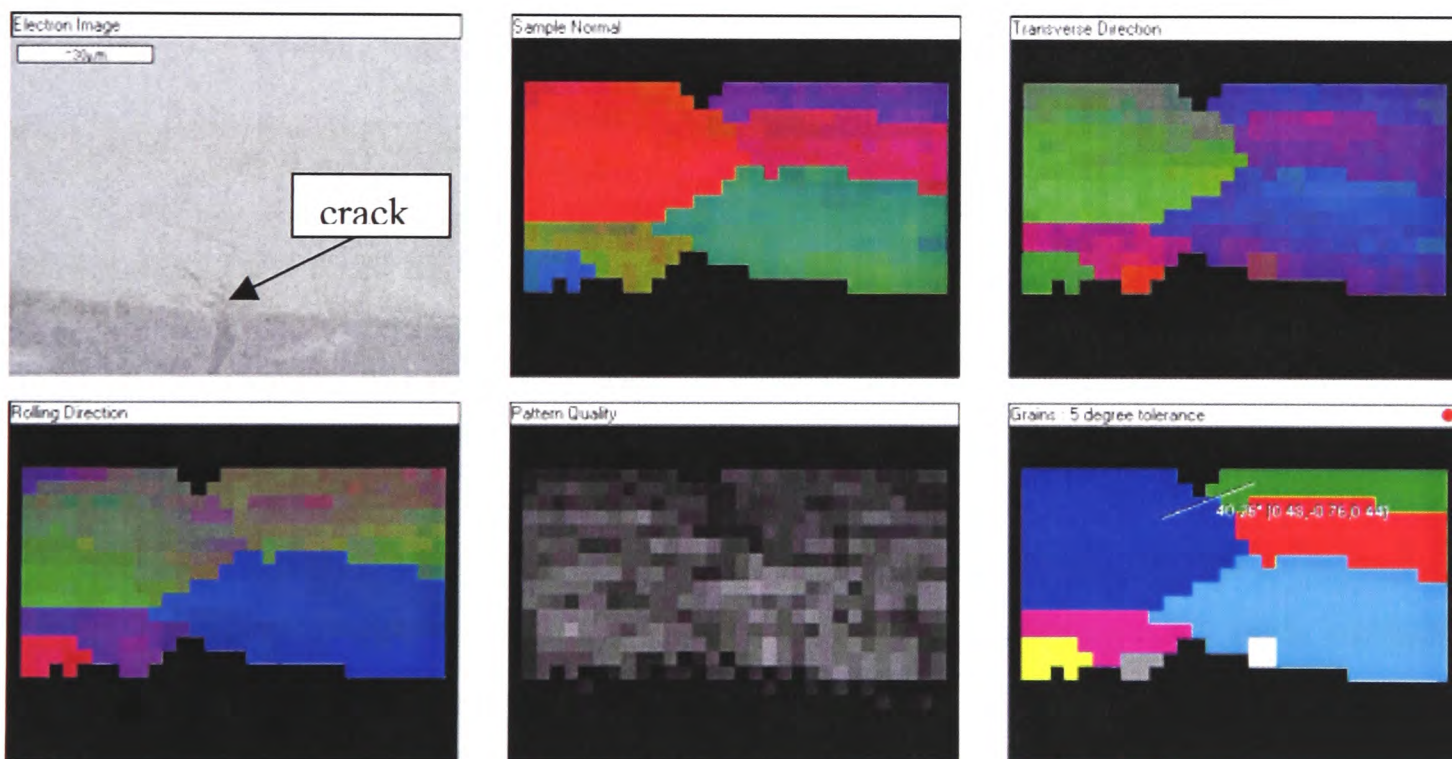


Fig. 3.8. EBSD mapping on a 304SS sample showing different grain orientations (acquired with the OPAL system in the J6300).

The grain orientations are shown through 3 different axis:

- Sample normal: Normal to the surface of the sample
- Transverse direction: Parallel to the edge of the sample
- Rolling direction: Normal to the surface below the edge

The colour code used to show the orientations is shown in Fig. 3.9.

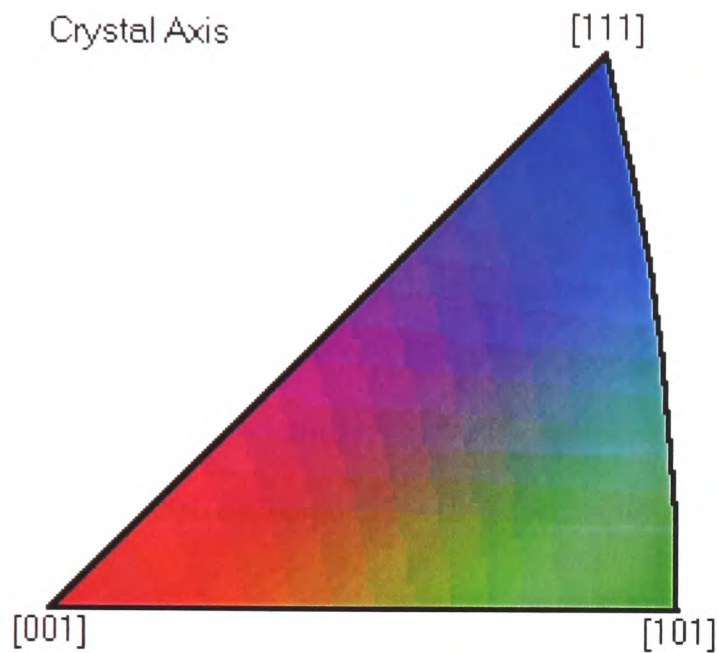


Fig. 3.9. Colour coding for understanding EBSD data presented in this work.

All the samples analysed had a fcc structure.

3.3.2.4 Jeol JSM 6300 SEM

For this research, a Jeol JSM 6300 SEM has been mainly used.

The Jeol JSM 6300 has a LaB_6 electron gun and operates between 30 and 1.0 kV.

Using secondary electron imaging, the best resolution attainable on high contrast samples (Au on C) is ~6 nm at 30 kV.

The following facilities on this instrument have been used :

- Conventional secondary electron imaging of surface topography.
- Back scattered electron imaging with annular detector, for compositional contrast and channelling contrast imaging.
- Digital image capture to PC via Oxford Instrument's INCA system.

- Automated electron back scatter diffraction (EBSD) analysis for crystal orientation measurement and phase identification with Oxford Instrument's OPAL system (replaced by Oxford Instruments INCA Crystal in May 2002).
- EDX spectroscopy via Oxford Instrument's INCA

The BSE detector in this microscope operates in 2 modes: "Topo" (topographical) and "Compo" (compositional). In "Topo" mode, only one quadrant of the detector is active, so the image detects changes in orientation on the surface, such as grain structure. In "Compo" mode the signals from the 4 quadrants of the detector are combined to minimise topographic information and maximize variations in Z on the surface of the sample. However, any asymmetric information (such as crystalline) is lost.

3.3.3 TEM

In transmission electron microscopy (TEM), a beam of highly focused electrons are directed toward a thinned sample (<200 nm). These highly energetic incident electrons interact with the atoms in the sample producing characteristic radiation and particles providing information for materials characterization. Information is obtained from both deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons. The following TEM imaging and diffraction techniques were used during this project:

3.3.3.1 BF/DF

In order to obtain good images in TEM we need a good contrast. Contrast in TEM might come from differences in Z, in thickness or in electron scattering in the sample. By separating the diffracted from the direct beam, information on the crystallographic structure can be acquired. Either the direct beam or some of the diffracted beams in the SAD pattern can be selected to form a Bright Field (BF) image or a Dark Field (DF) image, respectively (Fig. 3.9). BF/DF selection applies to "diffraction contrast imaging" methods and are very useful for revealing grain boundaries, second phases, dislocations, voids, etc.

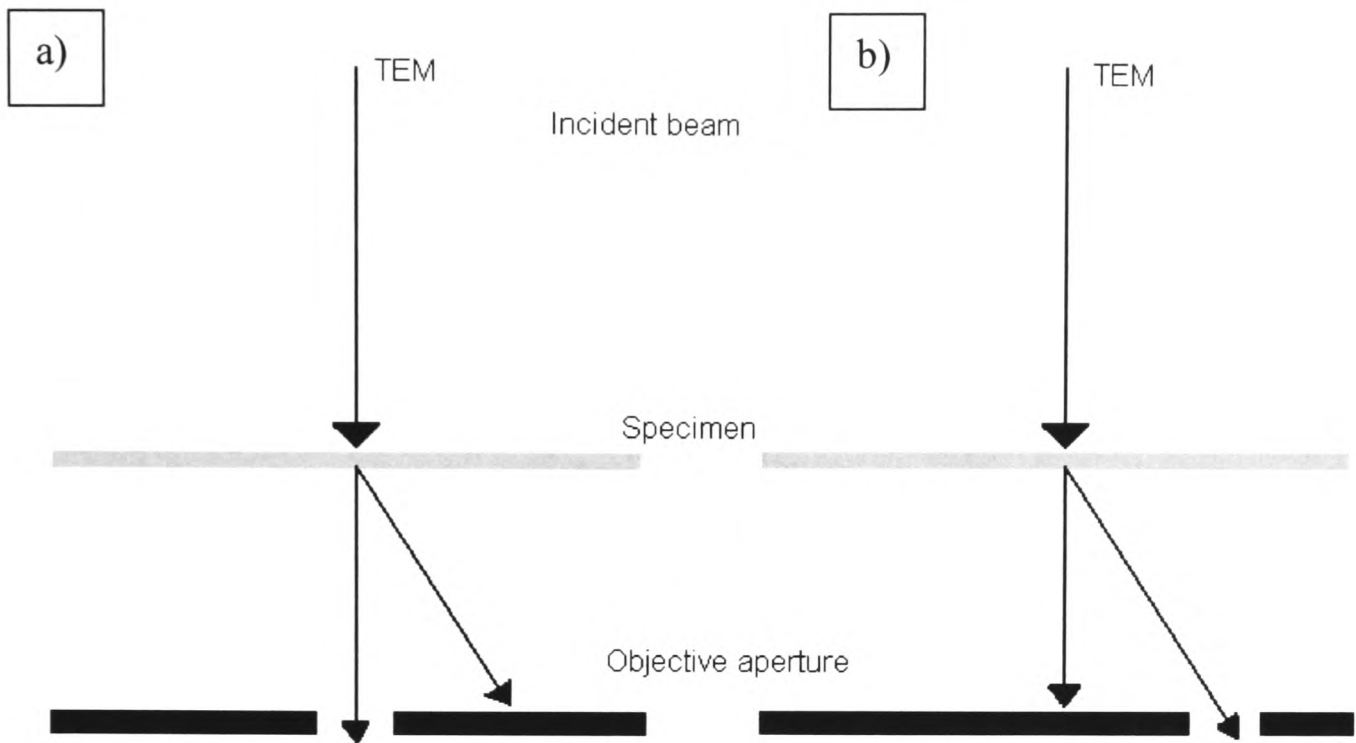


Fig. 3.9. Comparison of the use of an objective aperture to select (a) the direct or (b) the scattered electrons forming BF and DF images.

In Figs 3.10a and 3.10b, the same area of the sample is shown in BF (Fig. 3.10a) and DF (Fig. 3.10b), with the grain on the left in a zone axis orientation (appears dark in BF and bright in DF).

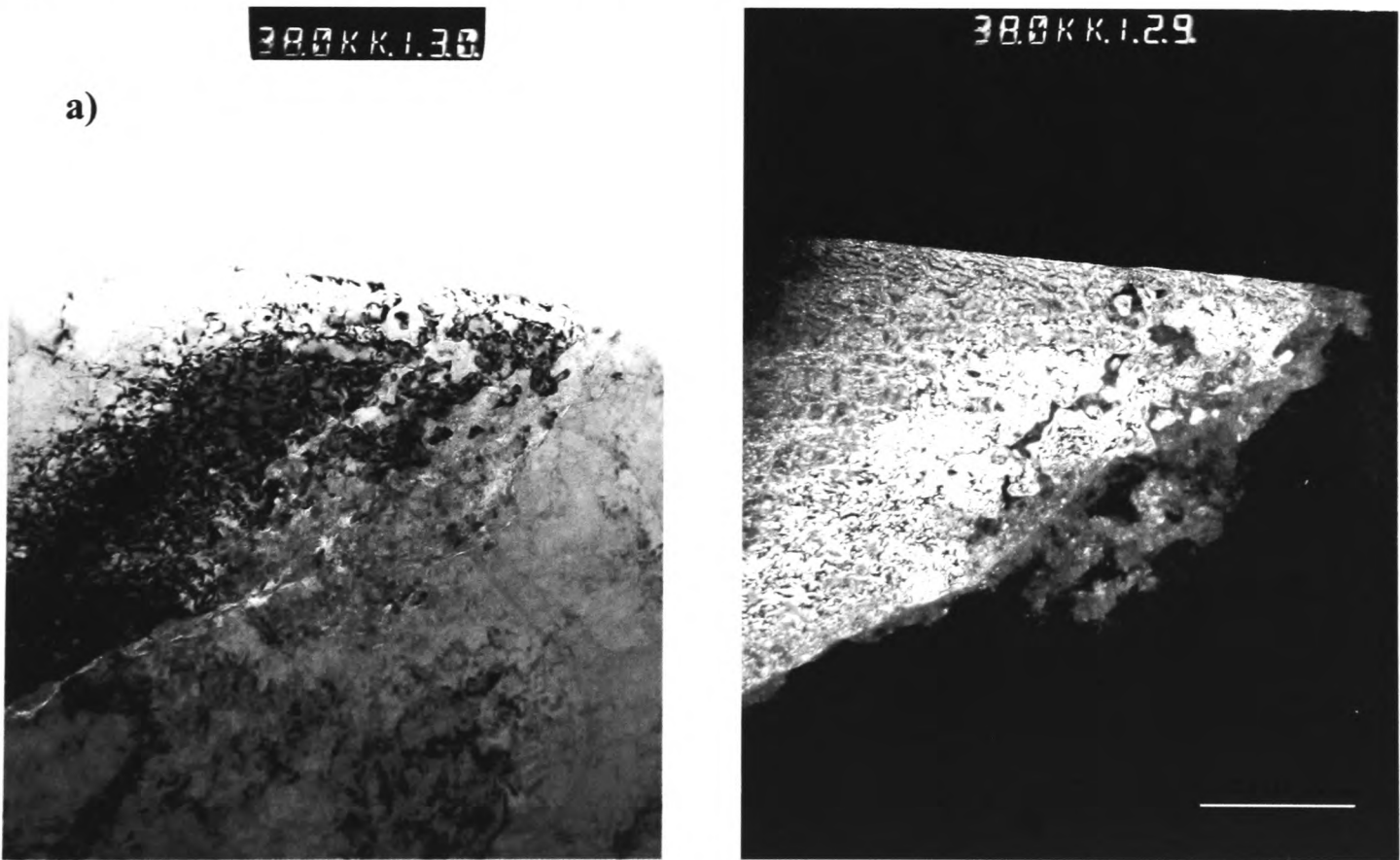


Fig. 3.10. BF (a) and DF (b) of the same region of the sample. The grain on the left is in zone axis and the grain boundary is attacked with some oxide formation (acquired with the CM20).

3.3.3.2 Selected area diffraction (SAD)

When a diffraction pattern is formed, it contains information from the area of the specimen that is illuminated with the beam if the beam is defocussed. The specimen can be buckled, or the feature of interest can be smaller than the illuminated area, and the beam intensity can be too high to record a high resolution, sharply focussed picture, so the intensity has to be reduced and a specific area of the specimen should be chosen. There are two ways of reducing the illuminated area of the specimen contributing to the diffraction pattern (DP): one is making the beam smaller and the other implies inserting an aperture below the specimen which will only let pass the electrons coming from the area of interest. The first option involves converging the beam on the specimen and it is called convergent beam electron diffraction (CBED) and the second is called selected area diffraction (SAD).

SAD is the best choice when we want to form BF or DF images, when diffraction spots are very close to one another and would overlap in CBED patterns or when we are looking for fine structure in the DP²⁸.

SAD has been used to characterize the microstructure of the matrix, big particles such as carbides or amorphous/polycrystalline regions .

Two different SADP are shown in Fig. 3.11. In Fig. 3.11a a DP from a monocrystal that consists basically of spots is shown. In Fig. 3.11b, a DP from a nanocrystalline oxide, consisting of rings, is shown.

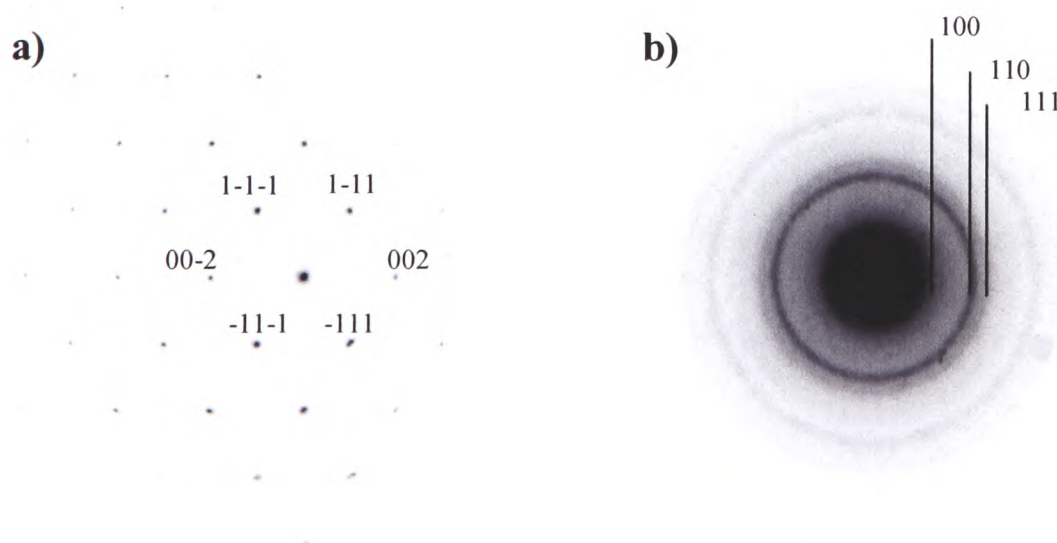


Fig. 3.11. SAD patterns showing a [110] zone axis in Alloy 600 (a) and nanocrystalline NiO (b) (acquired with the CM20).

3.3.3.3 Convergent beam electron diffraction (CBED)

Although SAD can give us very useful information about the specimen, it has some disadvantages. The minimum size of the area selected (using the smallest SA aperture) is about 5 μm , and particles smaller than this cannot be analysed without contributions from neighbouring areas. As the dimensions of most of the corrosion products were usually smaller than 0.5 μm , another diffraction technique had to be used: microdiffraction (μD or Kossel-Möllenstedt diffraction). This last technique is just a special case of CBED, when 2α (with α the semi-angle of the beam convergence) is small (small condenser aperture), and the disks do not overlap on the screen (Fig. 3.12).

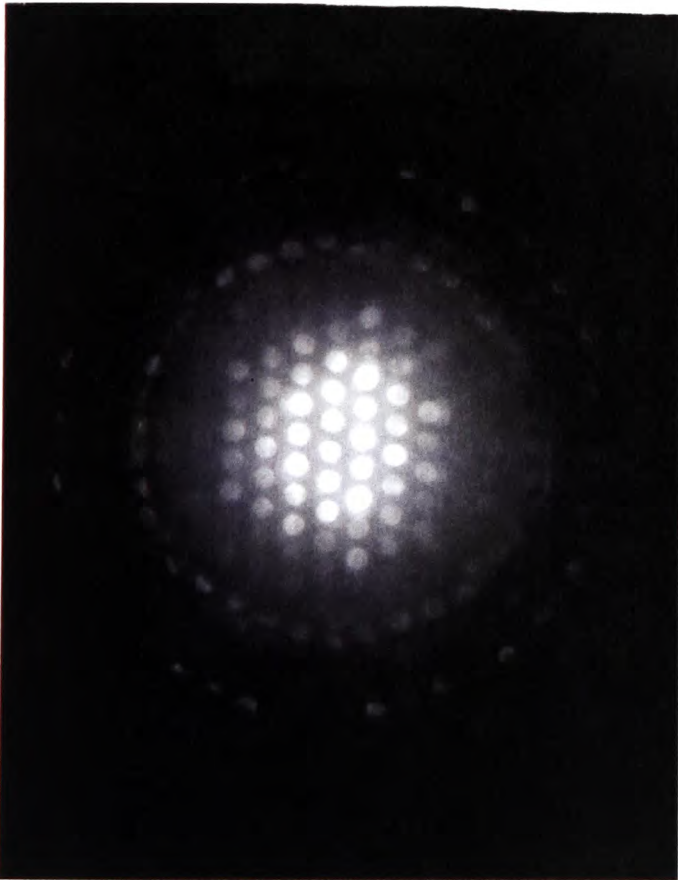


Fig. 3.12. μD pattern of a $[110]$ zone axis in NiFe_2O_4 (acquired with the CM20).

This technique has also been used to measure specimen thickness.

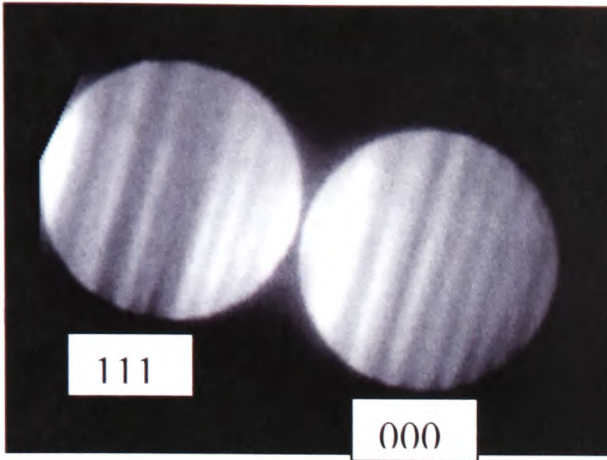


Fig. 13. CBED pattern from a 2 beam condition area close to a $[110]$ zone axis (acquire with the CM20).

The fringe spacing corresponds to angles $\Delta\theta_i$ from Fig. 3.13 are shown in Fig. 3.14.

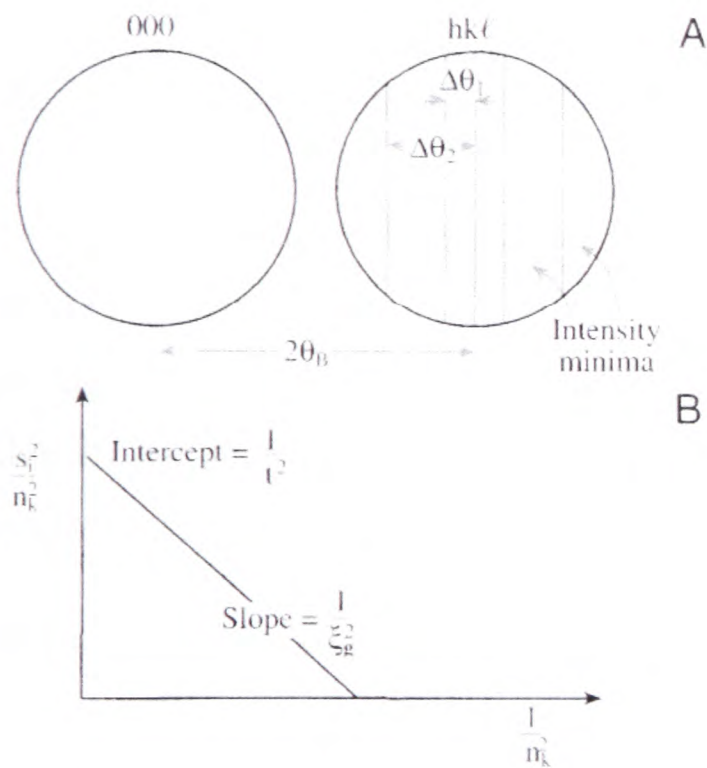


Fig. 3.14. Measurements necessary to extract thickness from the Kossel-Möllenstedt fringes.

and from the spacings, we can get a deviation s_i for the i^{th} fringe from the equation

$$s_i = \lambda \frac{\Delta\theta_i}{2\theta_B d^2} \quad \text{Eq. 3.1}$$

where θ_B is the Bragg angle for the diffracting hkl plane, d is the hkl interplanar spacing. $2\theta_B$ is determined from the separation of the 000 and the hkl disks. For

Alloy 600 $d_{111} = 0.207$ nm and for the sample of the figure, $\Delta\theta_i = 2, 3.5, 5$ and $d = 17$ mm. So, we can determine the foil thickness using the formula:

$$\frac{s_i^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} = \frac{1}{t^2}$$

where n_k is an integer, ξ_g the extinction distance and t the thickness.

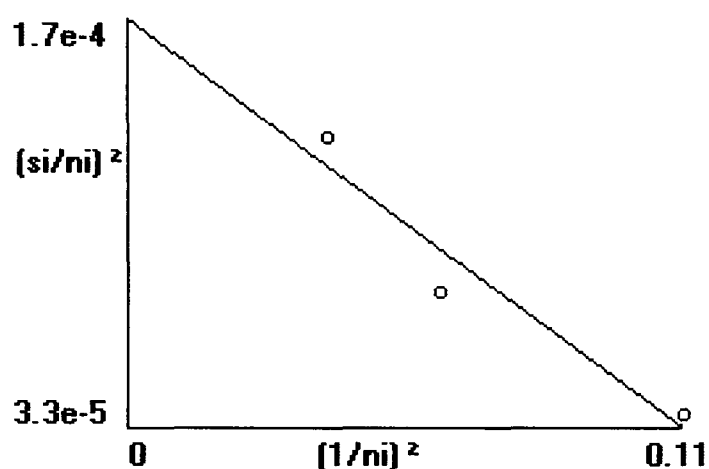


Fig. 3.15. Plot used to calculate the linear regression that better fits the data.

After plotting and calculating the linear regression that fits better with the data (Fig. 15), we get the best value for the correlation coefficient ($R = -0.96$) if we assign the value $n=3$ to the first fringe. Thus, the value for the thickness is 77.1 nm. This value for the thickness is usual for samples prepared with the FIB using the methods described in chapter 4.

3.3.3.4 High resolution electron microscopy (HREM)

Spatial resolution is always important for any electron microscopy work. However, it has to be taken into account that the HRTEM image is an interference pattern between the forward-scattered and diffracted electron waves from the specimen. Interference patterns require close attention to the phases of the waves. In TEM, the ray optics approach is useful for most explanations but the most important issues in HRTEM are best understood in terms of the phase of the electron wavefront and how this phase is altered by the specimen and by the objective lens. The specimen itself is approximated as an object that provides phase shifts to the electron wavefront, sometimes in proportion to its scattering potential. The method of HRTEM also demands close attention to the performance of the objective lens and other

characteristics of the microscope. For HRTEM to provide information on atom arrangements in a material, computer simulations of the image are usually required ¹⁰.

In this project HREM has been used to assess the quality of the samples prepared with FIB. In all samples, the damage layer was found to be smaller than 10 nm, in agreement with the literature ¹³. Fig. 3.16 shows lattice fringes in the nanocrystalline NiO that filled the stress corrosion cracks in the Alloy 600 samples analyzed.

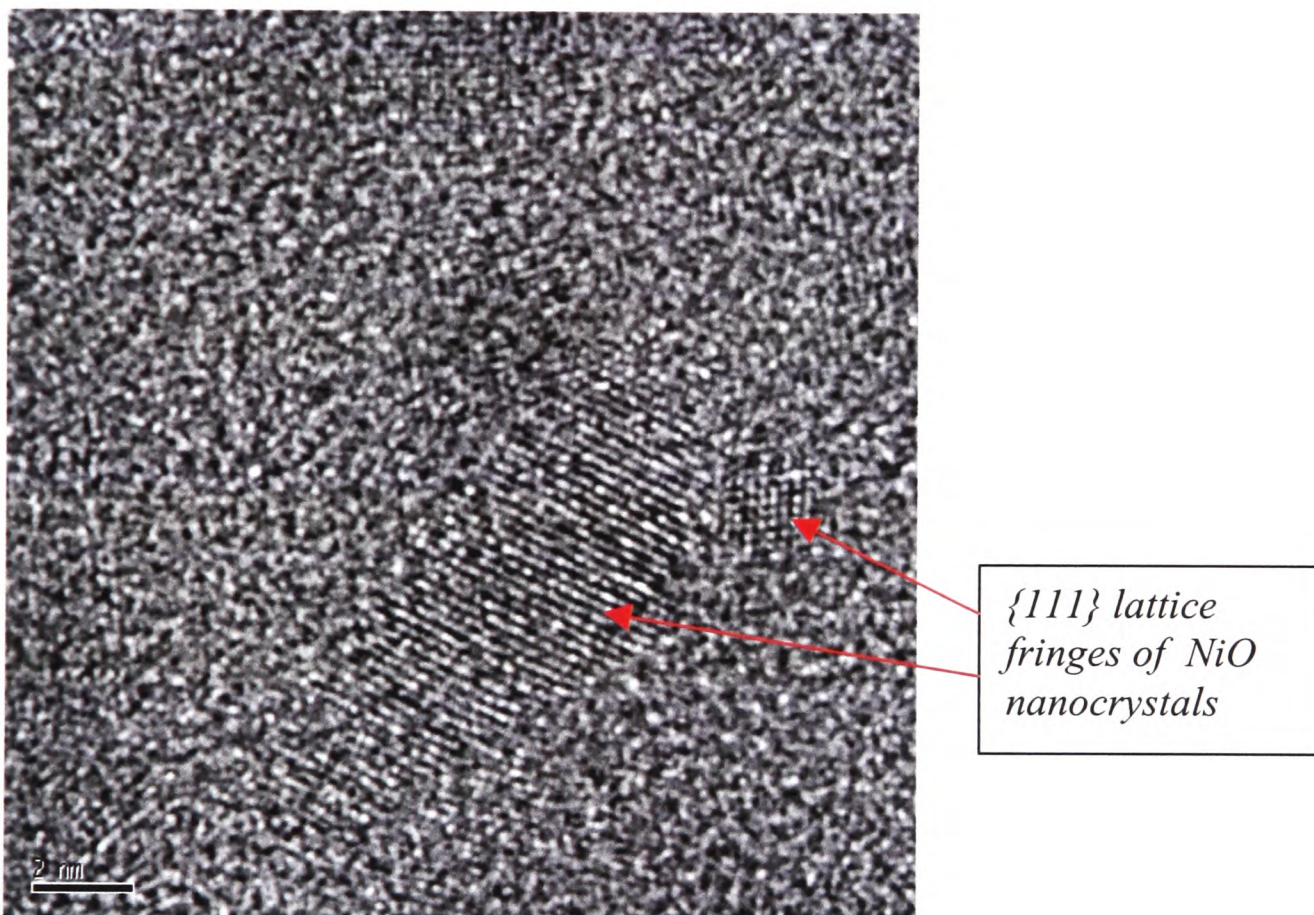


Fig. 3.16. Nanocrystalline NiO inside a crack. The $\{111\}$ lattice planes can be seen in this HR picture (acquired with the 3000F).

3.3.3.5 Instruments

The instruments used during this project were:

3.3.3.5.1 JEOL JEM-3000F FEGTEM

The JEOL 3000F is a field emission gun (FEG) TEM, which operates between 100 and 300kV.

The improved brightness and coherence of the Schottky field emission electron source, over either a LaB_6 or a tungsten thermal emitter, makes this a powerful analytical instrument.

The high-resolution performance (a point resolution of 0.16 nm) is complemented by the ability to perform chemical microanalysis from sub-nanometre areas (below 0.4nm in some cases).

The following facilities available on this instrument have been used:

-Specimen holders:

-Single tilt (± 25 degrees)

-Low background Be double tilt (± 25 degrees)

-A piezoelectric stage that allows fine mechanical movements to be made. The signal from the TV-rate CCD camera can be used to carry out manual or automated specimen drift correction.

-An Oxford Instruments energy dispersive x-ray spectrometer (EDS) with a super atmospheric thin window (SATW) detector allows chemical analysis of elements down to boron under suitable conditions. This detector has an ISIS 300 processor, and the addition of a SemiStem unit allows two-dimensional chemical mapping of 25 nm^2 areas.

-A Gatan imaging filter (GIF) equipped with a 2k 794IF/20 MegaScan CCD camera that allows chemical analysis using electron energy loss spectroscopy (EELS), either by acquiring a full spectrum in parallel (PEELS) or by using part of the spectrum to reform the image of the sample. This technique can be used to select energy losses corresponding to particular chemical elements or states (compositional mapping) or to filter out unwanted inelastically scattered electrons to form higher contrast images or diffraction patterns from thicker samples.

-A 1k Gatan 794 MultiScan (MSC) camera that was installed before the GIF allowed low-magnification imaging and the acquisition of DPs.

3.3.3.5.2 Philips CM20

The Philips CM20 is an analytical TEM, has a LaB₆ electron gun, which can be operated between 20 and 200kV.

It enables convergent beam electron diffraction (CBED), nano-beam diffraction (NDB), high-resolution scanning imaging (3nm) and channelling, x-ray mapping and line-scanning as well as the usual TEM imaging and diffraction facilities.

The following facilities on this instrument have been used for this project:

- A resolution of 0.27nm and an electron probe size down to 1nm (with the objective lens twin pole-piece).
- Secondary electron and backscattered electron detectors, bright field and annular dark field scanning transmission electron detectors, and energy dispersive x-ray spectrometers.
- Specimen holders:
 - Double tilt (± 30 degrees along both axes)
 - Double tilt (± 30 degrees along both axes), low x-ray background (Be)
- An Oxford Instruments thin window energy dispersive x-ray spectrometers (EDS), controlled via Oxford Instruments' INCA software.

3.3.4 STEM

The techniques used in STEM during this project were:

3.3.4.1 BF/DF imaging

In a STEM, the direct or scattered beams are selected in an equivalent way as in a TEM, but we use detectors rather than apertures. It is evident that for DF images,

the annular dark field detector (ADF) gathers many more electrons than the objective aperture (Fig. 3.17).

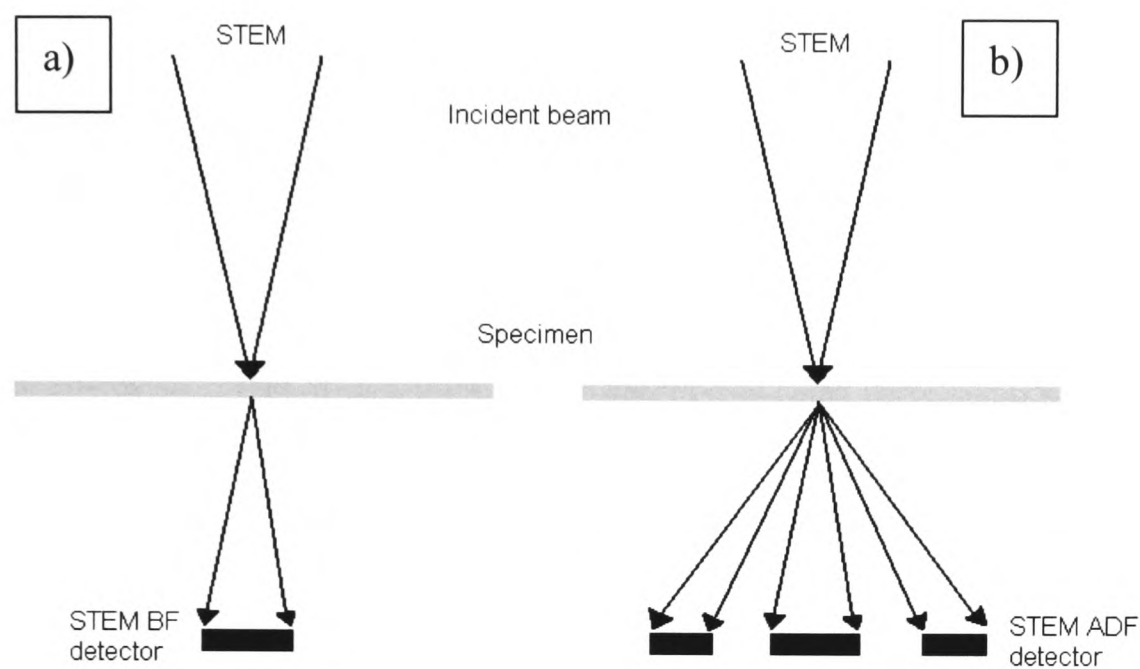
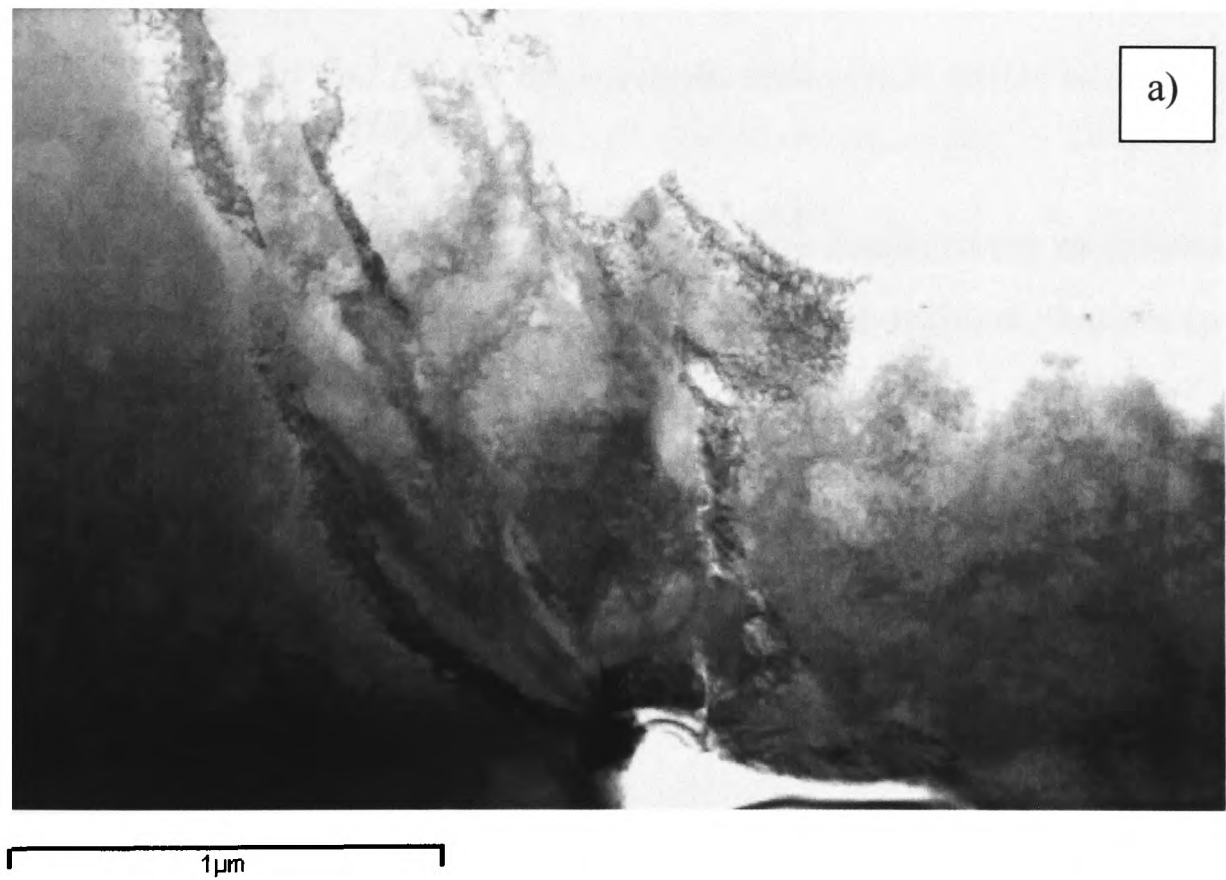


Fig. 3.17. In STEM, we use (a) an on-axis detector or (b) an annular dark field detector (ADF).



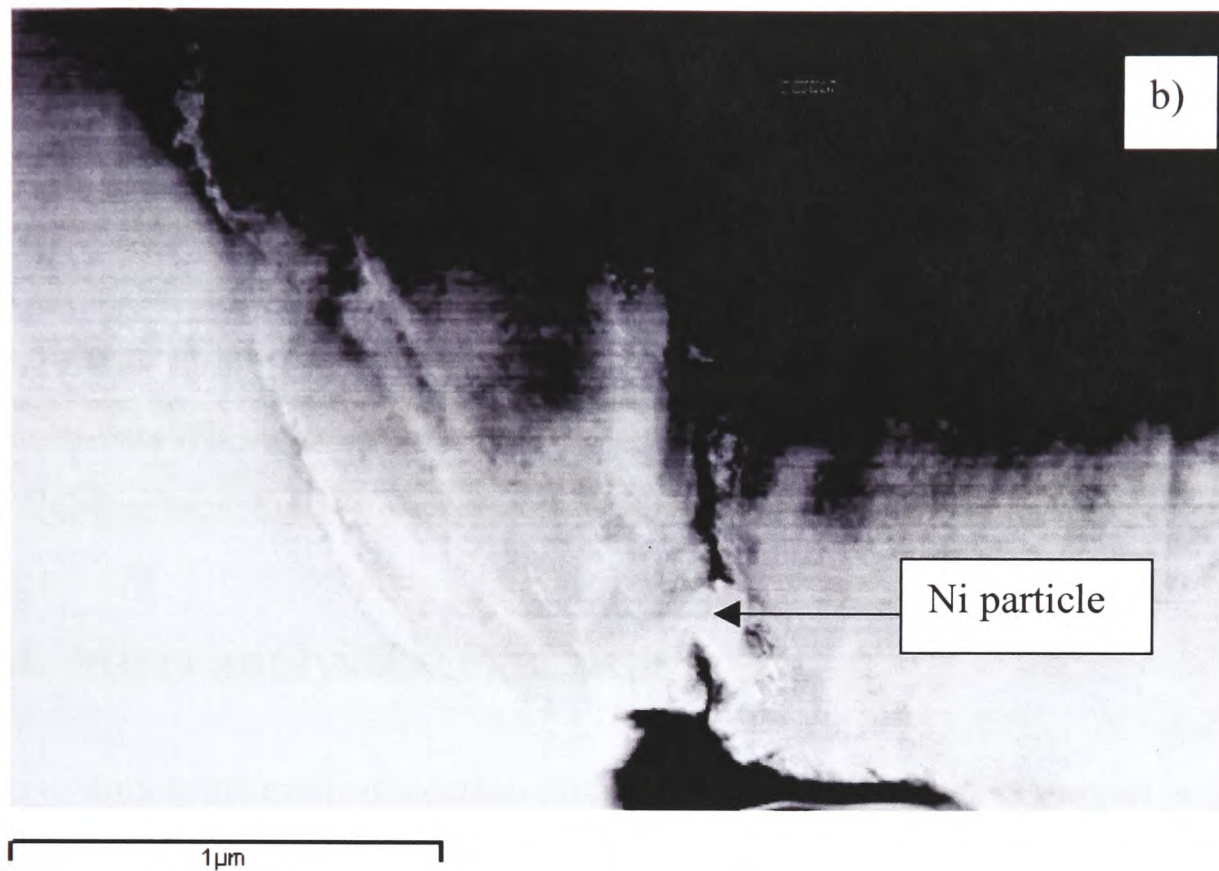


Fig. 3.18. BF (a) and DF (b) micrographs obtained in STEM mode (acquired with the INCA system in the HB501).

In Fig. 3.18, the BF image shows more details of the microstructure while the DF image is more sensitive to thickness and compositional changes (pure-Ni particle can be distinguished).

3.3.4.2 Instruments

The two STEM microscopes used during this research were the VG HB501 and the Philips CM20 (which has been already described).

3.3.4.2.1 VG HB501

The Vacuum Generators HB501 instrument is a dedicated scanning transmission electron microscope with a cold field emission electron source (FEG-STEM).

The instrument operates at an accelerating voltage of 100keV and provides conventional bright and annular dark field signals for imaging.

The primary use of the HB501 is for EDX chemical analysis and elemental mapping with 1-2nm spatial resolution.

Facilities used on this instrument for this project include:

- An analytical objective lens pole-piece with a +/- 30 degree specimen tilting holder.
- A LINK windowless energy-dispersive x-ray detection system (Substituted in May 2002 by an Oxford Instrument ultra thin window EDX detector controlled by Oxford Instruments INCA software).
- A VG gun lens, double o-ring seals and additional column pumping.

3.4. Microanalysis techniques

In a transmission electron microscope, microanalysis is unique in allowing the determination of composition with spatial dimensions ranging from a few atoms to a few microns. Whilst viewing an image of the microstructure and accurately pinpointing the area of interest for analysis. A non destructive technique, analysis identifies which elements are present, (qualitative analysis), how much is present, (quantitative analysis), where the elements are distributed over a chosen area, (x-ray elemental mapping) and crystal orientation. Combined analysis and image measurement is also possible.

Two well-established analysis techniques have been used during the present project: EDX and EELS, and both have been used for spectroscopy and elemental mapping.

3.4.1 EDX

3.4.1.1 Introduction

Within the electron microscope, when the beam of electrons impacts the sample, x-rays are generated. Two types of x-rays are produced, background

radiation, (Bremsstrahlung) and characteristic radiation. The energy range of the Bremsstrahlung x-rays produced is from zero up to the energy of the incoming electrons. Characteristic x-rays are manifest as peaks centred at energies that are very specific and dependent on the chemical species of the atom from which they are generated. Each type of x-ray is produced by a specific type of interaction. It is the characteristic x-rays that are of prime interest in x-ray analysis as these are determined by the elemental composition of the sample.

The measurement of chemical composition by energy dispersive x-ray analysis (EDX) both of bulk samples in the scanning microscope (SEM) and of thin foils in the transmission electron microscope (TEM) has been widely used for the last two decades. However, EDX still represents a challenge for the microscopist as a consequence of the design and physical construction of the specimen/microscope/detector interface and the laws of electron scattering, x-ray production and detection. Highly energetic electrons lose energy through a combination of scattering, ionisation and fluorescence processes which are not confined only to the volume of the specimen selected for analysis. Some of the resulting artefacts can be minimised by good instrument design²².

The EDX (Energy Dispersive x-ray) detector is positioned on the electron microscope with the detection unit close to the sample in order to capture x-rays as they emerge from the sample surface. Under typical operating conditions on the electron microscope, it is possible for the EDX system to detect all elements from Beryllium to Uranium in concentrations of around 0.1% (not for some light elements) and upwards.

The detected x-rays give three important types of information: which elements are present (qualitative analysis), how much of each element is present (quantitative analysis), and how the elements are distributed (x-ray imaging).

Although x-ray analysis in the AEM is a very straight-forward technique, it is surprising that relatively few users take the trouble to extract good quantitative data from their spectra, considering that numerical data are the basis for all scientific investigations. That is the reason why special attention was paid to all the factors that

could lead to a wrong interpretation of the spectra^{29; 28} and to a correct analysis of the data^{9; 29; 23; 22}.

3.4.1.2 The EDX System

The basic steps in detecting x-rays with an EDX system are as follows:

- x-rays pass through a thin vacuum-tight window into a cooled crystal where the x-ray energy is converted into a pulse of electrical charge. The magnitude of the pulse is directly proportional to the x-ray photon energy.

- The charge pulse is converted into a voltage pulse by a FET (Field-Effect Transistor). Further amplification of the pulse takes place prior to the pulse passing along cables to the pulse processor .

- At the pulse processor the pulse is simultaneously digitised and its magnitude measured.

- The digitised pulse is placed into a Multi Channel Analyser (MCA) at a position within the channel array consistent with the pulse magnitude. It is the contents of this MCA that we view as “the spectrum” on the screen.

3.4.1.3 Artefacts

Energy dispersive x-ray spectrometry is subject to artefacts of the measurement process that distort the recorded spectrum from the true x-ray spectrum that is generated in the specimen. Artefacts can be classified as physically inevitable or experimentally reducible or avoidable. Physically inevitable artefacts include absorption in window and detector materials, peak broadening, incomplete charge collection, distortion of symmetry, detector materials, peak broadening, incomplete charge collection, distortion on the low energy side of the peak, and silicon escape peaks. Artefacts that are reducible or avoidable are stray radiation, direct entry of electrons into the detector, dead time, pulse pileup, microphony/electromagnetic interference, and ground loops. Williams et al.²⁹ give further details.

3.4.1.4 Experimental

The EDX spectra were acquired in the Philips CM-20, Jeol JM-3000F and VG HB-501, during the course of the project.

The CM-20 was operated at 200 keV and it has an Oxford Instruments ultra-thin window detector controlled via Oxford Instruments INCA software. The detector is positioned in the same plane as the specimen, so the holder has to be tilted 40° towards the detector in order to get the maximum number of x-rays reaching the detector. A special double-tilt Be holder was used to minimise the background radiation. The probe size was controlled by changing the current of the 2 condenser lenses and allowed the characterization of particles with a diameter greater than ~20 nm. The spectra were acquired either in TEM or STEM modes.

The 3000F was operated at 300 keV and it has an Oxford Instrument ultra-thin window detector controlled via Oxford Instruments ISIS software. The detector take-off angle above the sample plane is 20°. A special double-tilt Be holder was used to minimise the background radiation. The probe size was controlled by changing the current of the 2 condenser lenses and allowed the characterization of particles with a diameter of a few nm. The current of the probe was high enough to perforate some thin parts of the sample, which made its use inadequate for the relatively long EDX acquisition times (100s). This problem could have been overcome by using a lower voltage, but this would have implied recalibrating the GIF system and the EDX detector. So for thin areas, the HB-501 was used.

The HB-501 had a LINK windowless detector controlled via LINK AN100 software until May-2002, when it was substituted by an Oxford Instruments ultra-thin window detector controlled by INCA software. Most of the analyses were performed with the “old” detector. In the results section, the detector used will be specified. This microscope proved to be the best choice for EDX microanalysis. Its cold-FEG source is bright enough to excite the required x-rays, even though the maximum operating voltage is 100 keV. This way only some very thin amorphous oxide layers were perforated after long exposures (>100s). The probe diameter was configured to be ~2 nm, allowing the detection of compositional changes at a very high magnification.

The LINK system was set up so that the C peak together with the strobe peak were removed automatically from the spectrum and its software cannot quantify light elements, including C and O.

3.4.2 Grain boundary segregation

Grain boundaries were studied in order to detect any traces of impurities. The detrimental effect of P and other impurities in the grain boundaries has been reported in the literature^{26; 4; 27}.

A grain boundary is a 2-dimensional defect which is usually assumed to have a “thickness” of only a few atom spacings. Consequently, to get information exclusively from the grain boundary, special attention has to be paid to the orientation of the sample: The grain boundary has to be parallel to the electron beam, so that most of the generated x-rays come from regions close to the boundary (Fig. 3.19).

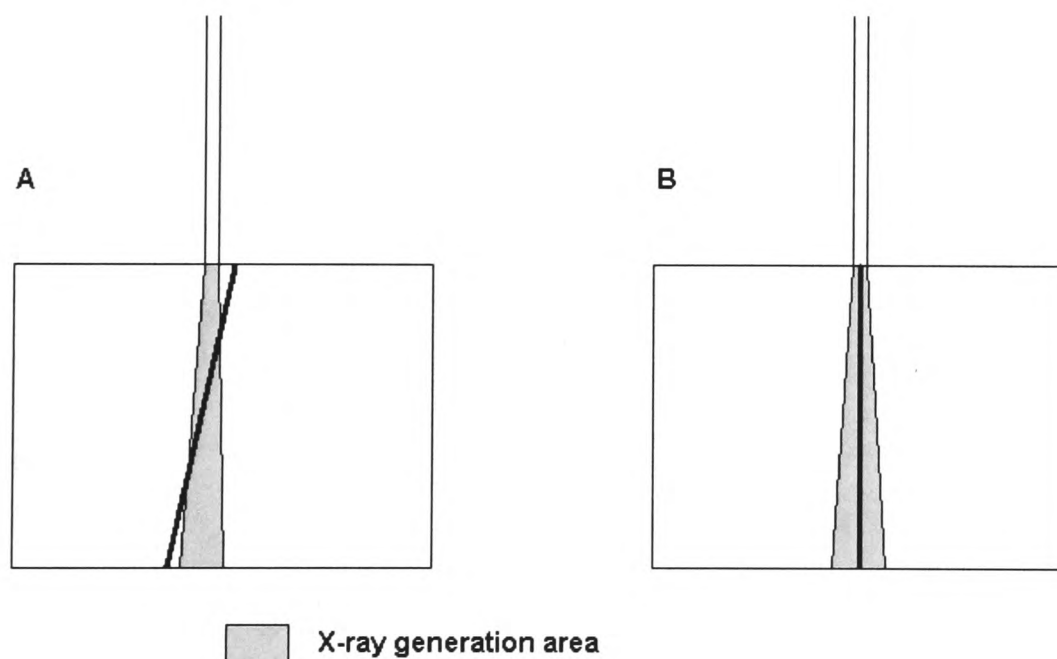


Fig. 3.19. In A, the grain boundary is not parallel to the electron beam and not all the generated x-rays come from the boundary region. In B, the grain boundary is parallel to the electron beam and is completely included in the x-ray generation area.

To check that the grain boundary is orientated parallel to the electron beam we use Fresnel contrast. By getting a slightly overfocused image, the grain boundary

should have a bright shadow that disappears when in focus. This indicates that the grain boundary is orientated parallel to the electron beam. As the tilt of the grain boundary away from ideal orientation increases, the projected width of the line image increases.

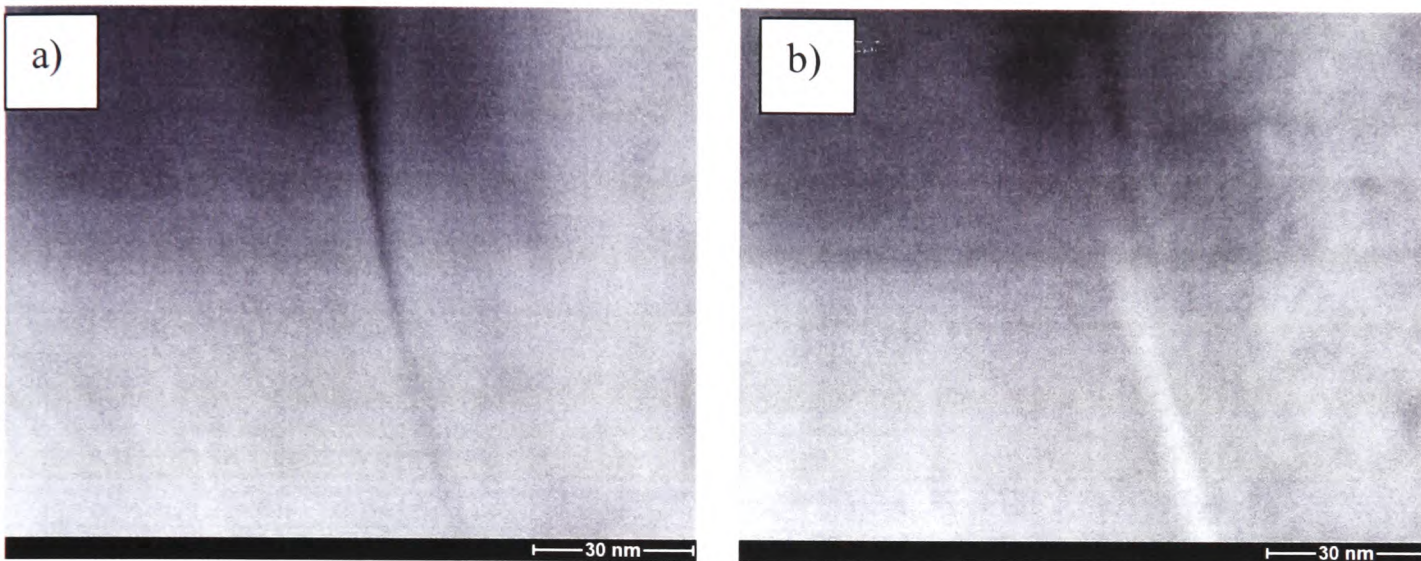


Fig. 3.20. STEM BF images showing: (a) a grain boundary in 304 SS in focus and (b) underfocused (acquired with the HB501).

3.4.3 EELS

This technique was found to be very valuable in our studies because due to the refinement of electron lenses, transmission EELS has one of the highest spatial resolutions of all analysis techniques and there are no beam broadening effects.

EELS can be applied in various types of apparatus, but always involves the bombardment of a sample with a monoenergetic beam of electrons. The technique is frequently used in association with Transmission Electron Microscopy (TEM) or Scanning TEM (STEM). The electrons impinging on the sample may lose energy by a variety of mechanisms. These losses can reveal the composition of the sample in TEM or STEM. Plasmon losses are a frequent cause of energy loss. Plasmons are collective excitations of the electron gas in the material and result in energy losses typically of 10-30 eV^{1; 8; 9; 17; 28}.

In TEM or STEM, the losses predominantly occur in the bulk of the sample, as the beam travels through the thin specimen to the EELS detector the other side. In

surface science techniques, the electron beam is usually reflected off the surface resulting in a sharp peak corresponding to elastically scattered electrons with a number of peaks at lower energy which correspond to plasmon or other excitations.

EELS spectra were acquired in the 3000F using Gatan EL/P software. The use of a carbon support film gave very high carbon edges in the spectra, although the software was able to deconvolute and remove it. The use of holey carbon support films helped, as it was possible to choose some points for analysis where the sample laid across holes in the carbon film. All the results will be shown with the background extrapolation from below the O edge removed, as shown in Fig. 3.21 for an EELS spectrum from the nanocrystalline NiO that filled a stress corrosion crack in an Alloy 600 sample.

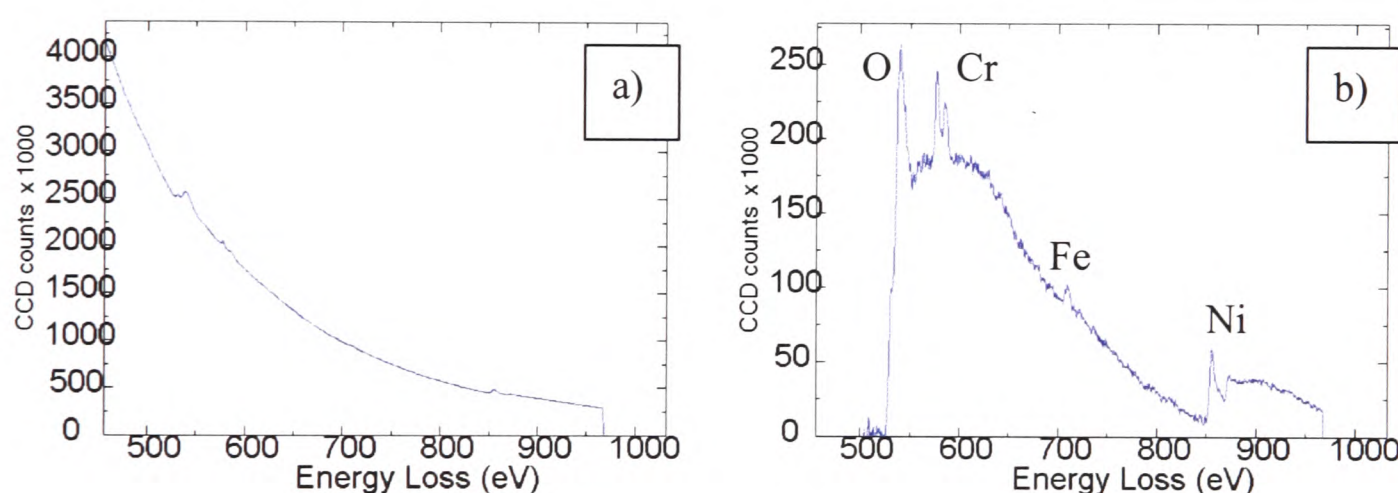


Fig. 3.21. EELS spectra from NiO; a) as acquired; b) after background extrapolation from below the O edge removed (acquired with the 3000F).

3.4.4 Chemical mapping

The intensity in any part of the EDX or EELS spectrum can be selected and be used to form an image, either in a digital manner by modulating the signal to the STEM image-screen or in an analog manner in the energy-selecting TEM. A variety of images can be formed in this way and they have several advantages over conventional TEM and STEM images³⁰.

In this research a LINK EDX system (substituted by an Oxford Instrument INCA system in May 2002) in the VG HB501 FEG-STEM and the GIF system in the JEOL JEM-3000F FEG-TEM were used. The Gatan Imaging Filter (GIF) is equipped

with a 2k 794IF/20 MegaScan CCD camera that allows chemical analysis using electron energy loss spectroscopy (EELS), either by acquiring a full spectrum in parallel (PEELS) or by using part of the spectrum to reform the image of the sample. This technique can be used to select energy losses corresponding to particular chemical elements or states (compositional mapping) or to filter out unwanted inelastically scattered electrons to form higher contrast images or diffraction patterns from thicker samples.

These techniques are particularly important when doing microanalysis of light elements. This is a difficult task, mainly when high spatial resolution and/or high analytical sensitivity combined with quantification are required. A crucial advantage of mapping is that it facilitates a one-to-one comparison between any composition variation in the specimen and the specimen microstructure. More details about detecting light elements can be found in ⁹.

The use of the GIF system in the 3000F was proven to be very useful but restricted to high-magnifications (>150kx), due to the manner in which the GIF is coupled to the microscope imaging optics. Attempts were made to use it at reduced magnifications, but the quality of the results was not high enough to use it instead of EDX mapping. The main advantage of the GIF is its ability to map light elements. In our experiments, oxygen was the main light-element analysed, as boron was not detected and it is not possible to analyse hydrogen with any of these techniques.

The 3000F worked well for EDX mapping using dwell times of 30 ms and due to the FEG source, the quality of the maps increased considerably in comparison to the CM-20 (for the same probe diameter). However, the use of Oxford Instruments “semi STEM” mode was proven to be inferior in quality to the dedicated STEM in the HB-501, as high dwell times could only be reached by scanning the probe several times over the same area in the TEM system.

In the HB-501, the total control of the software over the probe enabled single frame and high dwell-time (50 ms) mapping with a superb quality. Even at magnifications of 1 million times and higher (up to 10Mx) the quality of the maps was acceptable. Any drift only distorted slightly the features in the map, instead of

spreading the information, as in the case of multiple-frame maps (Semi-STEM in the 3000F). In Fig. 3.22, this effect is described. While in the single-frame scan, the feature appears distorted but with the right width, in the multiple-frame scan, the information coming from the feature has spread, so the feature appears wider.

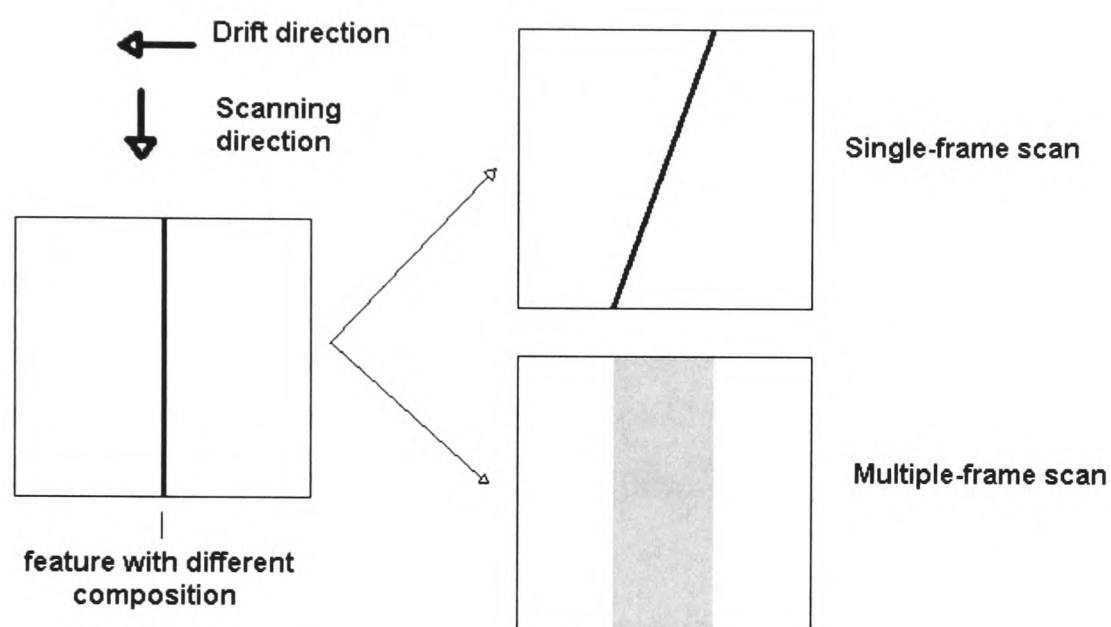


Fig. 3.22. Effect of drift in a single-frame and multiple-frame map.

When using EDX mapping in Alloy 600 and SS304 samples, the following positions were chosen for the energy windows: Ni: Ni- K_{α} peak, Fe: Fe- K_{α} peak, Cr: Cr- K_{α} peak, O: O- K_{α} peak, Ti: Ti- K_{α} peak. The only overlapping problems were found between the O- K_{α} peak and the Cr L_{α} peak, so special care was taken when mapping regions with Cr and O. O K_{α} peak has an energy of 0.52 KeV, while Cr L_{α} peak has an energy of 0.57 keV. To overcome this problem, the oxygen window was chosen so that it only included the left half of the oxygen peak. In this way, the possible contributions from Cr were minimised. As the Cr and O maps were not always correlated (apart from when mapping Cr oxide), it is assumed that this method is adequate. Unfortunately, the latest version of Oxford Instruments software for EDX microanalysis, INCA, does not allow the user to define the windows, in this new system the overlapping problem is treated automatically by the software. The results

did not show any obvious correlation between the maps, so it was assumed that the software worked properly.

The elemental maps acquired using the LINK system always had a resolution of 128x128 pixels. If a probe size of 3 nm is assumed, depending of the magnification used, undersampling or oversampling might have occurred. The magnifications used in the HB501 were 50kx, 100kx, 200kx, 500kx and 1Mx. The ideal mapping area for the probe size mentioned before would be (128x3 nm = 384nm) 384nm x 384nm, which is equivalent to a magnification of ~260kx. This means at lower magnifications some undersampling occurs unless the number of pixels is increased. So, for the maps acquired with the LINK system, undersampling occurred for the magnifications: 50kx, 100kx and 200kx, and oversampling for the rest (500kx and 1Mx). When the INCA system was used, 256x256 pixels were used for the mapping, and the ideal magnification is found to be ~1.3kx.

3.5 References

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Chapter 4:

TEM sample preparation

4.1. Introduction

The TEM sample preparation has been a key issue in this project. When it was started in 1999, there were only a few reports in the literature on TEM of crack tips. Some work had been done on “in-situ” TEM deformation experiments^{15; 5; 4; 20; 2; 11; 3}, but this way of observing cracks was not suitable for stress corrosion cracks, as the environment plays a crucial role in the growth. This and the following reasons, made this method unsuitable:

- The stress state in the “in-situ” experiments is “plane-stress” rather than “plane-strain” that is the general state of deformation in bulky components.
- The time of corrosion attack is unrealistically short in the TEM experiments
- Electron irradiation might affect any diffusion effects.

In other cases, crack tips were observed by chance in electropolished specimens⁹. However, the uncertainty in the final location of the transparent region makes electropolishing an unsuitable technique for studying stress corrosion cracks.

The cracks to study were generally smaller than 15 μm , so it was a priority to develop a suitable sample preparation method. The first serious attempt to study crack tips in austenitic steels using TEM was performed in 1996, by Thomas¹⁹. He used ion beam milling to produce transparent regions close to the expected location of the crack tip. This technique has been used since then by Thomas and Bruemmer^{18; 1} and it appears to be reliable for preparing cross sectional TEM samples of relatively long cracks ($\geq 50\mu\text{m}$). The only instrument capable of giving the required spatial accuracy for the present project was the FIB, and it will be shown that it was an excellent choice.

The first technique to be described will be the ion beam milling, because it will be later modified to allow a better crack tip area observation. Next, the different FIB techniques will be described, as well as the modifications developed specifically during this project to overcome limitations of these standard methods to make them suitable for the preparation of samples with cracks.

The samples were received from INSS in 2 formats:

- All the Alloy 600 pieces had the geometry shown in Fig. 4.1. As a normal procedure, the samples were cut from the red dashed line and one half was sent to Oxford and the other half was kept by INSS. As an exception, only the section contained between the two red lines was received from Alloy B.

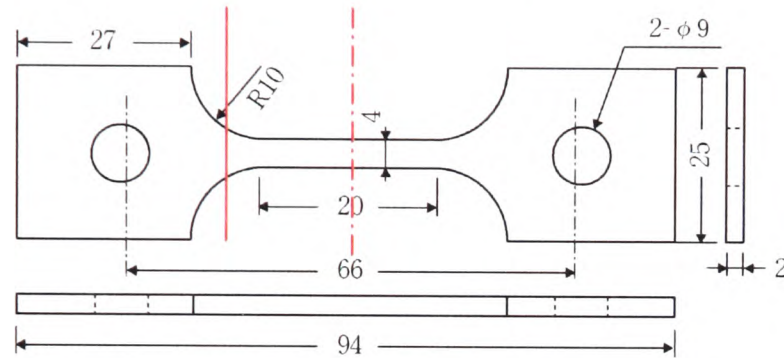


Fig. 4.1. Alloy 600 sample geometry. All distances are in mm (Courtesy of Dr. K. Fujii, INSS).

- The 304 SS samples had the geometry shown in Fig. 4.2.

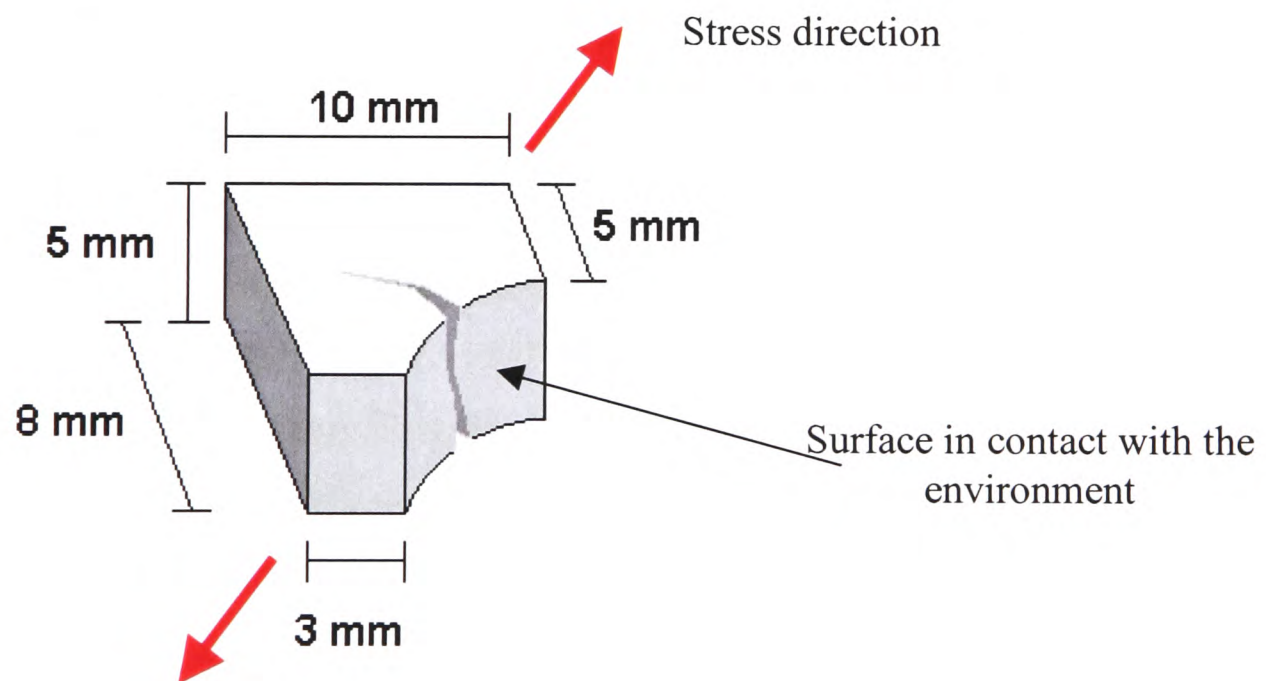


Fig. 4.2. Schematic view of the 304SS sample as received.

4.2. Ion beam milling sample preparation

As was mentioned earlier, this technique was used to prepare samples which contained long cracks, of the order of millimetres. The preparation procedure prior to the actual ion milling is as follows:

- The bulk piece of material was studied using SEM or optical microscopy and the positions of the cracks identified.
- A diamond saw was used to cut a piece of reduced dimensions containing a few cracks. An appropriate cut-off wheel was chosen, and a low feed rate was used.
- This piece was ground using SiC papers of different grading until its thickness was $\sim 100\mu\text{m}$. Then, depending of the available area, there are two possibilities:
 - If the available area was too small to allow cutting a 3 mm disc, the sample was ground using lapping diamond film until its thickness was $\sim 20\mu\text{m}$ (Fig. 4.3), then cut carefully using a scalpel so that it could be mounted on a Cu ring. The cracks to be studied were positioned off-centred, so that their tips were not in the expected position of the hole, once the ion beam milling process finished (Fig. 4.4).

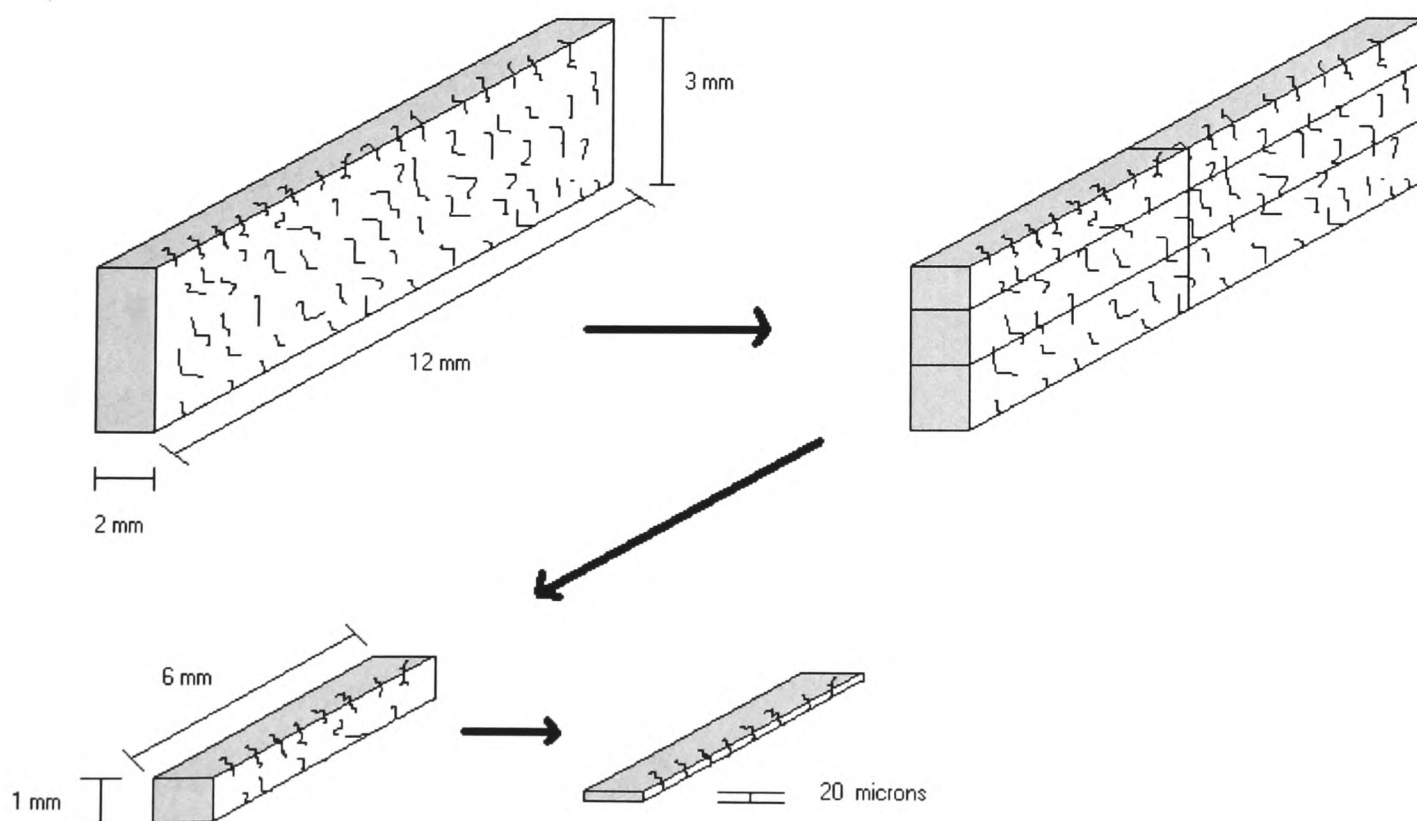


Fig. 4.3. Steps previous to PIPS milling: From the bulk piece with cracks “as-received”, to a $20\mu\text{m}$ foil.

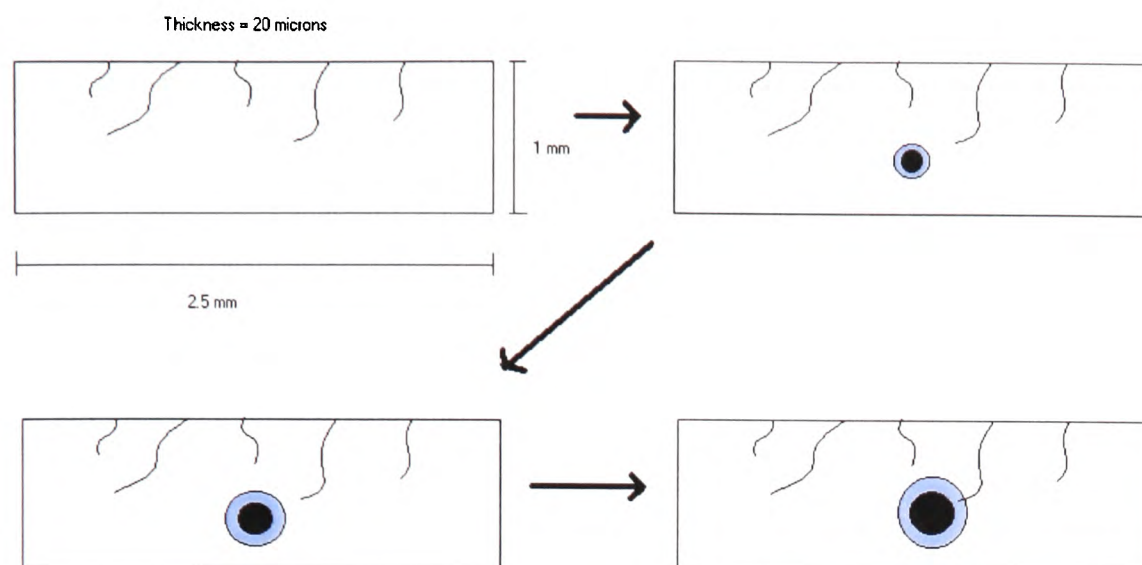


Fig. 4.4. Process of milling a hole in the sample close to the expected position of the crack tip.

- If the area was big enough to cut a 3 mm disc, a spark machine with a hollow copper electrode was used to minimise the damage to the sample during cutting. Again, the electrode was positioned on the bulk-sample so that the crack tips were slightly off-centred once the 3mm disc was ready. After this, the disc was ion beam thinned in the PIPS as usual.

4.3. FIB sample preparation

The most commonly used techniques reported in the literature for the preparation of cross section specimens by FIB are the “trench” and the “lift-out” techniques, although they are still not ideal and present some disadvantages^{12; 16}. The “trench” technique is the more reliable because the risk of losing a sample in the “lift-out” step is eliminated but disadvantages such as the restricted tilt angles for TEM imaging and Energy Dispersive Spectroscopy analysis often make it unsuitable for samples with cracks. Modifications have been developed to overcome this. The “lift-out” technique permits greater tilt in the TEM but sample buckling and possible fracturing of the sample during plucking make it unreliable for samples with cracks. The “framed membrane” technique has been developed by the author during the course of this project and proved to be a huge improvement over the conventional “lift-out” technique.

A cross-section slice of cracked material is mechanically polished to a thickness less than $\sim 30\ \mu\text{m}$ and mounted on a U-shaped support grid (Fig. 4.5a). Trenches are FIB milled from the edges to generate an electron transparent membrane containing the crack tip (Fig. 4.5b). Details of the method have been widely described in the literature^{6; 7; 8}. This procedure has been modified to minimise shadowing and scattering contributions in EDS in the following manner. BIB (Broad Ion Beam) is initially used to reduce the thickness of the slice to $\sim 5\ \mu\text{m}$ (Fig. 4.5c). The trench technique can then be used as normal. For deep cracks, FIB is used to remove a block of material through the slice to reduce the distance from the crack tip to the surface. Trenches are then cut deeper into the specimen (Fig. 4.5d) and the electron-transparent membrane is the surface ABCD.

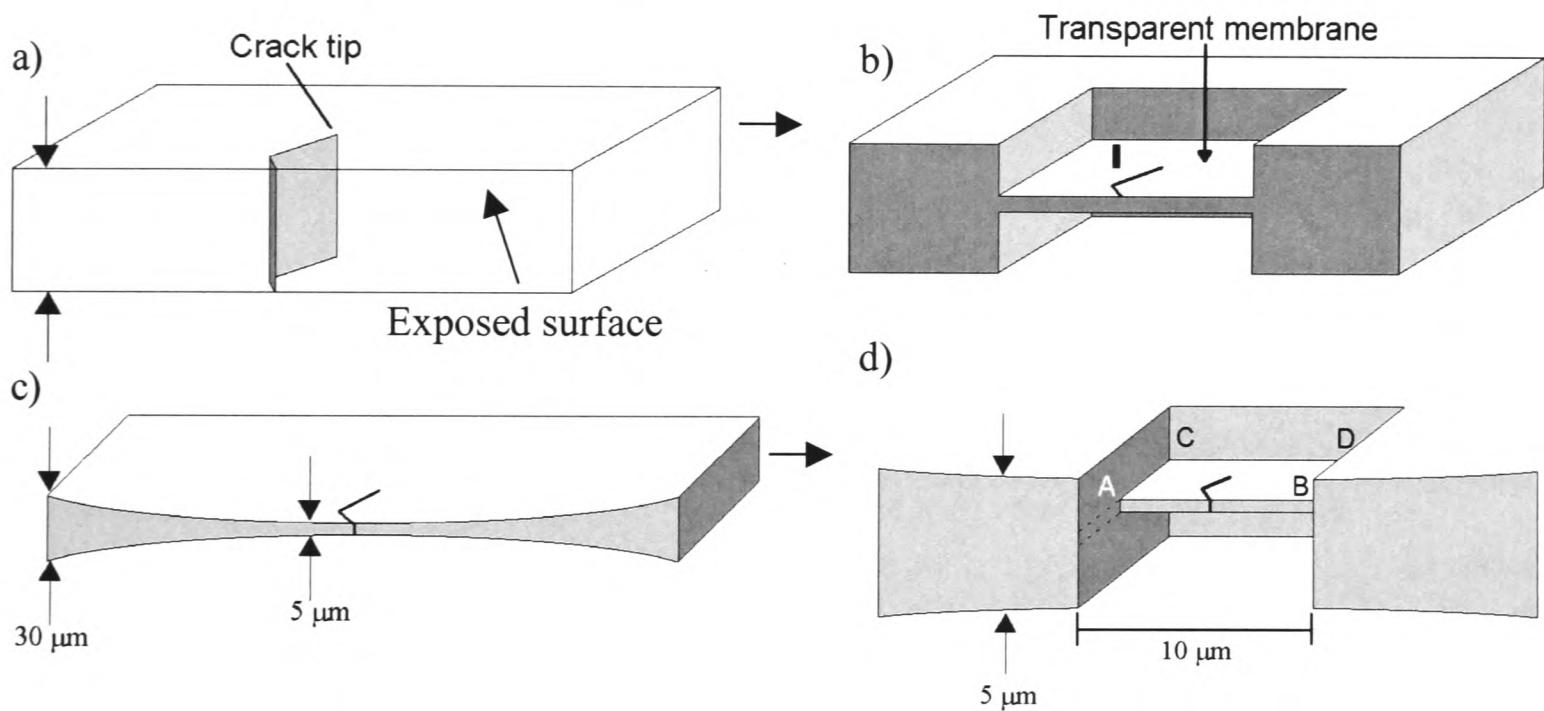


Fig. 4.5: Schematic views of: a) and b) Traditional “Trench technique” and c) and d) “BIB combined trench technique”

The bulk of the trench machining was performed using a 20nA beam current at 30 keV in a direction normal to the original sample surface. The final stages of machining were performed using a current of $\sim 1\text{nA}$ and 30 keV, alternately tilting the sample by $\pm 1.2^\circ$ from the normal until the membrane thickness is less than 100nm. This minimises tapering in the membrane thickness profile¹⁷. Final cleaning was performed using 5 keV ions. A typical sample imaged using secondary electrons in the FIB, before the final machining, is shown in Fig. 4.6. Images such as that in Fig. 4.6 were not normally recorded because every frame scanned by the ion beam causes

milling and damage. Image recording is not, therefore, beneficial to the machining process. Fig. 4.7 shows the same sample imaged in the TEM.

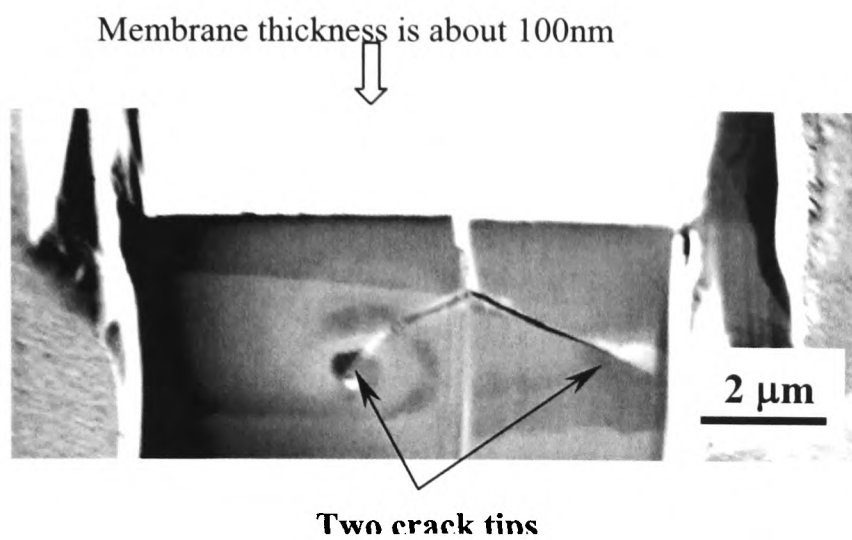


Fig. 4.6. FIB SE plan view image showing the crack (acquired with the FEI FIB)

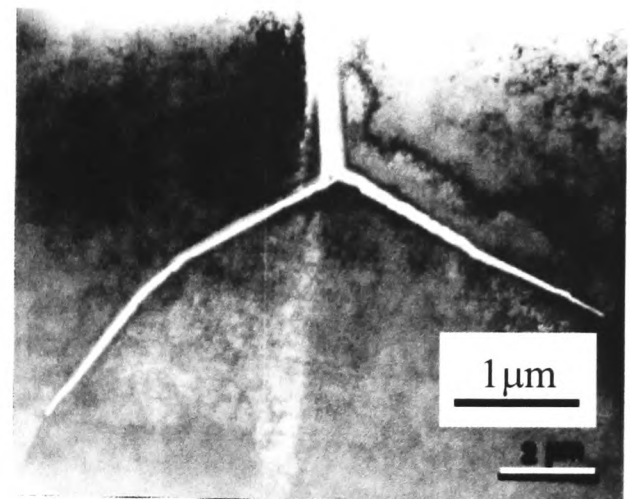


Fig. 4.7. TEM image of the crack region including the crack tip (acquired with the CM20)

4.3.1 Modified “Lift out” technique

In the lift-out technique the sidewalls and the base of a cross-section are cut so that the final specimen is completely free from the original substrate. This technique is especially useful when shallow cracks are the subject of study, too small to be isolated using any other technique, as with the stress corrosion crack in Fig. 4.8.

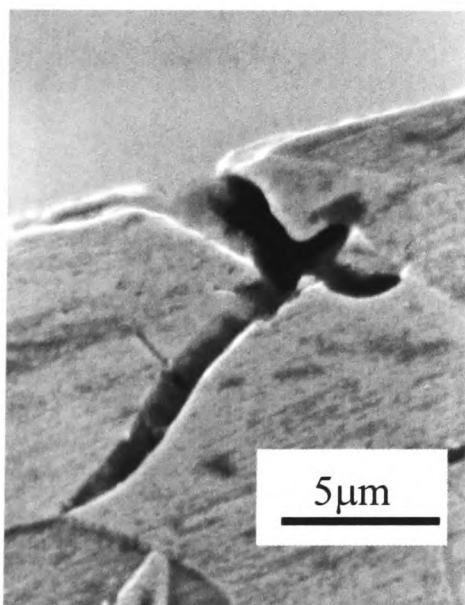


Fig. 4.8. FIB SE image of a typical SCC crack in Alloy 600 (acquired with the FEI FIB)

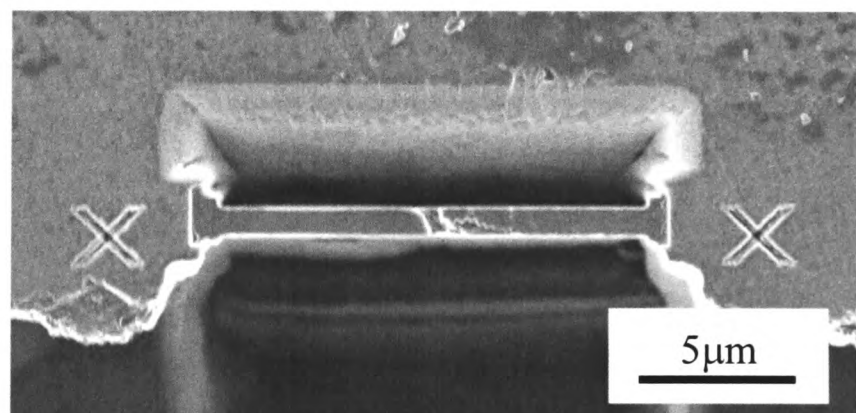
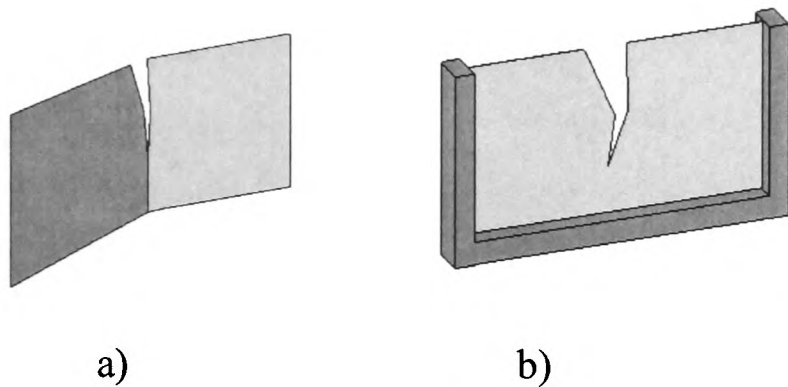


Fig. 4.9. FIB SE image showing the membrane including the crack (acquired with the FEI FIB)

Some extra problems occur when working with samples containing cracks. Once the sample is thinned to 100-200 nm, it was found that it could buckle, due to the high

residual stress, with a high risk of fracture along the crack (Fig. 4.10a). In order to avoid buckling the method is modified as follows. Preparation proceeds exactly as in the conventional “lift-out” technique until the membrane is 500 nm thick (Fig. 4.9). A thicker region at both sides and bottom of the sample is then left to act as a supporting frame (Fig. 4.10b). The process itself does not require extra work, as it can be incorporated into the final milling (Fig. 4.11) and “plucking” is performed in the standard manner.



*Fig. 4.10. a) Model of a buckled TEM sample
b) Model of the “framed-membrane” technique*

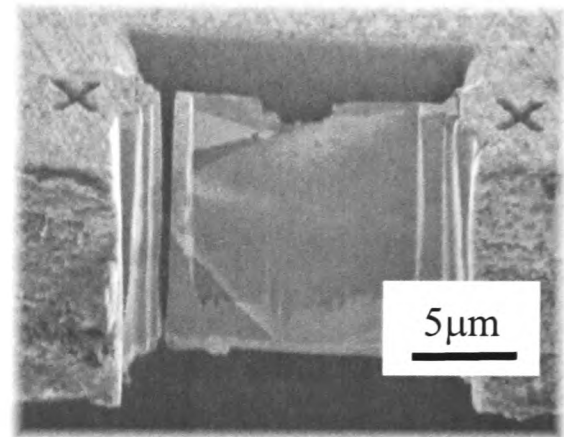


Fig. 4.11. FIB SE image showing the framed-membrane (acquired with the FEI FIB)

The resulting TEM specimen allows observation of the crack sides, the crack tip (Fig. 4.12a) and the corrosion products in the crack (Fig. 4.12b).

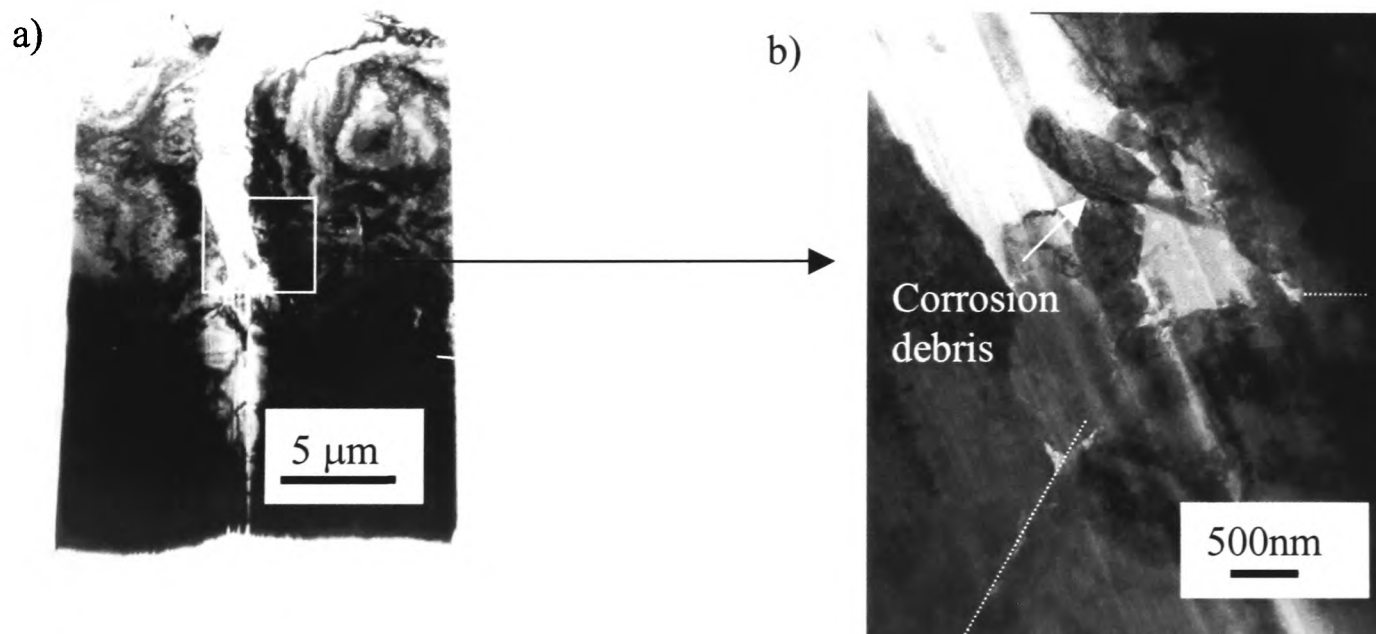


Fig. 4.12. TEM micrographs of a) whole membrane fabricated by the “framed membrane” procedure and b) detail from the highlighted area in a) showing corrosion products at the crack tip (acquired with the CM20).

In summary, it has been demonstrated how the FIB system can be used as a tool for the preparation of TEM cross-sections through cracks in metal alloys such as

steels. The study by TEM of the faces of the cracks and the tips should give important insight into crack growth mechanisms, especially when the cracks are the result of corrosion processes^{10; 13; 14}. Modifications have been developed for both FIB methods commonly used for the preparation of TEM foils from selected locations to overcome the specific problems arising with cracked and stressed materials. The preparation methods have been used successfully and applied to image crack tips and corrosion products in bulk stainless steel and Alloy 600 containing stress corrosion cracks. Such results are described in Chapter 8 and 9 of this thesis.

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Chapter 5:

Stress and IGSCC test methods

5.1. Study of Stress

5.1.1 Introduction

Reviewing the Classical Theory of Elasticity^{9; 15; 12; 10; 13} in order to study crack problems, it is found that the stress fields governed by the equations of plane strain or by the equations of plane stress have to be determined. As a first approach to a crack, a two-dimensional diagram can be represented by a segment of a straight line, and it is in reality a long flat ribbon-shaped cavity in a solid. It is stressed in such a way that there is no variation in the stress pattern as we pass in a direction parallel to the plane of the crack. In both cases the crack is called a "Griffith crack"⁷.

5.1.2 Modes of loading

In two dimensions there are three basic modes of loading. In the first mode, shown in Fig. 5.1, there is a Griffith crack (of length $2c$) in a solid under a tension which is in a direction perpendicular to the line of the crack.

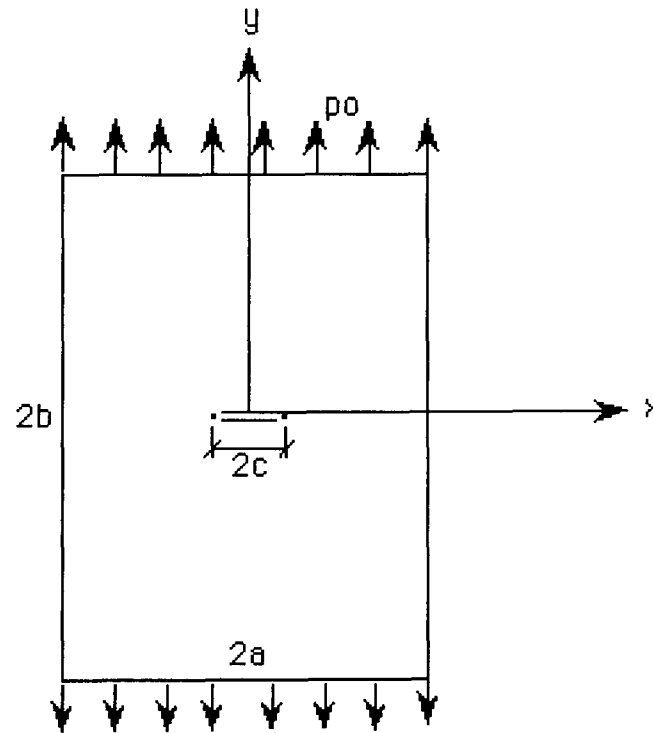


Fig. 5.1: Mode I geometry

Here we are interested in calculating the "stress intensity factor" K_I , defined by the equation 5.1:

$$K_I = \lim_{x \rightarrow c^+} \left[\sqrt{2(x-c)} \sigma_{yy}(x, 0) \right] \quad \text{Eq. 5.1}$$

where the x-axis is along the crack and the origin is at the crack centre.

In the second mode, shown in Fig 5.2a, the solid is under an applied shear parallel to the crack. In this case we should be interested in calculating the stress intensity factor:

$$K_2 = \lim_{x \rightarrow c^+} \left[\sqrt{2(x-c)} \sigma_{xy}(x, 0) \right] \quad \text{Eq.5. 2}$$

And also the strain energy W_2 , and the corresponding strain energy release rate.

In the third mode, shown in Fig. 5.2b, the solid is under an applied shear perpendicular to the crack. Here, we should be interested in calculating:

$$K_3 = \lim_{x \rightarrow c^+} \left[\sqrt{2(x-c)} \sigma_{xz}(x, 0, z) \right] \quad \text{Eq. 5.3}$$

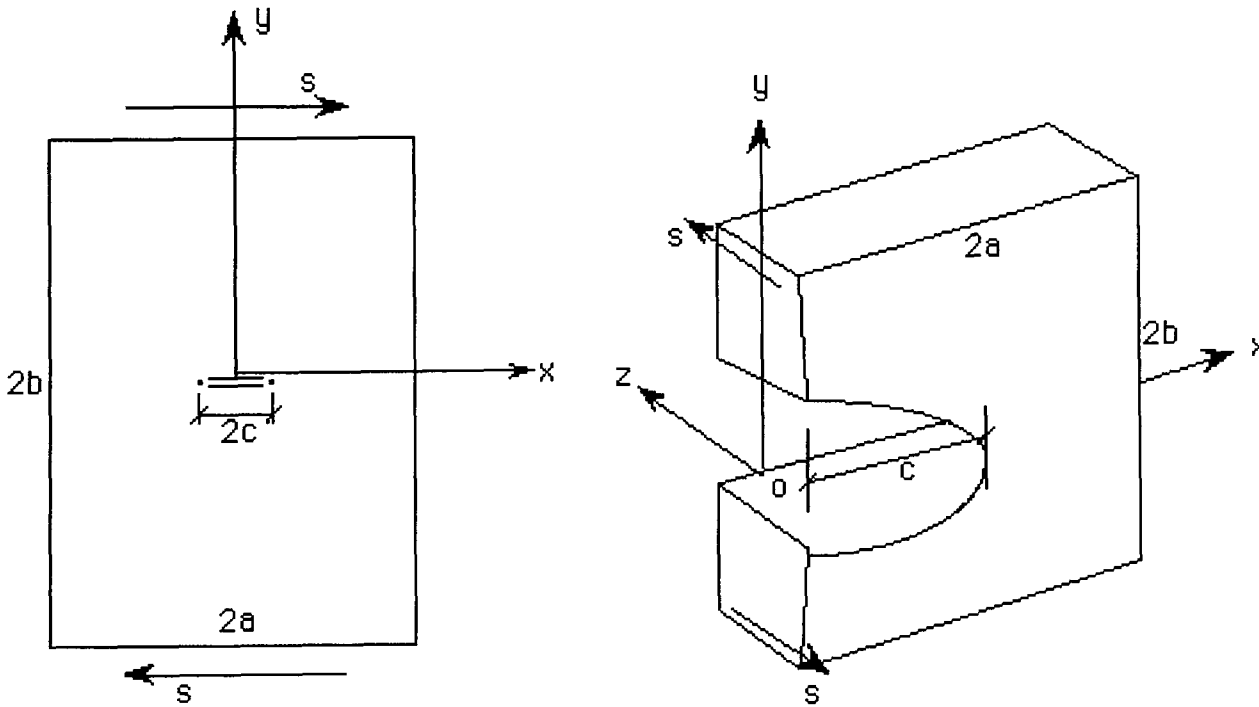


Fig. 5.2. a) Mode II displacement, b) Mode III displacement.

It is important to remark that , in a bulk component, the nature of the stress field is likely to contain components of all of the 3 modes and, as the crack advances, the stress field will change, particularly if the crack follows the grain boundary.

5.1.3 Strain Energy

It is also useful to calculate the strain energy W_1 required to form the crack. In two dimensions we define the strain energy rate of a Griffith crack of length Z as:

$$J = \frac{\partial W}{\partial Z} \quad \text{Eq. 5.4}$$

Thus in this case, we have the equation:

$$J_1 = \frac{1}{2} \frac{\partial W_1}{\partial c} \quad \text{Eq. 5.5}$$

The Griffith criterion for failure is that the crack will begin to grow catastrophically when the applied tension reaches the value given by the equation:

$$\frac{\partial (W - U)}{\partial c} = 0 \quad \text{Eq. 5.6}$$

where U is the surface energy of the crack. Griffith expresses U in terms of a "surface tension" γ of the solid by the equation $U=4c\gamma$. Thus, we can write the last equation in the form $J = 2\gamma$.

When a crack is nucleated, the condition of brittle crack extension is governed by the Griffith formula, $J=2\gamma$, which balances the release of elastic energy against the work of fracture, i.e. the surface energy, during the growth of the crack. The Griffith condition may be expressed in terms of when potential energy release rate J per unit thickness reaches a critical value:

$$J_c = 2\gamma \quad \text{Eq. 5.7}$$

where J_c is the critical energy release rate, or the fracture toughness of a material, and γ is the surface energy.

It is well known that the fracture toughness of many of the structural materials is greater than that predicted by the Griffith formula because of plastic deformation that occurs at a crack tip. It was suggested by Orowan ¹¹ that Eq. 5.7 should be modified:

$$J_c = 2\gamma + \gamma_p \quad \text{Eq. 5.8}$$

here γ_p is the plastic work. It is usually found in many metals that γ_p is much greater than 2γ . Under an extreme temperature or a harsh chemical or nuclear environment, however, the fracture toughness of a metal can be reduced drastically and the metal fails in a brittle manner. It is not known at present which of the material parameters are important in determining the extent of crack tip deformation and how the crack tip deformation is related to the onset of brittle crack extension ¹¹.

5.1.4 Crack growth rate

Traditionally, the growth rate of SCC can be expressed as a function of the stress intensity factor (K) :

$$\frac{da}{dt} = D_P K_I^{m_P} \quad \text{Eq. 5.9}$$

where da/dt is the crack growth rate and m_P and D_P are constants. The value of the stress intensity factor can be expressed as:

$$K_I = F_I \sigma_0 \sqrt{\pi a} \quad \text{Eq. 5.10}$$

where σ_0 is the applied stress, a is the crack size and F_I is a constant determined by crack configuration and boundary conditions. Eq. 5.9 is used widely and much experimental data has been accumulated to specify the constants values for different materials and environments.

Some recent work by Kamaya ⁸ has proven that the local K value of short cracks may deviate from the macroscopic K value, which is calculated from the applied stress and crack configuration. He suggested that when predicting the crack growth behaviour using Eq. 5.9, and macroscopic growth data, the variation in the K due to microstructure has to be taken into account. The microstructures considered were crystal grain orientation and specially the effect of anisotropic elastic of crystal grains and the crack kink. For the anisotropic elastic effect he found that:

- The K values are changed due to the anisotropic elastic effect.
- The variation of the K value is 51% at its maximum, becoming smaller as the crack size becomes larger.

For the crack kink effect:

- The K values are changed due to the crack kink effect.
- The change in the K value depends on the crack kink angle, but not on the number of kinked points and crack configuration.
- The variation in the K value can be given by the following equation: “New K_I ” = $K_I \cos^3 (\alpha/2)$

So, the effect of the microstructures in K was found to be remarkable until a crack length of approximately 10 times the grain size.

5.2. Stress Corrosion Cracking test methods

5.2.1 Introduction

Most SCC testing is performed to determine the best material for a specific application or to compare the behaviour of the material to environmental variations. Test conditions for the first case should be representative of the most severe conditions predicted during service. For the second case, test conditions are usually chosen to produce various degrees of cracking in a reasonable time.

As traditionally service failures due to SCC have been identified with sustained tensile stress, SCC testing has developed around the use of static loading. Before 1965, only constant-load or constant-strain tests of smooth and notched test specimens were used to assess SCC. Currently, many more test methods are available. Of special relevance are two accelerated testing techniques developed in the 60s. One tests and analyses statically loaded, mechanically precracked test specimens using linear elastic fracture mechanics concepts. The second consists of constant (slow) strain rate tests on smooth or pre-cracked specimens. These techniques produced SCC in some samples and conditions where the older, traditional test did not ⁴.

The purpose of the tests is to determine whether cracking will occur in the stressed test piece in the specific corrosive environment used during a specified maximum test period. In cases in which the objective of the test is to predict service behaviour, it is normally necessary to acquire the information in a short period of time. This is achieved by increasing the severity of some variables ¹⁴, e.g.:

- by increasing the stress intensity to a value above the yield stress
- by using a slow continuous straining
- by using pre-cracked specimens
- by using more aggressive environment or higher temperature

5.2.2 Types of Stress Corrosion Test

The first thing to do when testing SCC is to decide which kind of test is going to be used. Some tests try to reproduce service conditions as closely as possible, while others are designed to study the mechanistic aspects of SCC. In our case, in order to reproduce primary water conditions in PWRs, constant load and slow strain rate tests in autoclaves were chosen.

Test specimens can be divided into 2 categories:

- Smooth: Normally several specimens are exposed to the given stress condition and inspected regularly for surface cracks. Alternatively, specimens can be withdrawn at

intervals and inspected destructively by cross-sectioning and polishing them. This category can also include abraded specimens that could be considered “rough” but not precracked. The specimen geometry is generally a round bar or a flat tensile.

- Notched or pre-cracked: The notch serves to concentrate the applied stress and to induce a triaxial stress system (provided that the specimen is not plate-like). It will also makes the inspection easier, as the induced crack will be easily found. The geometries used are usually 3-dimensional, i.e. compact tension specimen with pre-cracking by fatigue. Such specimens are especially useful for measuring crack-growth rates without a long initiation stage.

The mode of stressing can also be divided into:

- Constant strain tests (fixed displacement): The applied stress decreases as the crack grows. This results from the opening of the crack(s) under the high stress concentration at the crack tip(s) and causes some of the applied elastic strains to change to plastic strain. One of the main reasons for their use is that a great variety of simple and inexpensive jigs can be devised. However, the exposure stress cannot be reproduced accurately. Therefore, more sophisticated techniques have been developed to improve this facet of testing.

- Constant load tests: The applied stress at the crack increases as the crack grows. The load is usually applied by a lever arm. Tests using uniaxially loaded tensile specimens are often used to define threshold stress. However, recent work by Andresen² suggests that a threshold defined that way would be useful. Many results from short time tests invoking a threshold stress are perhaps not very useful for applying to real components under stress for many years.

- Slow strain rate stress: The specimen is subjected to slow dynamic straining as the crack grows. It is one of the most recently developed methods for accelerating the SCC process. To accelerate SCC initiation a slow dynamic strain exceeding the elastic limit is applied. This technique is consistent with many proposed mechanisms of SCC, which involve plastic microstrain and film rupture. However, the validity of

SSRT is questionable in that the testing conditions are unlikely to be typical of those experienced by plant components.

5.2.3 Pre-testing considerations

5.2.3.1 Alloy grain orientation

Rolling, extruding and forging are the most common processing operations used in the production of wrought forms of alloys. All produce a flow of metal in a predominant direction so that, microscopically, the grains are often elongated in the direction of flow. In cases in which the SCC is intergranular (i.e., the cracks follow grain boundary paths), the SCC resistance may be strongly related to the grain shape and orientation with respect to the applied stress ¹⁴..

5.2.3.2 Residual stresses

Tensile stresses are believed to be necessary for SCC to occur. The total stress in a stress corrosion test is supplied by both the test load and residual stresses. While the test loads can be calculated, the amount of residual stress is not estimated that easily. Residual stresses may result from quenching after heat treatment, rolling, extrusion, deformation during construction, welding, and service abuse. They may be eliminated either in the bulk material or in test specimens by stress relief annealing ¹⁴.

5.2.3.3 Surface condition

The initiation of SCC involves some initial surface reactions, so the surface condition may play an important role on test results. Specimen surface can be mechanically prepared (ground or polished) or chemically treated (electropolished).

5.2.4 Alloy 600

In this project all the samples were tested by INSS. The following scheme describes the steps they followed prior to testing (Fig. 5.3a) and the sample geometry used (Fig. 5.3b) :

Sample preparation

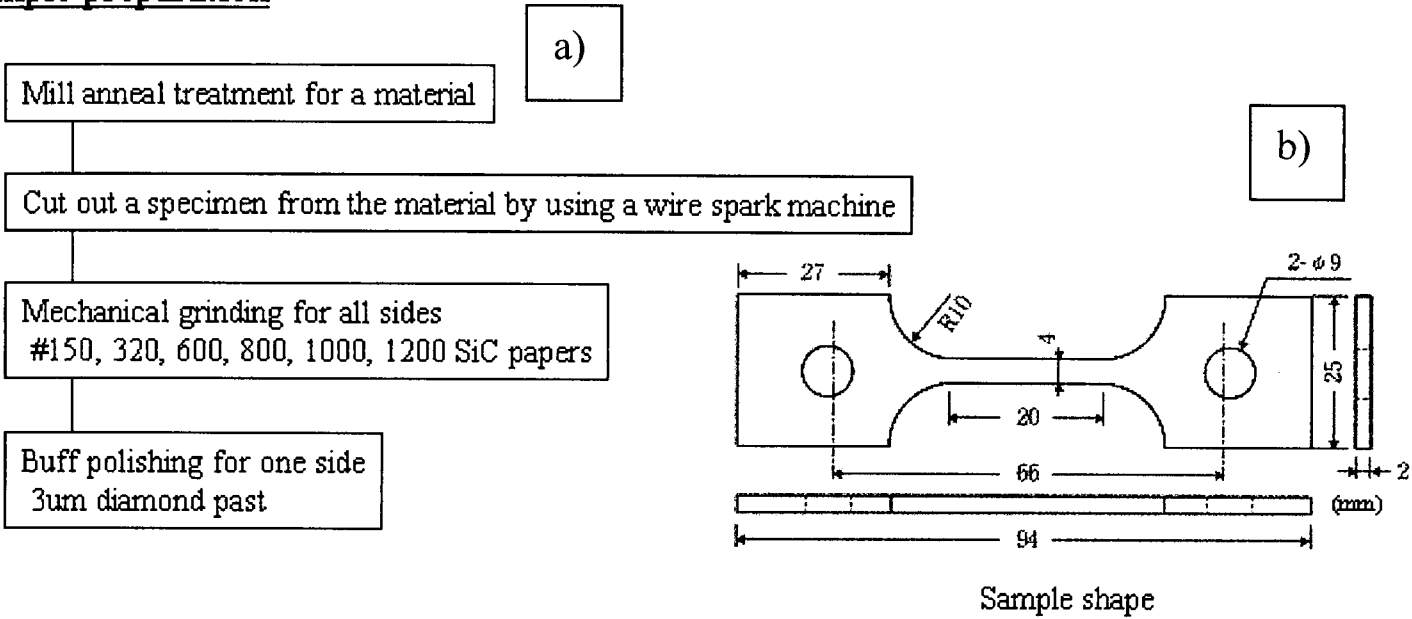


Fig. 5.3. a) Steps followed prior to testing and b) geometry of the test sample (courtesy of Dr. K. Fujii, INSS)

5.2.5 Autoclaves

SCC tests are generally performed in environment controlled vessels called autoclaves. This involves elevated-pressure and elevated-temperature experiments.

The autoclave vessel should be constructed of a corrosion-resistant alloy that does not introduce corrosion products to the test solution. Autoclave testing is generally conducted in either static or refreshed mode. In a static arrangement, the solution is not changed during the test, while in a refreshed arrangement, a flow of solution is maintained through the autoclave during the test ¹⁴. The autoclaves used for our experiments have worked in refreshed mode, so only this mode will be described in detail.

5.2.5.1 Refreshed autoclave systems

The autoclaves used have been manufactured by Toshin Kogyo Co., LTD (Japan) and are similar to that shown in Fig. 5.4.

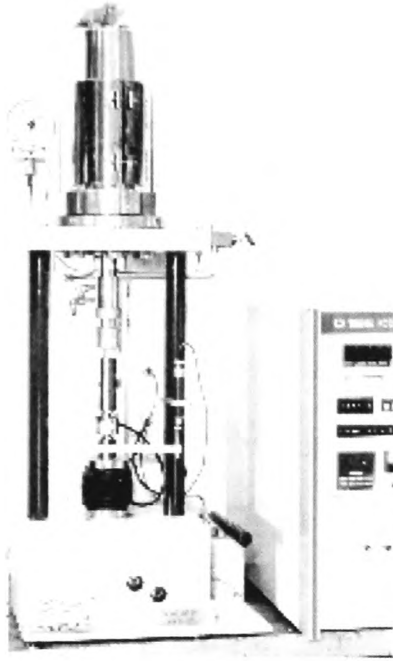


Fig. 5.4. Standard Toshin Kogyo autoclave similar to that used in this project.

In refreshed autoclaves, the test solution is pumped through the autoclave at a preselected rate. Fresh solution enters at the bottom of the autoclave from a pipe through the lid extending to the bottom of the autoclave vessel. A concentric outside pipe surrounding the inlet pipe takes the outgoing solution also through the lid port, but the outer pipe is shorter than the inner pipe to avoid fresh liquid from being sucked right out again. The concentric pipe arrangement serves to preheat the entering solution. A diagram with all the details of the configuration used by INSS can be seen in Fig. 5.5.

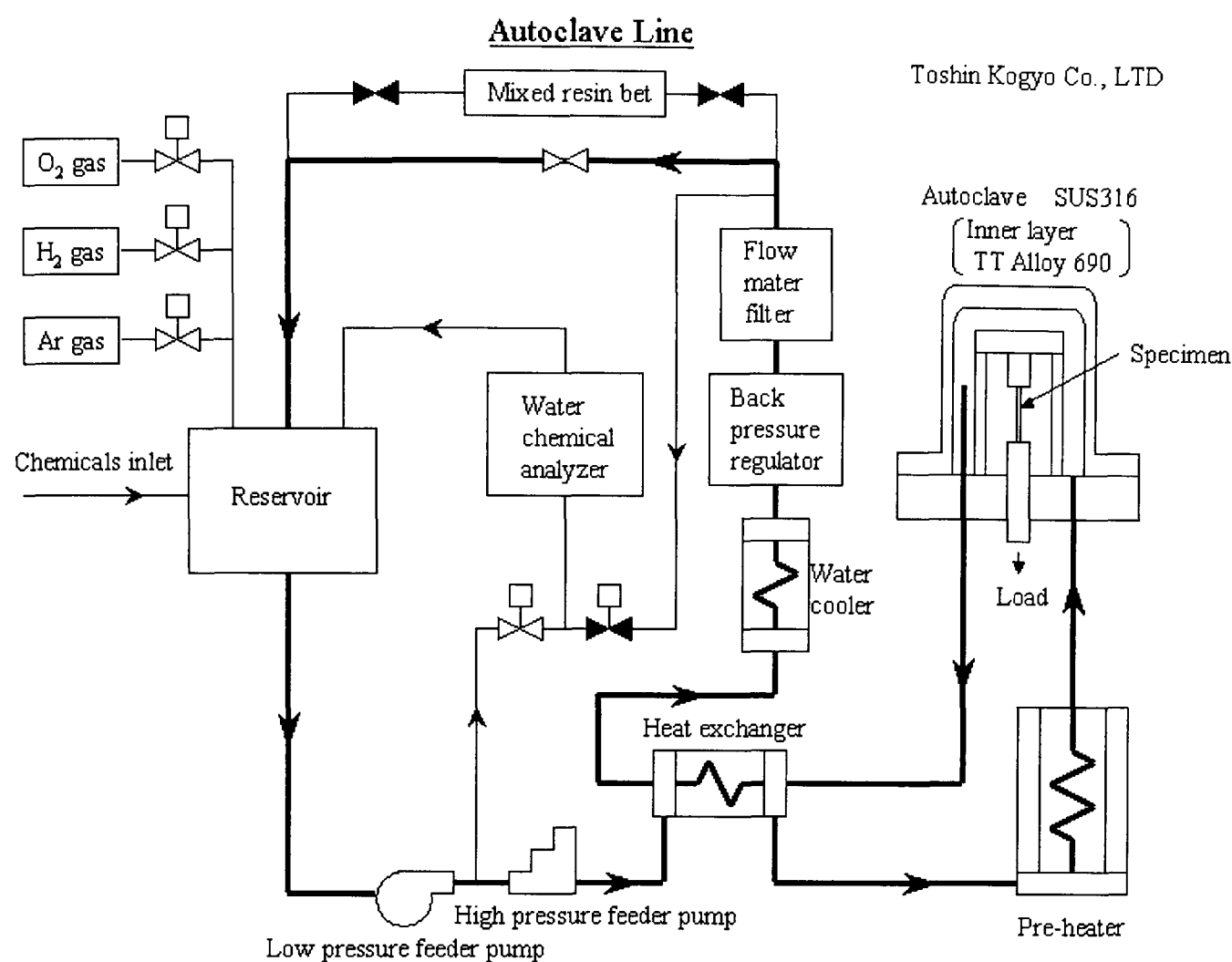
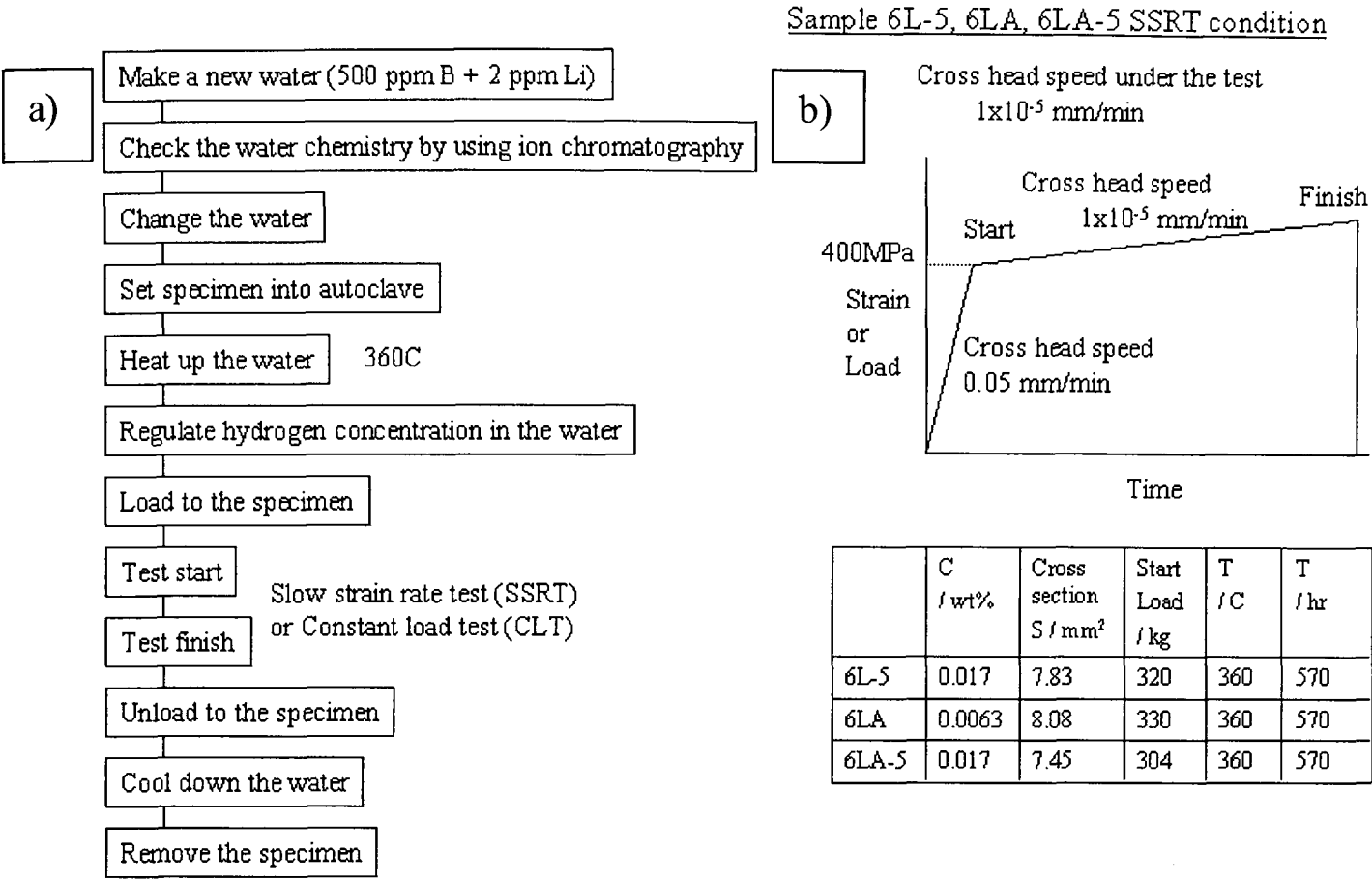


Fig. 5.5. Autoclave used by INSS for the slow strain rate tests and constant load tests (courtesy of Dr. K. Fujii, INSS)

5.2.6 Testing details for Alloy 600 samples

The exact procedure used by INSS for the tests is detailed in Fig. 5.6.

Corrosion test follow



more effective than tests with statically loaded U-bend specimens ⁵, although the validity of this test method is arguable.

When Ni alloys are tested in simulated PWR primary water conditions, some problems may arise, e.g. corrosion of autoclave components affecting water chemistry and particulate deposition.

Samples 6L5, 6LA5 and 6LA were tested at slow strain rate, while Sample B and the 304SS sample were tested at constant load.

5.2.6.1 Slow strain rate test data

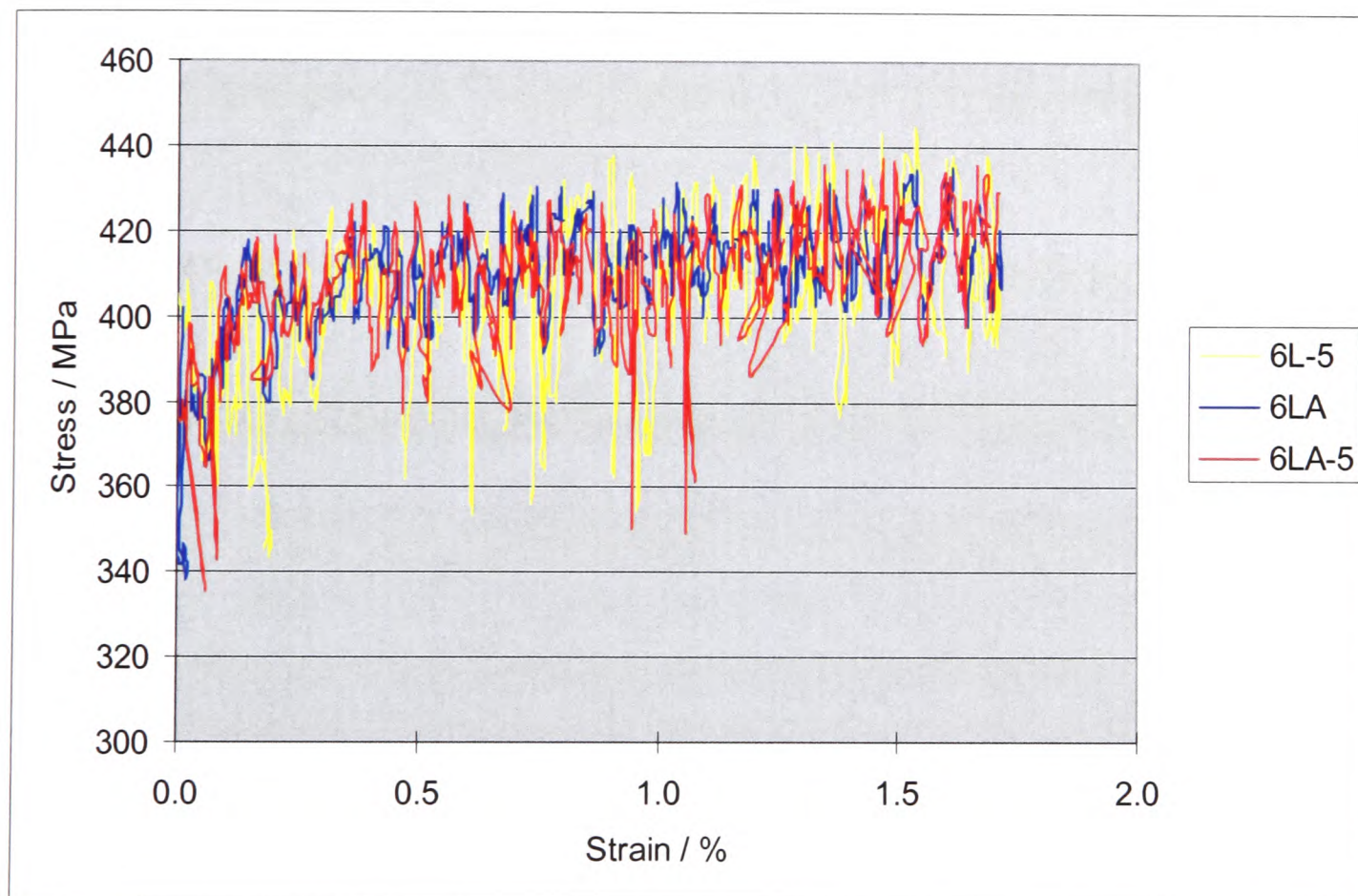


Fig. 5.7. Stress/strain curves for samples 6L-5, 6LA and 6LA-5 (courtesy of Dr. K. Fujii, INSS).

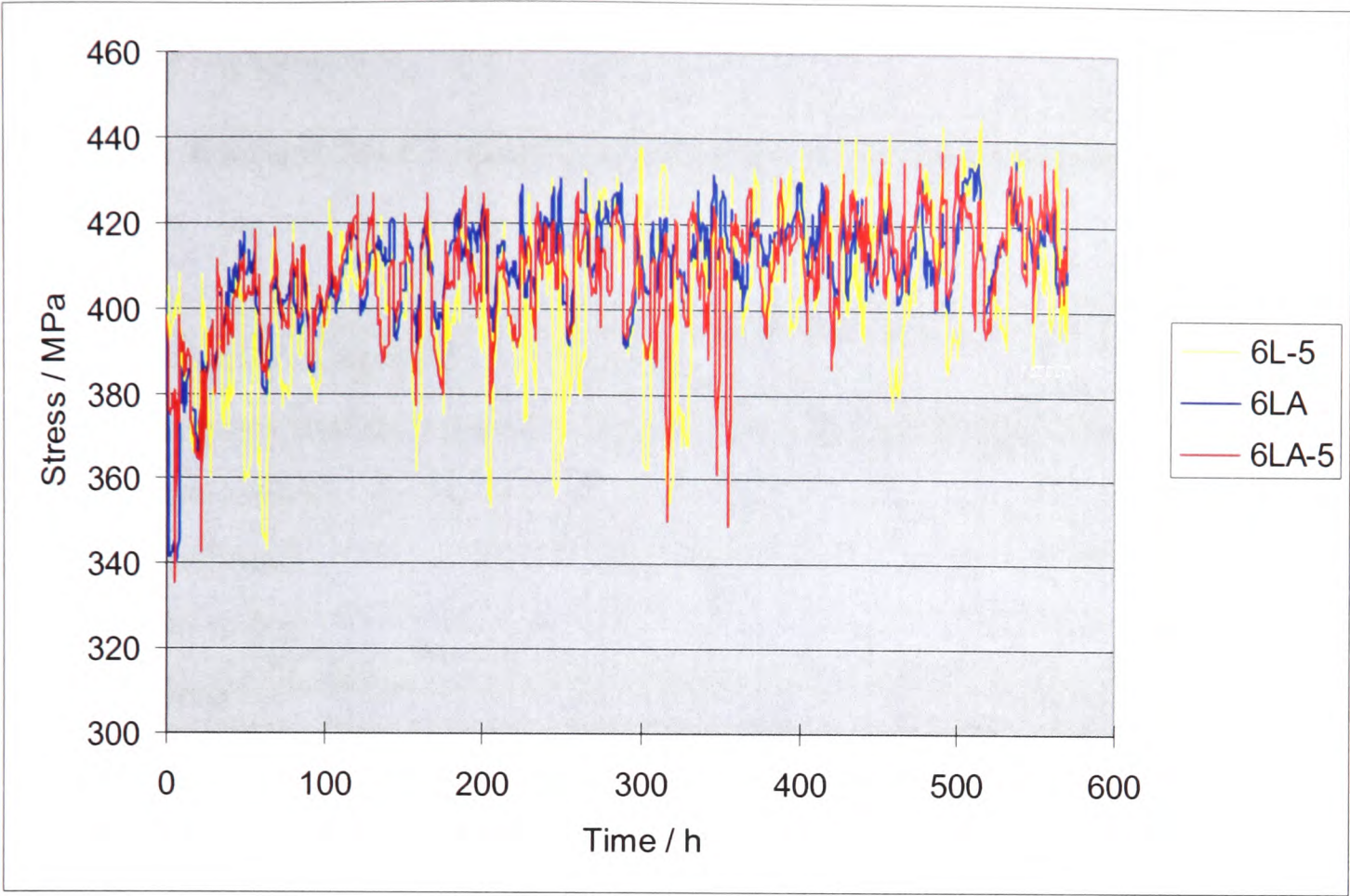


Fig. 5.8. Stress/time curve for alloys 6L-5, 6LA and 6LA-5(courtesy of Dr. K. Fujii, INSS).

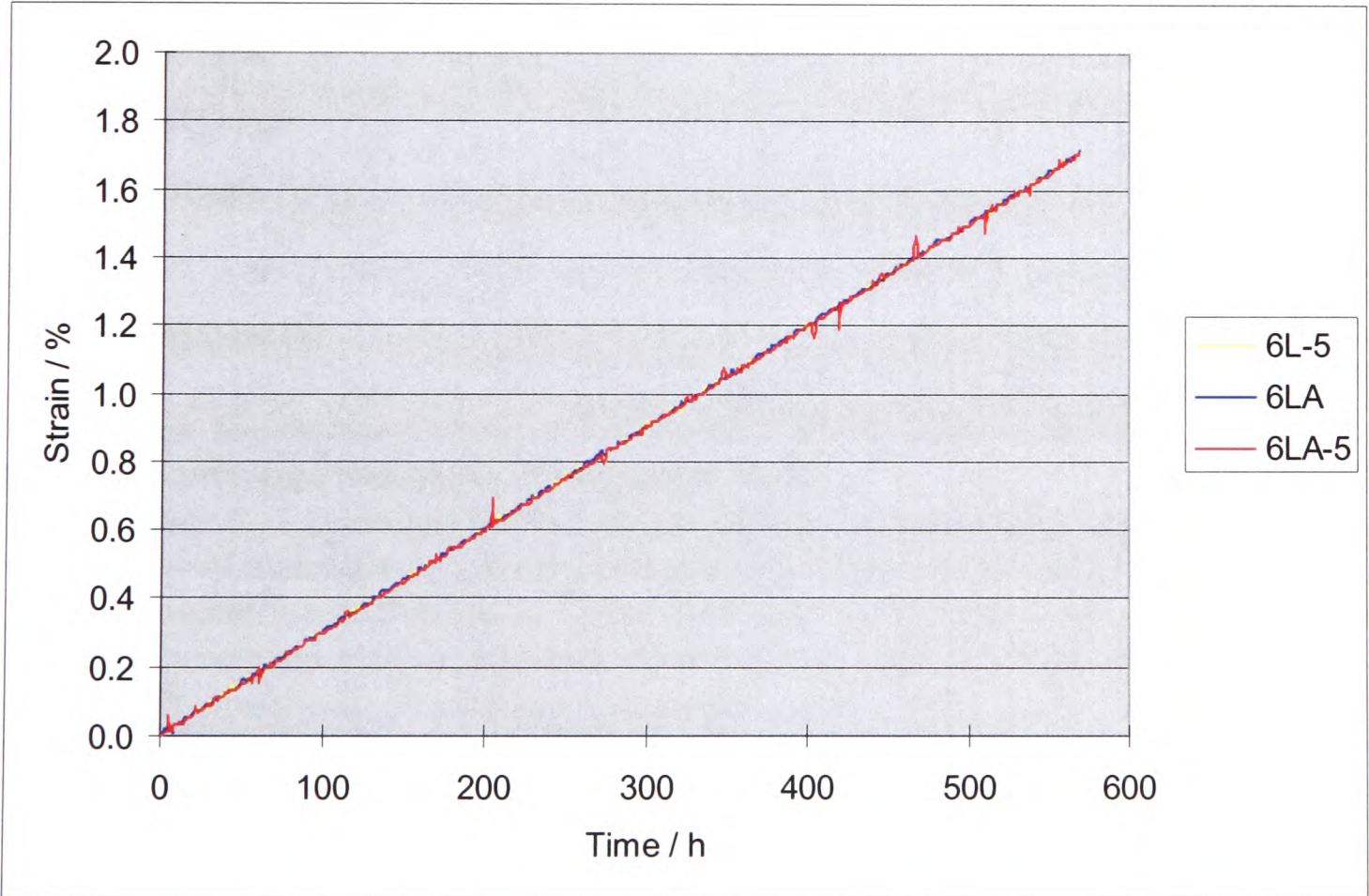


Fig. 5.9. Strain/time curve for alloys 6L-5, 6LA and 6LA-5 (courtesy of Dr. K. Fujii, INSS).

5.2.6.2 Constant load test data:

The constant load testing conditions for Alloy 600 (Sample B) were the following:

- It was performed in aqueous environment
- Solution composition: 500 ppm B + 2 ppm Li + 2.75 ppm H₂ (30 ccH₂/kgH₂O)
- Temperature: 360°C
- Load: 35 kgf/mm²
- Time: 4840 hours
- Did not break

For the 304SS sample were:

- It was performed in aqueous environment
- Solution composition: 500 ppm B + 2 ppm Li + 0.5 ppm DO₂
- Temperature: 240°C
- Load: 410 Mpa
- Time: 1008 hours
- Did not break

5.3 References

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Chapter 6:

EBSD results

6.1 Introduction

EBSD was used during this project to identify if any grain boundary orientations and/or misorientations were more susceptible to SCC than others. Two bulk samples were analyzed: Alloy 600 and 304 SS, both from Constant Load Tests. Details about this technique can be found in section 3.3.2.3 of this thesis. Samples will be shown in a cross-sectional view, with the loading direction parallel to the edge of the sample.

The results showed some similarities between both materials: They cracked preferentially along high-angle grain boundaries in a preferential orientation perpendicular to the load direction. No twin boundaries were found to crack nor to suffer IGA.

It was also checked if any grain orientation were particularly preferred for cracking, both in the transverse and rolling direction, without finding any significant differences.

6.2 Alloy 600

69 boundaries were studied. Of these, 19 cracked, all high-angle boundaries. 50 boundaries did not crack: 7 were low angle boundaries, 34 were twins and 9 were high-angle boundaries. The high-angle boundaries that did not crack belonged to small grains with elongated shapes parallel to the surface.

In Fig. 6.1, a typical SC crack in a grain boundary with an orientation almost exactly perpendicular to the load direction is shown. It was a common observation that when these kind of boundaries were found opened, the flanks of the crack showed complementary features, suggesting an abrupt and elastic opening of the boundary, while the region close to the blunt crack tip was found to have some plastic deformation. The crack usually arrested at triple points, when the grain boundary plane changed its orientation (decreasing mode I loading) or when a precipitate was present in the grain boundary. In Fig. 6.1, the reason for the arresting seemed to be the combined effect of a triple point and twin boundaries at either sides of the flanks.

In Fig. 6.2, a crack which opened 2 grain boundaries is shown. While the first grain boundary was in pure mode I loading, the second grain boundary was in a less favourable mixed I+II mode, due to its orientation. The propagation in this mode showed some different features: e.g. the crack tip was not blunt but sharp. The reason for the arrest seemed to be a triple point. The same features are shown in Fig. 6.3, but in this case, the two boundaries after the first triple point opened. Both also arrested when reaching further triple points.

An area without cracks has been analyzed in Fig. 6.4, showing that all the boundaries that did not crack have a small misorientation angle ($<19^\circ$).

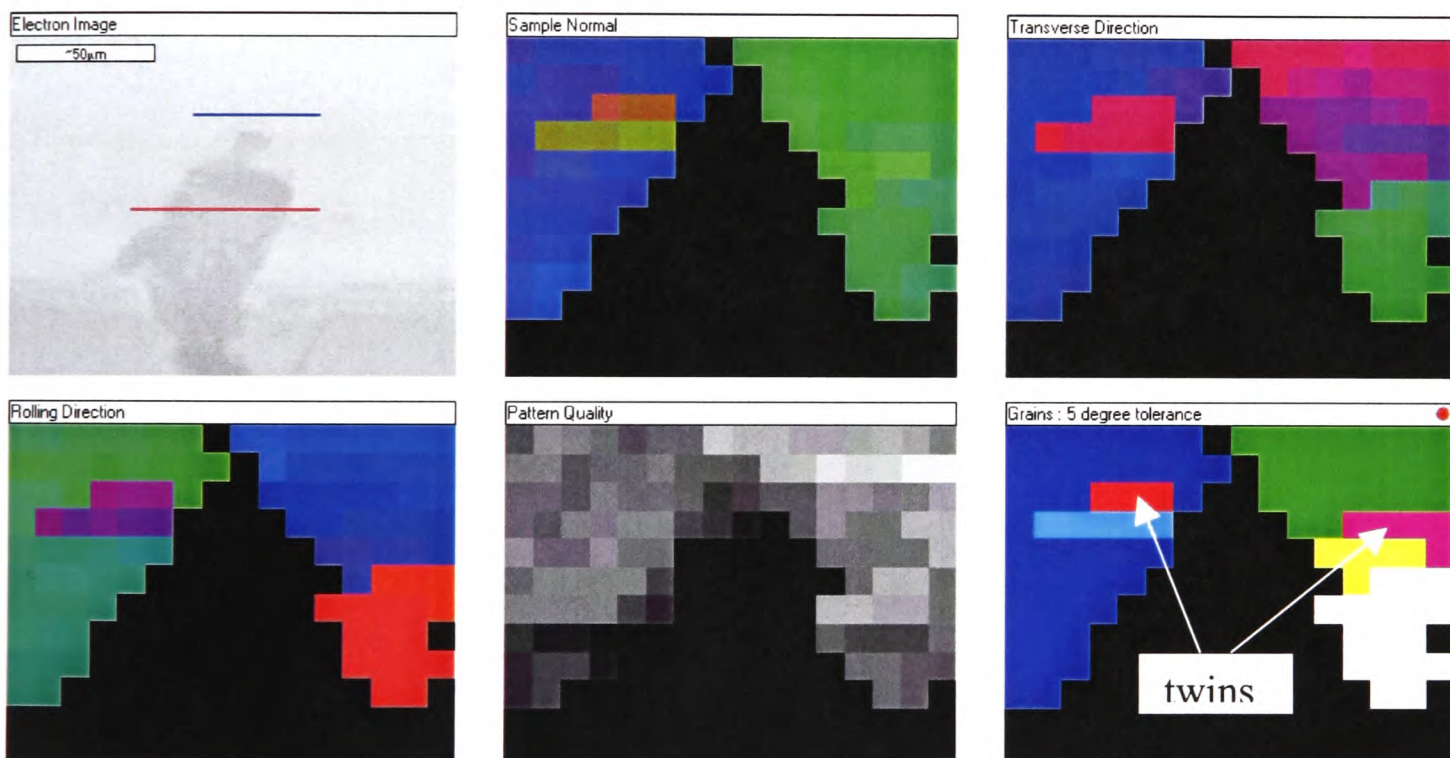


Fig. 6.1. Stress Corrosion Crack in Alloy 600. Misorientations: 45° , 35° (acquired with the OPAL system in the 6300)

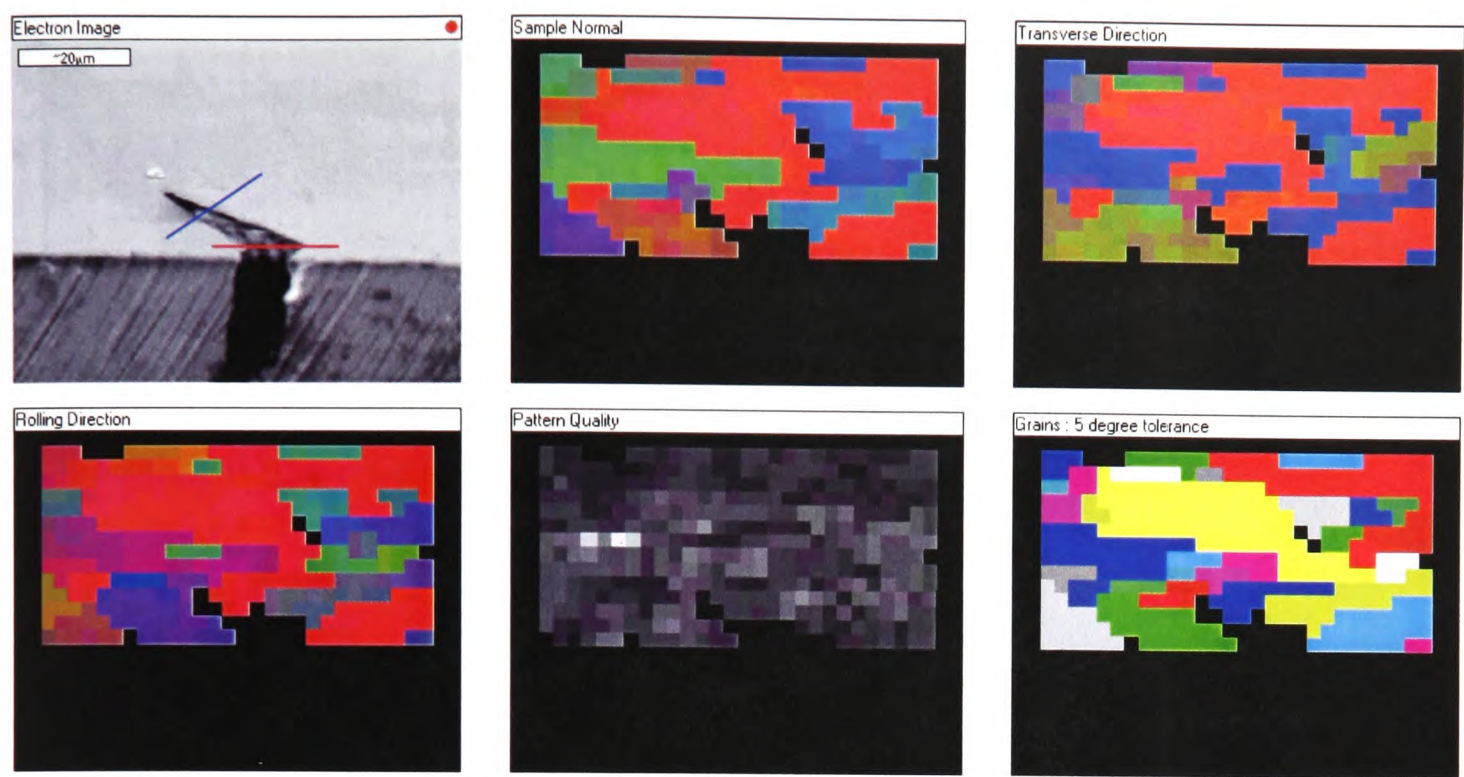


Fig. 6.2. Stress Corrosion Crack in Alloy 600. Misorientations: 27°, 47° (acquired with the OPAL system in the 6300).

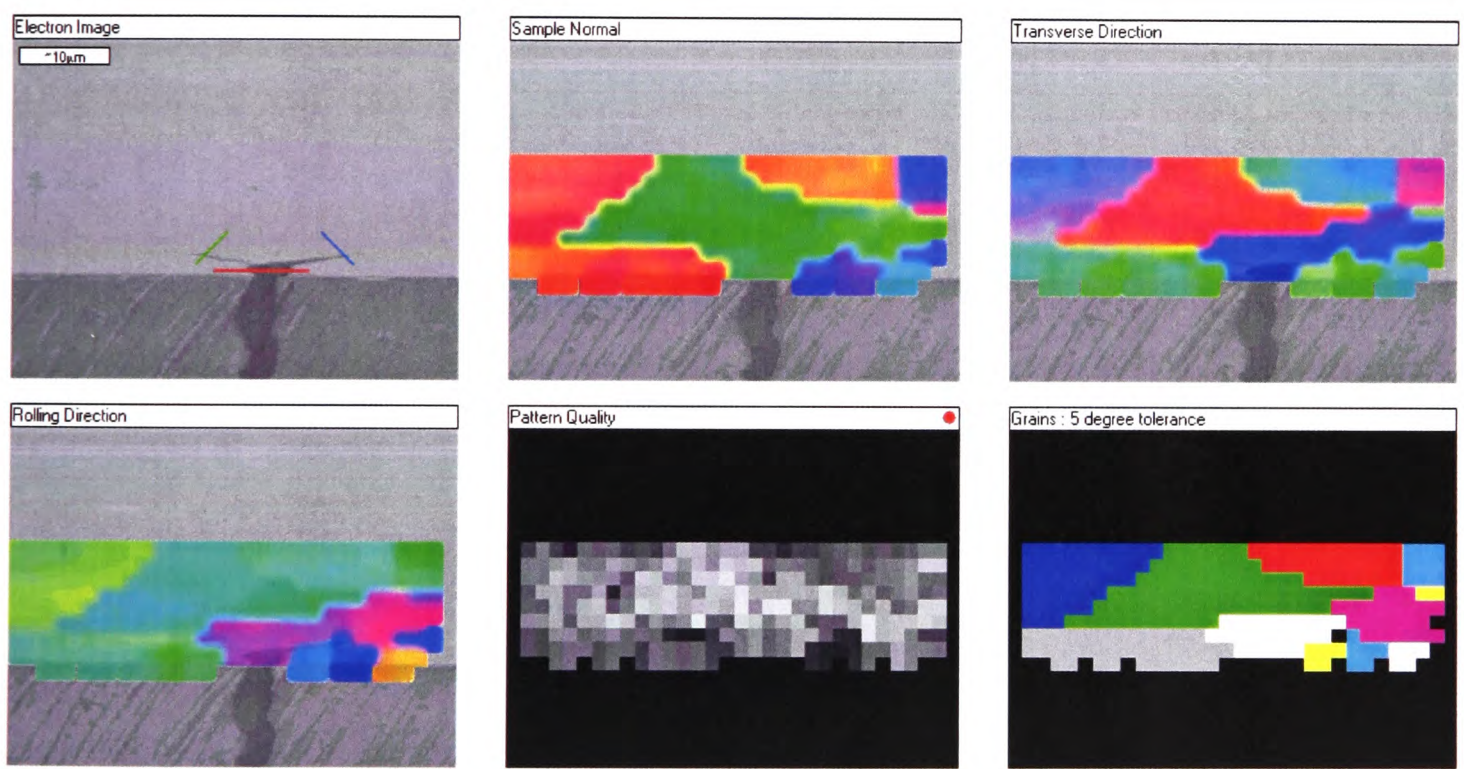


Fig. 6.3. Stress Corrosion Crack in Alloy 600. Misorientations: 44°, 33°, 37° (acquired with the OPAL system in the 6300)

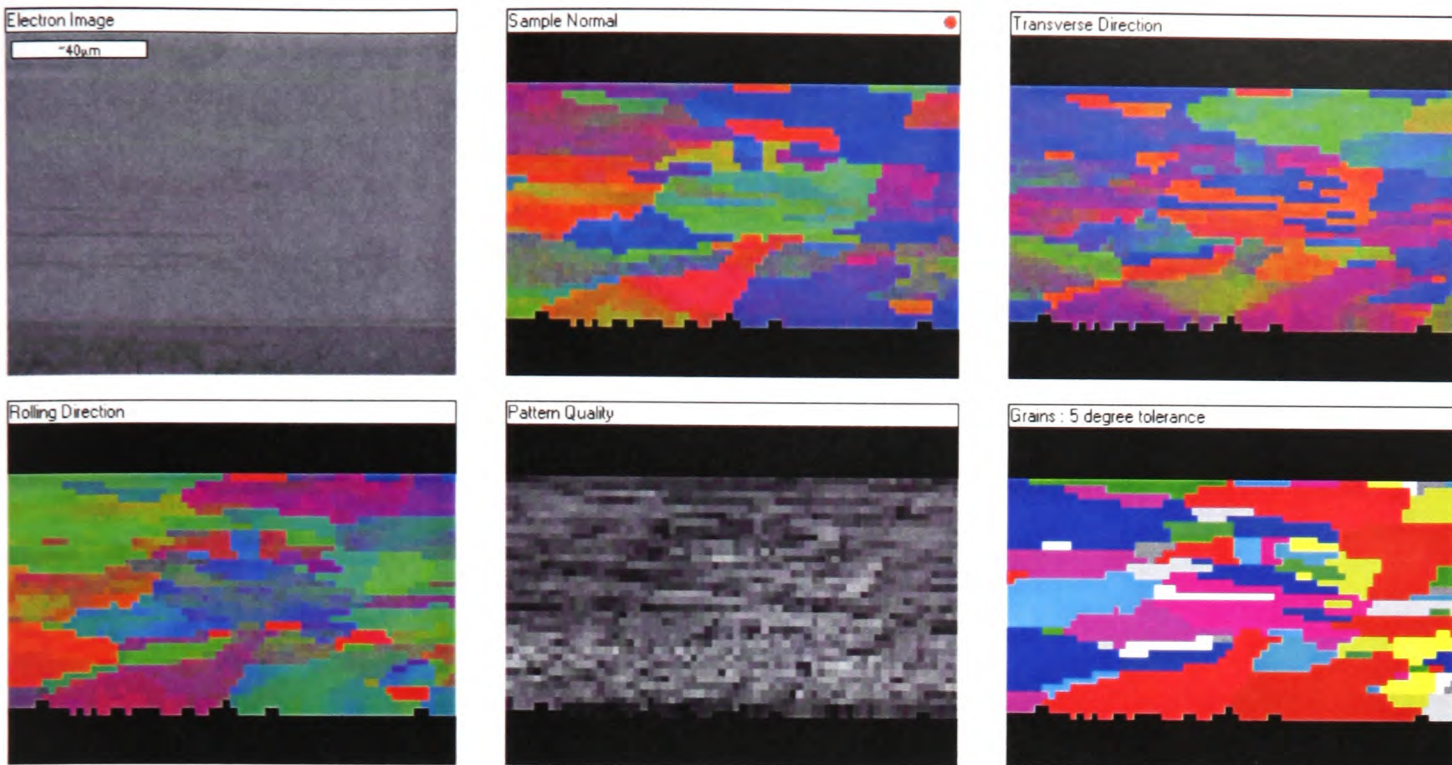


Fig. 6.4. Area without cracks in Alloy 600. Misorientations of boundaries intersecting the surface (from left to right): 13°, 50°, 18° (acquired with the OPAL system in the 6300)

6.3 SS304

50 boundaries were studied. Of these, 17 cracked, all high-angle boundaries.

33 boundaries did not crack: 12 were low angle boundaries, 8 were twins and 6 were high angle boundaries.

The sample chosen for analysis had 2 major cracks with lengths of several mm. These cracks showed many bifurcations as they penetrated the sample, but always maintained a general tendency to grow in a perpendicular direction to the loading. In Fig. 6.5, one of the main cracks is shown and 3 of the grain boundaries analyzed. As can be seen, the flanks of the crack are separated by $\sim 100\ \mu\text{m}$ and some grains have been completely attacked and become detached, apparently, from their neighboring grains (see arrow in Fig. 6.5). The attacked boundaries were found to have a high misorientation.

In Fig. 6.6, a crack similar to that found in Alloy 600 is shown (see Fig. 6.3). The first boundary was close to pure mode I loading and seems to have been opened abruptly, while the cracks in grain boundaries crossed by the blue and green lines appear sharper.

In Fig. 6.7 the other main crack is shown, exhibiting similar features to those in the crack shown in Fig. 6.5. Another completely attacked grain can be see (arrowed in Fig. 6.7).

A region without cracks is shown in Fig. 6.8 and it can be seen that most of the uncracked boundaries are low-angle boundaries. The presence of small and elongated grains close to the surface exposed to the environment was a common observation and is assumed to be due to final polishing or grinding of the sample before testing.

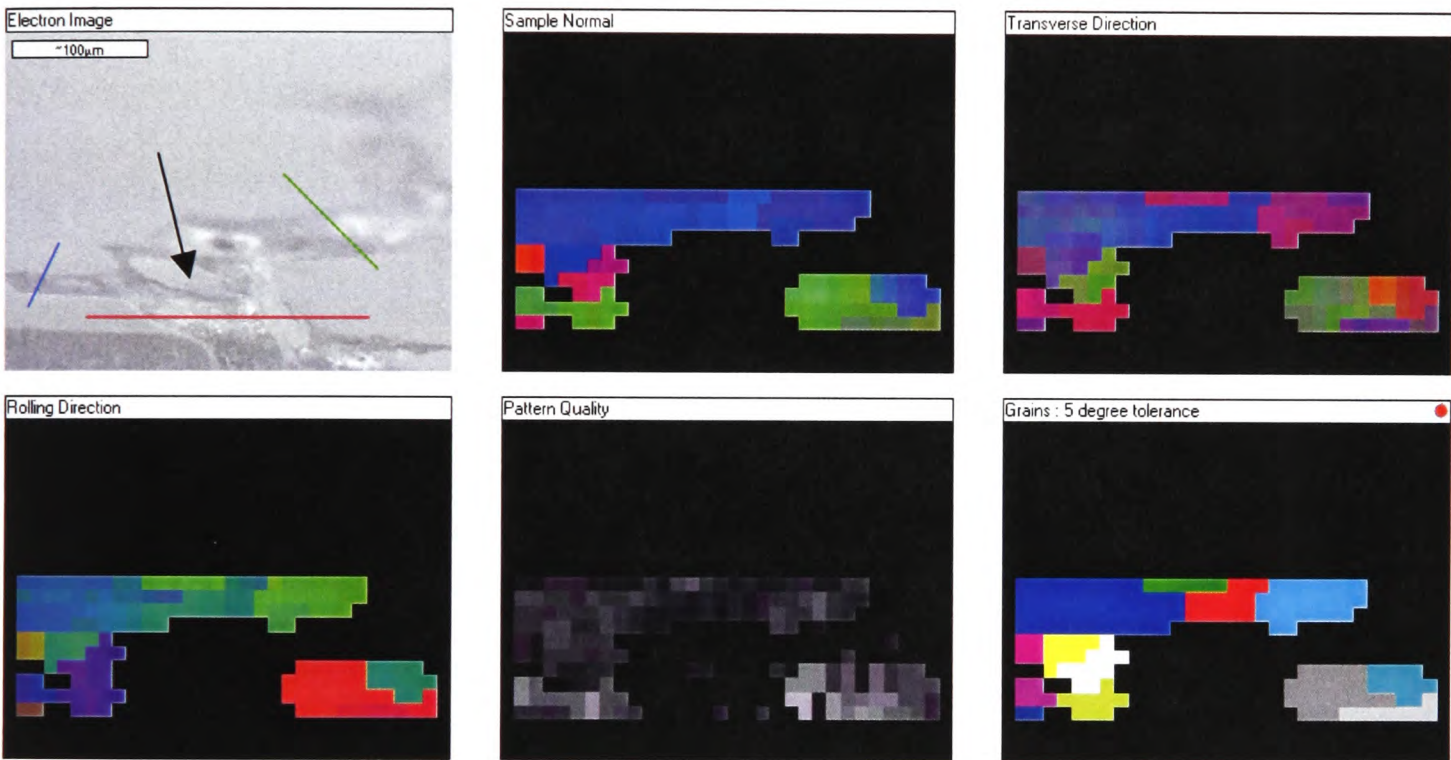


Fig. 6.5. Stress Corrosion Crack in 304 SS. . Misorientations: 60°, 43°, 45° (acquired with the OPAL system in the 6300).

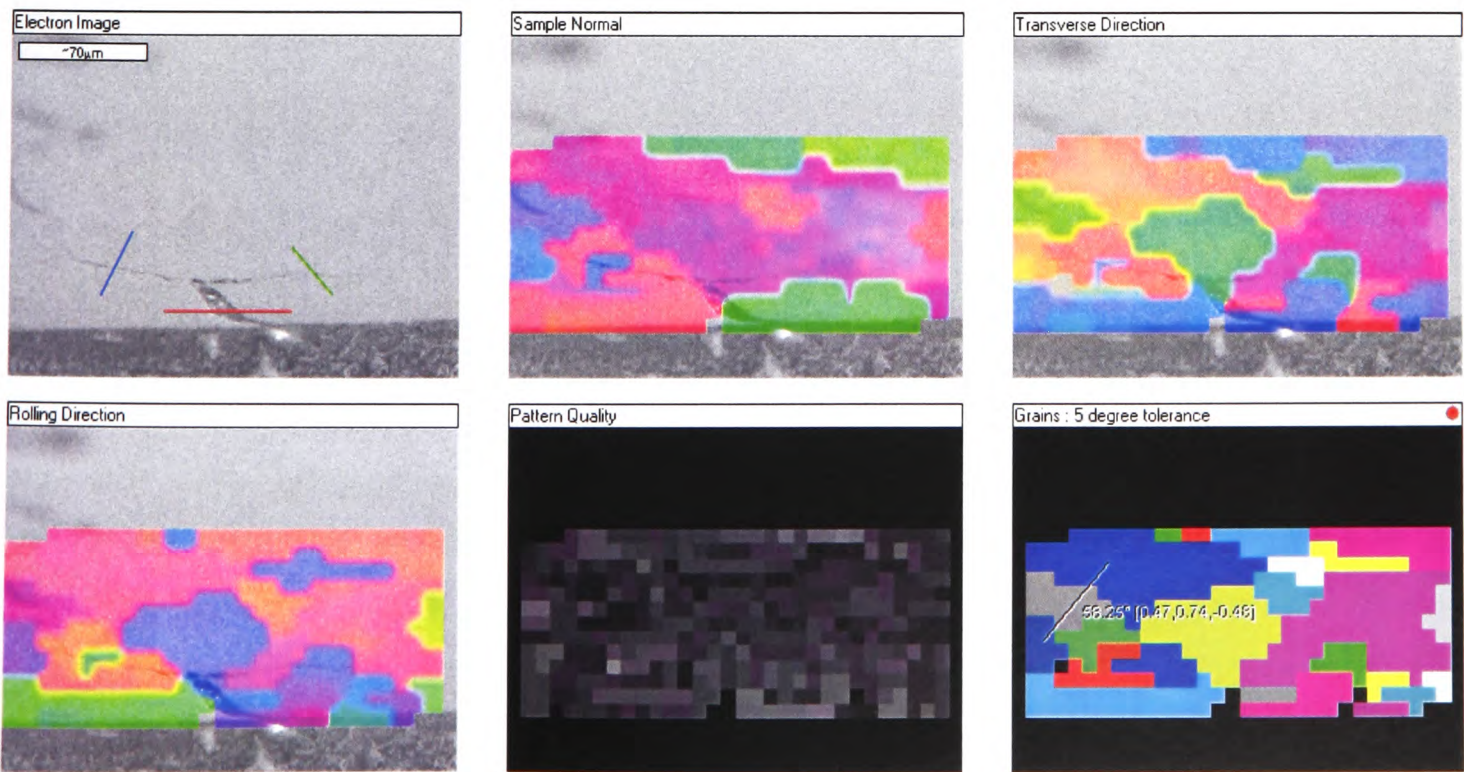


Fig. 6.6. Stress Corrosion Crack in 304 SS. . Misorientations: 35°, 44°, 55° (acquired with the OPAL system in the 6300).

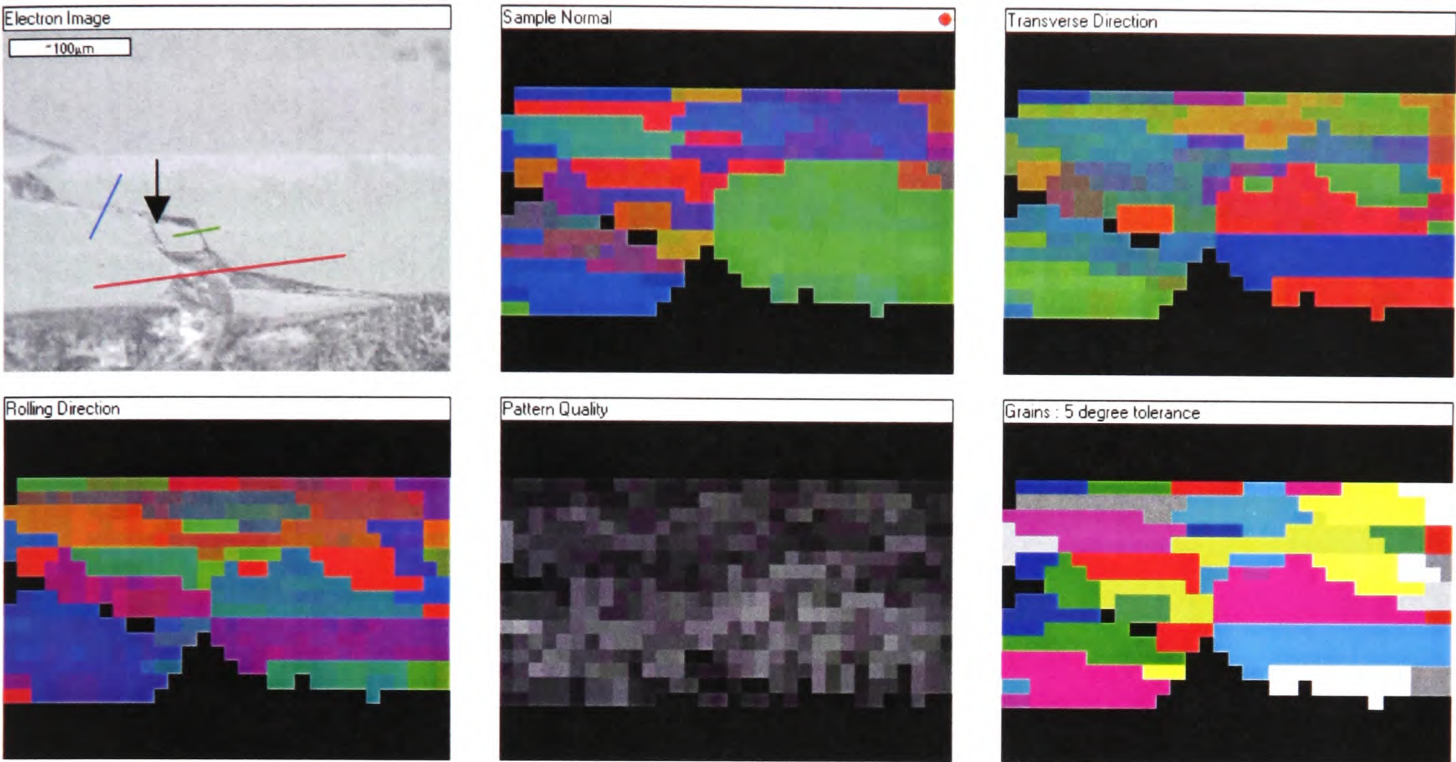


Fig. 6.7. Stress Corrosion Crack in 304 SS. . Misorientations: 43°, 55°, 50° (acquired with the OPAL system in the 6300).

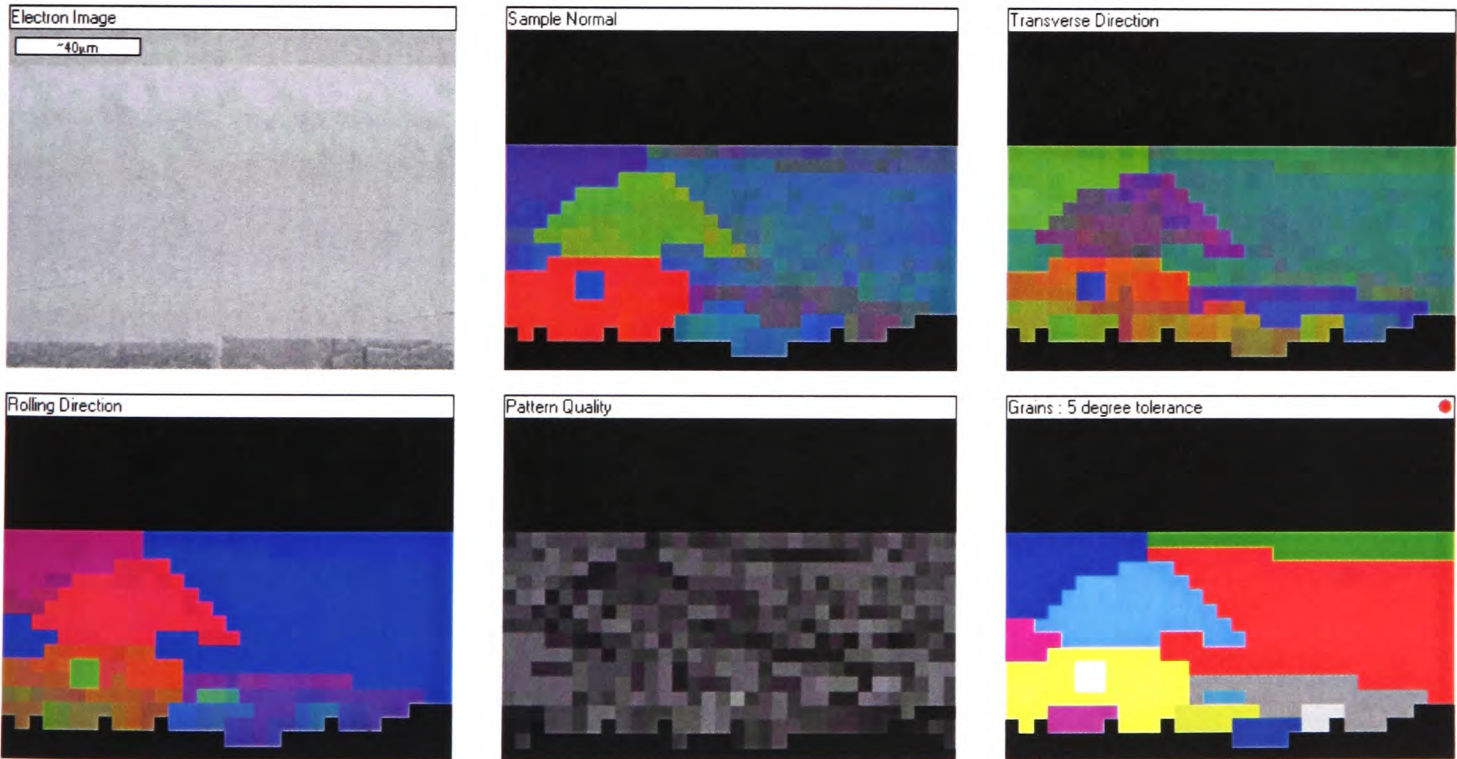


Fig. 6.8. Area without cracks in 304 SS. Misorientations of boundaries intersecting the surface (from left to right): 3°, 5°, 45°, 15° (acquired with the OPAL system in the 6300)

6.4 Conclusions

EBSD has proven to be a very useful technique to reveal grain orientation prior to TEM sample preparation. It is also a very fast and reliable way of obtaining grain misorientation data and its influence on SCC.

Both samples examined have exhibited a preference to crack along high-angle boundaries. Twins and low-angle boundary have appeared as very resistant to SCC.

Chapter 7:

Alloy SS304

7.1 Introduction

Stainless steels are iron-based alloys designed to be corrosion-resistant containing a maximum of 1.2% carbon and a minimum of 10.5% chromium by weight. Their corrosion resistance is provided by a very thin and protective surface film, known as the passive film, which has the peculiarity of being self-healing when damaged by a corrosive environment ³. The most common austenitic steel is the so-called 18/8, containing around 18% Cr and 8% Ni. It has the lowest nickel content which allows a fully austenitic structure. When a greater stability towards the formation of martensite is required, the nickel content is increased. Resistance to pitting and crevice corrosion is usually improved by further alloying the austenitic grades with Cr, Mo and N. By increasing the Cr, a greater resistance to intergranular corrosion is achieved. Intergranular corrosion results from chromium depletion in the alloy matrix near grain boundary chromium carbides precipitated during high temperature exposures ¹.

Typical applications for 304 include hollowware, architecture, food and beverage processing, equipment and utensils, commercial and domestic kitchen construction, sinks, and plant for chemical, petrochemical, mineral processing and other industries.

In this project, the 304SS sample has been used to develop a suitable TEM sample preparation technique which allowed the study of “long” cracks (~ 3 mm). The length of the cracks was a limitation when using FIB, so a combined PIPS- FIB technique was developed (See Chapter 4). However, as it will be shown, FIB was also used alone to prepare x-sectional samples containing sections of the crack which were found to be very useful for characterising the oxide layers and the interaction of the crack with carbides.

7.2 Sample description

Material: 304SS

The type 304SS sample composition plus test condition were as follows:

Chemical composition (wt%):

C: 0.054, Si: 0.52, Mn: 1.48, P: 0.024, S: 0.001, Ni: 9.74, Cr: 18.44, Fe: Bal.

Pre-test heat treatment:

Sensitization: Heat treatment 1050°C for 30 min + 750°C for 100 min + 615°C for 5h

Constant load testing conditions:

In aqueous environment

Solution: 500 ppm B + 2 ppm Li + 0.5 ppm DO₂

Temperature: 240°C

Load: 410MPa

Time: 1008 h

Did not break

Two pieces of 304 SS have been analyzed, both tested under constant load conditions as described in the Section 5.2.6.2. Both samples had developed some long cracks of the order of the mm, always perpendicular to the stress direction.

The geometry of the original sample can be seen schematically in Fig. 7.1.

The bulk sample contained the two big cracks examined by EBSD with lengths of the order of mm (as can be seen in Fig. 7.2). These cracks are shown individually in Figs. 7.3 and 7.4. and were found to bifurcate into smaller ones (Fig. 7.5), so that the main trend of the crack was to grown in a direction perpendicular to

the applied stress. Several small cracks were also found perpendicular to the samples edge.

In order to study the long cracks, the TEM samples were prepared using PIPS, as described in Section 3.2.2, while for the small ones, FIB was used. FIB was also used to try to reach the crack tip of the secondary cracks from the cross-sectional plane.

The 3 mm disc containing cracks after the first PIPS polishing is shown in Fig. 7.6. The crack tip area was position close to the centre of the disc. The effects of the PIPS polishing in the sample can be seen in Fig. 7.7. The details at the big crack entrance (Figs. 7.7a, 7.7c) and the secondary cracks (Figs. 7.7b and 7.7d) are shown. It can also be noted how the oxides in the crack flanks are preferentially milled by the Ar ion beam.

Some of the positions chosen for the preparation of the FIB cross-sections are shown in Fig. 7.8. These x-sections were prepared from the previously polished x-sectional surface, which facilitated the identification of the attacked boundaries and the positions of the multiple crack tips. In Fig. 7.9, one of the membranes is shown after tilting 40° from the milling direction prior to final thinning, cutting and plucking.

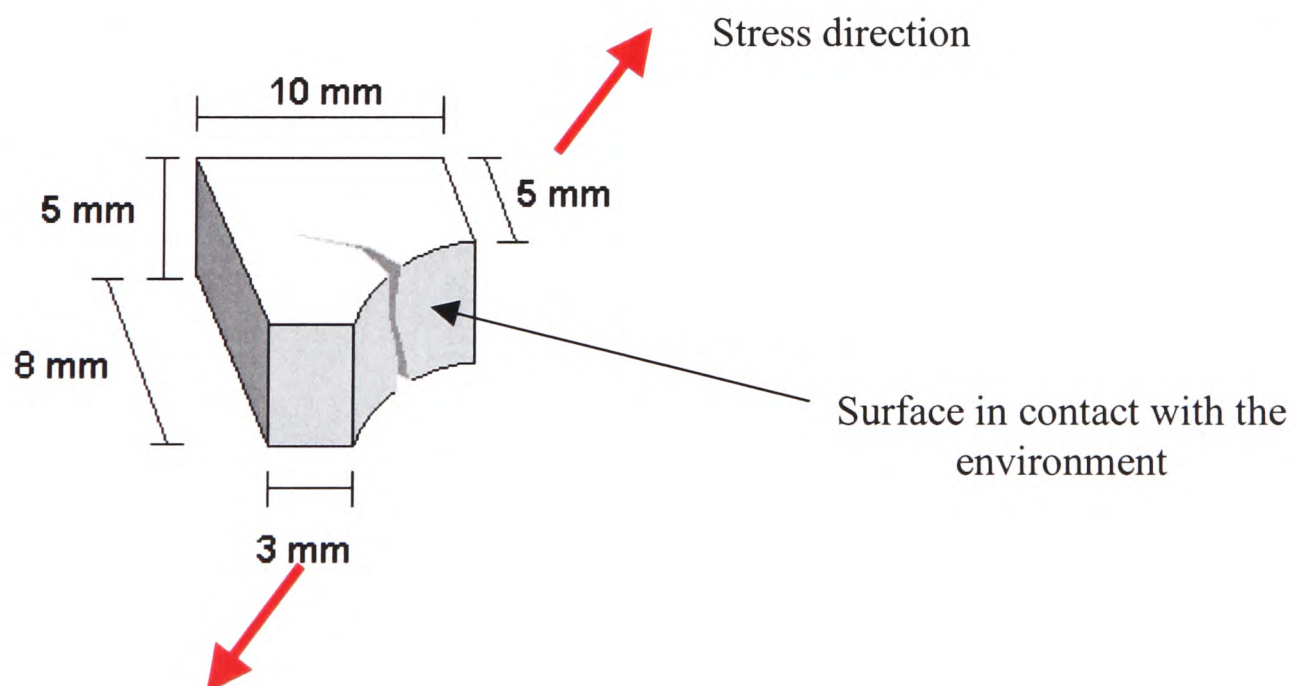


Fig. 7.1. Schematic view of the 304SS sample as received.

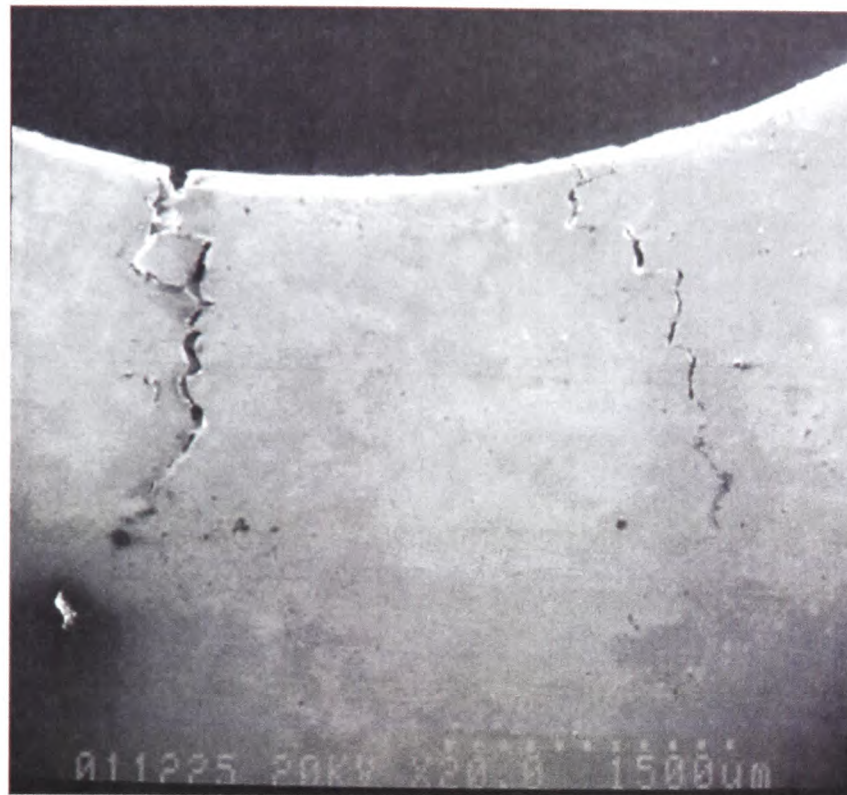


Fig. 7.2. SEM SE micrograph showing 2 long cracks on the cross-sectional side.

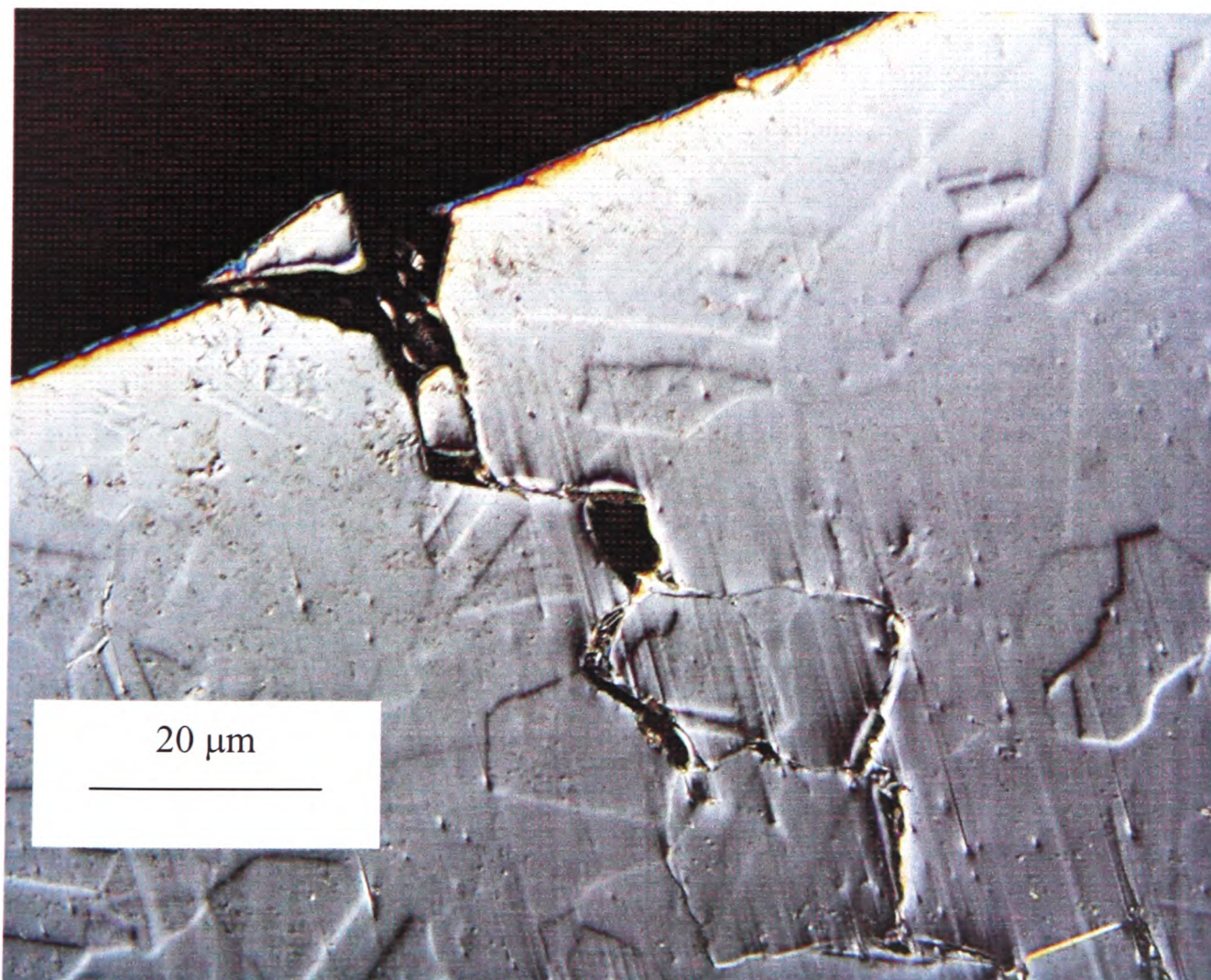


Fig. 7.3. Optical micrograph of 304SS. Cross-section etched with syton (silica).

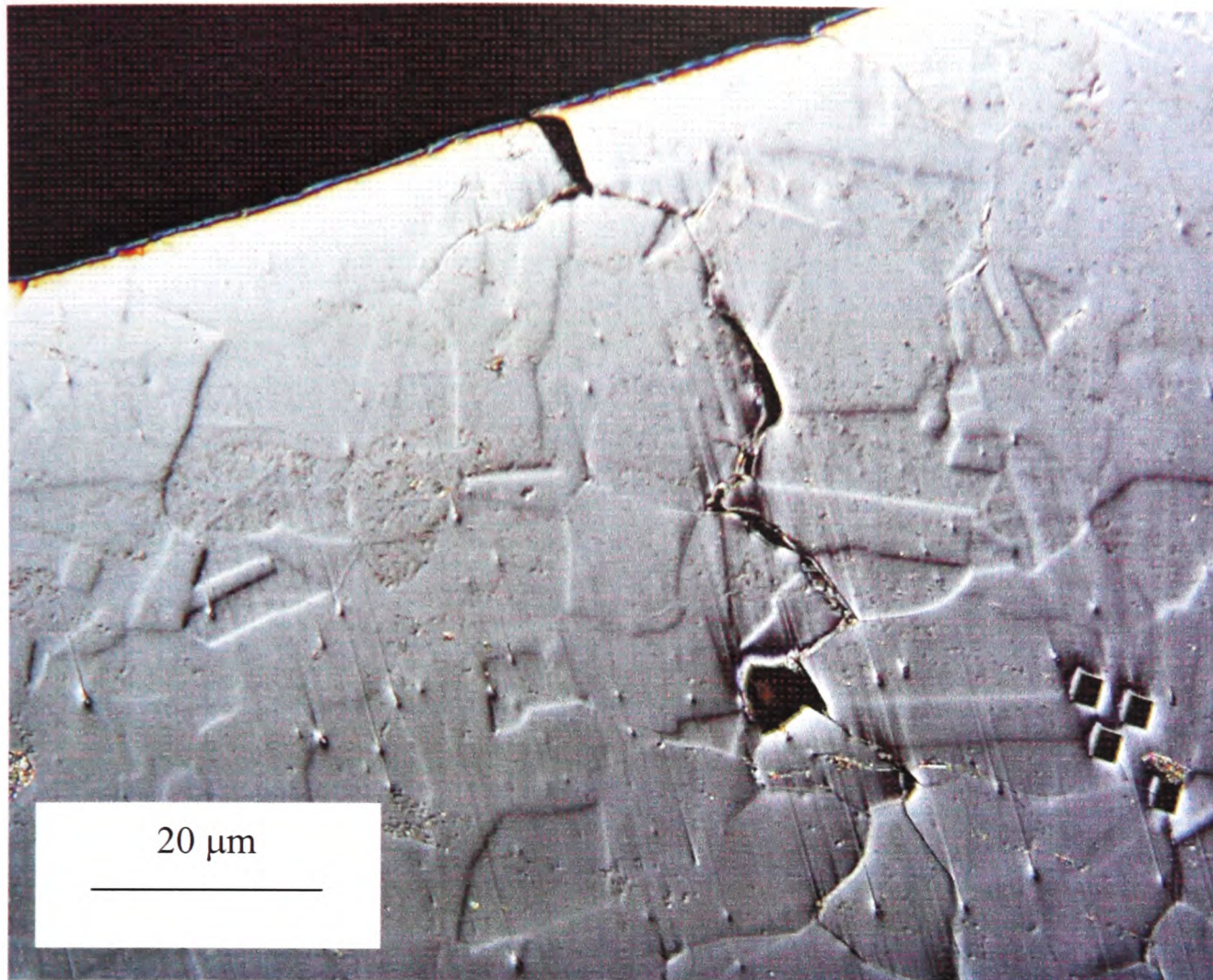


Fig. 7.4. Optical micrograph of 304SS. Cross-section etched with syton (silica) with some FIB trenches in the right bottom corner.

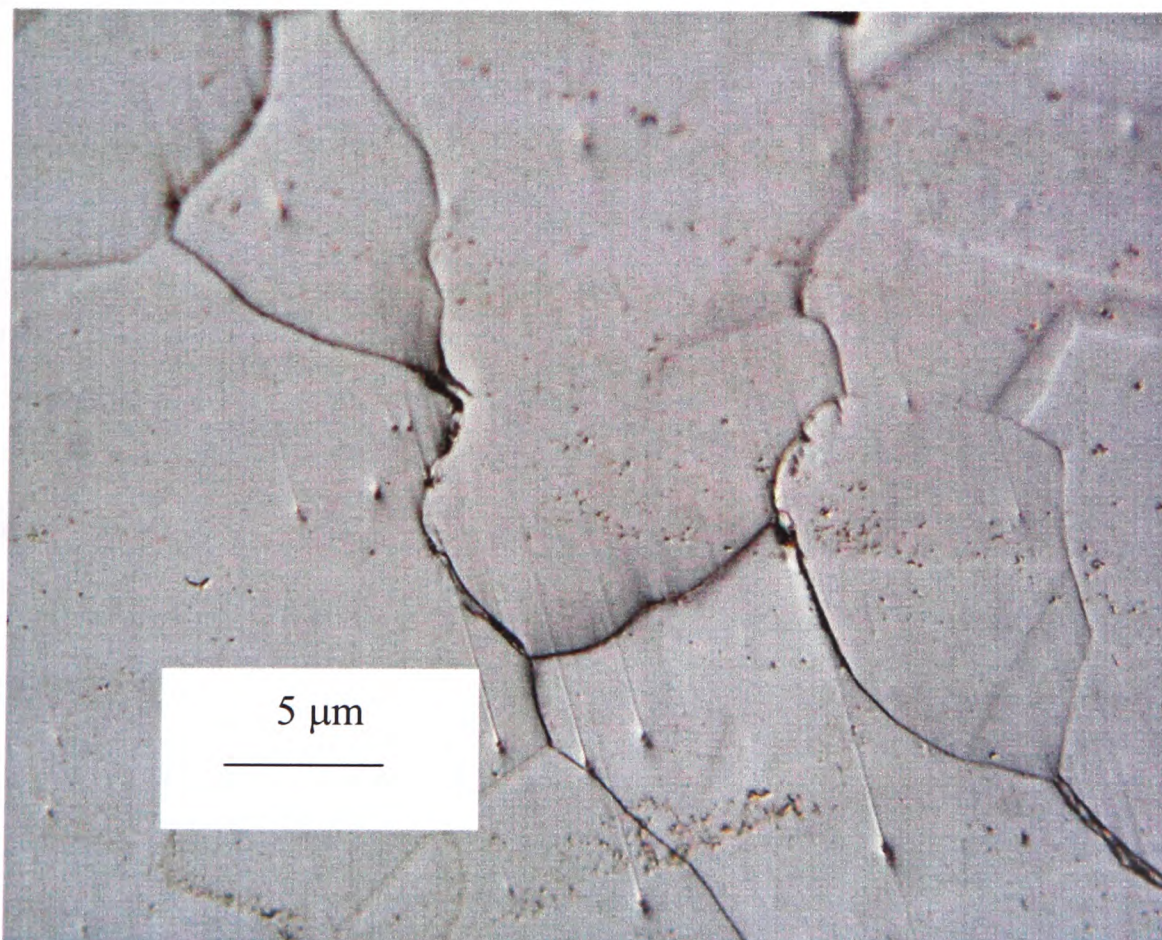


Fig. 7.5. Optical micrograph of 304SS. Cross-section etched with syton (silica) showing IGSCC.

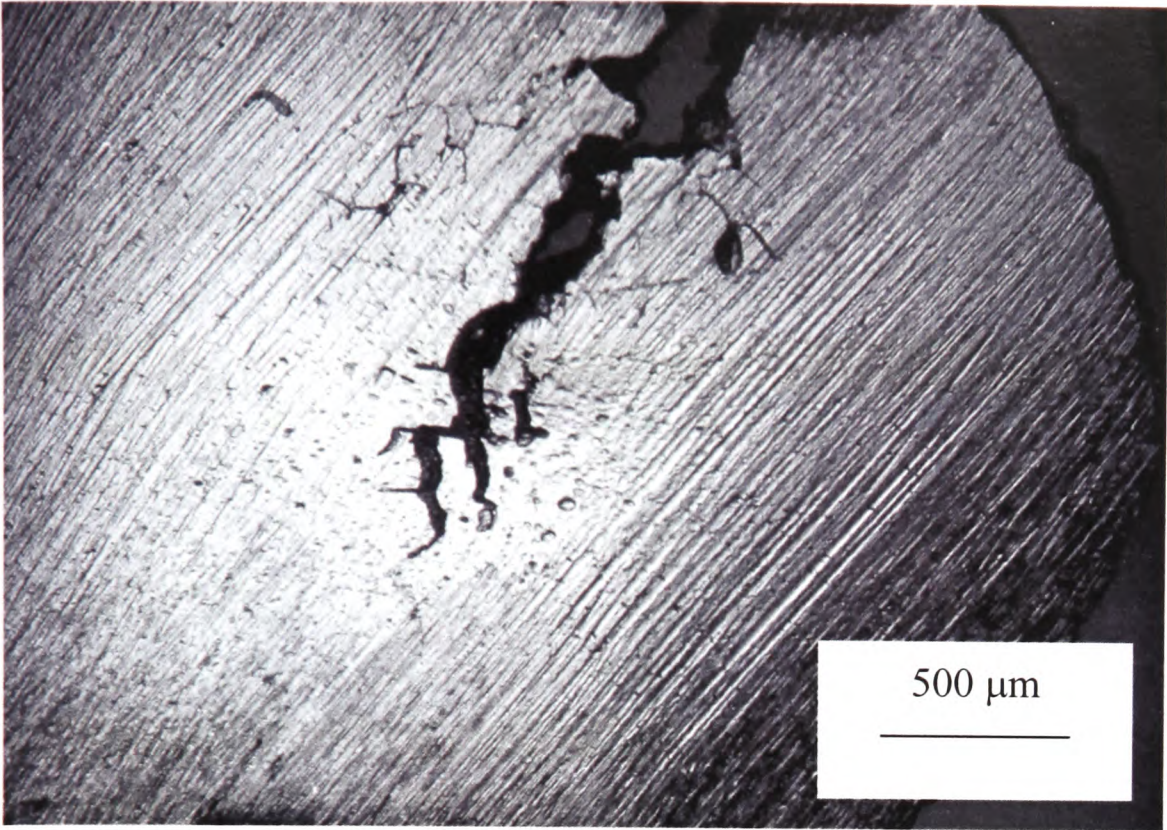


Fig. 7.6. Optical micrograph of a 3mm disk after the first PIPS milling, showing how the crack tip is located at the centre of the disk.

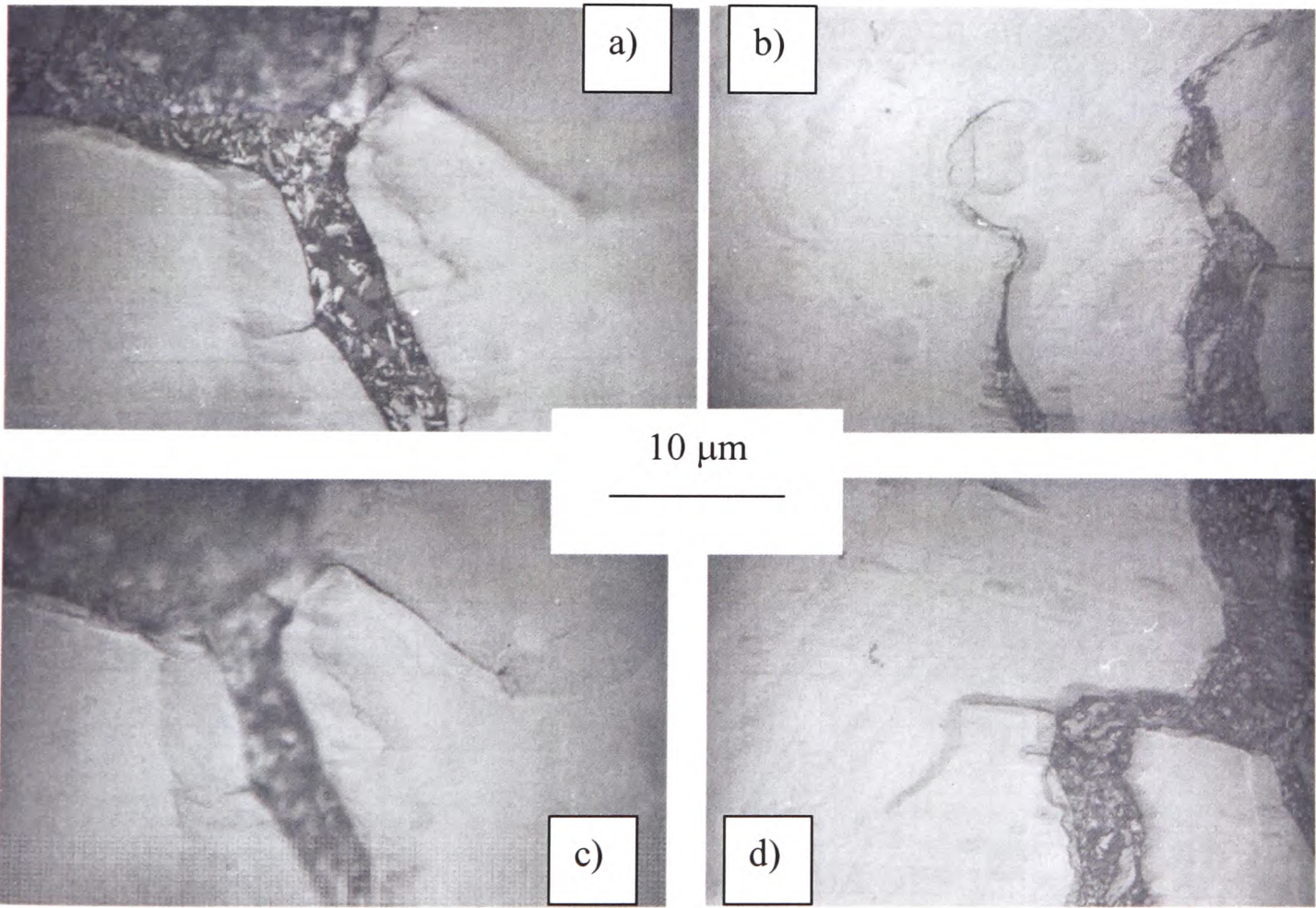


Fig. 7.7. Optical micrographs of different views of cracks in the sample after further PIPS polishing.

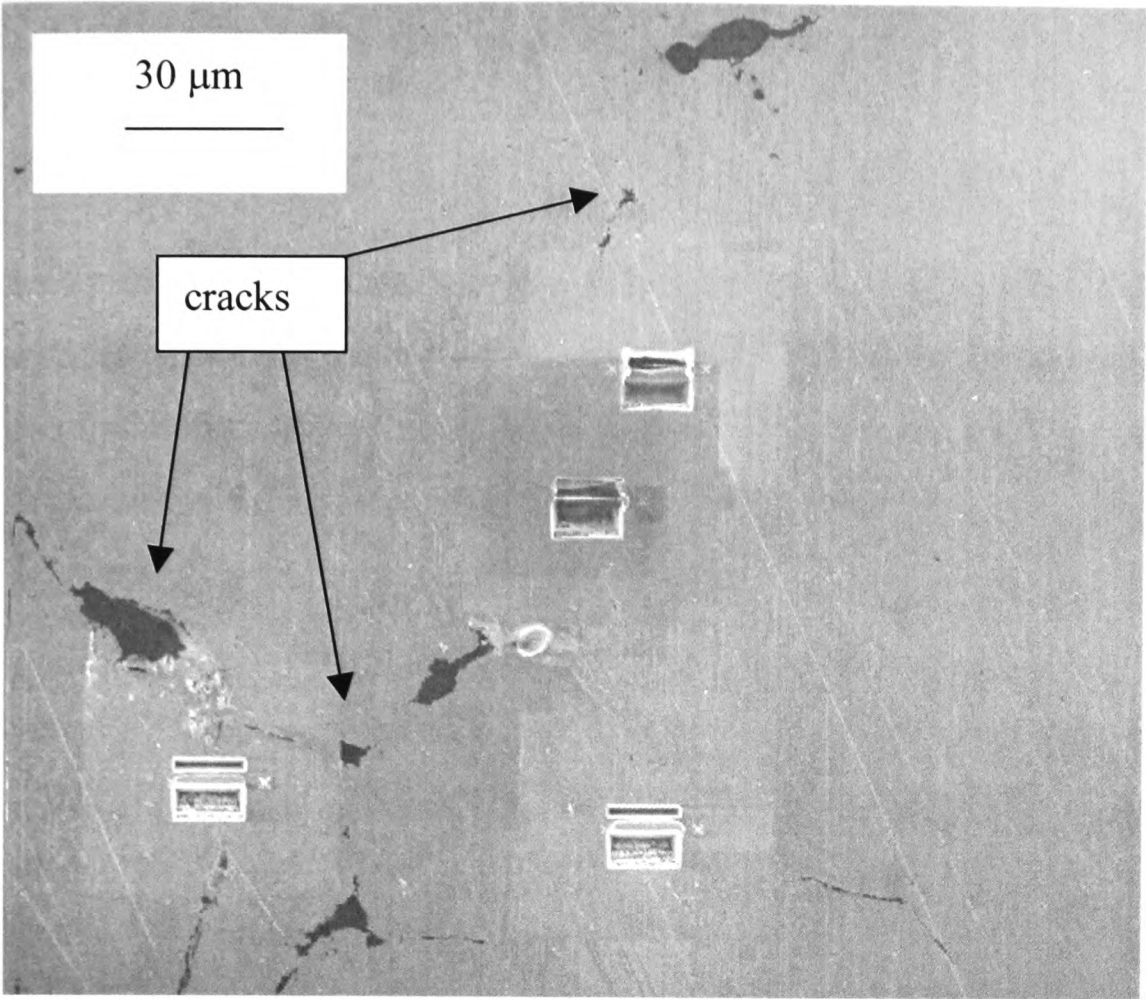


Fig. 7.8. FIB SE micrograph showing four x-sections prepared using the “lift-out” technique in a 304 SS sample.

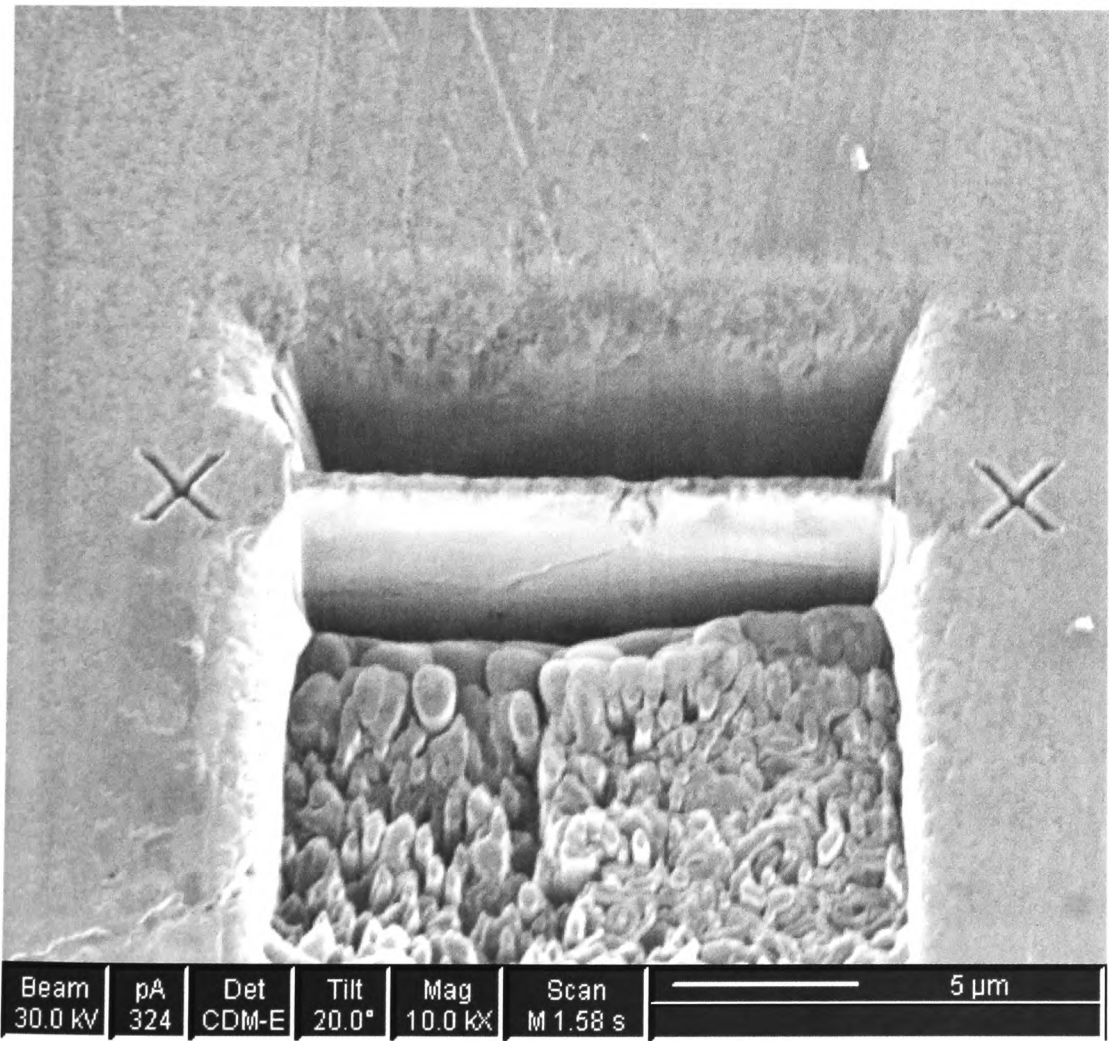


Fig. 7.9. FIB SE micrograph showing a x-section containing a crack that has bifurcated.

7.3 Microstructure

As expected³, $M_{23}C_6$ carbides together with some Ti nitrides were the only precipitates found in the sample. 304SS grain boundaries were found to be decorated with Cr-carbides, with a high density in some areas, as can be seen in Fig. 7.10. Such precipitation can have an adverse effect on the mechanical properties, due to the Cr depletion in the adjacent regions. The surface film in these regions is likely to be depleted in chromium and as a result the steel is more susceptible to corrosive attack

In Fig. 7.11 an intergranular carbide, identified as $Cr_{23}C_6$, is shown at a higher magnification. An EDX spectrum from the carbide in Fig. 7.11 is shown in Fig. 7.12 and from the matrix in Fig. 7.13. No sensitization nor segregation was found in unattacked boundaries, according to EDX analysis (of elements with $Z > 7$).

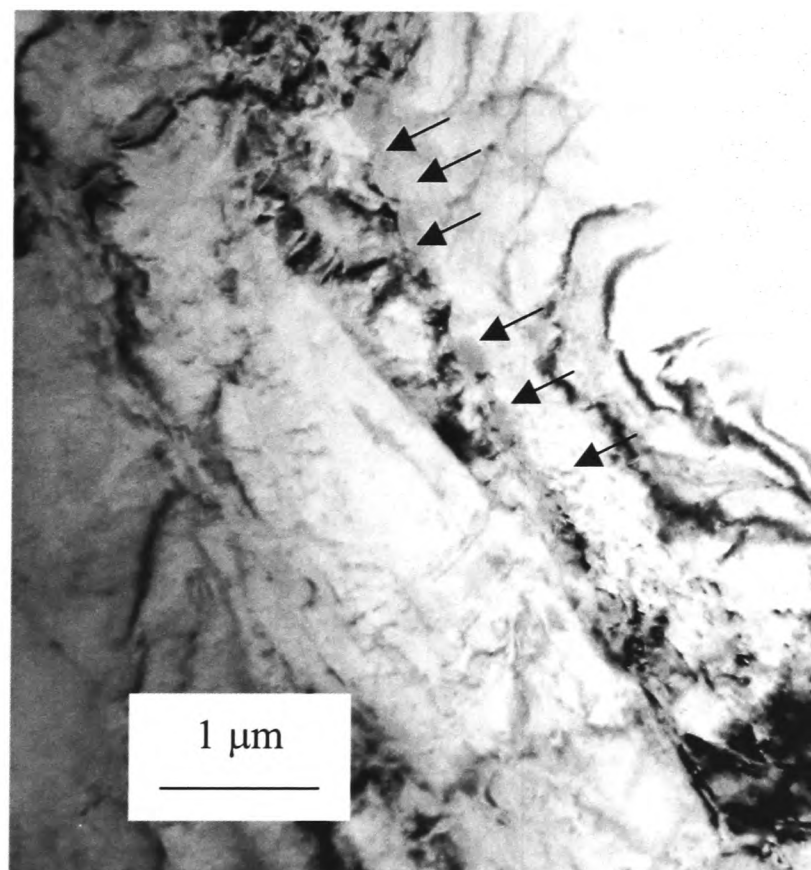


Fig. 7.10. TEM BF micrographs showing grain boundaries decorated with carbides. The grain boundaries did not show any traces of segregation neither impurities, apart from Cr carbides, identified as $Cr_{23}C_6$ (acquired with the CM20).

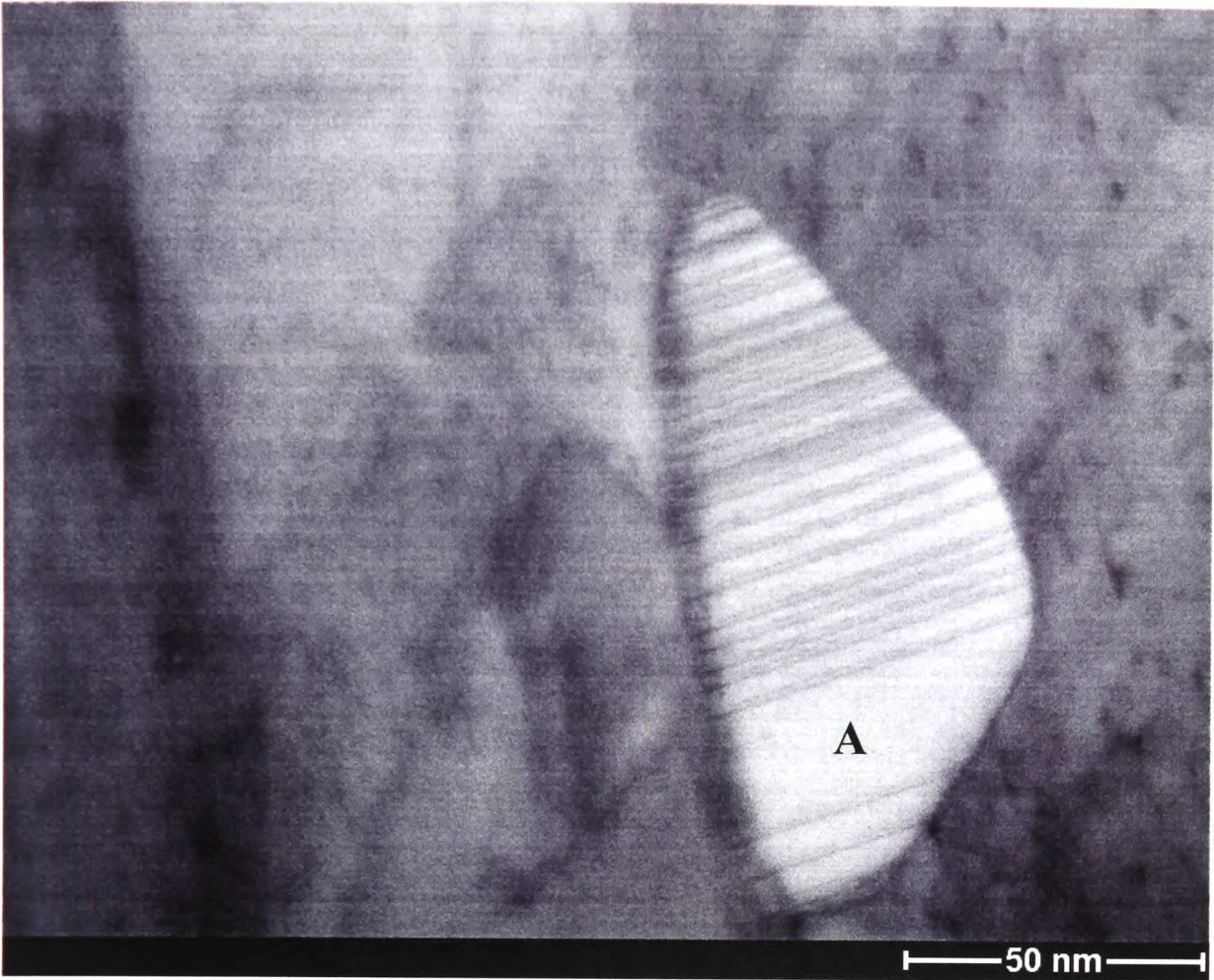


Fig. 7.11. STEM BF micrograph of a typical intergranular Cr-carbide (labelled as A) in 304 SS (acquired with the HB501).

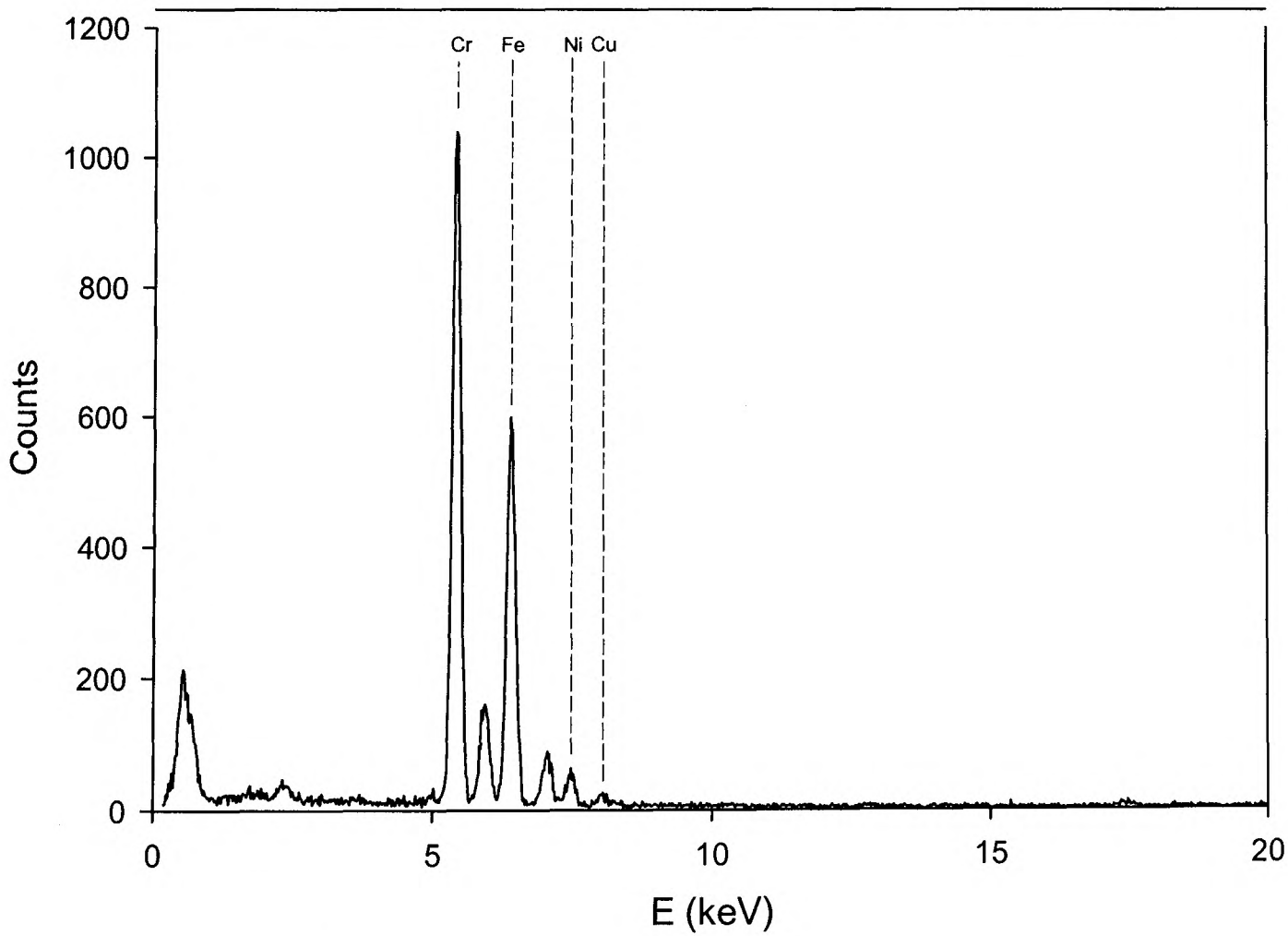


Fig. 7.12. EDX spectrum of particle A showed in Fig. 11 (acquired with the Link system in the HB501).

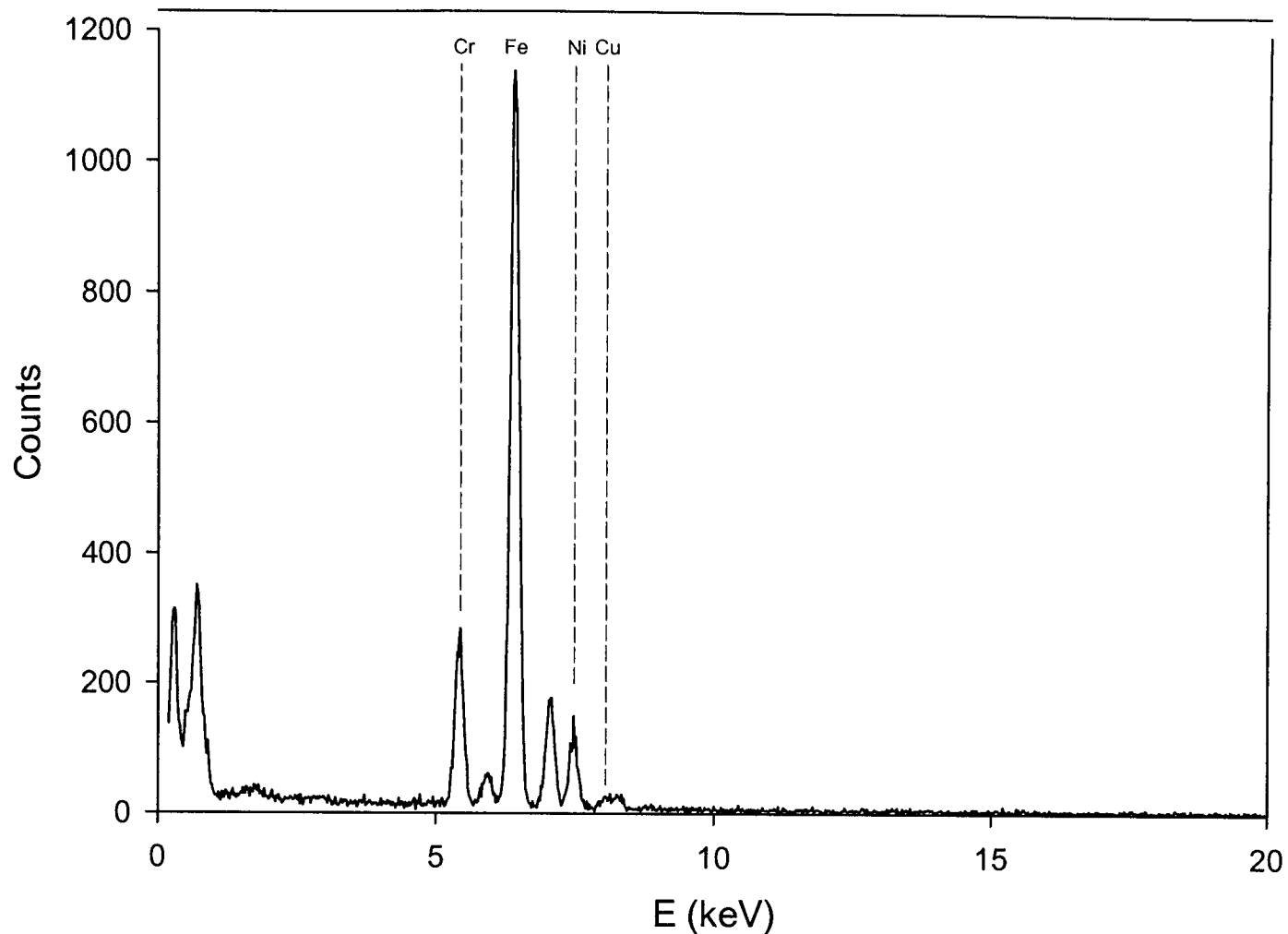


Fig. 7.13. EDX spectrum of the 304 SS matrix (Acquired with the Link system in the HB501).

7.4 Sample prepared using FIB

The FIB was used to prepare samples from the deepest cracks, when they had bifurcated many times and their width was very small, almost a line on the FIB SE image (Fig. 7.14). The sample was prepared perpendicular to the x-sectional polished surface shown in Fig. 1 and between the crosses. The 304 SS had a bigger grain size than the Alloy 600 so it was more difficult to find a triple point contained in the FIB sample. No triple point was found in the samples prepared.

Only one sample will be illustrated, as the 6 samples prepared using this technique all showed the same kind of features. The sample chosen had a crack α that crossed the sample from top to bottom, opening only along one grain boundary (Fig. 7.14). This sample would have been structurally very weak if the modified “lift-out” technique had not been used. By leaving a thicker bottom and left and right edges and keeping the Pt layer, the sample remained flat and in one piece during the final thinning, cutting and plucking. Apart from the oxide layer structure, the main feature

of this sample is the presence of an intergranular Cr-carbide (labelled as **a** in Fig. 7.15) that has been attacked.

As can be seen in Fig. 7.16, the separation between the flanks was approximately 200 nm, so the crack can be considered just opened or in the process of opening. In some areas, the separation is almost non-existent, showing correspondence between the flanks, indicating that they once were together (features **1** and **1'** in Fig. 7.16), although this might be an effect of the sample tilt in the TEM or the grain boundary orientation during the FIB sectioning.

The area containing the Cr-carbide ('**a**' in Fig. 7.17) was studied using EDX mapping. The EDX maps in Fig. 7.18a reveal how the area between the carbide and the grain boundary has been preferentially oxidized (see O map). The Ni and Fe maps show that the flanks have mostly Ni-Fe rich particles with rectangular shape, which were found to be NiFe_2O_4 particles using microdiffraction. The RGB composition in Fig. 7.18b reveals how an inner Cr-oxide layer (as light blue) is developing between the outer Ni-Fe rich layer and the matrix. This layer is probably the same Cr-rich inner layer found in the PIPS sample, but at an early stage of growth.

The right flank was studied at a higher magnification in Fig. 7.19 and again, the same duplex oxide layer was revealed. An outer Fe and Ni-rich oxide layer was observed (Fig. 7.19a) and identified as NiFe_2O_4 and, although not directly evident from the EDX elemental maps, an inner Cr-rich layer was observed between the outer layer and the matrix (appears as light blue in Fig. 7.19b and blue in Fig. 7.19c). It was also observed that the interface between the matrix and Cr oxide is not flat and the oxide layer thickness is variable.

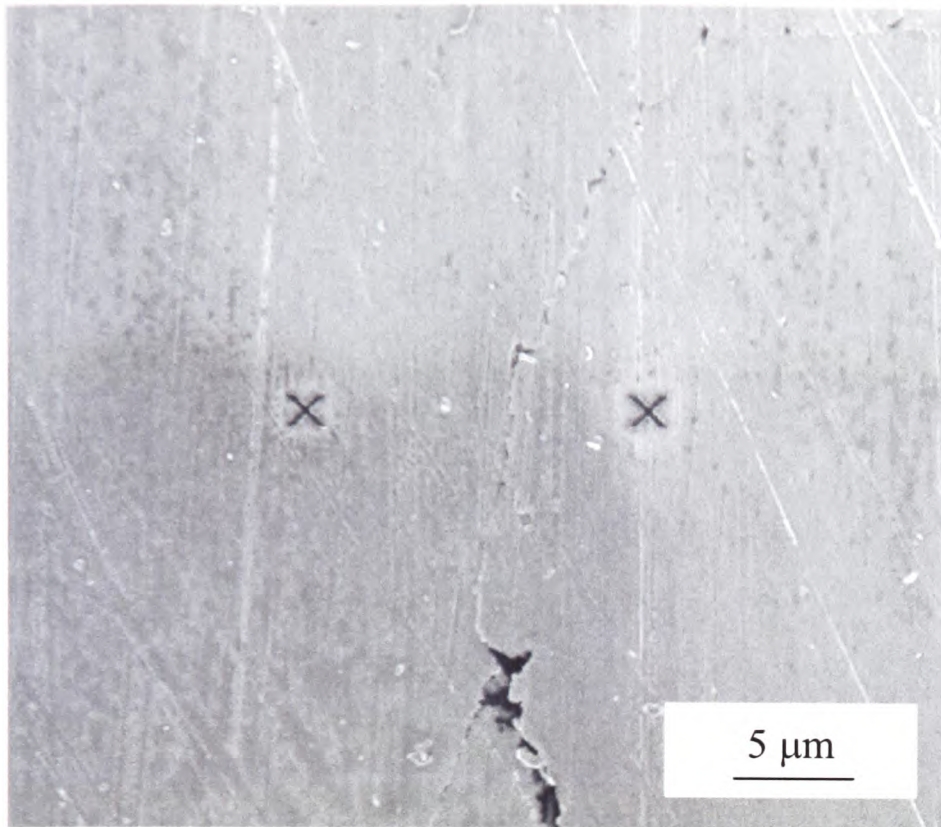


Fig. 7.14. FIB SE micrograph showing how the position of the x-sectional specimen is chosen.

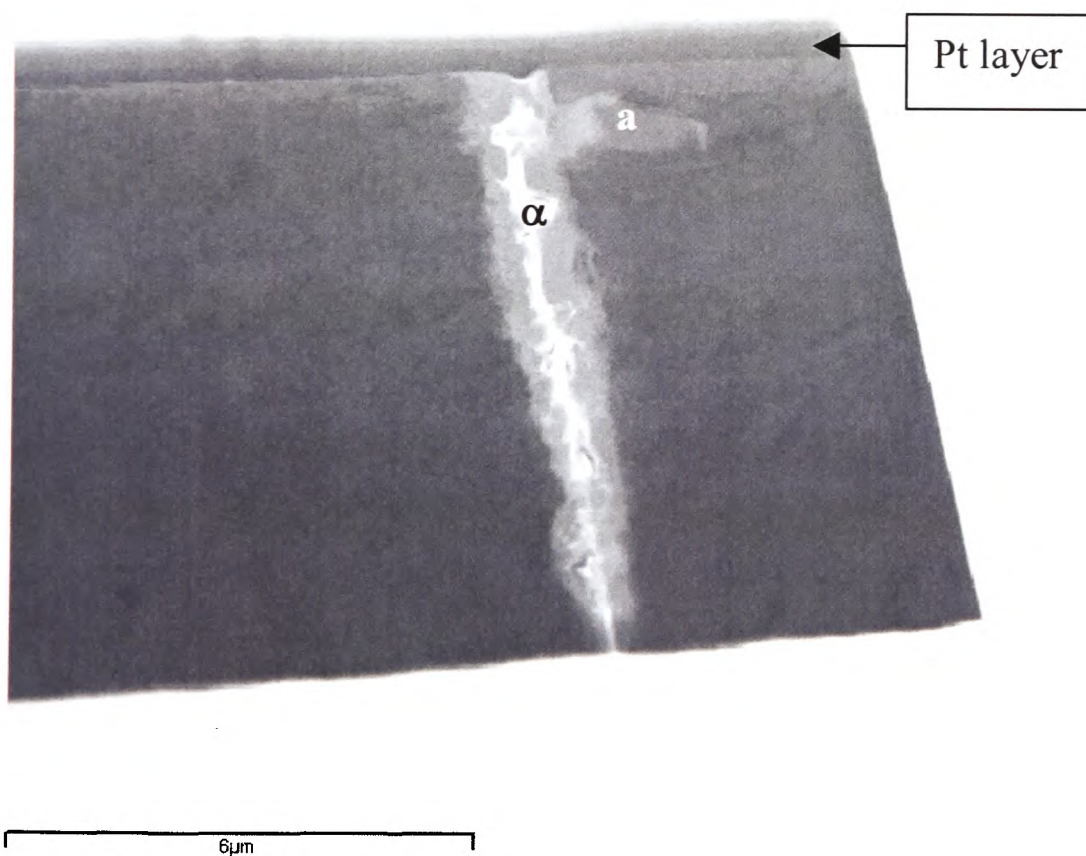


Fig. 7.15. STEM BF image of an FIB x-sectional sample prepared with the modified “lift-out” technique (acquired with the INCA system in the CM20).

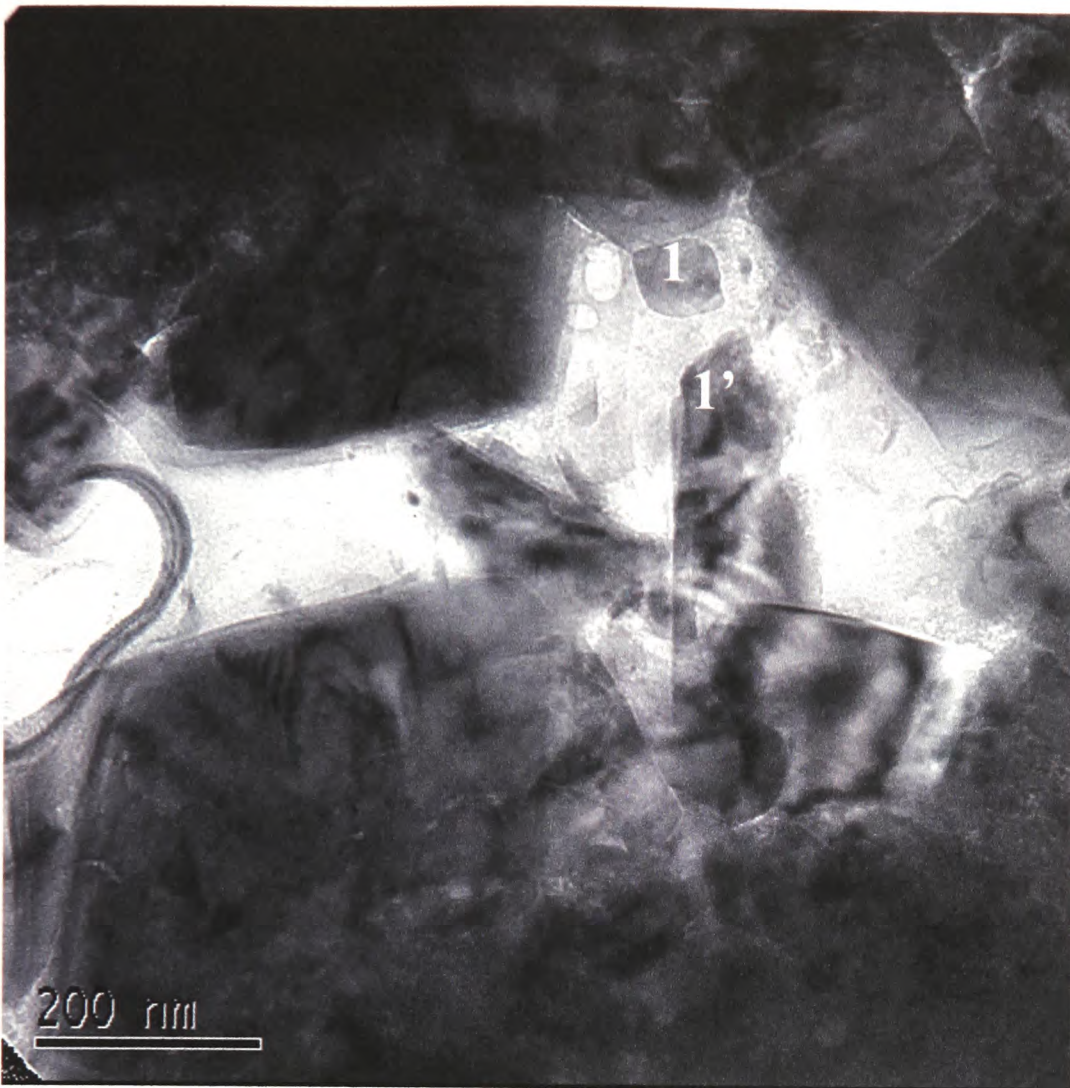
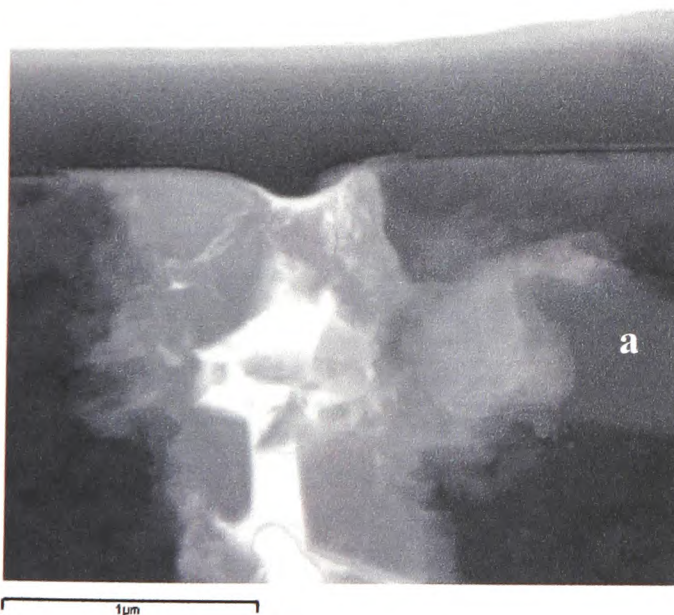


Fig. 7.16. TEM BF micrograph showing details of the corrosion products in the crack, most of them NiFe_2O_4 particles (with rectangular shape) (acquired with the multiscan CCD in the 3000F).



*Fig. 7.17. STEM BF image showing details of the crack and the attacked Cr-carbide (labelled as **a**) (acquired with the INCA system in the CM20).*

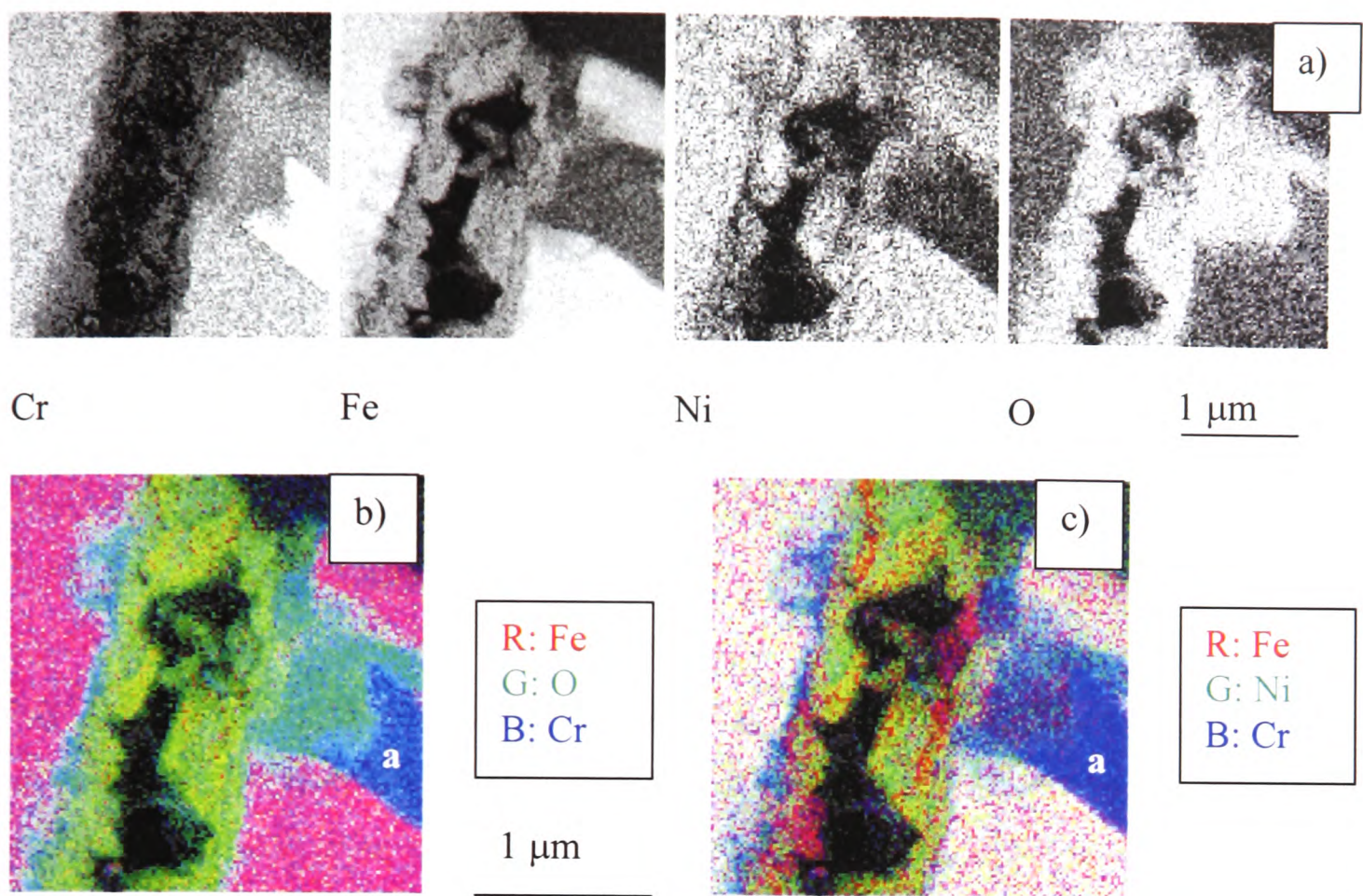


Fig. 7.18. a) EDX maps from the region with the carbide (labelled as **a**) and flanks (acquired with the LINK system in the HB501); b), c), d) and e) RGB composition of images.

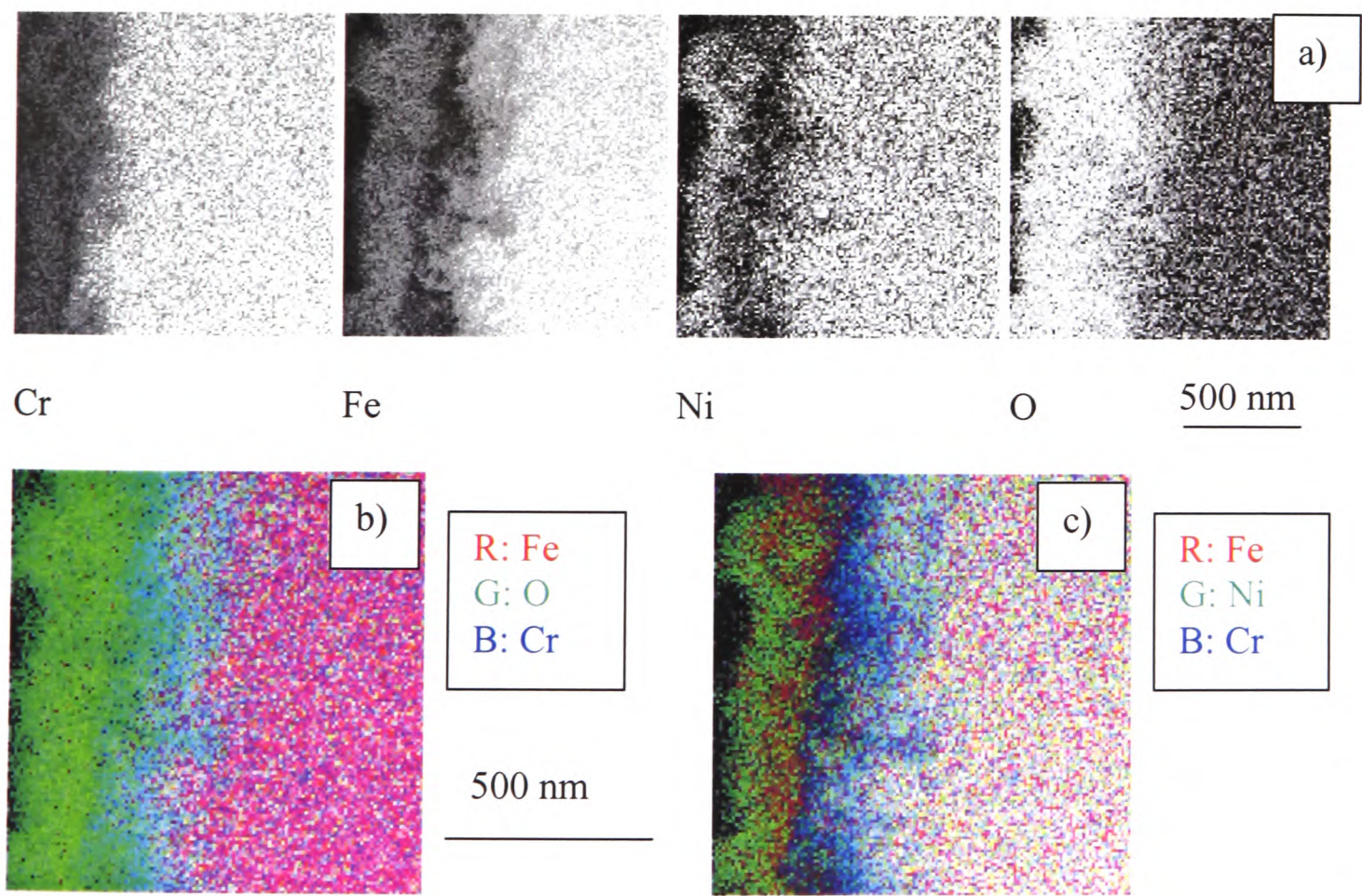


Fig. 7.19. a) EDX maps from the right flank of the crack; (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

7.5 Sample prepared using PIPS

The 3 mm disc used to study the following cracks was shown in Fig. 7.6. Some of the thinned areas around cracks were shown in detail in Fig. 7.7. One crack was contained in a particularly thin region and was chosen for analysis. Different views of the crack are shown in Figs. from 7.20 to 7.24, showing that the crack propagated along 2 different grain boundaries (**A** and **B**). In Fig. 7.20a, the entrance of crack α is shown. It can be seen that after the first micron, the damage from the ion beam thinning disappears and the duplex oxide layer starts. In Fig 7.20b the duplex oxide layer can be seen at a higher magnification and the polycrystalline nature of the outer oxide layer is revealed. This duplex oxide layer continued along grain boundary **A** (Fig. 7.21) and after the triple point along grain boundary **B** (feature **1** in Fig. 7.22). At the triple point, grain boundary **C** was also found attacked, but no open crack was found (Fig. 7.22).

The crack tip was found in grain boundary **B**, at approximately 12 μm from the triple point (**1** in Fig. 7.22), as shown in Fig. 7.23. The crack tip is defined as the position at which the flanks of the crack stop being in contact with the environment (labeled in Fig. 7.24). The attack continues for a few microns ahead of the crack tip along grain boundary **B** as a band of varying transmitted intensity but having greater transmission than the matrix. The greater transmission occurred because of the lower mass density of oxide, compared with matrix rather than voids or open cracks. This conclusion was reached following careful observations as the sample was slowly tilted in the TEM.

7.5.1 Analysis of the duplex oxide layer

The duplex oxide layer was found to be a nanocrystalline inner layer of FeCr_2O_4 (Fig. 7.25) and an outer layer of polycrystalline NiFe_2O_4 and FeCr_2O_4 , all with spinel structure (Figs. 7.26a). The fact that FeCr_2O_4 and NiFe_2O_4 have an identical lattice parameter made it very difficult to distinguish them in a SA DP. A deeper analysis of the outer layer revealed that all the big particles were NiFe_2O_4 (Fig. 7.26b), only FeCr_2O_4 being detected in nanocrystalline form. This is in agreement with some of the previous results in the literature^{2; 5; 4} and would explain 20% wt. Cr

detected in the outer layer. In order to check the validity of the results, EDX analysis was performed together with a characterization of the DP obtained from the different areas.

As both FeCr_2O_4 and NiFe_2O_4 have a similar lattice parameter: 0.837 nm they could not be differentiated using only microdiffraction (μD), and so EDX analysis was also necessary.

Compositional line profiles performed with the HB501 (Fig. 7.27) showed perfectly the difference in composition between the two layers. The inner layer was found to be rich in Cr, so it could only be FeCr_2O_4 . The outer layer was enriched in Fe and Ni, so together with the μD from the biggest particles (Fig. 7.26a) it is clear that it is NiFe_2O_4 .

Later analysis showed that the NiFe_2O_4 particles were aligned with the matrix, suggesting that they grew epitaxially orientated, in contact, the FeCr_2O_4 layer being developed afterwards.

The same duplex oxide layer structure was observed along the flanks of the crack up to the crack tip. Even at the triple point it was possible to distinguish the two layers (Fig. 7.28).

Elemental EDX maps were acquired to reveal the changes in composition in the duplex oxide layer. In Fig. 7.29a, it is easy to see how the inner layer is rich in Cr and O and the outer layer is rich in Fe and Ni. Note that the left flank of the crack (in Fig. 7.29) seems to have been preferentially thinned (an artefact), as it has less counts in the EDX maps than the right flank. The RGB composition in Fig. 7.29b shows the inner FeCr_2O_4 layer as light blue (blue in Fig. 7.29c) and the outer NiFe_2O_4 layer as green (red/green in Fig. 7.29c).

The triple point area was also analyzed revealing that, although grain boundary **C** had not opened, it was heavily attacked (Fig. 7.30a). Grain boundary **B** seemed to have opened more than grain boundary **A**, as suggested by the increased

separation of the flanks in Fig. 7.30. However, a similar duplex oxide layer grew from the triple point, along grain boundary **B**.

A quantitative line profile was acquired across the attacked grain boundary **C**, at a distance of 5 μm from the triple point. The results reveal an Fe-enrichment (Fig. 7.31a) and a Cr-depletion (Fig. 7.31b) at the grain boundary. No traces of the Cr-rich inner layer observed on the flanks was found. This was expected, as the NiFe_2O_4 particles on the outer oxide layer of the flanks were found aligned with the matrix, so they were supposed to have grown in contact.

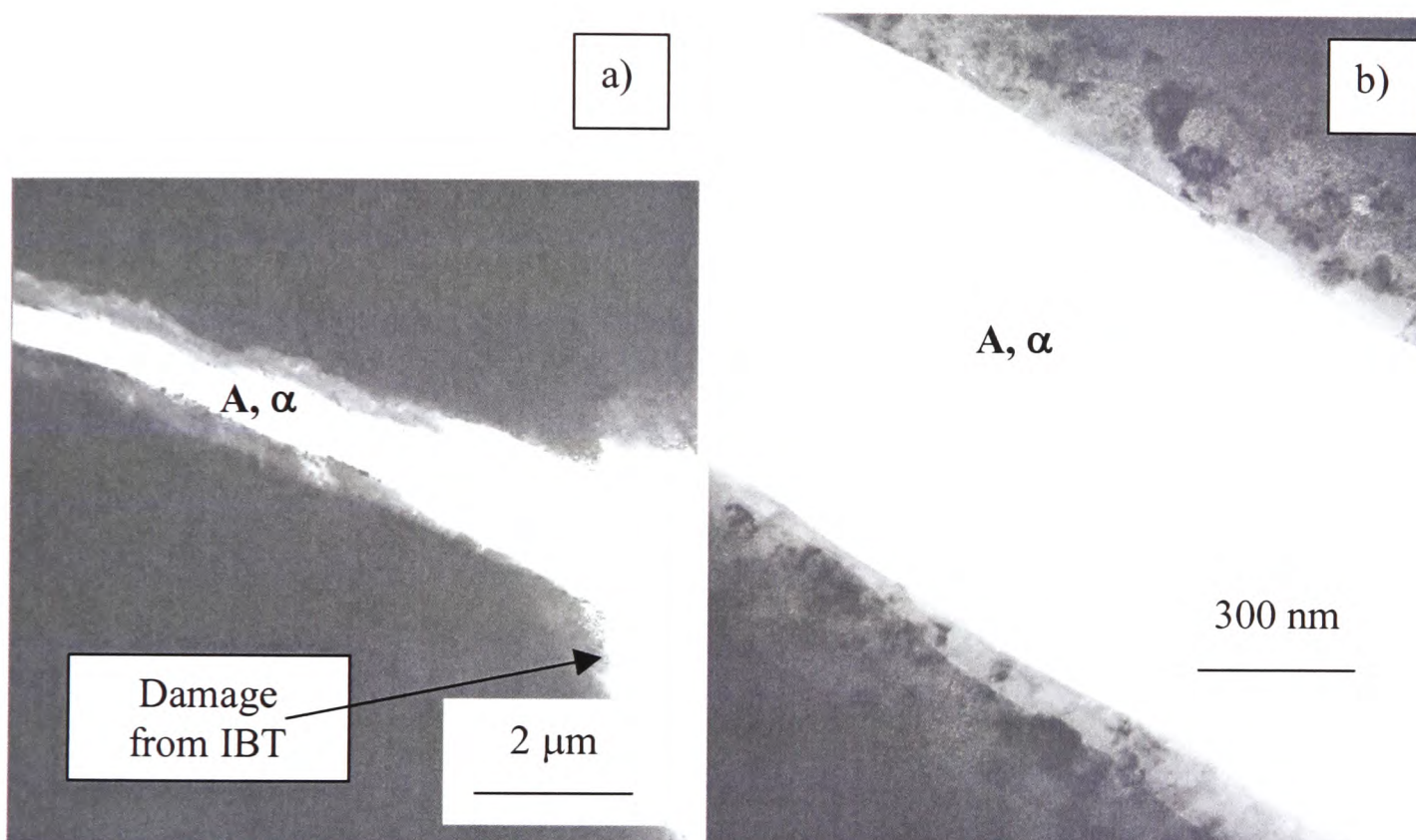


Fig. 7.20. BF TEM micrograph showing the entrance of the crack (a) and the flanks of the crack (b), both with a double oxide layer (acquired with the CM20).

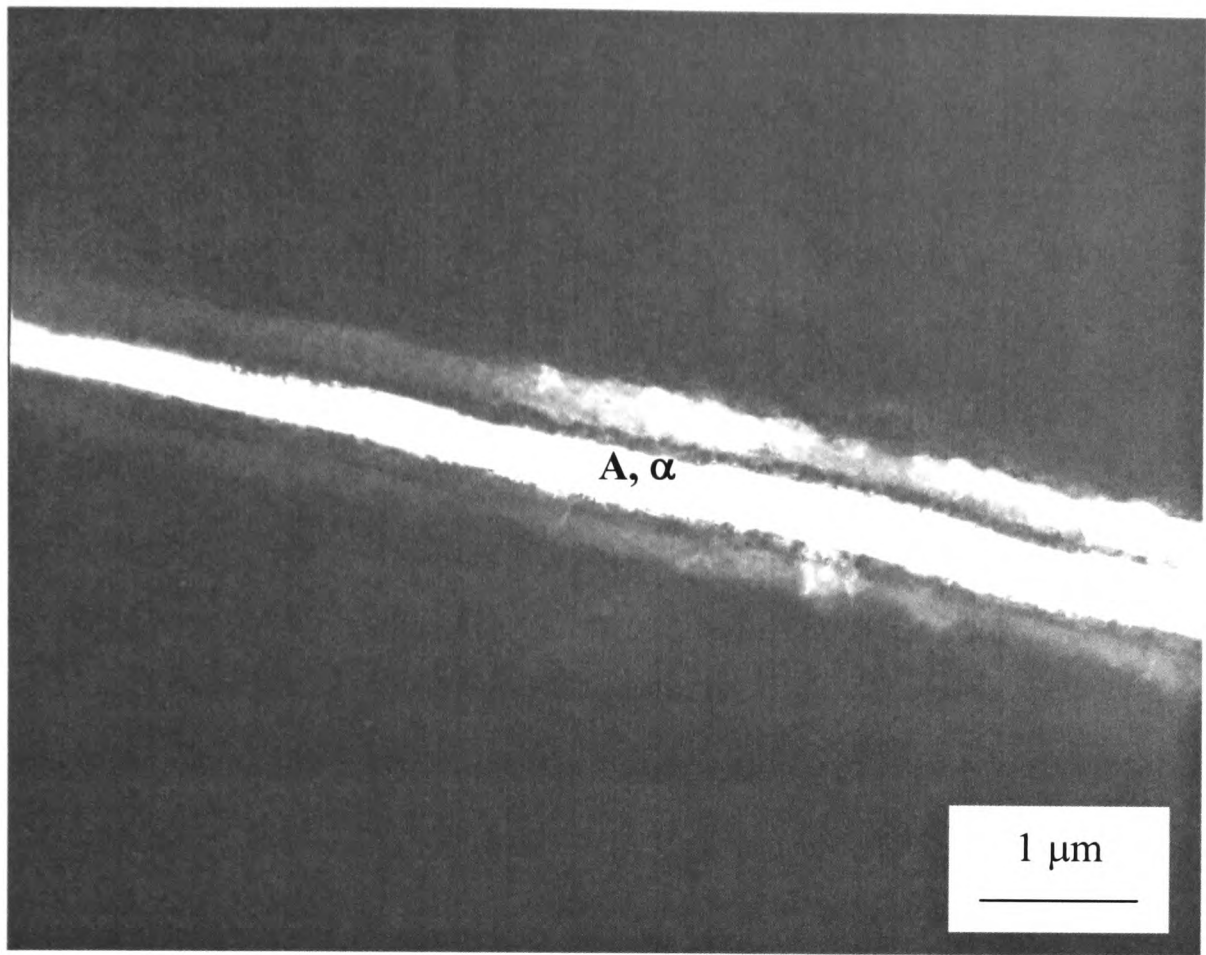


Fig. 7.21. BF TEM micrograph showing another part of the crack, closer to the tip, in which the double oxide layer is easily distinguishable (acquired with the CM20).

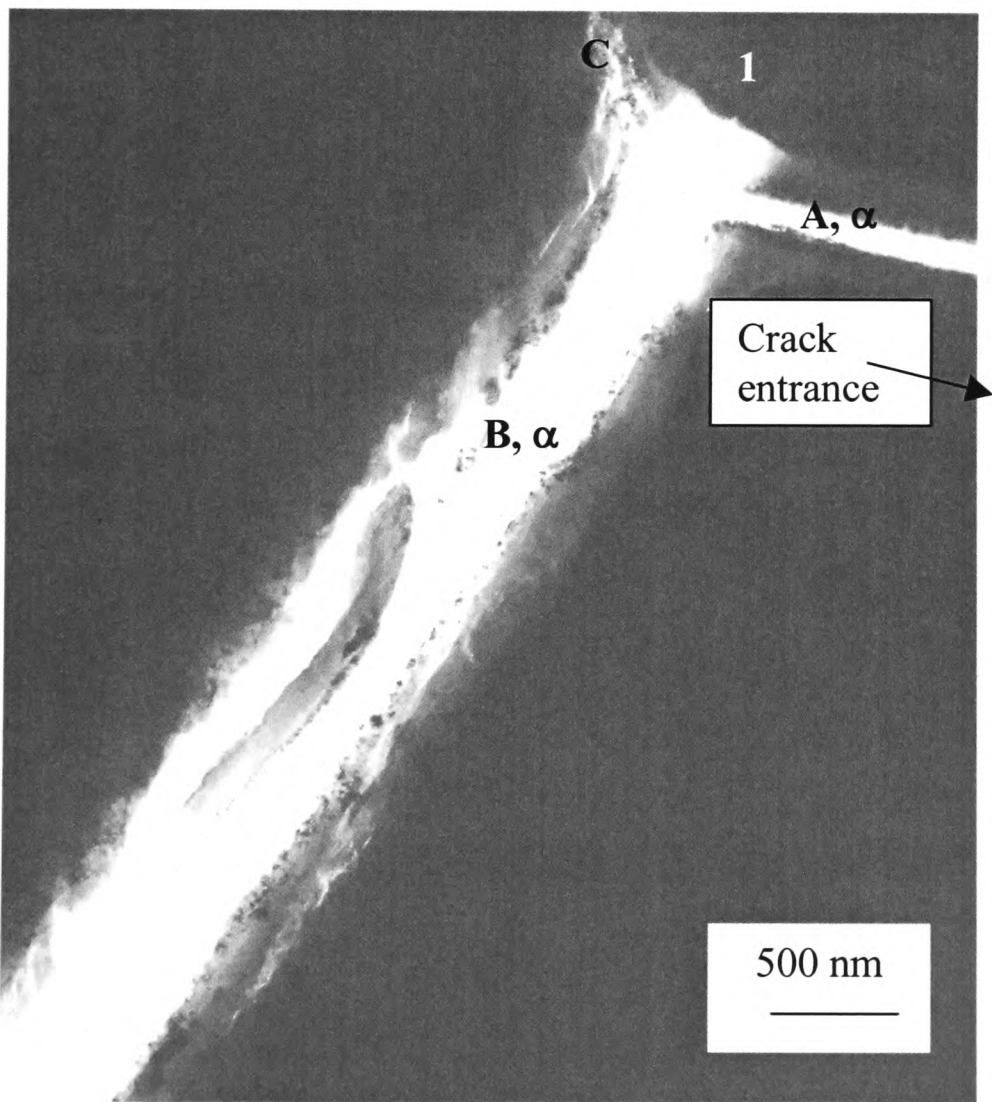


Fig. 7.22. BF TEM micrograph showing how the crack reaches a triple point and changes its direction, attacking the other boundary but not cracking it (acquired with the CM20).

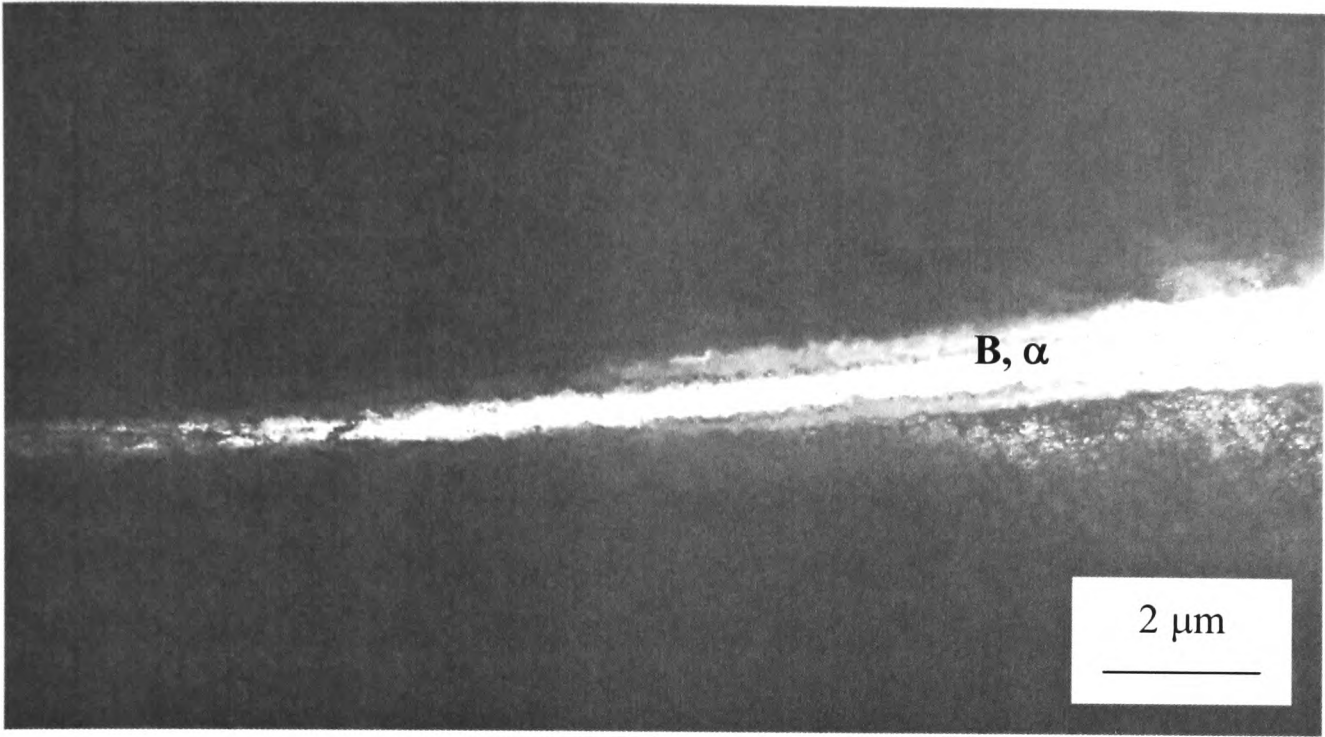


Fig. 7.23. BF TEM micrograph showing the crack tip (acquired with the CM20).

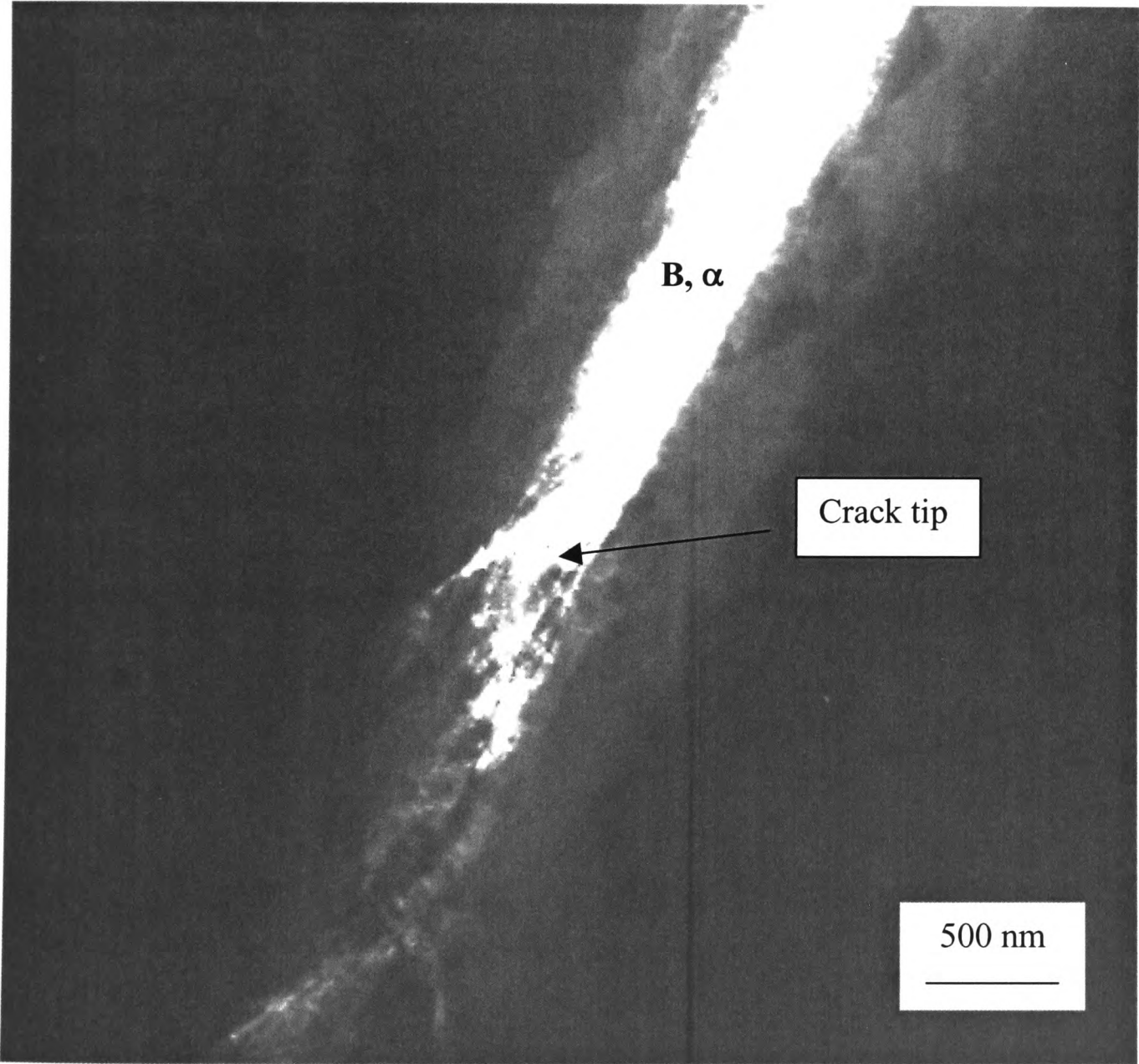


Fig. 7.24. BF TEM micrograph showing the crack tip region into more detail (acquired with the CM20).

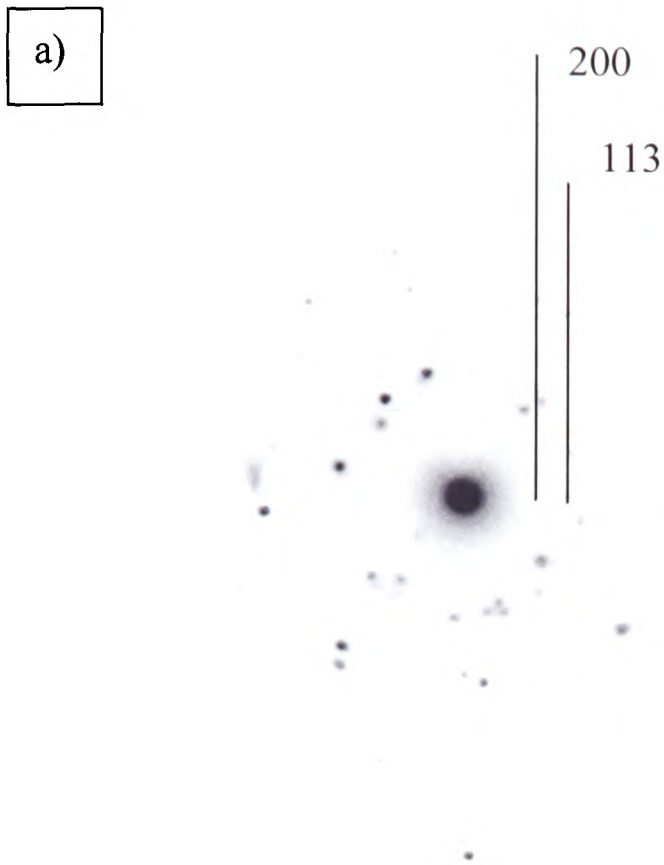


Fig. 7.25. SA DP showing some characteristic rings of FeCr_2O_4 (acquired with the CM20).

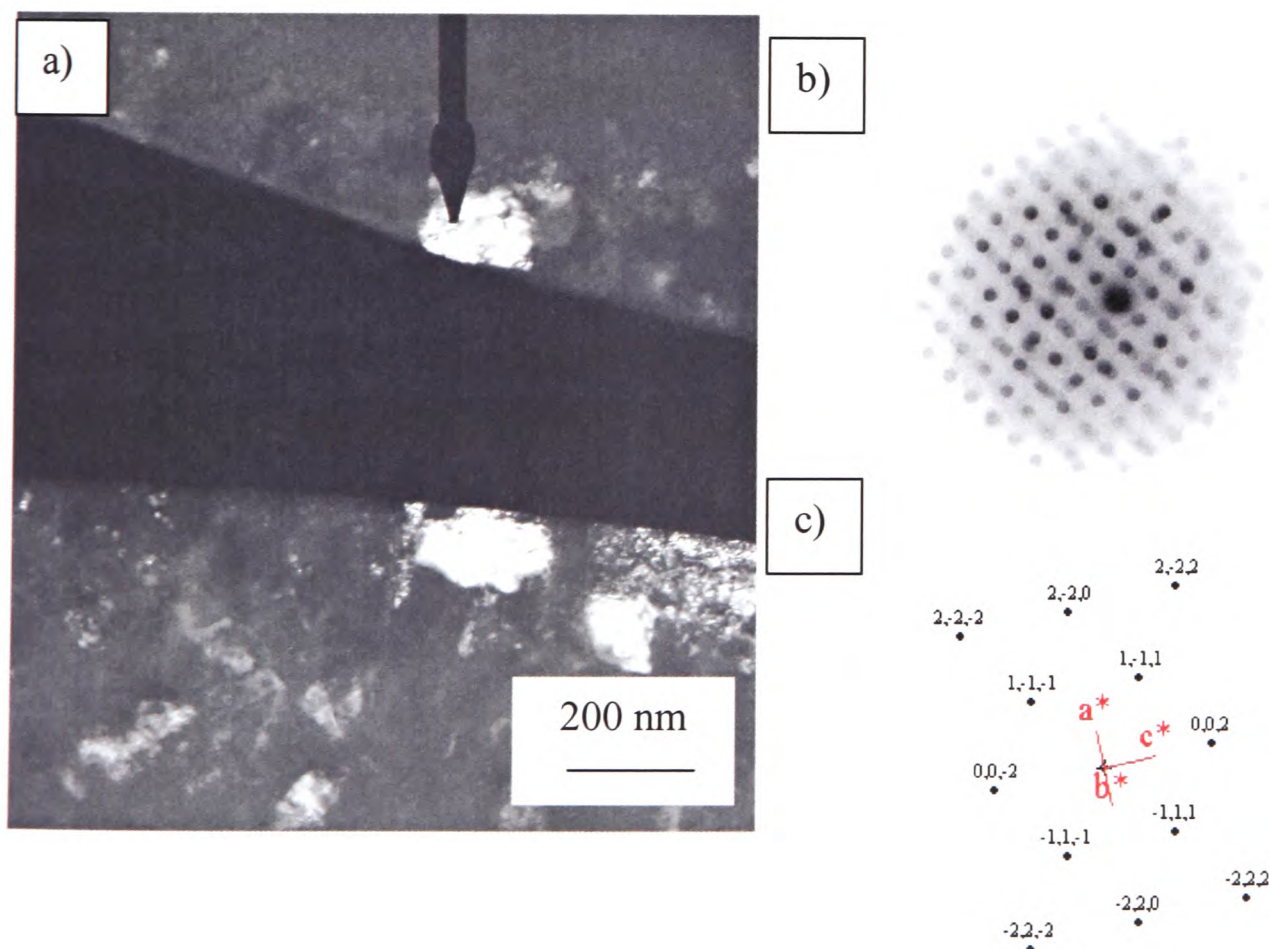


Fig. 7.26. a) DF TEM micrograph showing some NiFe_2O_4 diffracting in a $[110]$ zone axis; b) μDP is shown from the arrowed particle. The DP shows contributions from more than one particle, but all with similar orientation; c) Simulated DP.

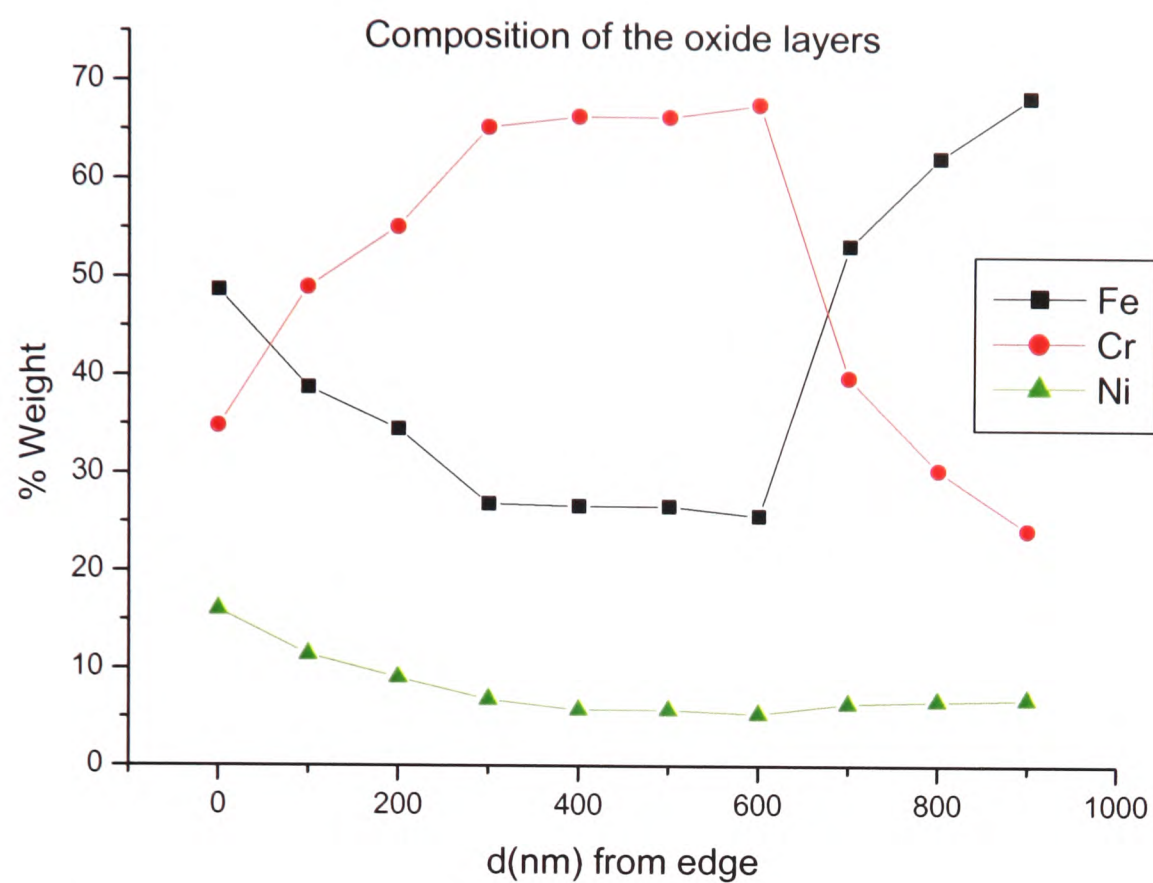


Fig. 7.27. EDX quantitative line profile across the duplex oxide layer (acquired with the LINK system in the HB501).

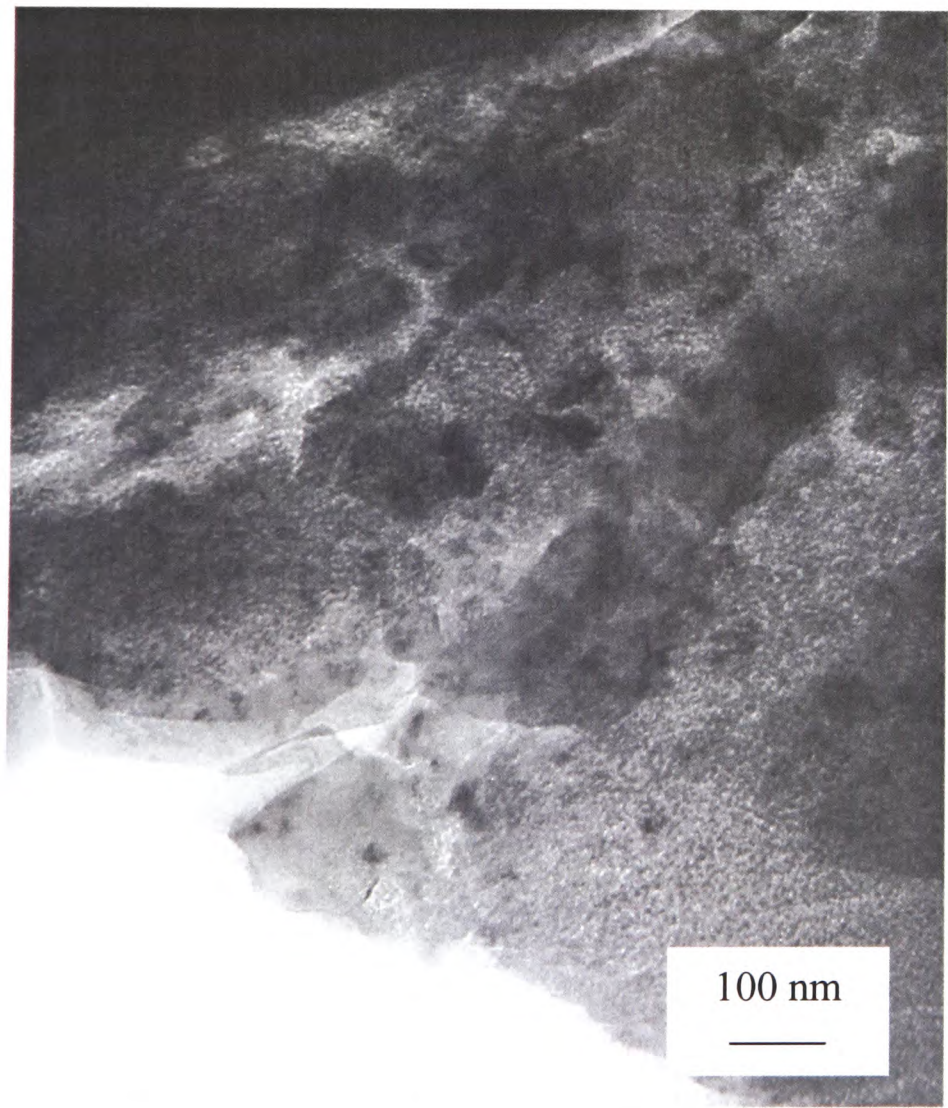


Fig. 7.28. BF TEM micrograph showing into detail the microstructures at the triple point. The big dark particles are NiFe_2O_4 (acquired with the CM20).

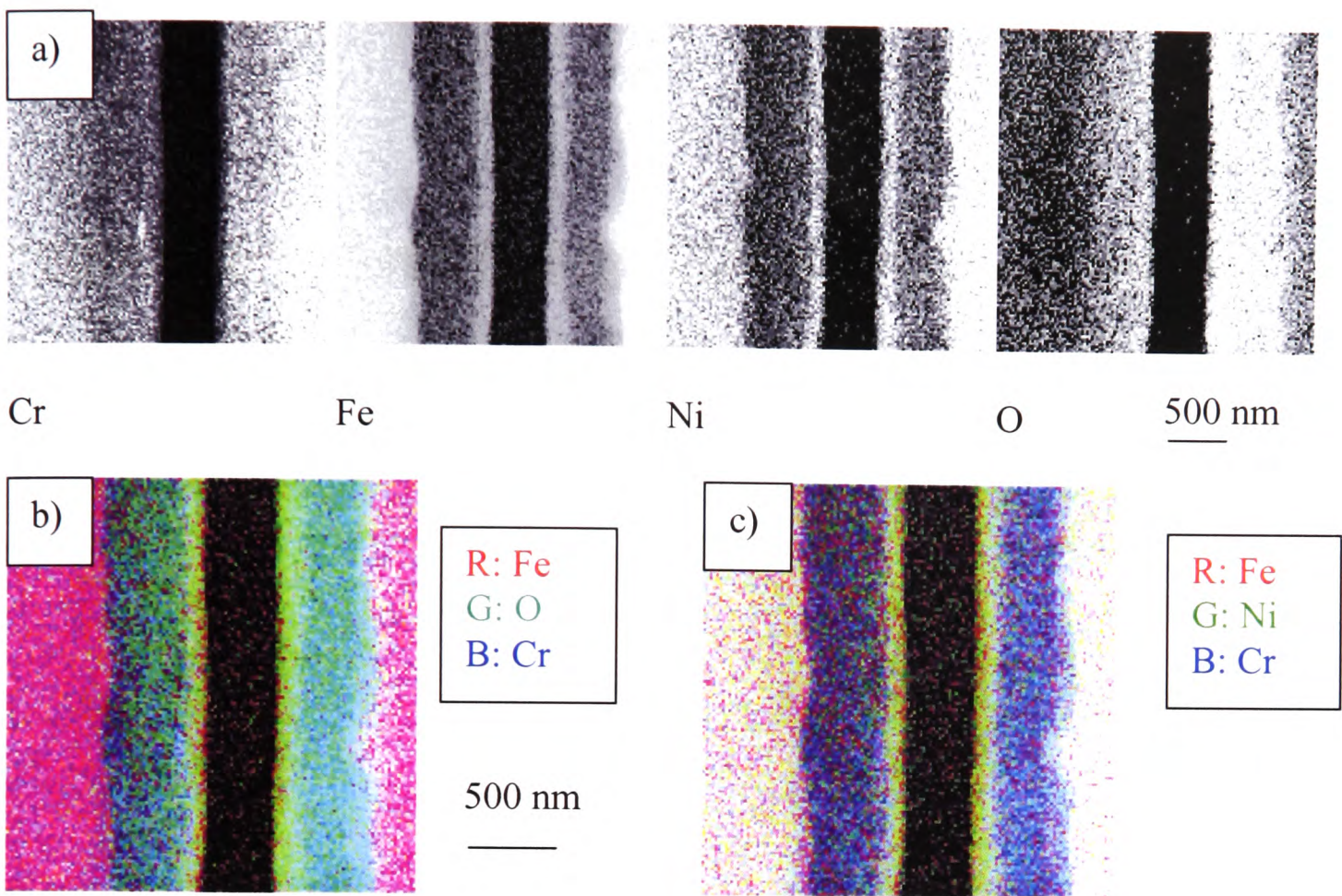


Fig. 7.29. a) EDX elemental maps from the duplex oxide layer; b) and c) RGB composition of images (acquired with the LINK system in the HB501)

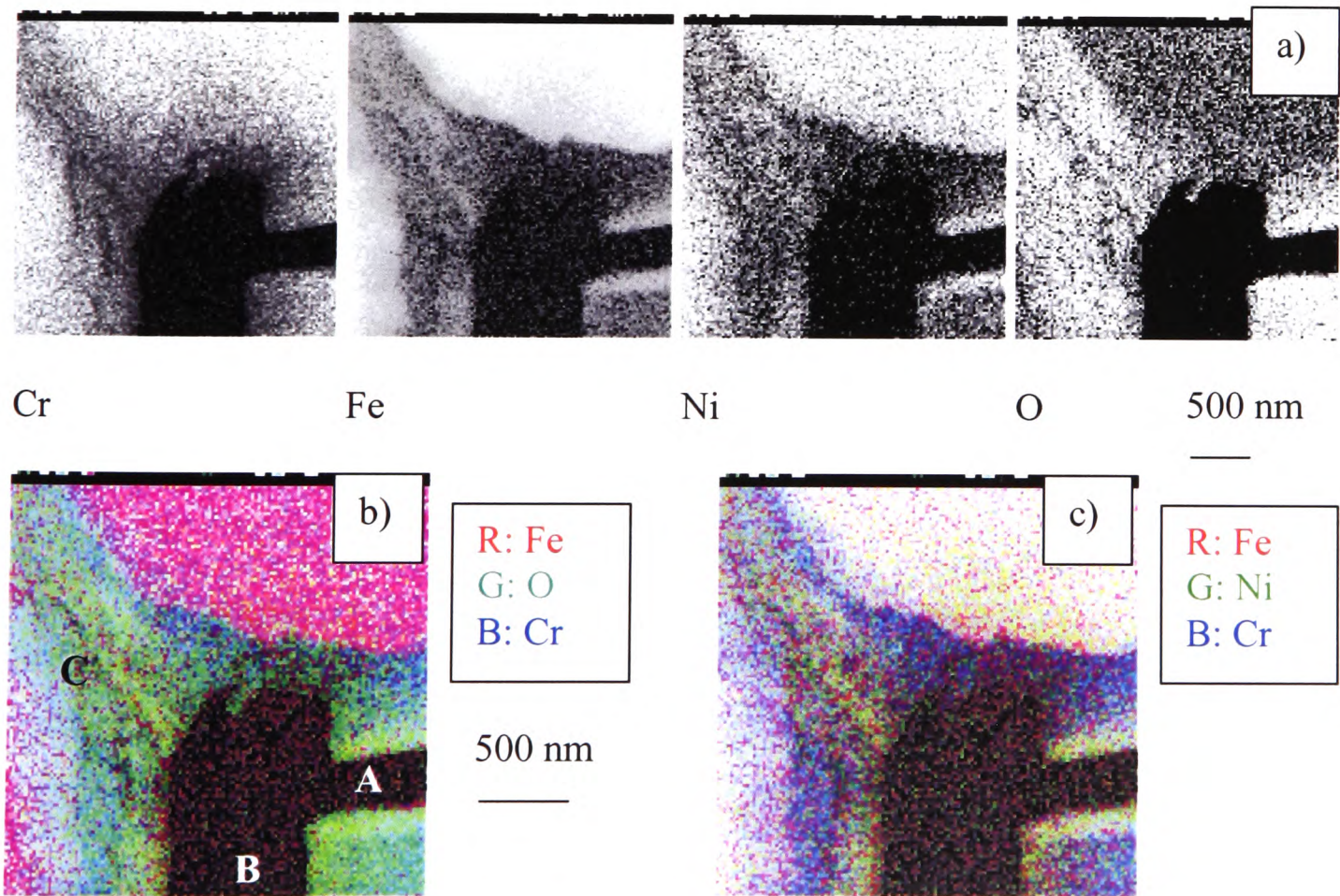


Fig. 7.30. a) EDX elemental maps from the triple point area; b) and c) RGB composition of images (acquired with the LINK system in the HB501)

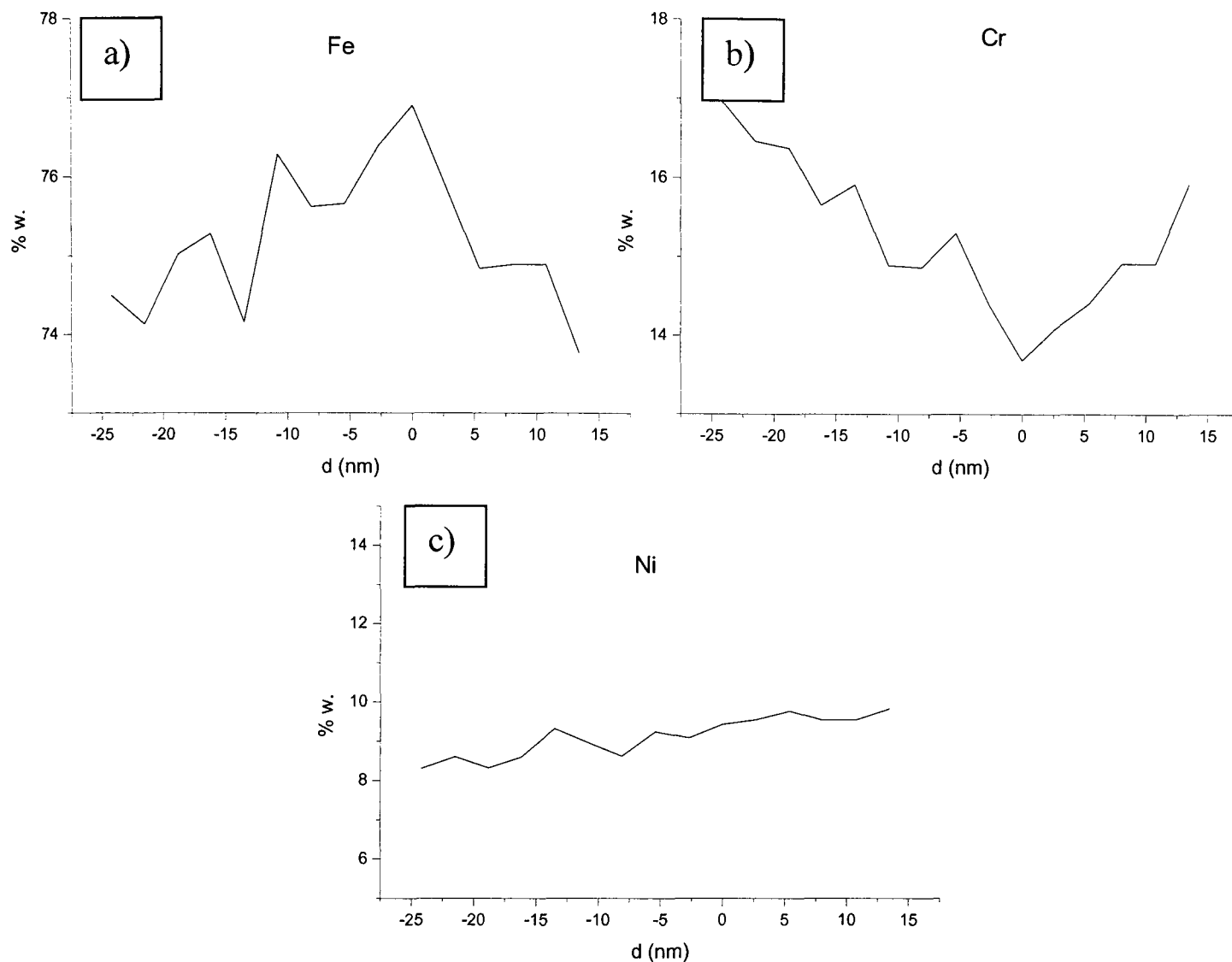


Fig. 7.31. Line profile across grain boundary C (which did not open) 5 μm ahead of the triple point.

7.6 References

1. ASM International. Handbook Committee. and Davis, J. R. (1989). **Metals handbook**. Metals Park, Ohio, ASM International.
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4. Kim, Y. J. (1999) Corrosion. vol.55, no.1; Jan. 1999; p.81-8.
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Chapter 8:

Results on Alloy 600 samples under constant load test

Material: Alloy 600

The composition and test conditions of the Alloy 600 specimens is as follows:

Chemical composition (wt%):

C: 0.030, **Si:** 0.35, **Mn:** 0.36, **P:** 0.009, **S:** 0.001, **Ni:** 74.85, **Cr:** 16.16, **Fe:** 8.64

Pre-test heat treatment: Mill annealed at 980°C

Constant load testing conditions:

In aqueous environment

Solution: 500 ppm B + 2 ppm Li + 2.75 ppm H₂ (30 cc H₂/kg H₂O)

Temperature: 360°C

Load: 35 kgf/mm²

Time: 4840 h

Did not break

This chapter will show the results obtained after the analysis of the Alloy 600 sample (sample B) tested under constant load simulating PWR primary water conditions. Results from 10 specimens will be described in detail, for a total of 25 examined. It has been considered important to include all these in detail as they illustrate the full range of observed behaviours and the reproducibility of the general trends. A general description of the specimen will be given in each case, including a sketch showing its orientation in the bulk sample and details of the analysis of the crack flanks, crack tip and particles.

Sample 10 was used to analyze the surface oxides, and it does not contain any crack.

8.1 Sample 1: General observations

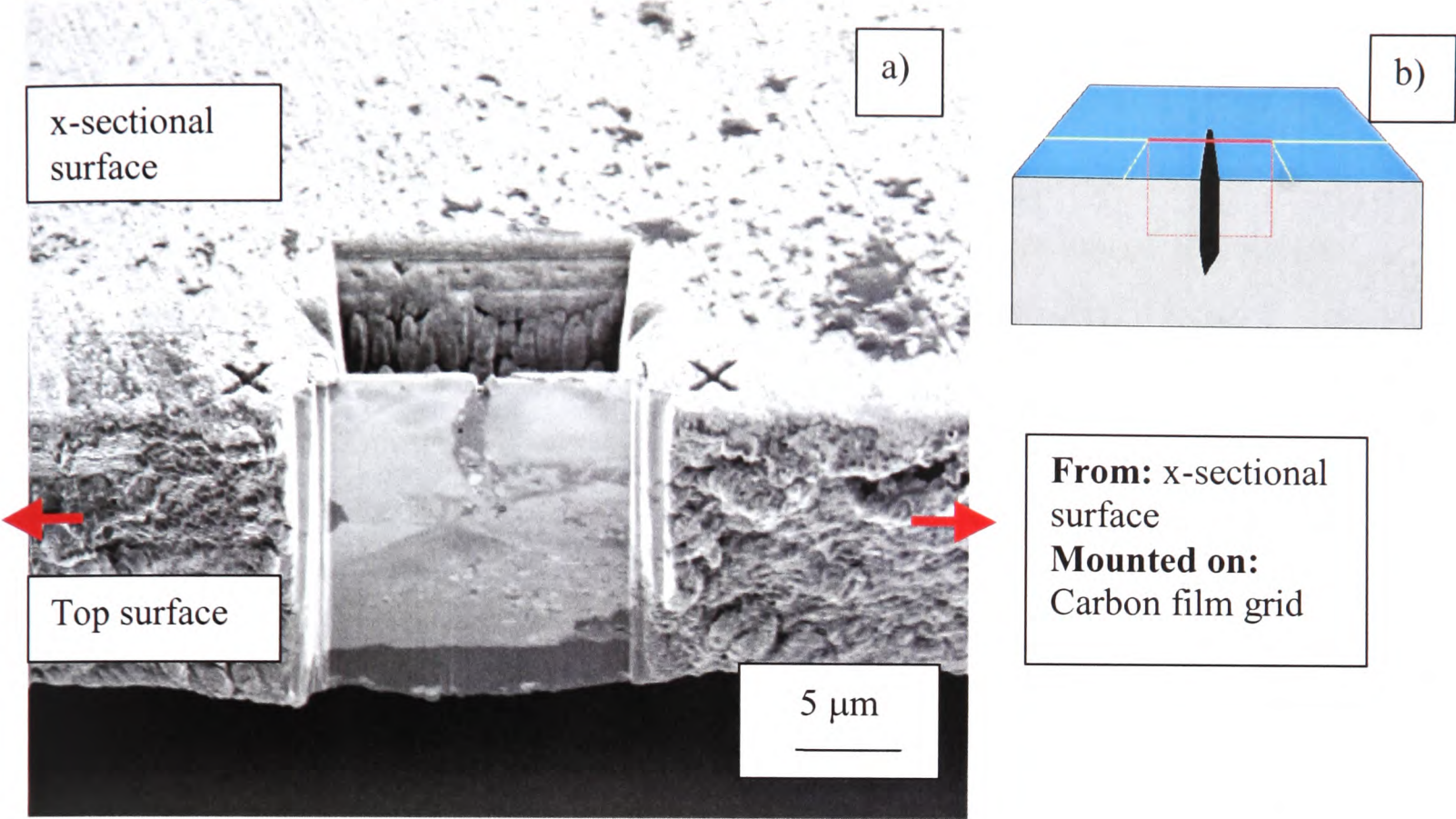


Fig. 8.1.1. a) FIB SE micrograph showing the relative orientation of sample 1 before the final cleaning and cutting in the FIB. The stage was tilted 40°, so the scale can only be used to measure horizontal distances. The loading direction is indicated by the red arrows (acquired with the FEI FIB 200), b) orientation of the crack in the sample.

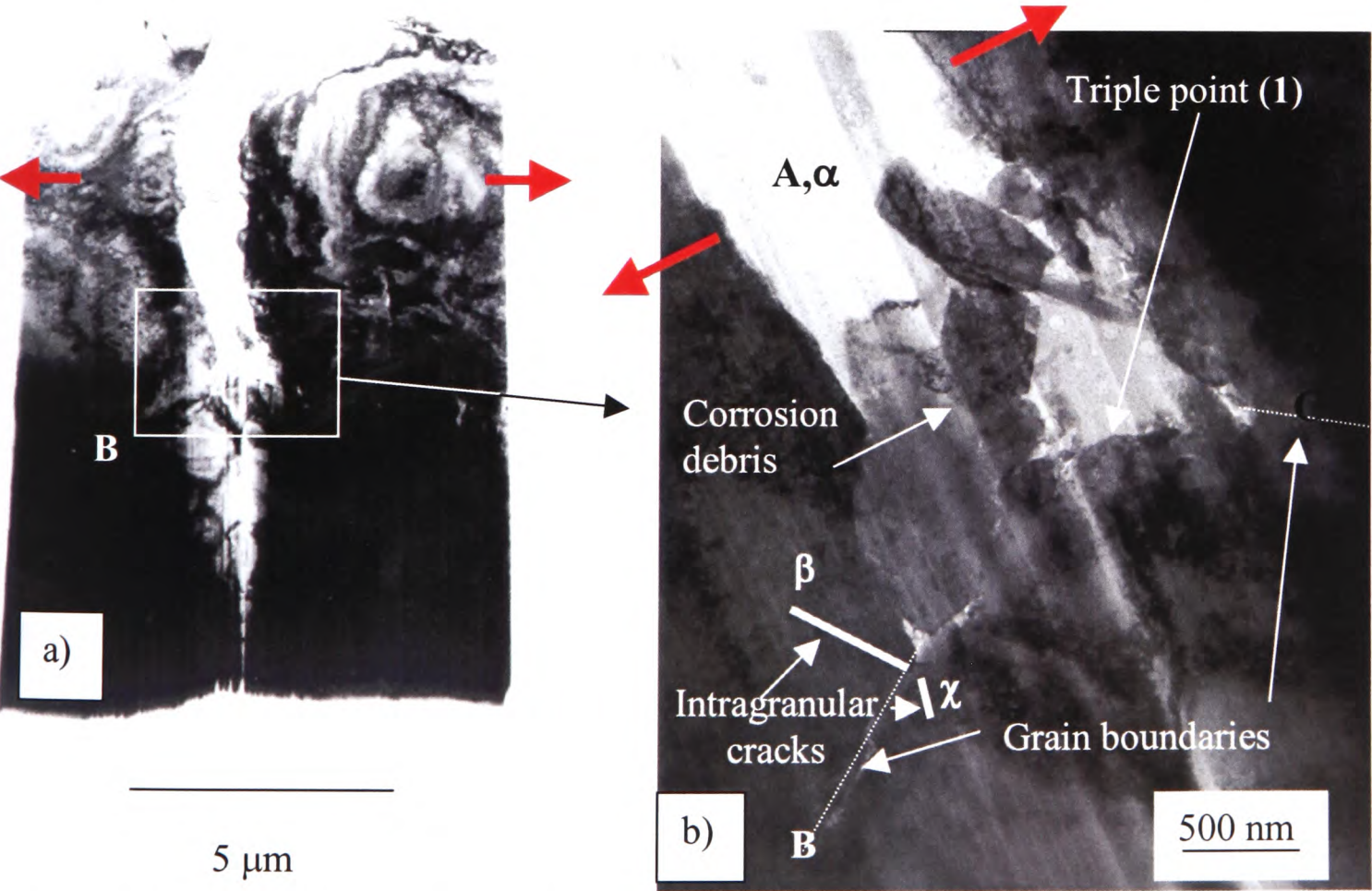


Fig. 8.1.2. a) TEM BF micrograph showing sample 1 after the final cleaning, cutting and plucking; b) Triple point area. The loading direction is indicated by the red arrows (acquired with the CM20).

Sample 1 was prepared from a thin foil x-sectioned perpendicularly to the top surface (Fig. 8.1.1b) and previously thinned to 20 μm using diamond impregnated polymeric paper (1 μm). Due to a technical problem with the Pt needle in the FIB, this sample was prepared without deposition of the protective Pt layer on the top. As a result, the material inside the crack was partly removed on the top of the sample during ion machining, but remained intact after a “depth” of 1 μm (Fig. 8.1.1a).

Sample 1 contained 3 grain boundaries (labelled **A**, **B**, **C** in Fig. 8.1.2a) and a triple point (labelled **1** in Fig. 8.1.2b)). Grain boundary **A** had an orientation where it was subjected to Mode I loading and it was found completely attacked. It is assumed that it had opened abruptly as a consequence of the applied stress forming crack α . Crack α had blunted after reaching a triple point (**1**) at the “bottom” of the sample and continue advancing presumably under mixed Mode I+II loading through the next two boundaries (**B** and **C**). Grain boundary **B**, showed intragranular cracks (β and χ) growing in orientations oblique to its primary crack. These cracks cannot be seen in Fig. 8.1.2b, only in the EDX maps of Figs. 8.1.7 and 8.1.8, and were indicated by solid white lines. This is not an isolated observation, as will be shown in the next samples, and it is similar to the intragranular attack mentioned by Hipsley².

Due to the FIB preparation, the sample developed some artefacts. In figure (Fig. 8.1.2b), are seen some striations, which were bigger than usual because of the lack of a Pt protective layer. Also the area just below the big crack appears artificially thinner, due to the difference in milling rate between the matrix and the material within the crack.

8.1.1 Analysis

8.1.1.1 Flanks

The composition and microstructure of the flanks of crack α were analysed. EDX compositional mapping of the left flank area are shown in Fig. 8.1.3a. The Cr rich outer layer and an inner depleted region (rich in Ni) are believed to be a consequence of the migration of the Cr to the outer layer to form Cr_2O_3 . The oxygen map suggests an O-rich layer coincident with the Cr-rich layer at the edge of the

flank. RGB composition of images in Figs. 8.1.3b and 8.1.3c show with different colours the different regions of the left flank area. Figs. 8.1.3b and 8.1.3c clearly show the extension of the Ni-rich and Cr-rich regions. In Fig. 8.1.3c the matrix appears in white, the Ni-rich region in green and the Cr-rich region in blue.

As can be seen in Figs. 8.1.2a and 8.1.2b, crack α was found completely filled. The material filling the crack was analyzed using SAD and as shown in Fig. 8.1.4, was identified as NiO. Although it could seem that it was amorphous, later analysis in another samples will show that it was nanocrystalline.

As the Cr-rich region did not appear very obvious on the EDX maps in Fig. 8.1.3a, an EDX quantitative line profile across the left flank was acquired (Fig. 8.1.5). In Fig. 8.1.6b the presence of a Cr-rich layer of around 20 nm in thickness on the flank of the crack is clear. In some areas of the right flank, this oxide layer was found to be thicker, but always at locations corresponding to thin areas in the left flank (Fig. 8.1.6).

The Cr-rich layer was identified as mostly Cr_2O_3 , after analyzing some Cr-rich particles which were found at the edge of the flank (indicated by the blue arrow in Fig. 8.1.7). The particle in Fig. 8.1.7 was analyzed using microdiffraction (μD) (Fig. 8.1.8a). A simulation of a Cr_2O_3 DP in the same orientation (Fig. 8.1.8b) and a model of the unit cell (Fig. 8.1.8c) are also shown in order to ease the identification of the DP in Fig. 8.1.8a. Although the Cr-rich layer was continuous along the flank, the particles were in general too small to be identified as Cr_2O_3 , although its presence was inferred by EDX, suggesting the presence of a nanocrystalline oxide layer.

8.1.1.2 Crack tip area

Several SADPs were acquired from the attacked boundaries in the crack tip area, revealing the presence of Cr_2O_3 as shown in Fig. 8.1.9. This task was not easy, as the Cr_2O_3 was believed to be in some nanocrystalline form and in most cases did not separate completely from the matrix. Only by using the smallest SA aperture in

the 3000F and tilting until the expected reflections appeared was it possible to confirm the presence of this phase.

The crack tip area was examined in detail using EDX compositional mapping. Several EDX maps at different magnifications were acquired (Figs. 8.1.10 and 8.1.11) to show the complexity and the variety of the phases found.

The RGB compositions of these EDX maps have been found very useful to identified the phases, as their compositions will be constant (assuming uniform sample thickness) and, thus, their colour in the RGB composition.

The Ni map in Fig. 8.1.10a shows the positions of the intragranular cracks β and χ , as they were depleted in Ni. These intragranular cracks (β and χ) are not visible in TEM mode due to the small misorientation at both sides of the crack (approximately 1°). The Ni map also showed some Ni-rich clusters, which were later analyzed using EDX and μ D and identified as pure-Ni (with fcc structure, almost identical to the matrix, see Fig. 8.1.12a.). The Cr map in Fig. 8.1.10a showed that the Ni-depleted regions did not suffer any depletion in Cr. This, together with the O-enrichment observed in the O map, suggests that the grain boundaries have suffered Intergranular Attack (IGA). The intragranular cracks β and χ were also found enriched in oxygen. Later studies showed that the Cr-rich areas in the grain boundaries and intragranular cracks were Cr_2O_3 .

Figs. 8.1.10d and 8.1.10e are RGB montages of the same area but with different combination of elements, as labeled, using the single elemental maps shown in Figs. 8.1.10a, 8.1.10b and 8.1.10c. In Fig. 8.1.10d, the intergranular Cr-oxide appears as light blue, indicating that boundaries **B** and **C** have been heavily attacked. Boundaries **B** and **C** show no evidence of de-cohesion, unlike boundary **A**, even though there is absolute evidence for IGA and Cr_2O_3 formation. Fig. 8.1.11 shows the triple point region at a higher magnification. In Figs. 8.1.11b and 8.1.11d, the Ni clusters are easily identified (they appear as red in Fig. 8.1.11e). The Cr-enrichment of the boundaries and intragranular cracks is also obvious in Fig. 8.1.11f.

Beyond the point where crack α reached the triple point (**1**) the mode of loading on grain boundaries **B** and **C** was mixed mode I+II. The change of loading mode appeared to have reduced the rate of boundary attack. The applied stress would have probably opened grain boundaries **B** and **C** if the test had not been interrupted. These grain boundaries were attacked and Cr_2O_3 was formed.

A quantitative line profile was acquired across crack β (Fig. 8.1.13) showing that the width of the attack was of the order of 40 nm, with an associated Ni-rich region of approx. 15 nm. The width of the Cr-rich region was similar to that of the Ni-depleted region, suggesting their correlation. It is probable that grain boundary **C** also has some intragranular cracks associated but the artefacts (striations plus artificial thinning) did not allow identification of such features.

8.1.1.3 Particles

Fig. 8.1.14 is a bright field TEM image of the triple point labeled **1** in Fig. 8.1.2a in which several particles can be seen. Individual particles are labeled from **a** to **f**. EDX analysis, SADP and μDP were used to identify these particles. They include NiO and two spinels, NiFe_2O_4 and FeCr_2O_4 . The key to Fig. 8.1.14 indicates the identities of the individual particles. These particles are believed to come from the outer oxide scales. However, if crack α had been opened long enough, it cannot be discounted that particles such as **a** or **b** (Figs. 8.1.14 and 8.1.15) could have grown on its flanks in the same way they would do on the external surface of the sample. Particles **a** (NiO) and **b** (FeCr_2O_4) in Fig. 8.1.15 were found to be correlated in orientation, but independently from the matrix. In Fig. 8.1.16a, particle **c** (Fig. 8.1.15) is characterized using μD . In Fig. 8.1.16b, a simulated DP from the same orientation is shown in order to help with the identification of the spots. A model of the NiO unit cell in the same orientation is also shown (Fig. 8.1.16c). This shows that as well as the nanocrystalline NiO which filled crack α , some NiO monocrystals can also be found. In Fig. 8.1.17, two epitaxially orientated particles can be seen. After μD , these particles were identified as NiO (**d**) and NiFe_2O_4 (**e**) and are shown in a [110] orientation in Fig. 8.1.17. Several other NiO/ NiFe_2O_4 particles were found embedded in crack α , e.g. particle **i_a/i_b** in Fig. 8.1.18b. A common feature of these duplex

particles is that they are always epitaxially orientated. In Fig. 8.1.18a a TiO particle (**k**) can be seen together with a Cr oxide particle (**h**) and a NiFe_2O_4 particle (**g**). In Fig. 8.1.18, the other duplex particle (**i**) is shown. As mentioned before, it was identified as NiO/ NiFe_2O_4 duplex particle.

The particles found close to the flank of crack α appeared completely embedded in the nanocrystalline NiO. In Fig. 8.1.19a, EDX maps from this area show the long particle **g** rich in Fe Ni and O which was identified as NiFe_2O_4 . titanium map reveals the presence of a Ti oxide particle (**k**). Fig. 8.1.19b shows a TEM BF image of the area, with crack α in a horizontal orientation (the triple point would be on the left). RGB compositions are also shown to enhance the diversity of particles and compositions in the area, as they appear with different colors (Figs. 8.1.19c, d, e, f and g).

8.1.2 Main observations

- Grain boundary **A** loaded in Mode I opened, unlike boundaries **B** and **C**, which were loaded in a mixed mode I+II.
- Flanks of the opened grain boundary **A** had complementary topography, suggesting an abrupt opening.
- Crack α was found filled by nanocrystalline NiO containing different embedded particles which are typical of the outer surface scales.
- Two intragranular cracks were found (β and χ) and there was evidence of intragranular attack below the triple point (**1**).
- A Cr-oxide layer was found on the flanks of the attacked grain boundaries (opened and not). In the opened grain boundary, the width of the layer on each flank correlated reciprocally (e.g. if wide on the left flank, narrow on the right one).
- Cr_2O_3 was found in both intragranular cracks and attacked grain boundaries.
- Cr_2O_3 was found to reject pure Ni in the attacked boundaries.

8.1.3 Sample 1- Data collection

8.1.3.1 Flanks of the crack

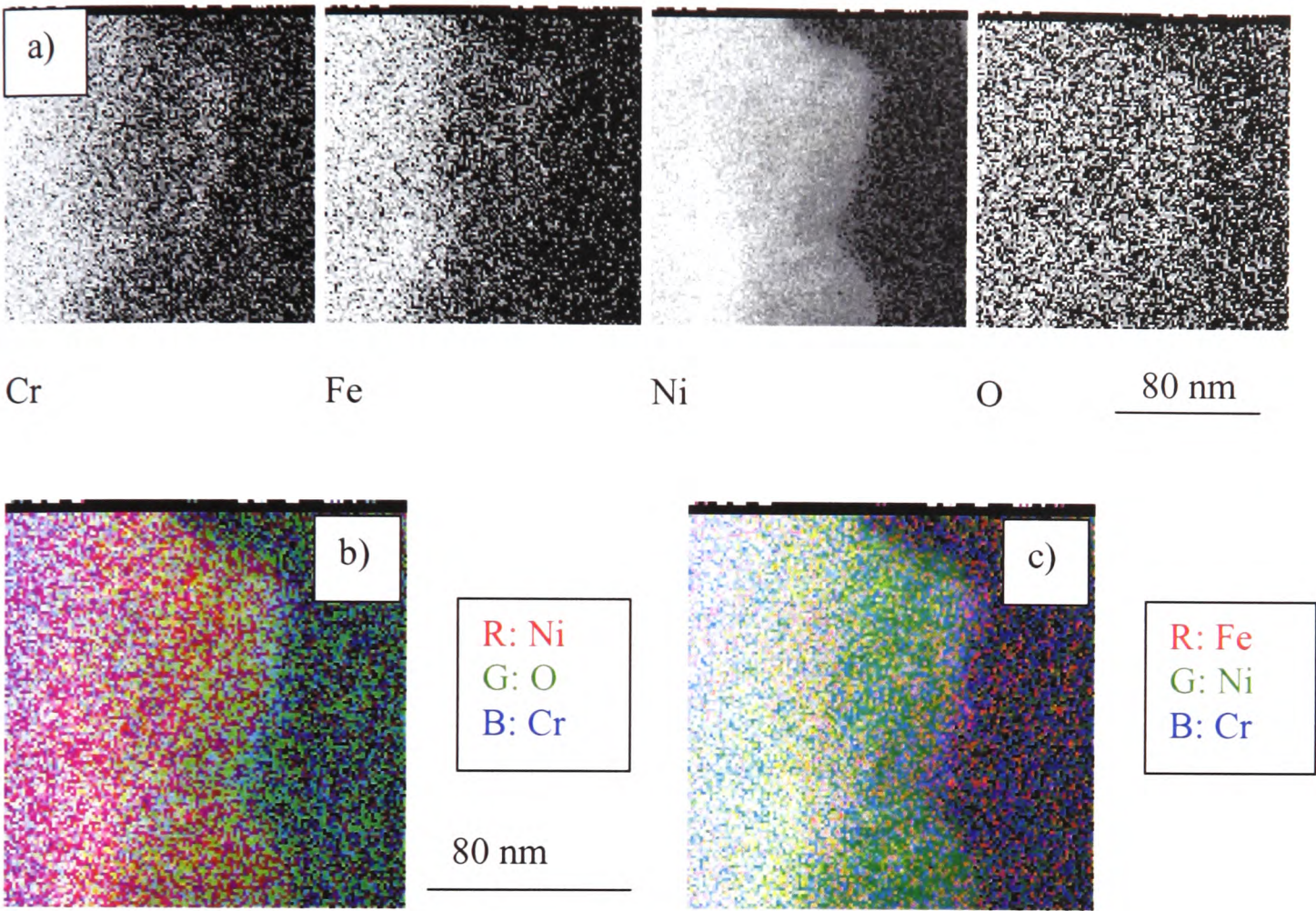


Fig. 8.1 3. a) EDX compositional mapping of the left flank region (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

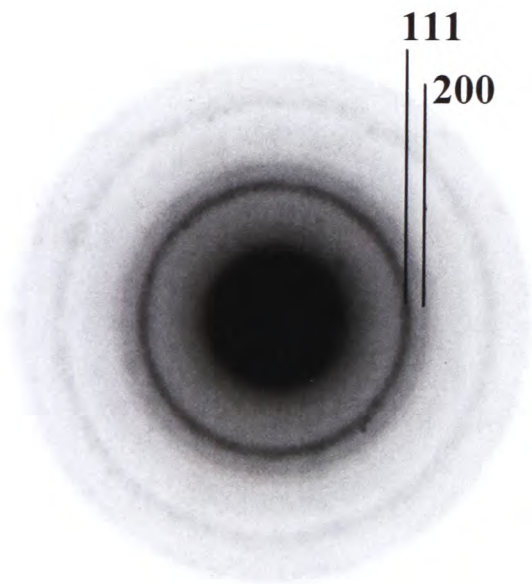


Fig. 8.1.4. TEM SA DP showing the nanocrystalline character of the oxide found filling completely crack α (acquired with the CM20).

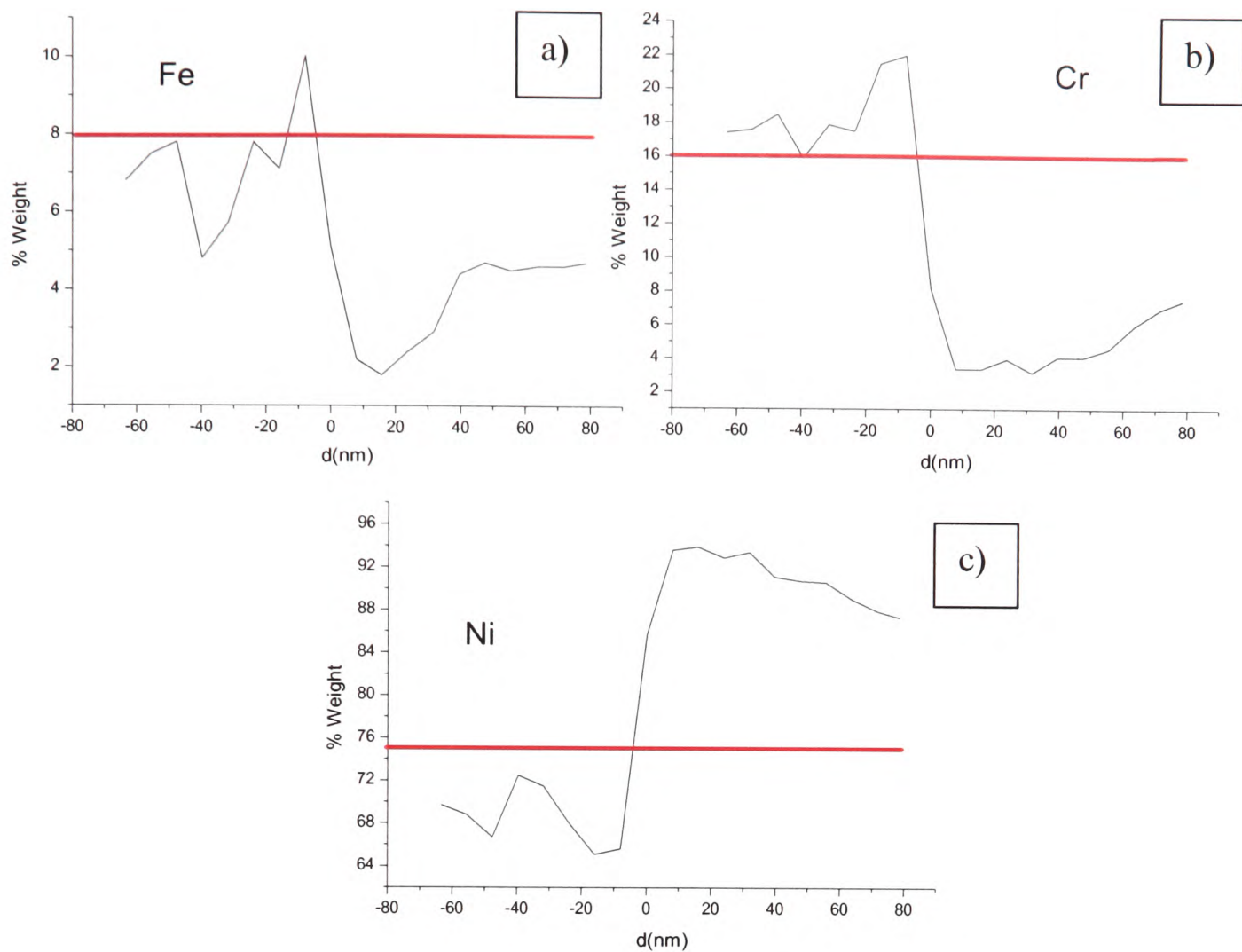


Fig. 8.1.5. Line profile showing the transition in composition between the matrix and the mode I crack α . Negative values of d represent points inside the matrix. For the oxide: $\sigma(\% \text{ wt. Ni}) = 4$, $\sigma(\% \text{ wt. Fe}) = 1.3$, $\sigma(\% \text{ wt. Cr}) = 1.6$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.7$, $\sigma(\% \text{ wt. Fe}) = 0.2$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red lines indicate the nominal composition (acquired with the LINK system in the HB501).

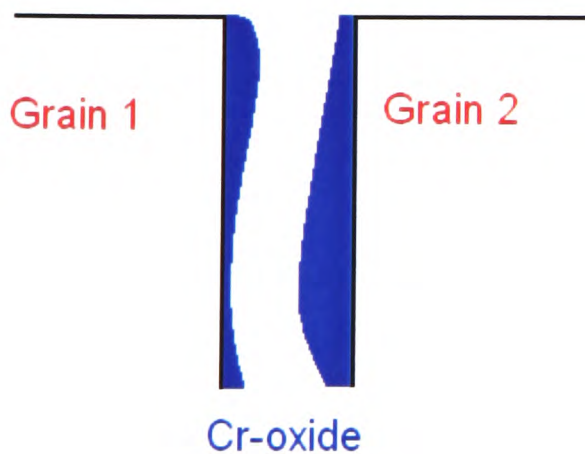


Fig. 8.1.6. Schematic diagram showing the differences in thickness in the Cr-oxide layer due to the grain boundary opening.

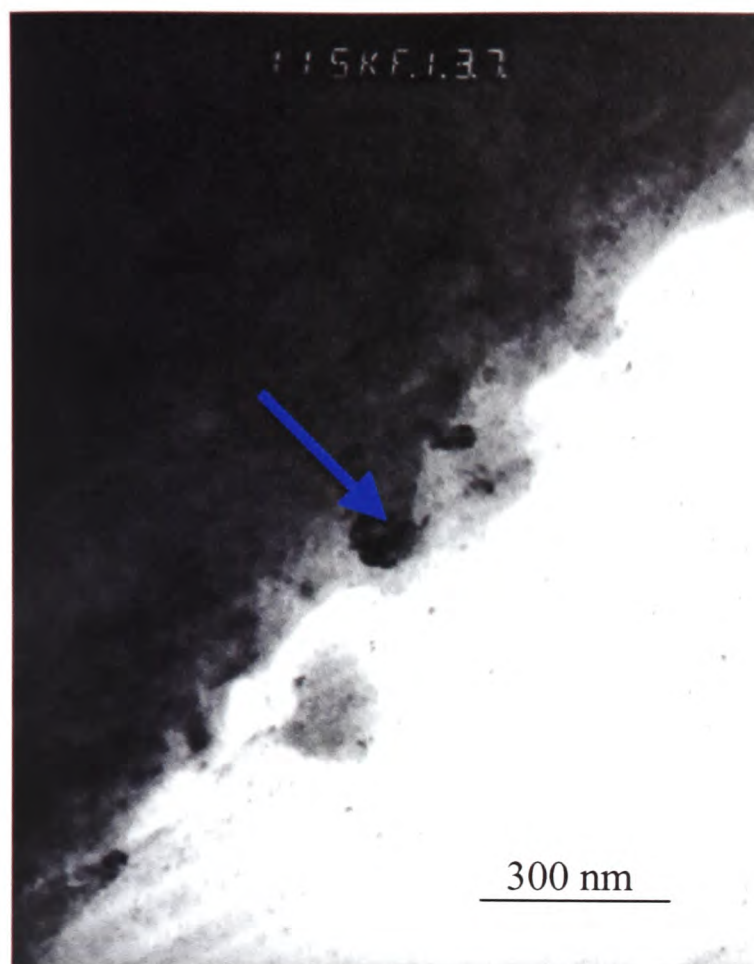


Fig. 8.1.7. TEM micrographs showing a Cr_2O_3 particle at the interface between the matrix and the NiO polycrystalline oxide (acquired with the CM20).

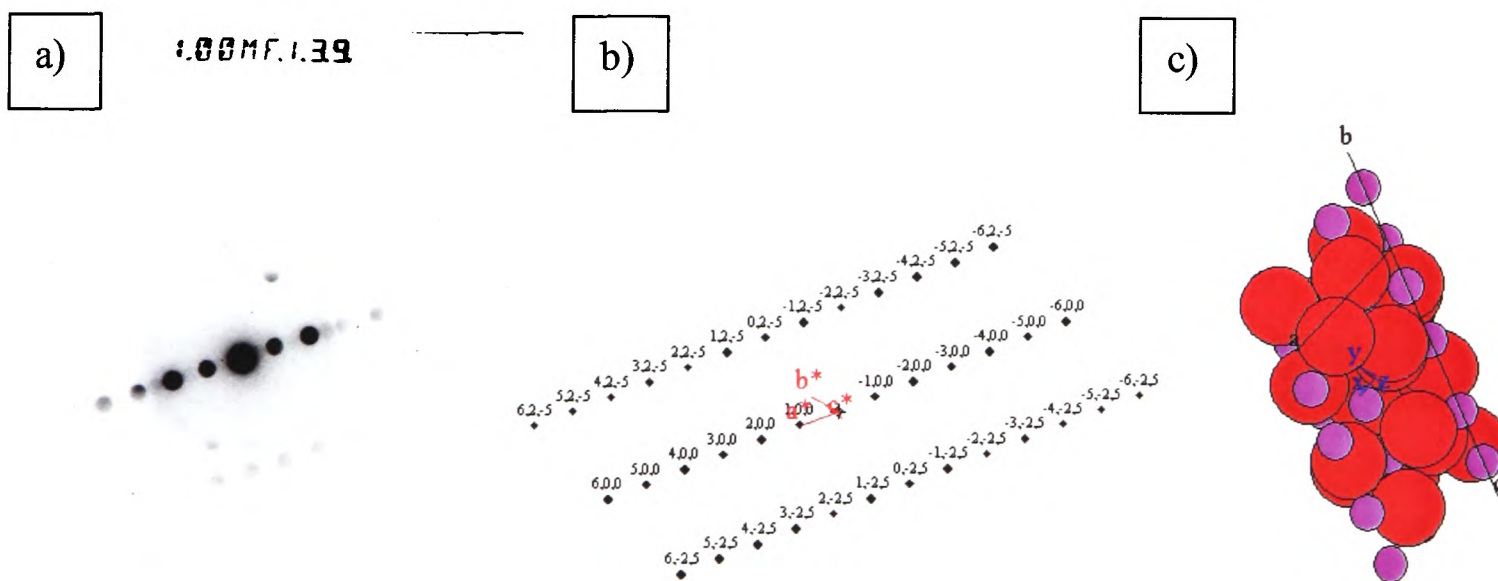


Fig. 8.1.8. a) TEM μD micrograph from the arrowed Cr_2O_3 particle in Fig. 8.1. 5, in a $[052]$ zone axis (acquired with the CM20); b) Simulation of a Cr_2O_3 DP in a $[025]$ zone axis ; c) Cr_2O_3 unit cell (Cr atoms in purple and O in red).

8.1.3.2 Crack tip area

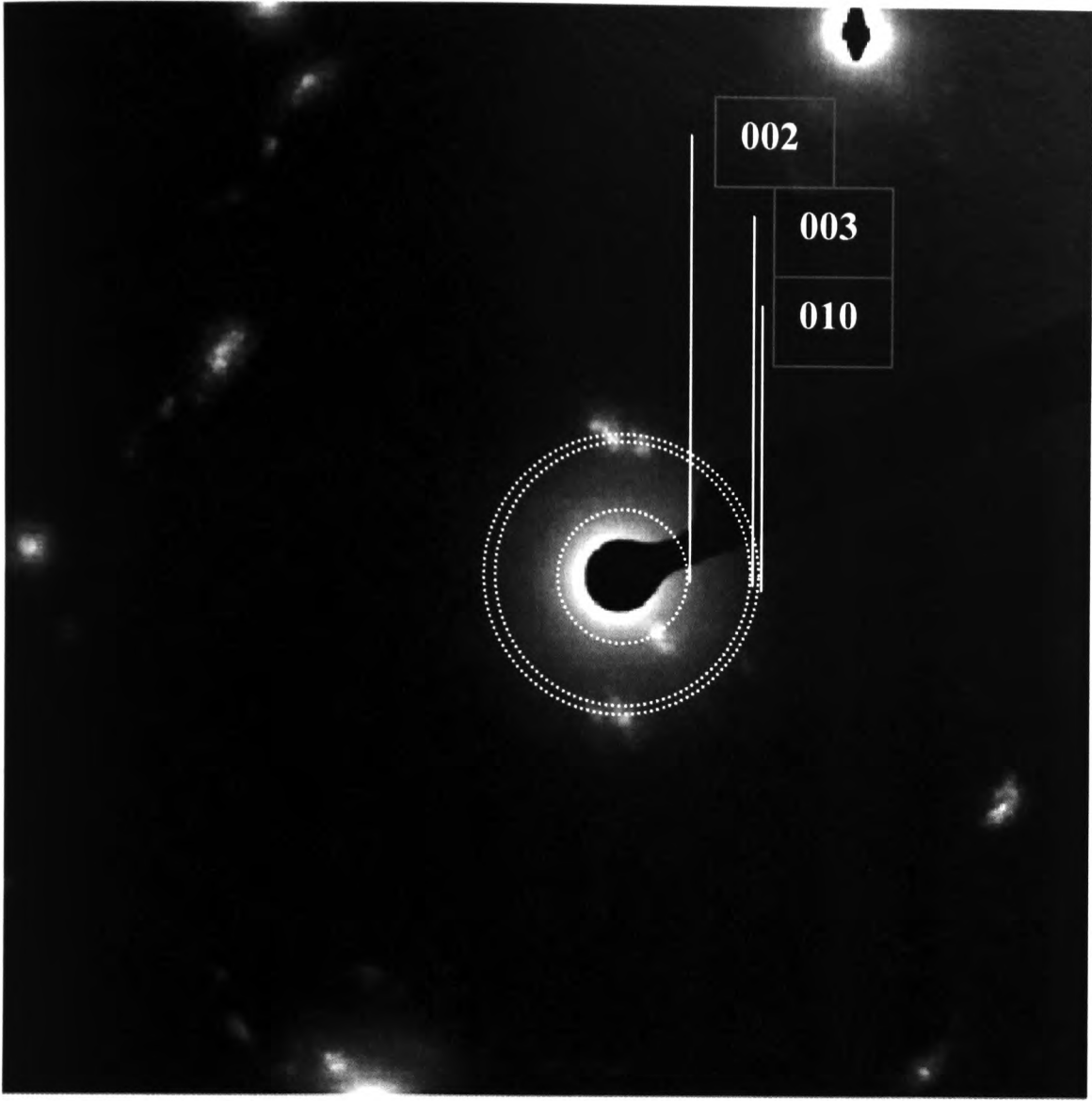
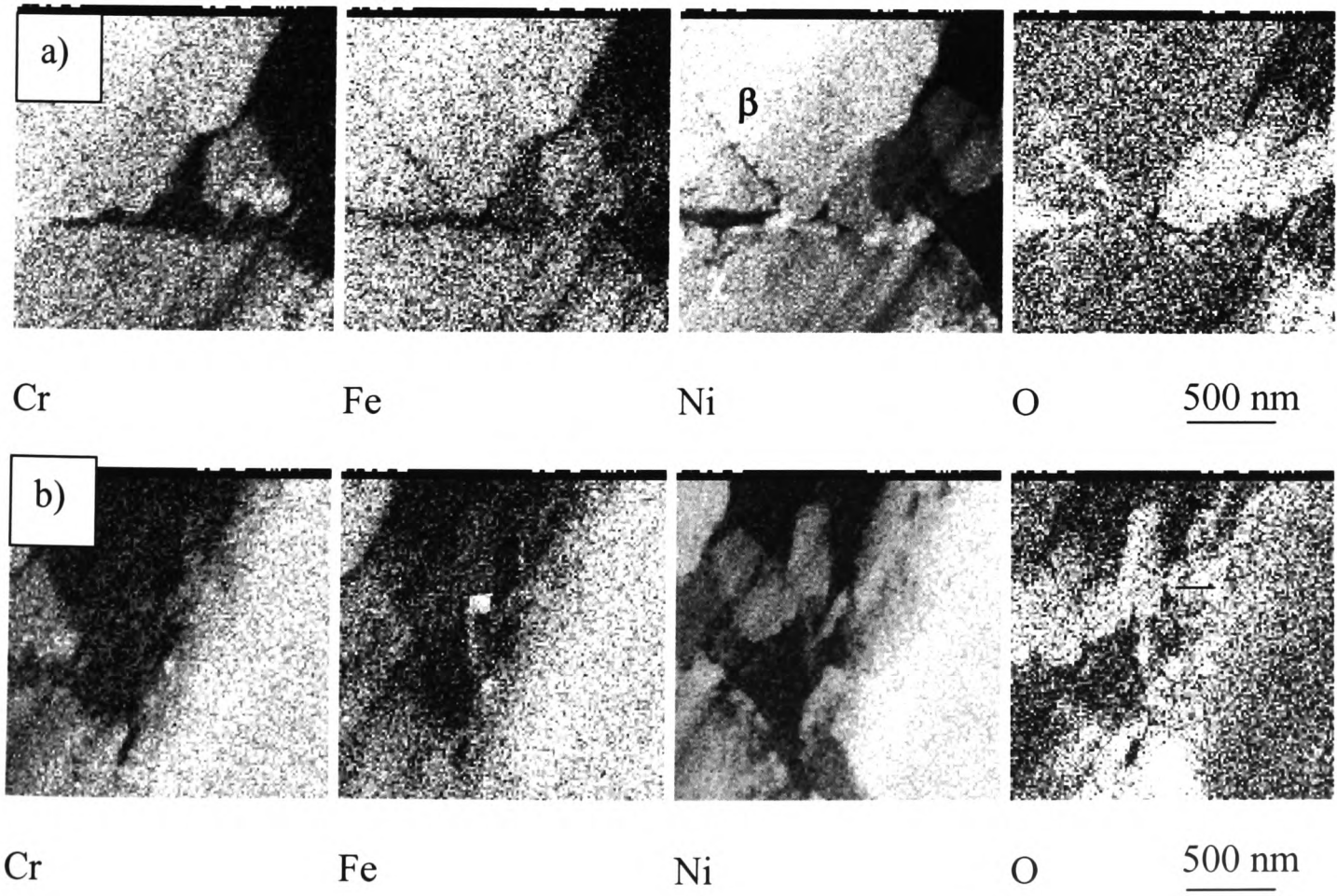


Fig. 8.1.9. SA DP showing some reflections of Cr_2O_3 (acquired using the multiscan CCD in the 3000F).



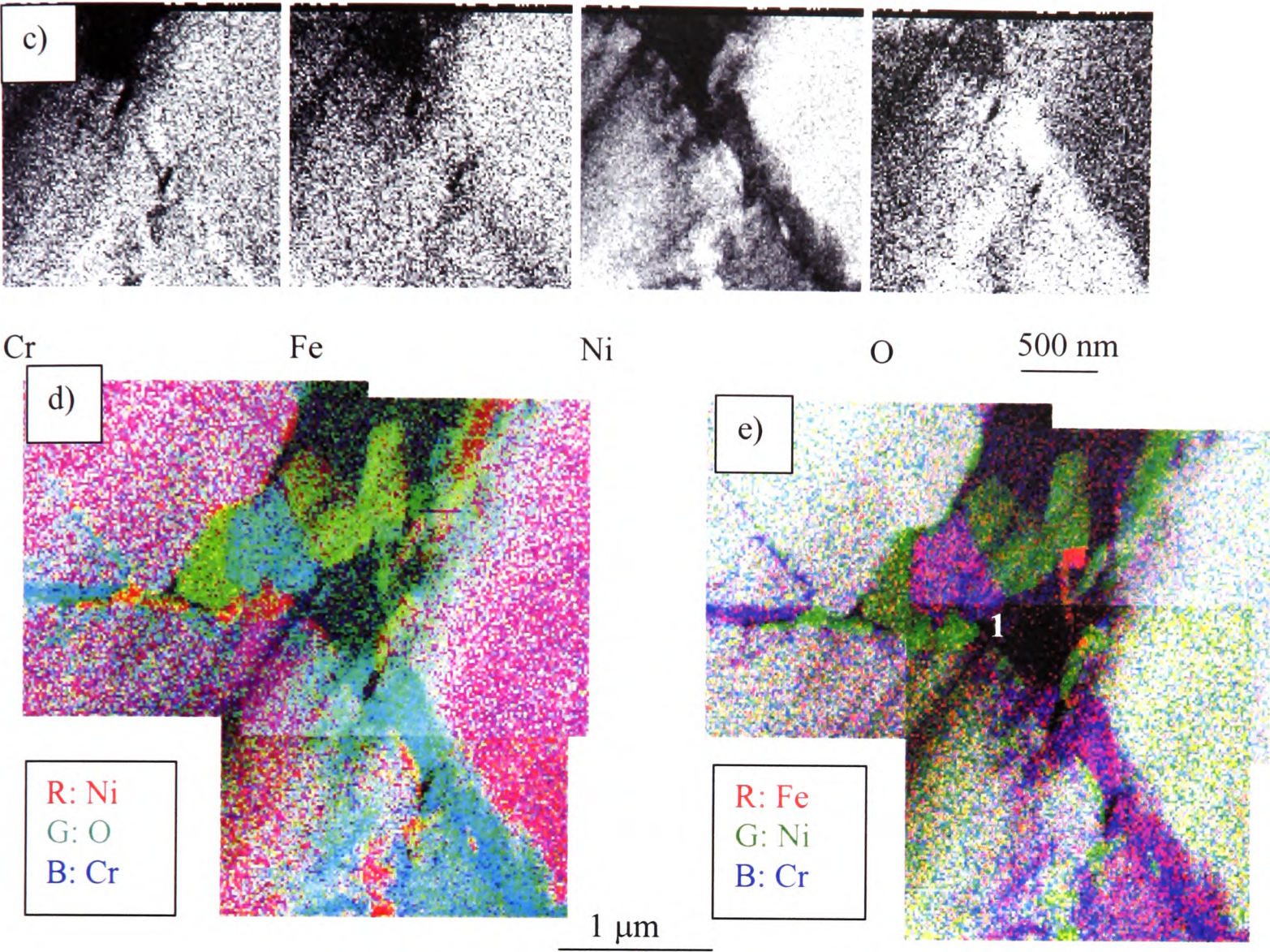
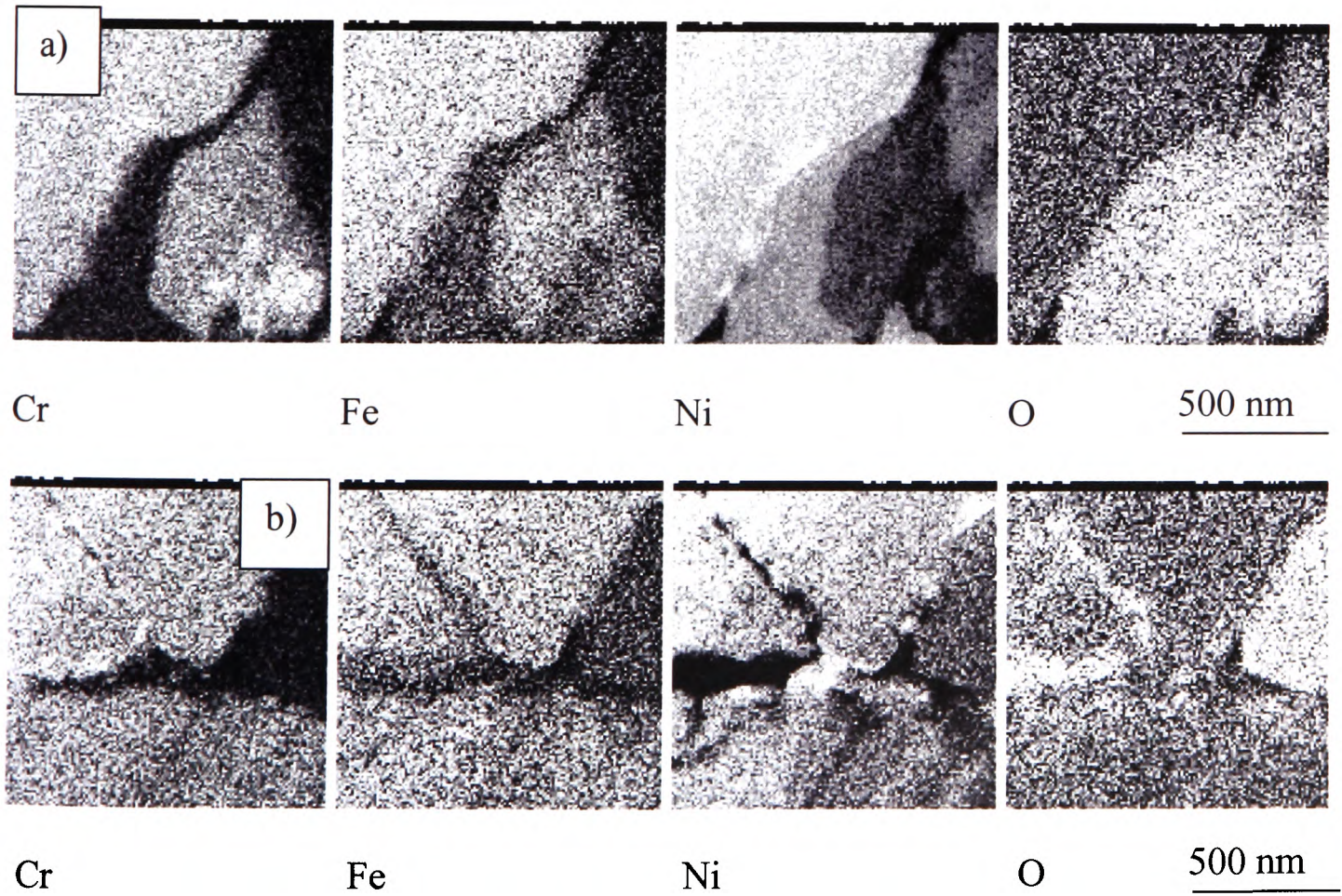


Fig. 8.1.10. a), b), c) EDX elemental maps showing the changes in composition in the triple point (1) area (acquired with the LINK system in the HB501); d), e) RGB composition of images.



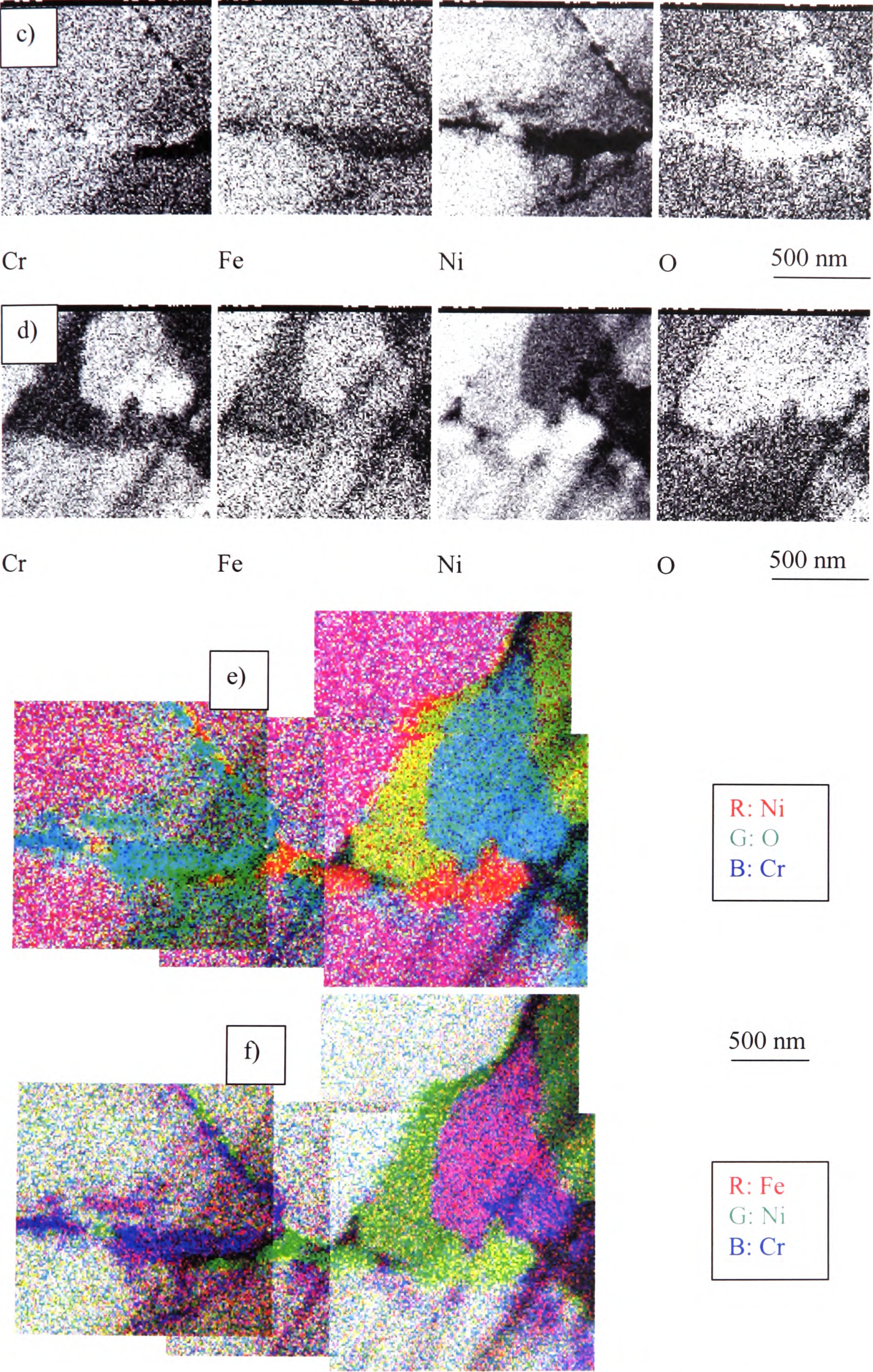


Fig. 8.1.11. a),b),c),d) EDX elemental maps showing at a higher magnification than previously the left boundary after the triple point (acquired with the LINK system in the HB501); e), f) RGB composition of images.

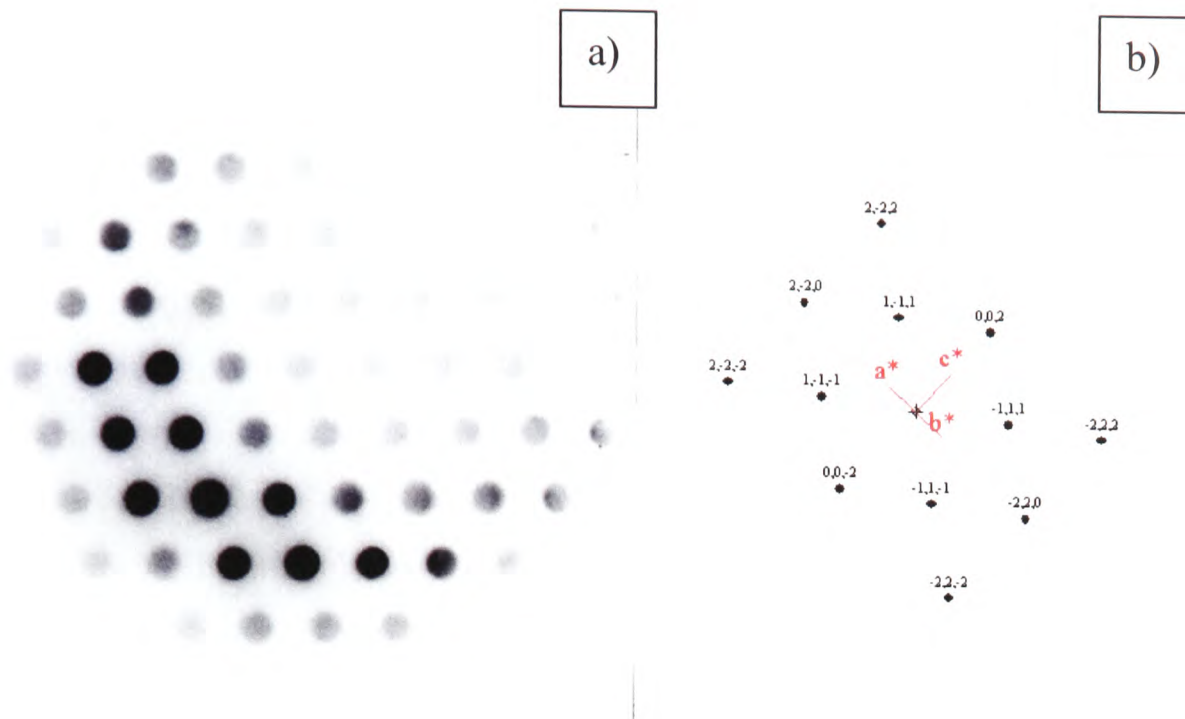


Fig. 8.1.12. a) μ DP from a Ni-cluster (acquired with the CM20); b) Simulated DP from pure Ni (fcc) in a [110] zone axis.

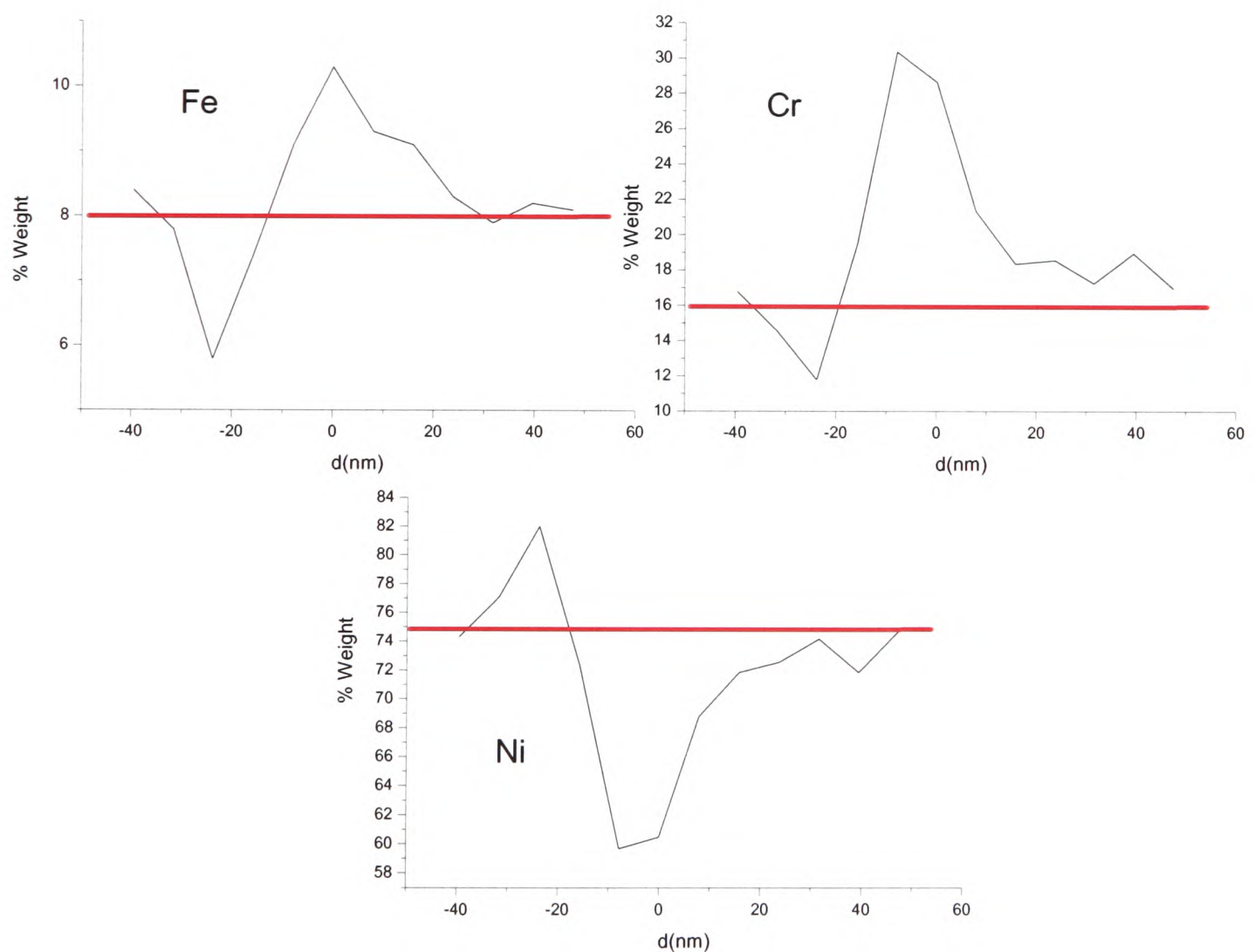


Fig. 8.1.13. Compositional line profile across transgranular crack β at 500kx. The red lines represent the nominal composition of the alloy. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.8$, $\sigma(\% \text{ wt. Fe}) = 0.4$, $\sigma(\% \text{ wt. Cr}) = 0.6$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.8$, $\sigma(\% \text{ wt. Fe}) = 0.2$, $\sigma(\% \text{ wt. Cr}) = 0.3$. (acquired with the LINK system in the HB501).

8.1.3.3 Particles

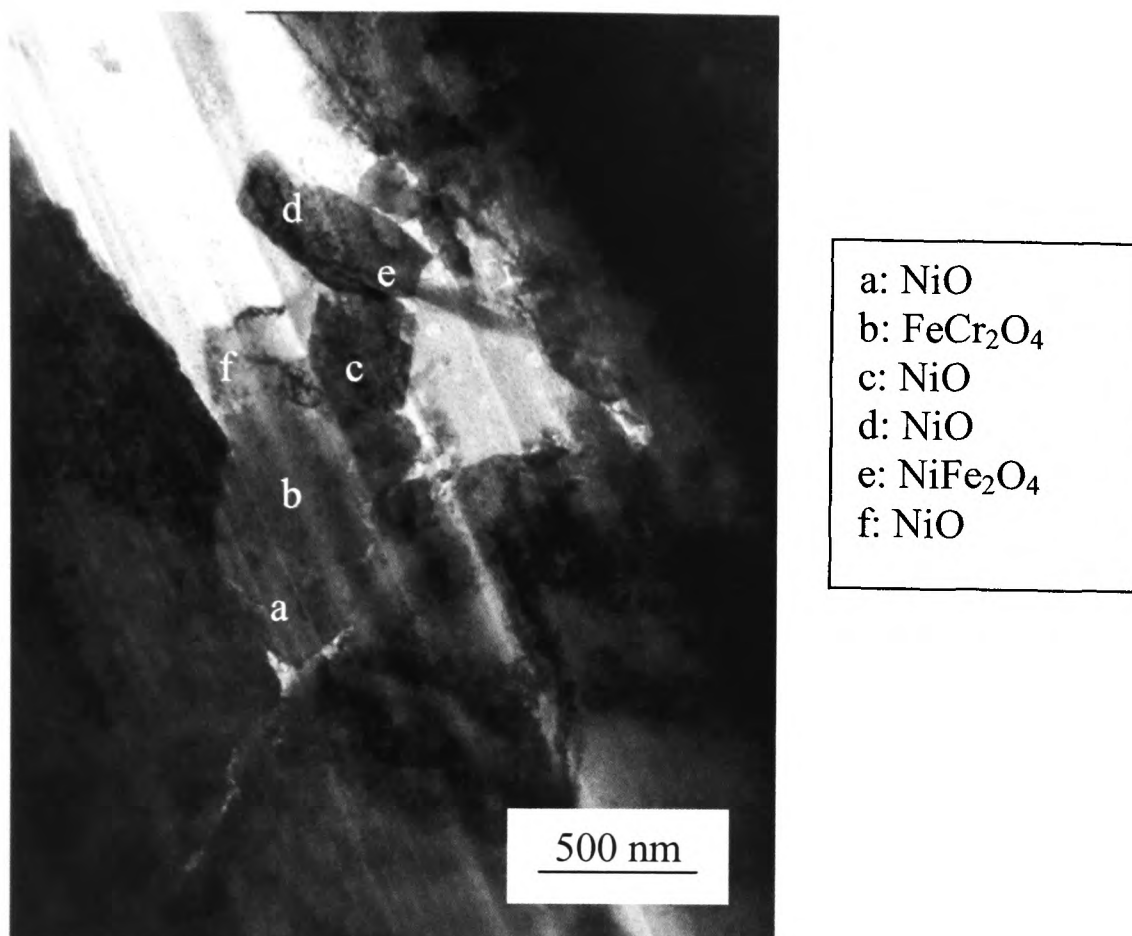
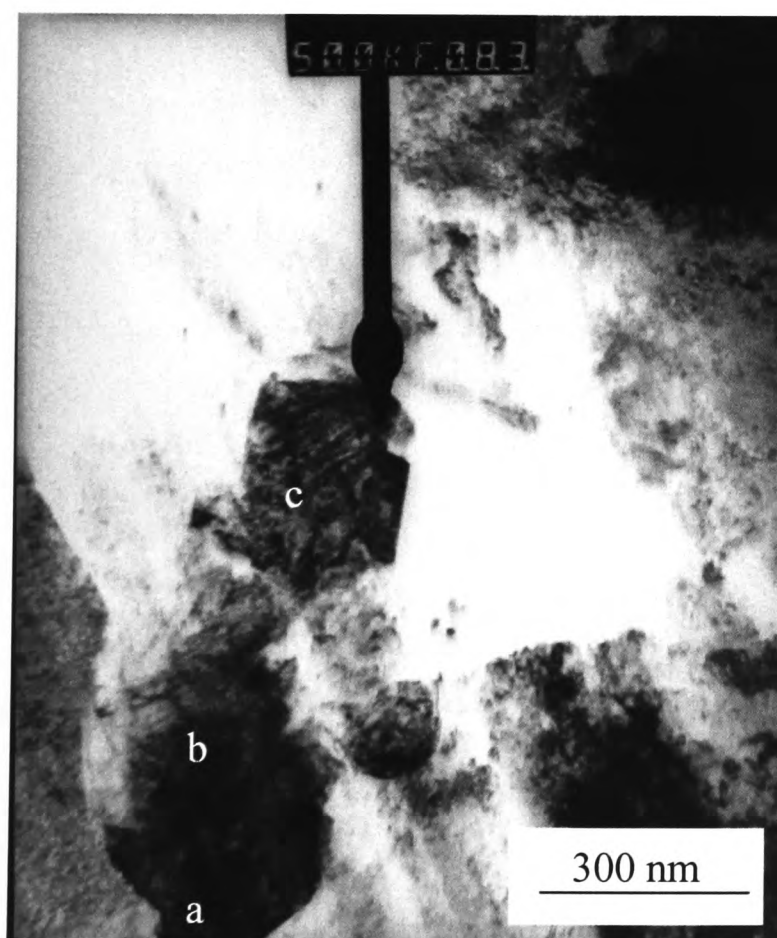


Fig. 8.1.14. TEM BF micrograph in which the different particles that have been identified are labeled (acquired with the CM20).



*Fig. 8.1.15. TEM BF micrograph showing particles **a**, **b** and **c** epitaxially orientated in an [110] zone axis (acquired with the CM20).*

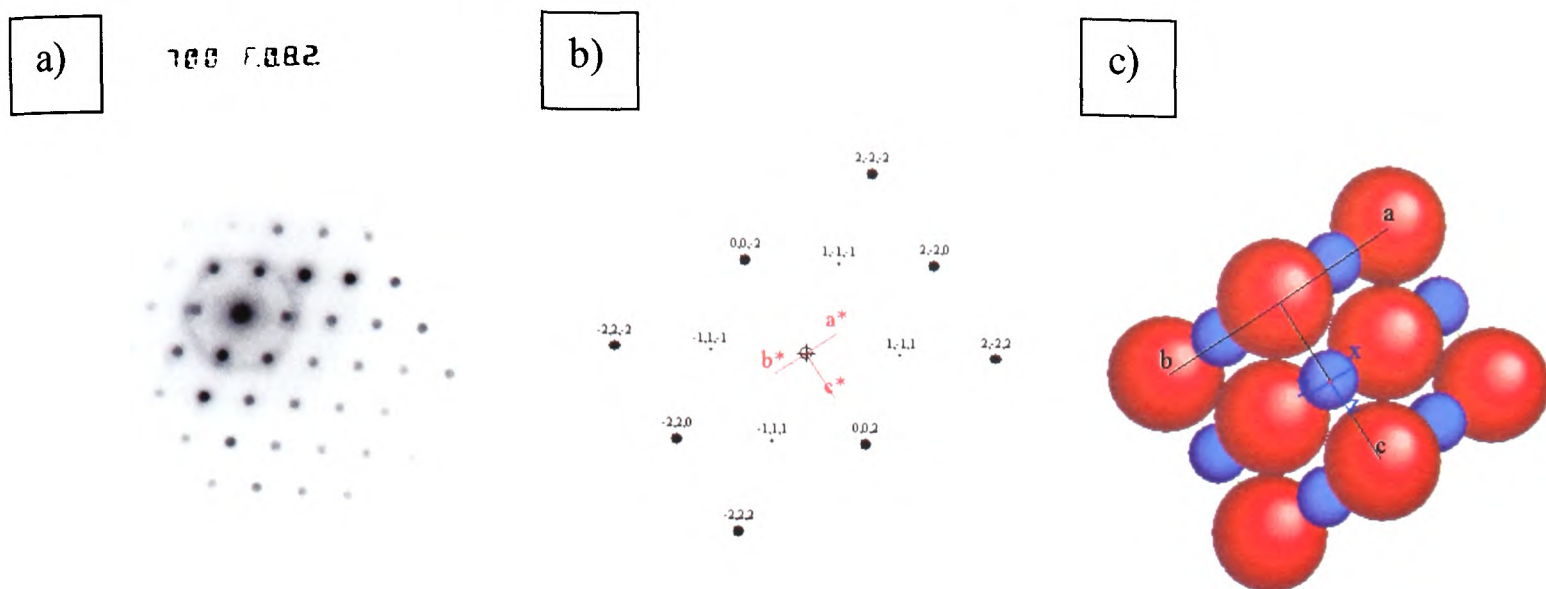


Fig. 8.1.16. a) TEM μ D micrograph showing a $[110]$ zone axis from the NiO particle c (acquired with the CM20), b) a simulation of a DP in the same orientation and c) a NiO unit cell (Ni atoms in blue and O in red).

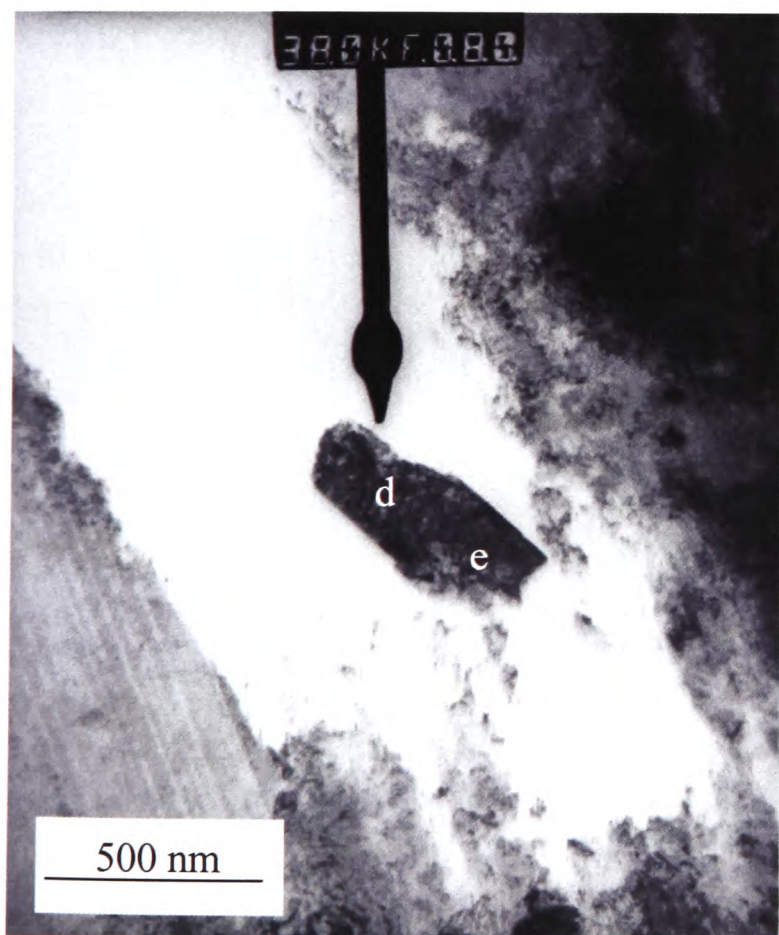


Fig. 8.1.17. TEM BF micrograph showing particles d (NiO) and e (NiFe₂O₄) epitaxially orientated in a $[110]$ zone axis (acquired with the CM20).

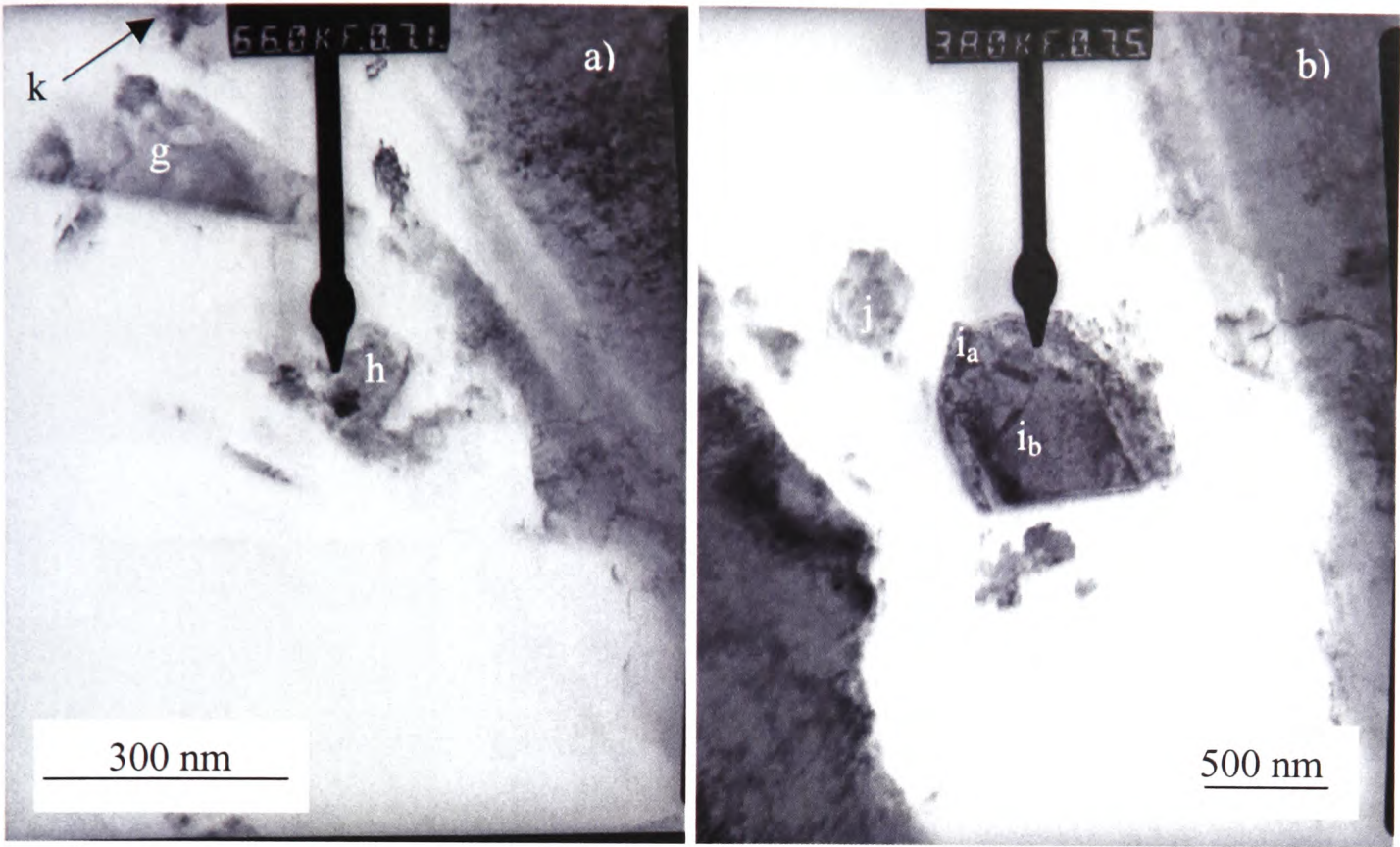
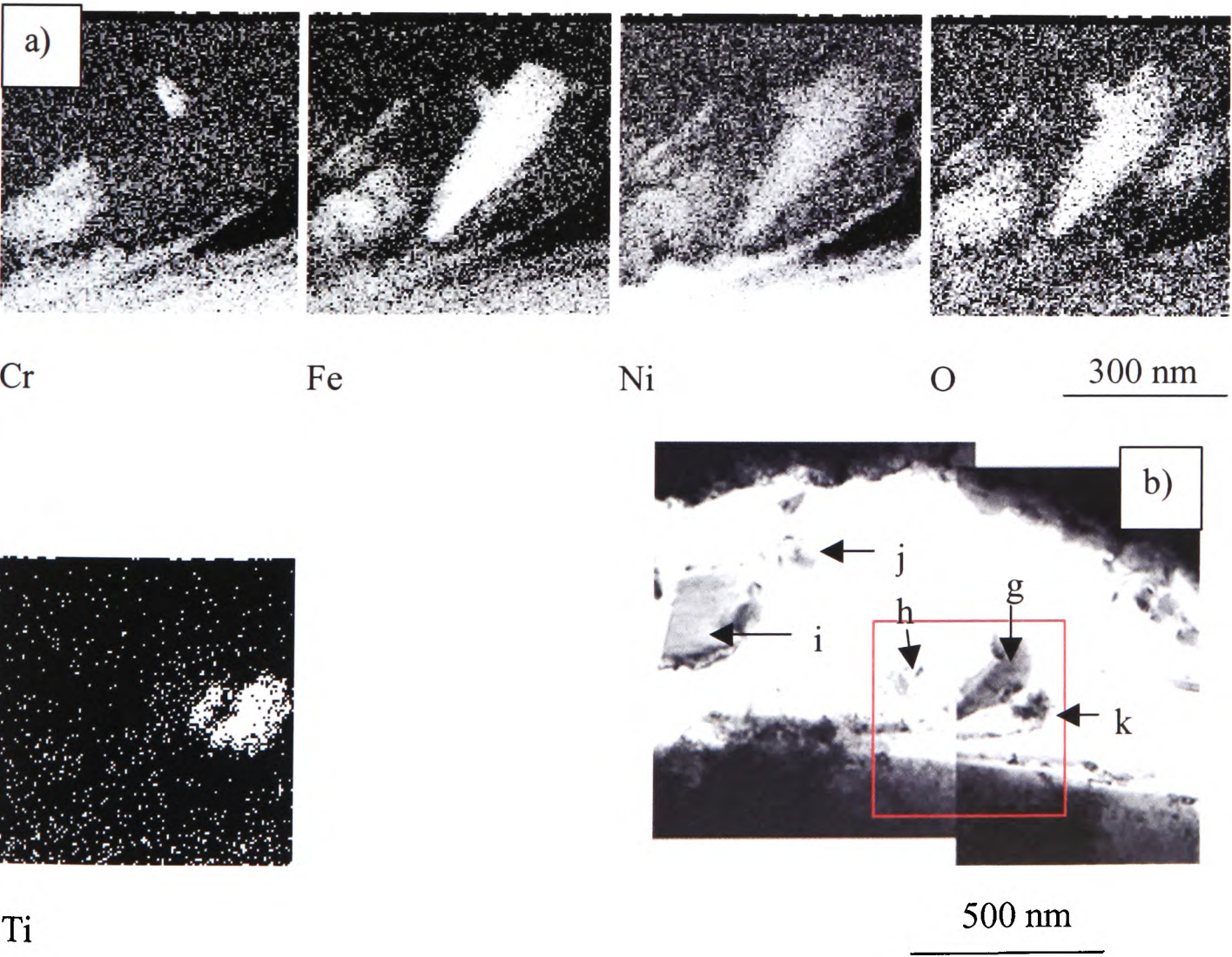


Fig. 8.1.18. TEM BF micrographs showing in a) a chromium oxide particle (h), a NiFe_2O_4 particle (g) and a TiO particle (k) ; in b) a compound $\text{NiO}/\text{NiFe}_2\text{O}_4$ particle (i) and a NiO particle (j). All the particles were embedded in the polycrystalline NiO .



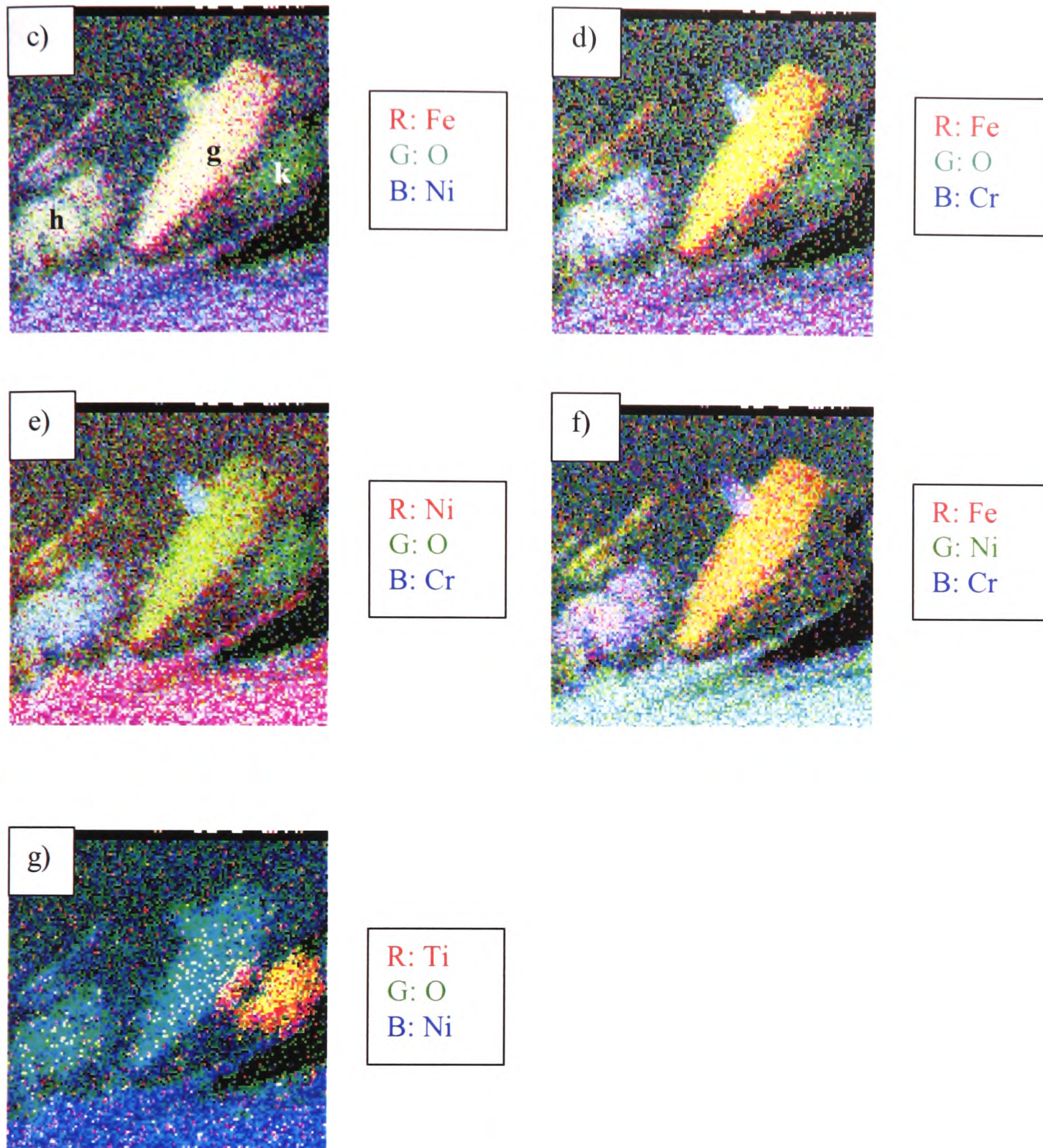


Fig. 8.1.19. a) EDX maps showing the differences in composition of particles **g**, **h** and **k** (acquired with the LINK system in the HB501); b) TEM BF micrograph showing how the particles were embedded in the nanocrystalline NiO in the crack (acquired with the CM20; c), d), e), f), g) RGB composition of images.

8.2 Sample 2: General observations

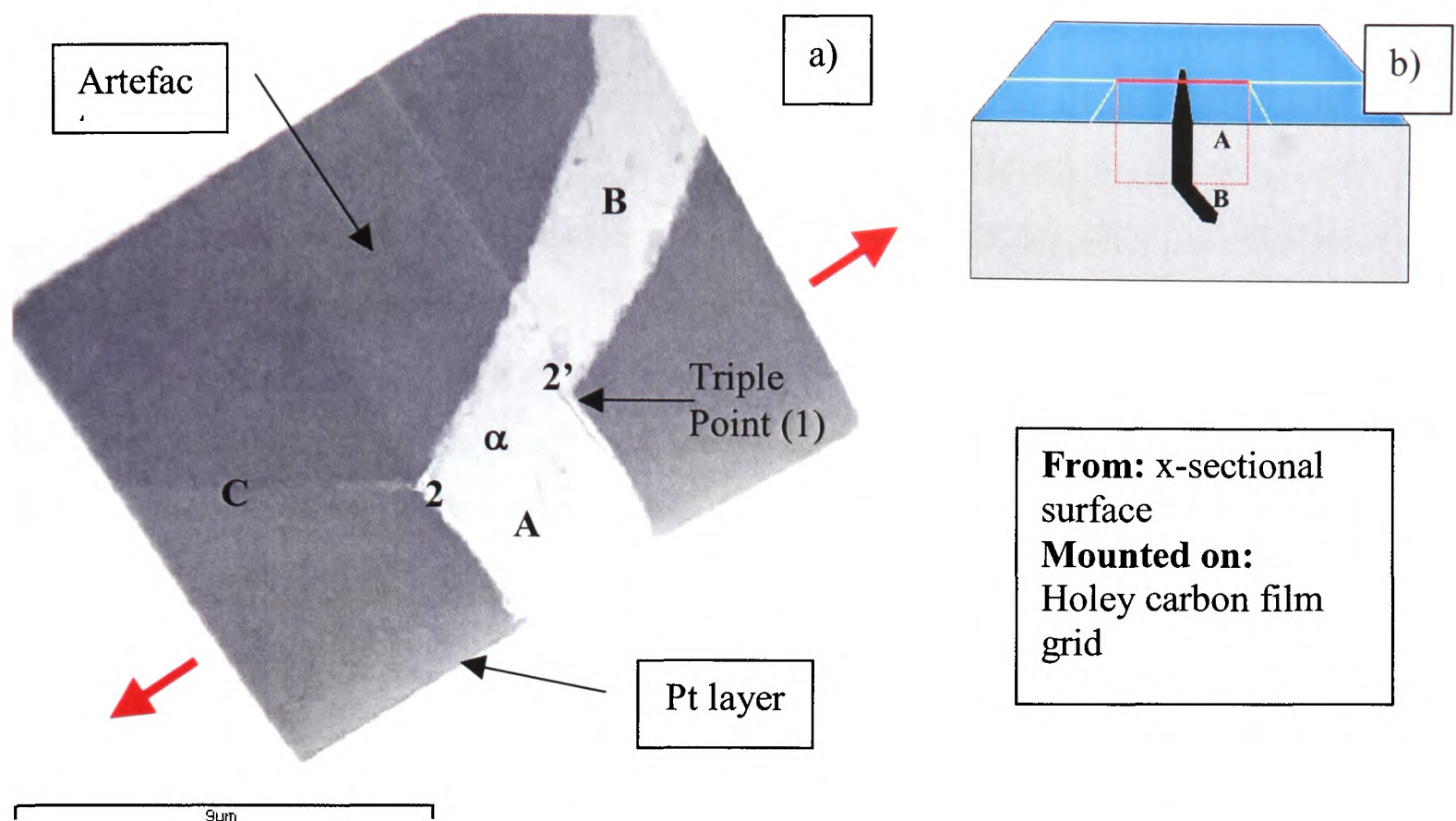


Fig. 8.2.1. a) STEM BF micrograph showing sample 2 after plucking. The loading direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) schematic diagram showing the orientation of the sample.

Sample 2 (Fig. 8.2.1a) was prepared from the x-sectional polished surface (in blue in Fig. 8.2.1b), at 1 μm from the edge. The sample contains 3 different grains and a triple point. Crack α grew perpendicular to the loading direction following grain boundary A until it reached a triple point (1) and chose boundary B to continue advancing.

It is interesting to note that the grains between boundaries A and B seem to have been pulled apart rather than internally corroded. If the grains were shifted inversely to the strain direction they would fit perfectly (2 and 2' would meet). This is not the only observation of this kind, several other samples have shown the same geometries.

The artefact arrowed in Fig. 8.2.1a is an artificially thin region below grain boundary A, due to the difference in milling rate between the matrix and the oxide. Due to the loss of the Pt protective layer in some areas, part of the nanocrystalline NiO that filled the crack is missing at the “entrance” of crack α in grain boundary A.

8.2.1 Analysis

8.2.1.1 Flanks

The composition and microstructure of the flanks of crack α were analysed. It was found that only a thin Cr oxide layer (a few nm) separated the matrix from the nanocrystalline NiO. This layer was found to be thinner than in the other samples. In Fig. 8.2.2, a higher magnification BF image of the region adjacent to the point labelled **2'** in Fig. 8.2.1a is shown. In this region, two EDX spectra were acquired in the nanocrystalline NiO (**a**) and in the almost separated layer next to the flank (**b**). The results of the quantification are shown in Table 1:

Spectrum	O	Cr	Fe	Ni	Total
a	12.48	6.16	7.83	73.53	100.00
b	40.17	17.90	7.50	34.42	100.00

Table 1: Compositions of points **a** and **b**. All results in Weight Percent

It can be seen that the nanocrystalline NiO (**a**) has considerable amounts of Fe and Cr, although the SADPs of the area do not show any other contributions apart from the NiO rings. This can be explained on the assumption that the Fe and Cr come from dissolved oxide particles from the outer surface of the sample which remain in ionic form in the solution. The other spectrum (**b**) shows a composition that would fit with that of a Ni-Cr spinel, although this was not observed in Sample 1.

8.2.1.1 Attacked boundary C

After studying the area where the crack α opened, it seems that it did not open until grain boundaries **A** and **B** had been completely attacked, as the flanks of the crack ran parallel for many microns and the features at both sides fitted each other. The reason why the crack did not open along grain boundary **C** seems to be the orientation of the grain boundary planes. Grain boundary **A** plane is completely perpendicular to the strain direction, so the crack was initially loaded in pure mode I. The intersection line of grain boundary **B** plane and grain boundary **A** is parallel to the top surface, while that of grain boundary **A** and grain boundary **C** is oblique to the

top surface. Thus, when grain boundary **A** opened the crack subsequently propagated along grain boundary **B**, as its orientation was more favourable than boundary **C**.

In Figs. 8.2.3a and 8.2.3b, it can be seen that the attack along grain boundary **C** is not limited to the plane of the grain boundary. The grains at both sides of the grain boundary have been attacked in a direction perpendicular to the grain boundary (e.g. at the points labelled **2** and **3** in Fig. 8.2.3a), as predicted by Hippsley². In Fig. 8.2.3b, an area a few microns ahead from the triple point in grain boundary **C** is shown, and it exhibits the same attacks as those found in the area of Fig. 8.2.3a. The attack seems to have happened in “zig-zags”, always obliquely to the grain boundary line, but never extending for more than 100 nm in a perpendicular direction to the grain boundary.

The entrance of the attacked boundary **C** (Fig. 8.2.4) shows many small particles, with sizes in the order of 100 nm. As they appeared only in the EDX Ni map (Fig. 8.2.5c) and O map (Fig. 8.2.5d) and since SAD patterns from these particles did not show any differences from those of the nanocrystalline NiO, they are believed to be small NiO particles. They were all embedded in the finer nanocrystalline NiO that completely fills crack α . The attacked boundary appears lighter in the TEM BF image in Fig. 8.2.4. This area was correlated with the Cr and O-rich regions in Figs. 8.2.5a and 8.2.5c and was identified as Cr₂O₃ using μ D. It is present continuously from the entrance of the crack to the end of the attacked region. In the EDX maps it can also be seen that Ni has been rejected preferentially, but not Fe, which can even be retained by the Cr-oxide to form a Fe-Cr spinel (Fig. 8.2.5a,b,c). In the RGB compositions the Cr-oxide can be seen as light blue (Cr+O) (Fig. 8.2.5e). Note that the orientation of the EDX maps and RGB compositions appears rotated 70° anticlockwise with respect to the image in Fig. 8.2.4.

The oblique orientation of grain boundary **C** can be appreciated in Fig. 8.2.6, as the tip of the attack seems to advance transgranularly parallel to the grain boundary. In fact, it is advancing through the grain boundary, but at a different height on the sample, so appears separated from the boundary in the TEM image. This effect can also widen the apparent region of attack in the image.

Compositional information at the tip of the attack along boundary **C** is shown in Fig. 8.2.7, revealing that there is no apparent diffusion of O ahead of the Cr_2O_3 in the grain boundary, as Cr and O intensities completely overlap (Fig. 8.2.9a). The apparent width of the attacked region varies while tapering away.

Fig. 8.2.8 shows a qualitative EDX line profile along the attacked boundary **C**. Although it has been acquired along a straight line, and at some points it might not have followed the exact position of the grain boundary, it was useful to reveal some details. For example, there is an Fe rich region (labelled as **1** in Fig. 8.2.8d) only at the entrance of the crack, which suggests that the Fe-Cr spinel phase forms only in contact with the environment. The O and the Cr profiles shapes (Figs. 8.2.8.2.8a and 8b) are not completely correlated, which indicates that the overlap between the Cr-L peak and the O-K peak has been resolved satisfactorily. The Cr content in the grain boundary is not significantly different from that of the matrix (Fig. 8.2.8c) (although this can be seen better in Fig. 8.2.9c). The oxygen content decreases considerably as the tip of the attack is reached (Fig. 8.2.8a).

In Fig. 8.2.9, a similar qualitative EDX line profile is shown, but acquired perpendicular to the attacked boundary. In Figs. 8.2.9d and 9c it can be seen that the Fe and Cr contents do not differ much from those of the matrix, but the O content changes considerably (Fig. 8.2.9b). The Ni is depleted in the attacked region (Fig. 8.2.9e) although in this boundary no Ni-clusters were found.

The presence of nanopores in the attacked boundary is revealed in Fig. 8.2.10. These nanopores might have an important role in explaining the fast diffusion of O through the Cr_2O_3 in the boundary. Many of them can be observed, running parallel to the grain boundaries, with lengths up to 500 nm. These features could also have been described as cracks, indicating a future opening of grain boundary **C**.

8.2.2 Main observations

- Grain boundary **A** (loaded in Mode I) and grain boundary **B** (loaded in mixed mode I+II) opened, but not grain boundary **C**.
- Clear optical evidence of grain boundaries **A** and **B** having been pulled apart rather than internally corroded.
- Attack in grain boundary **C** occurred in “zigzags” with wide penetrations of the attack in the matrix.
- Evidence of pores in grain boundary **C**.

8.2.3 Sample 2- Data collection

8.2.3.1 Flanks of the crack

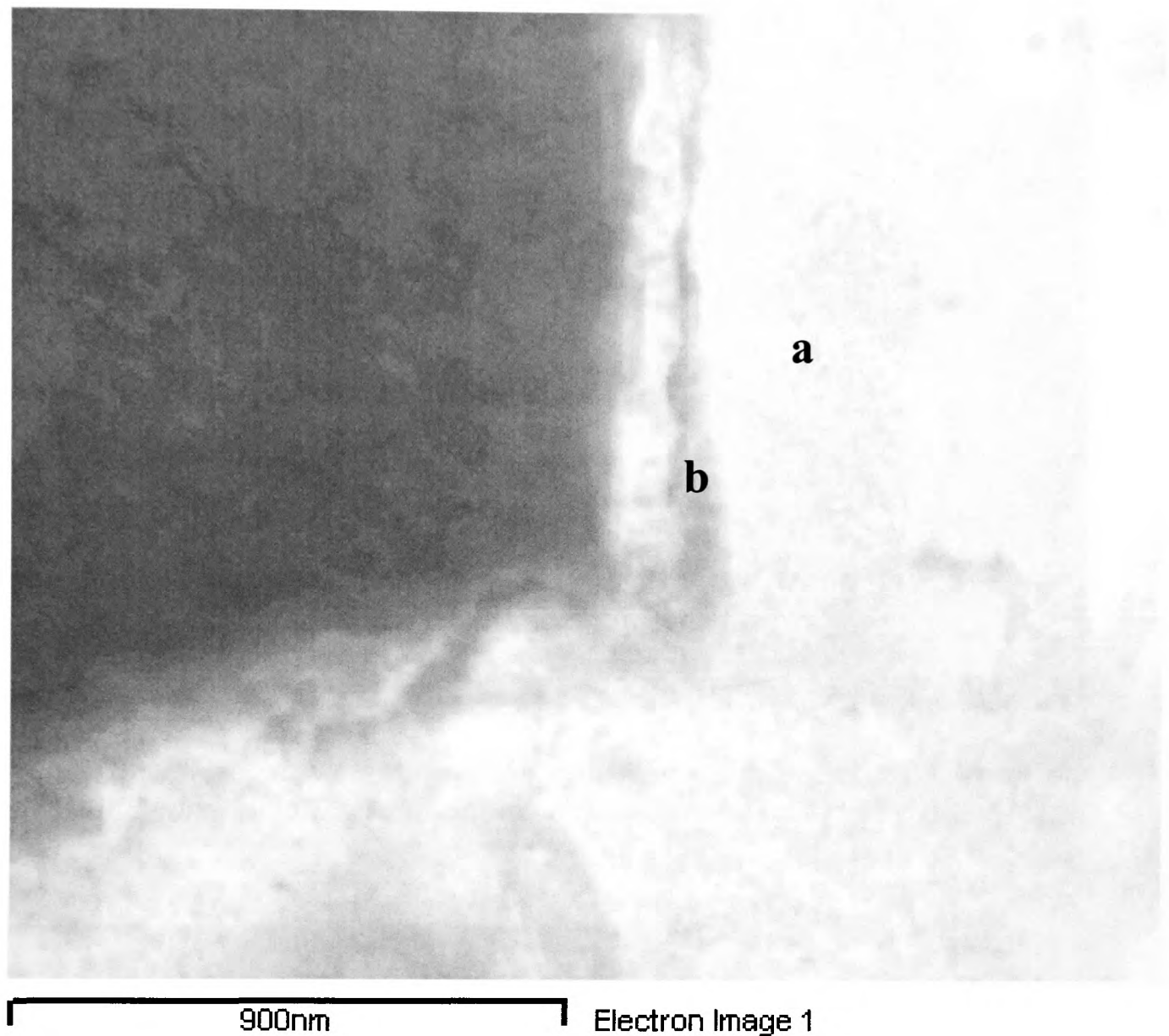


Fig. 8.2.2. STEM BF micrograph showing details of the flank of crack α at the triple point. (a) is nanocrystalline NiO and (b) is a Ni-Cr oxide layer (acquired with the INCA system in the CM20).

8.2.3.2 Attacked boundary C

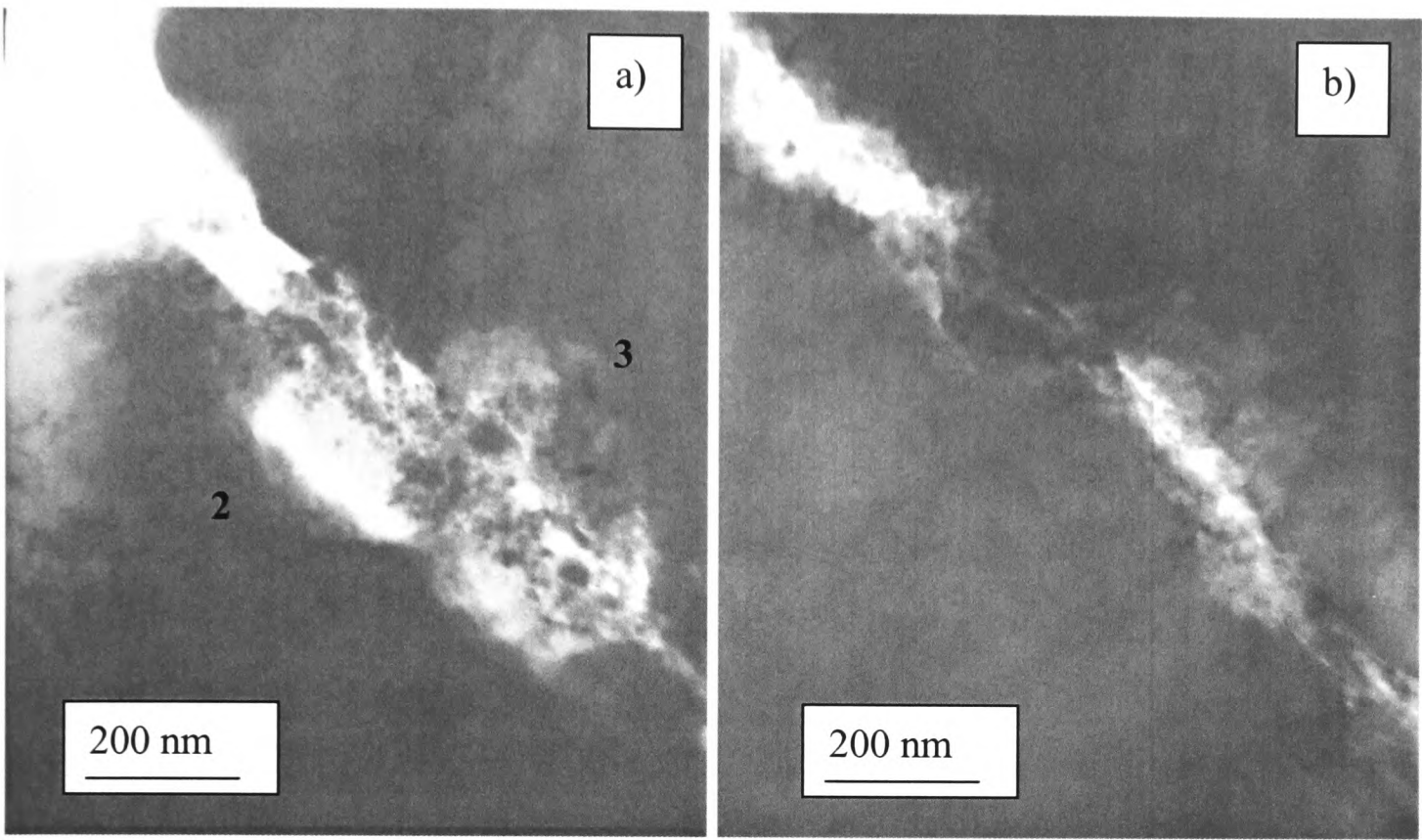


Fig. 8.2.3. TEM BF micrographs showing the attack in grain boundary C from the triple point (a) and some details of the attacked boundary ahead (b) (acquired with the CM20).

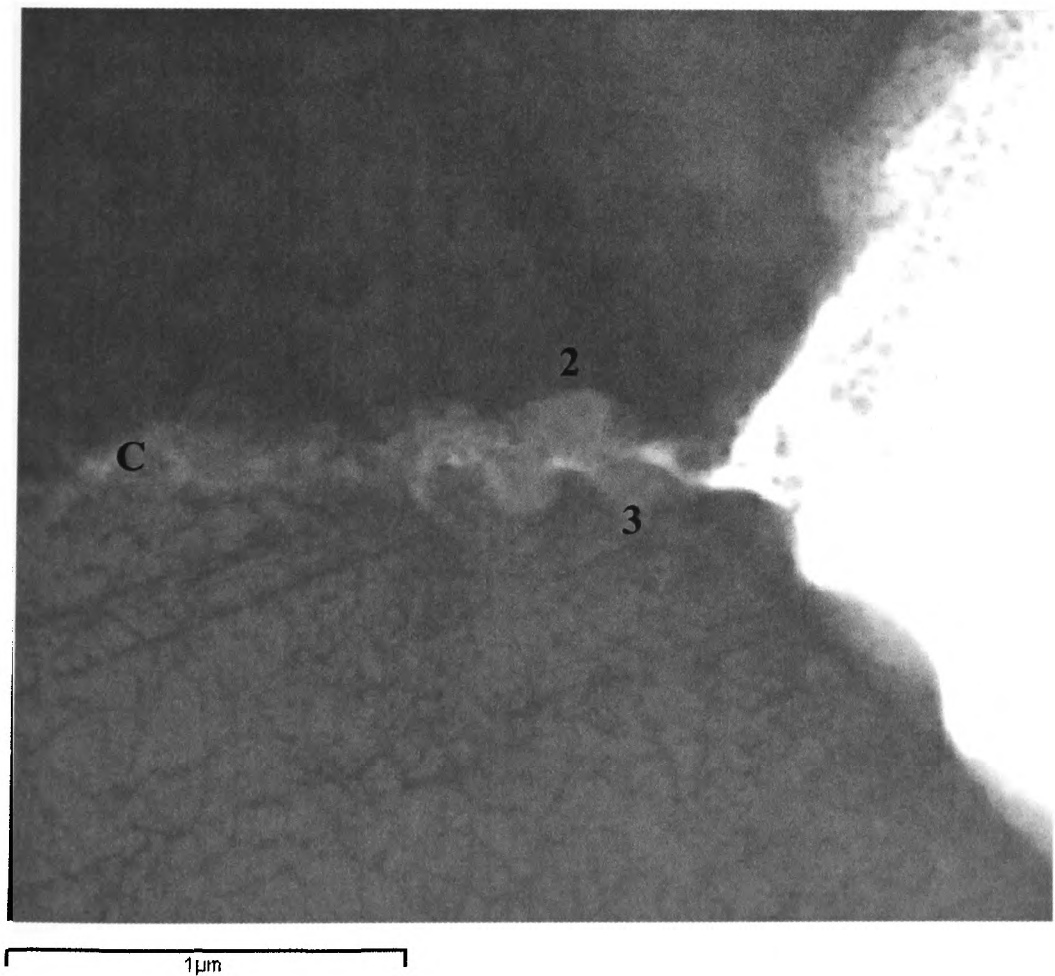
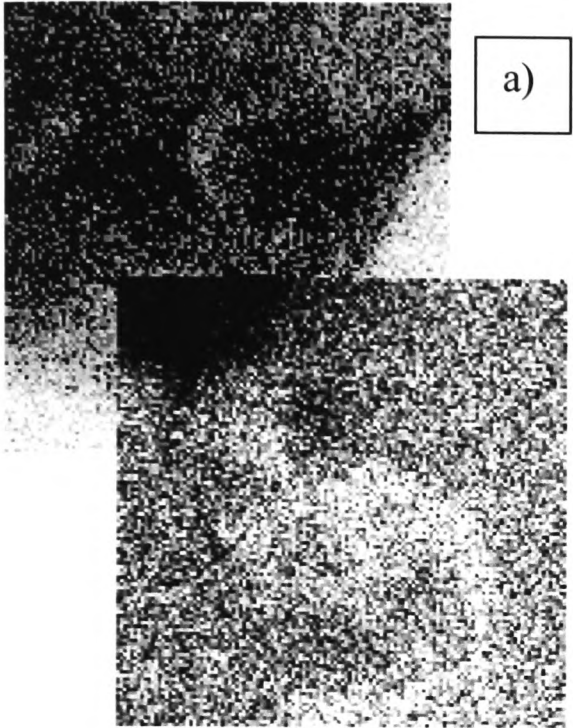
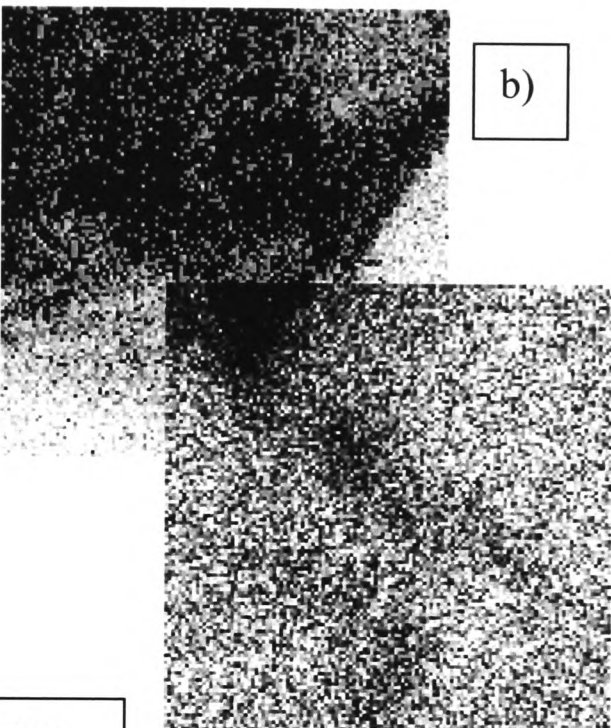


Fig. 8.2.4. STEM BF micrograph showing the triple point and the attack of grain boundary C (acquired with the INCA system in the CM20).

Cr

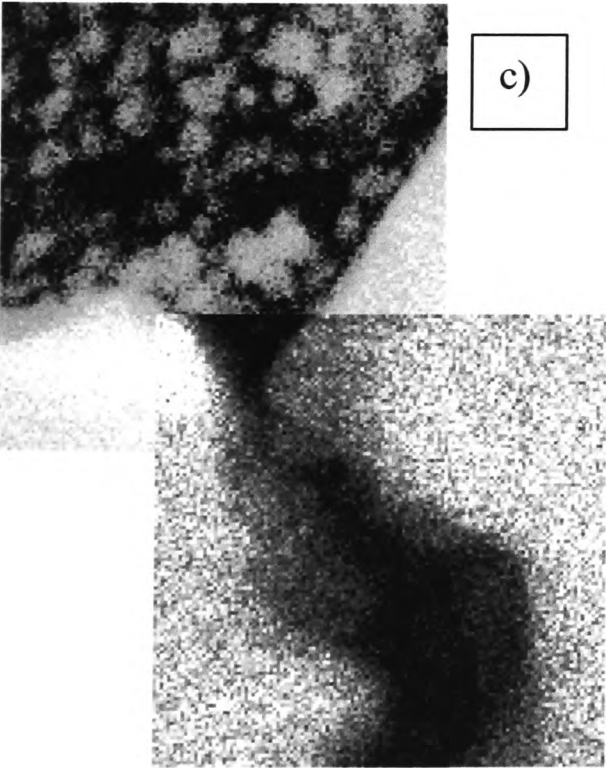


Fe

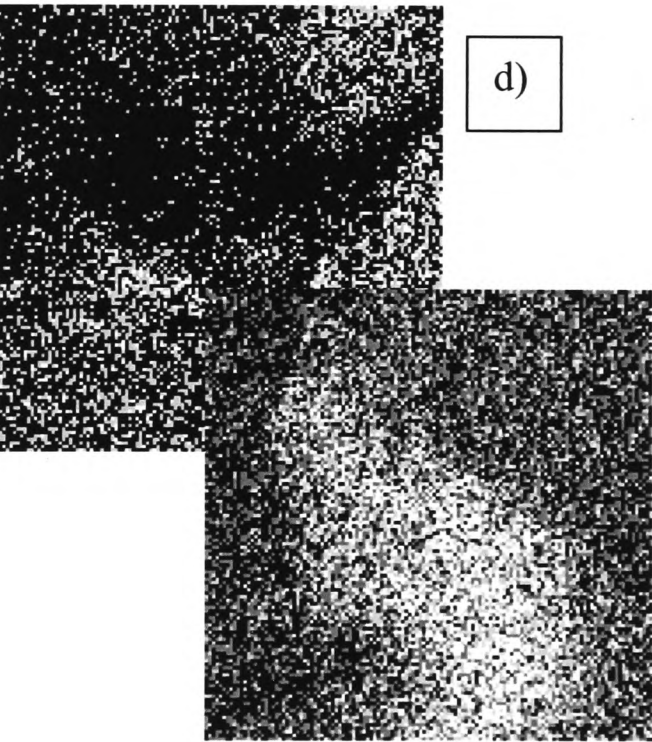


500 nm

Ni



O



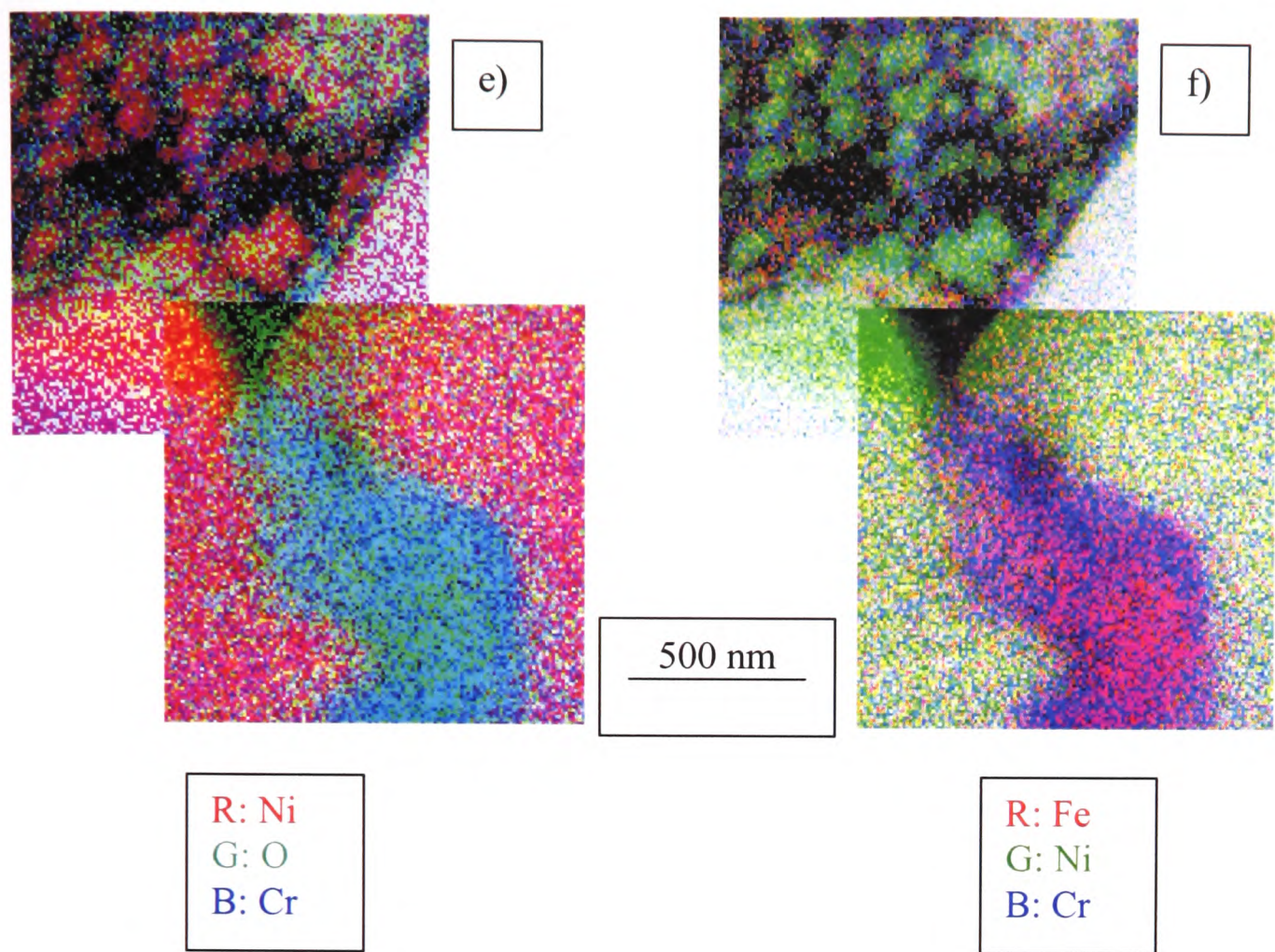


Fig. 8.2.5. a), b), c), d) EDX maps of the entrance of the attacked boundary C (acquired with the LINK system in the HB501)); e) and f) RGB composition of images.

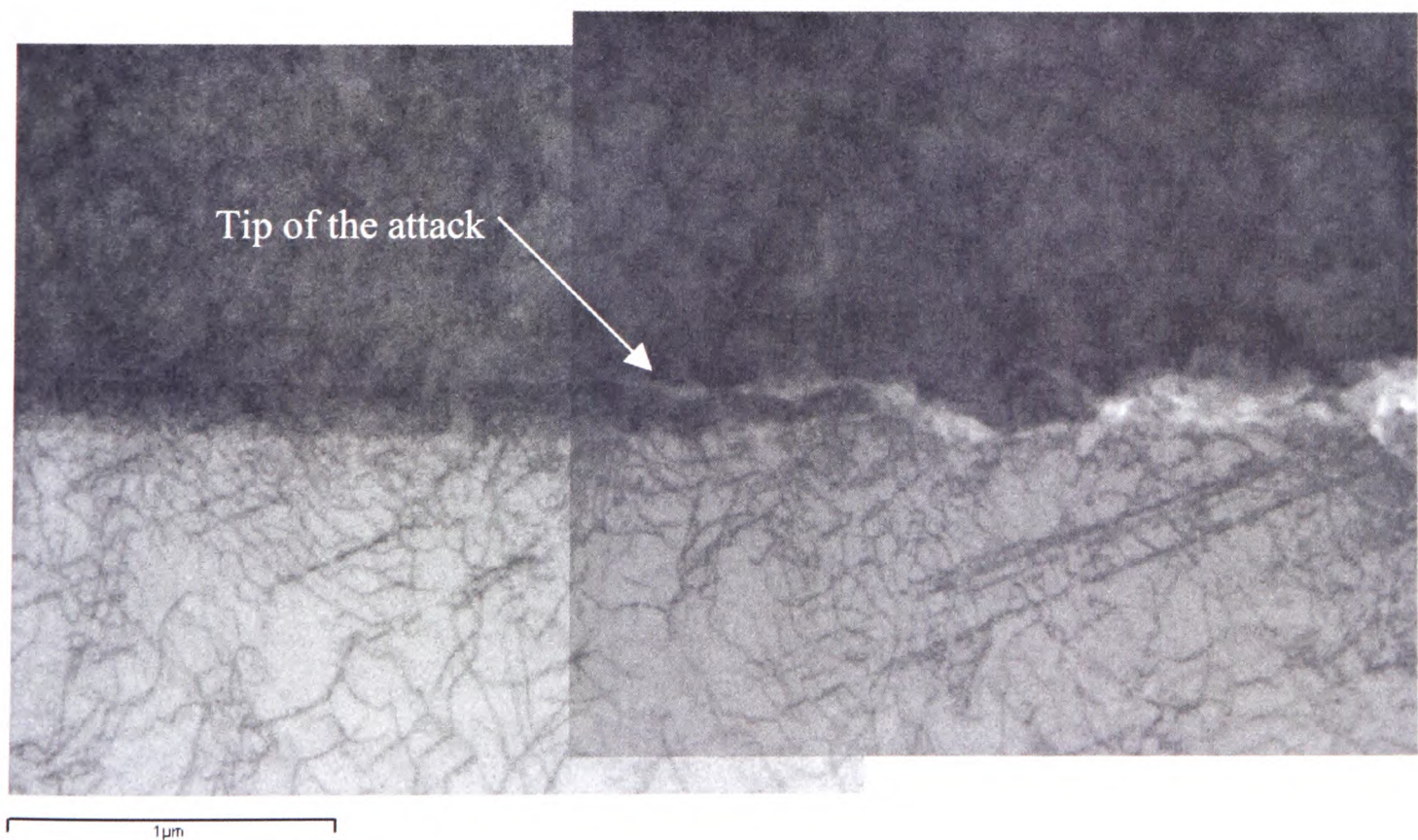


Fig. 8.2.6. STEM BF micrograph showing the attack of grain boundary C until the oxide reaches its tip (acquired with the INCA system in the CM20).

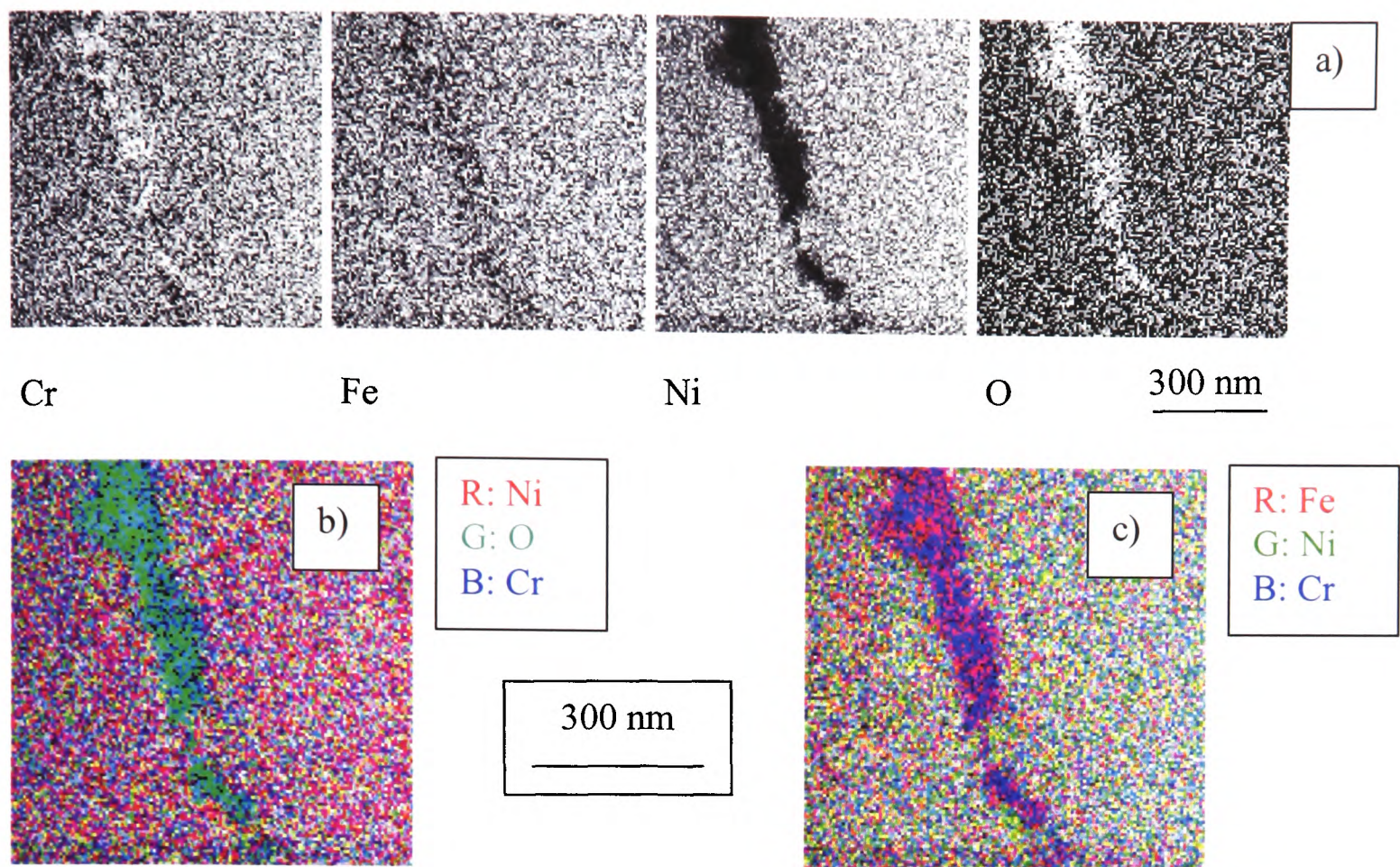
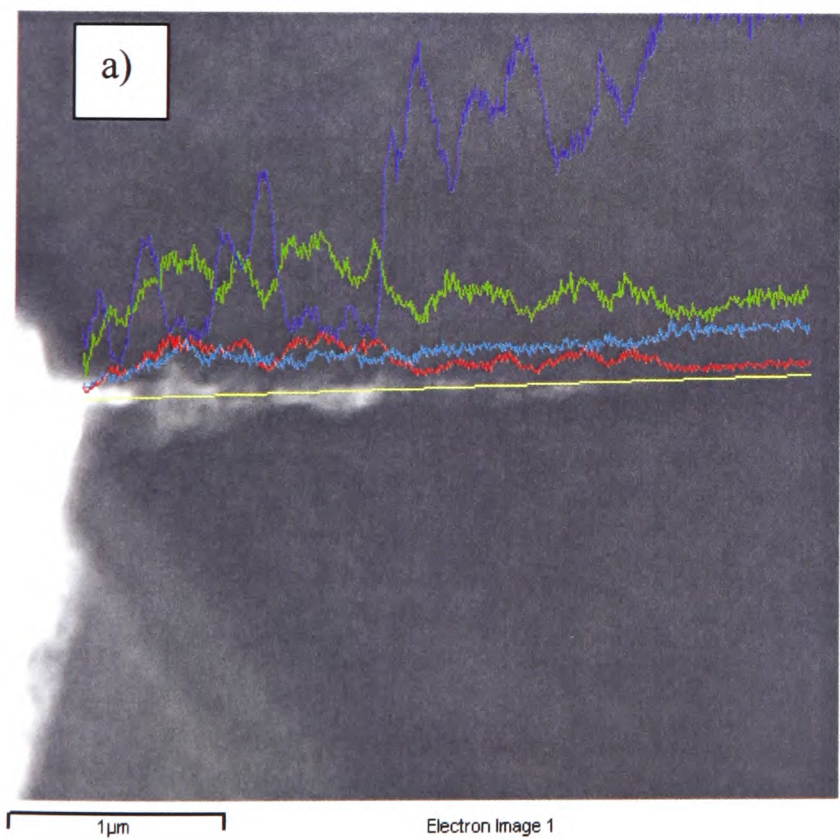


Fig. 8.2.7. a) EDX maps of the tip of the attacked region in boundary C (acquired with the LINK system in the HB501); b) and c) RGB compositions of images.



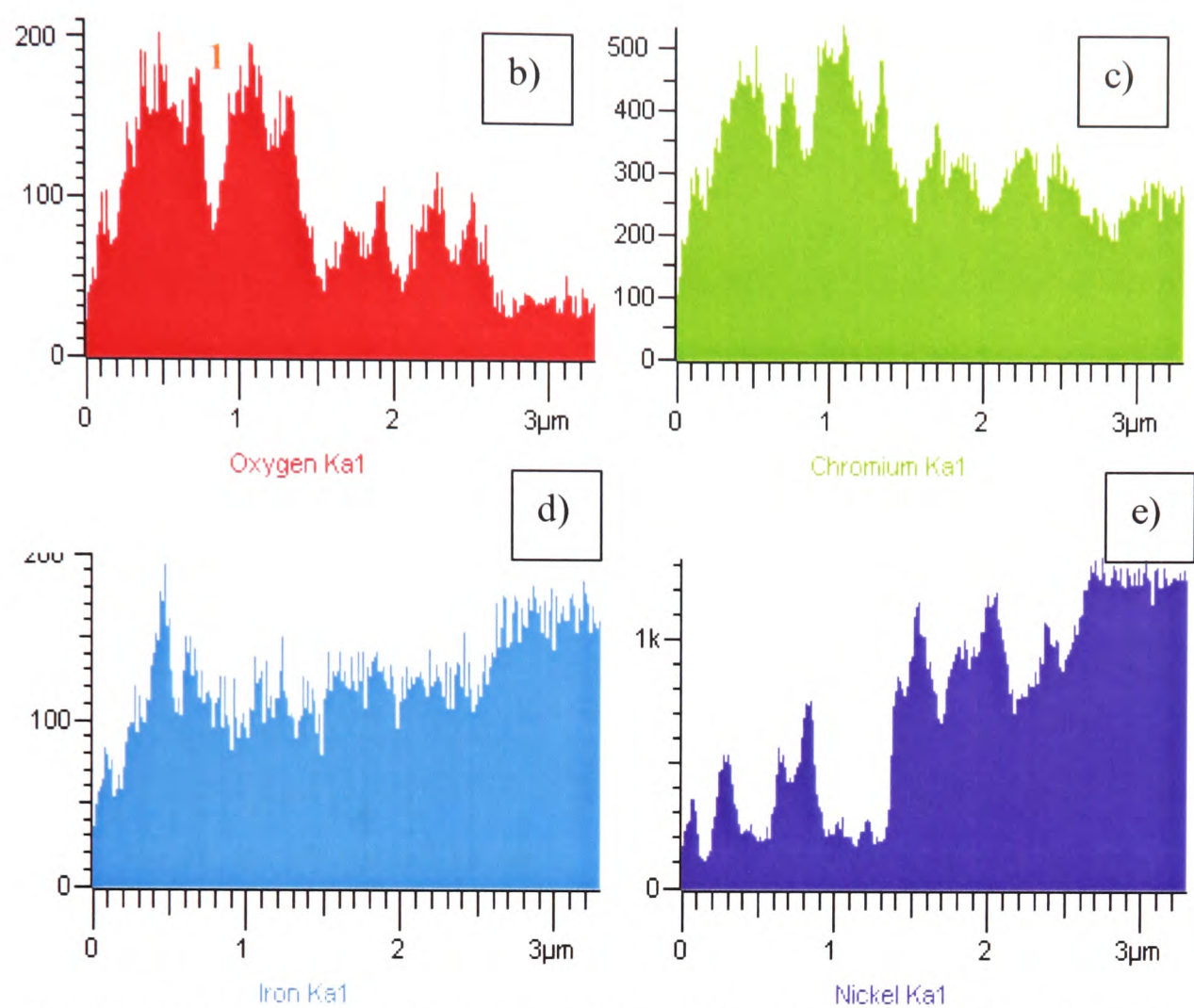
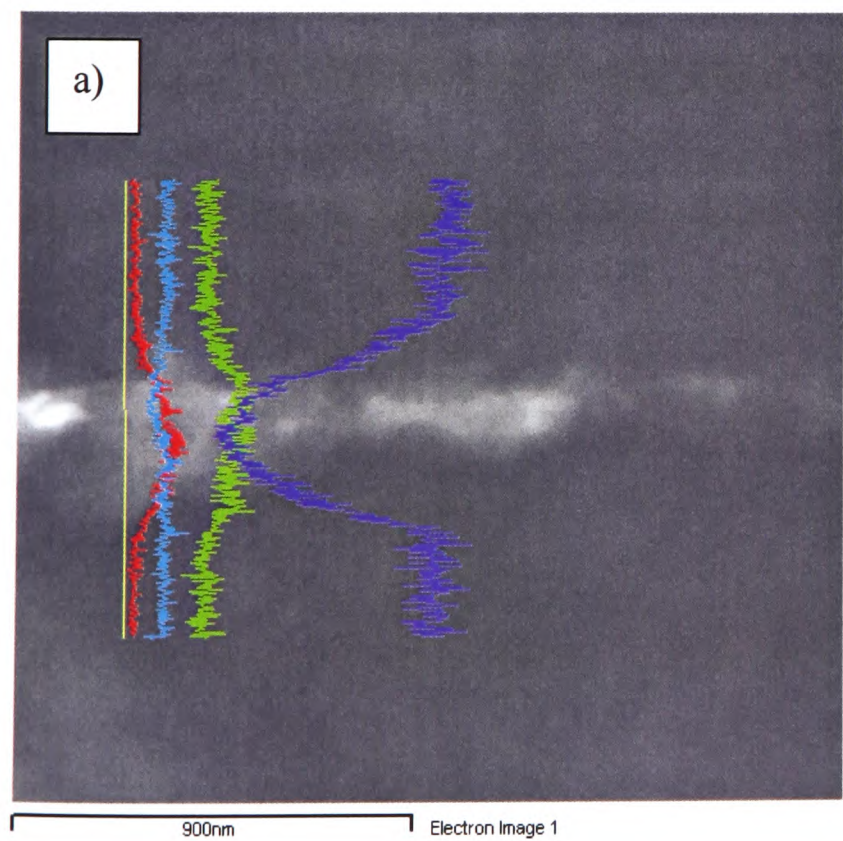


Fig. 8.2.8. EDX qualitative line profile along the attacked grain boundary C (acquired with the INCA system in the CM20).



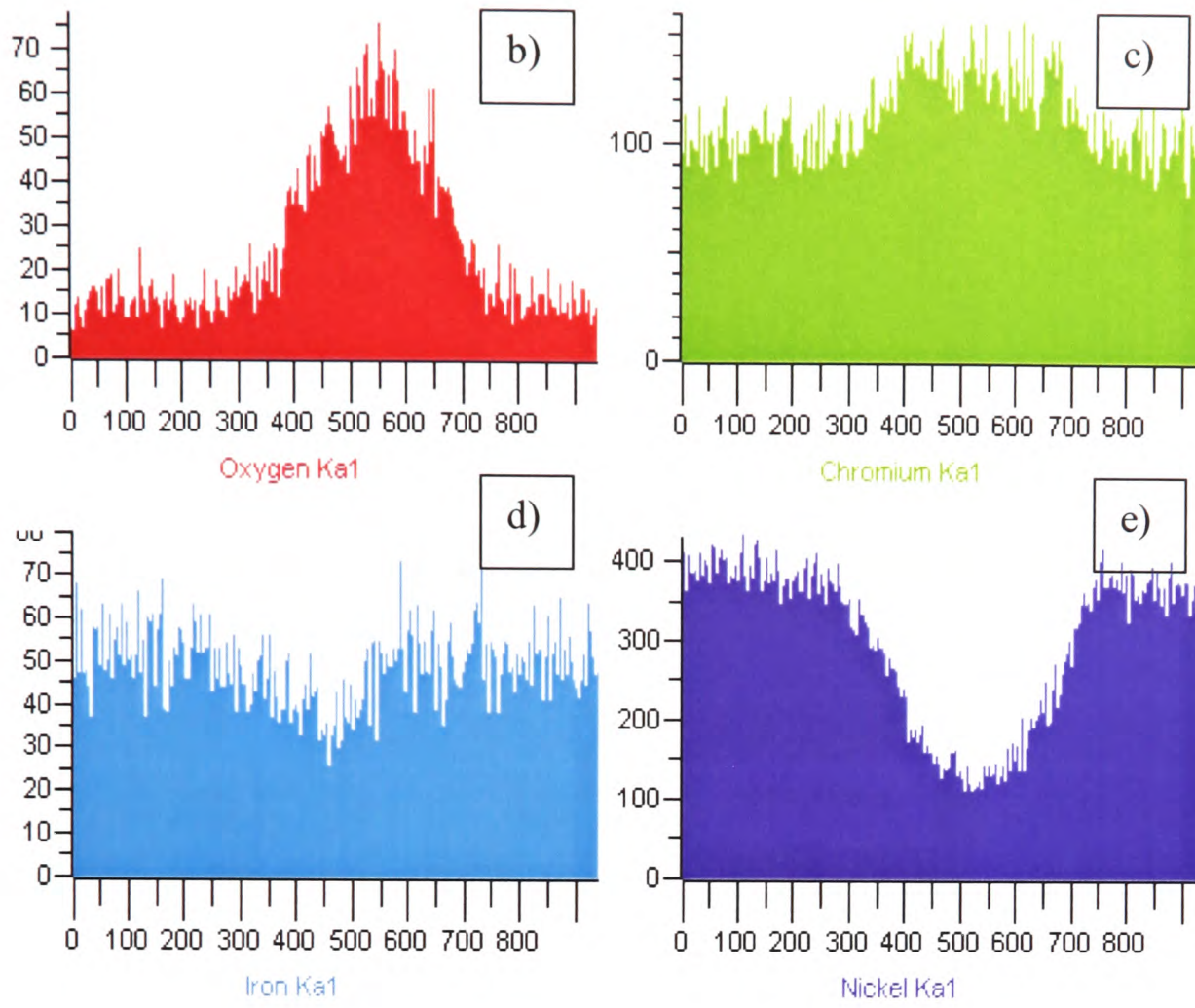


Fig. 8.2.9. EDX qualitative line profile across the attacked grain boundary C (acquired with the INCA system in the CM20).

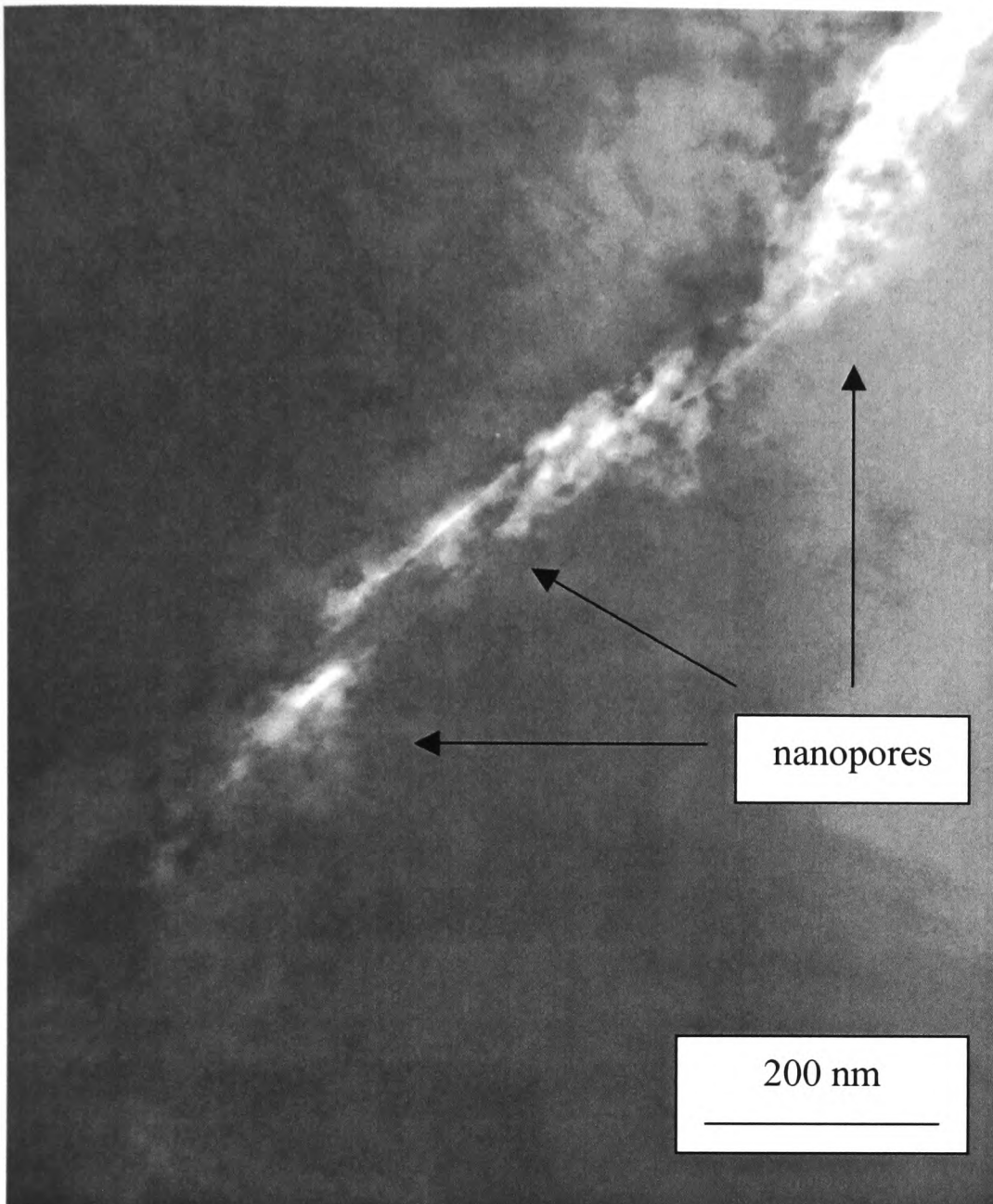


Fig. 8.2.10. TEM BF micrograph ($\Delta f = -700$ nm) showing nanopores in Cr_2O_3 of the attacked grain boundary C (acquired with the CM20).

8.3 Sample 3: General observations

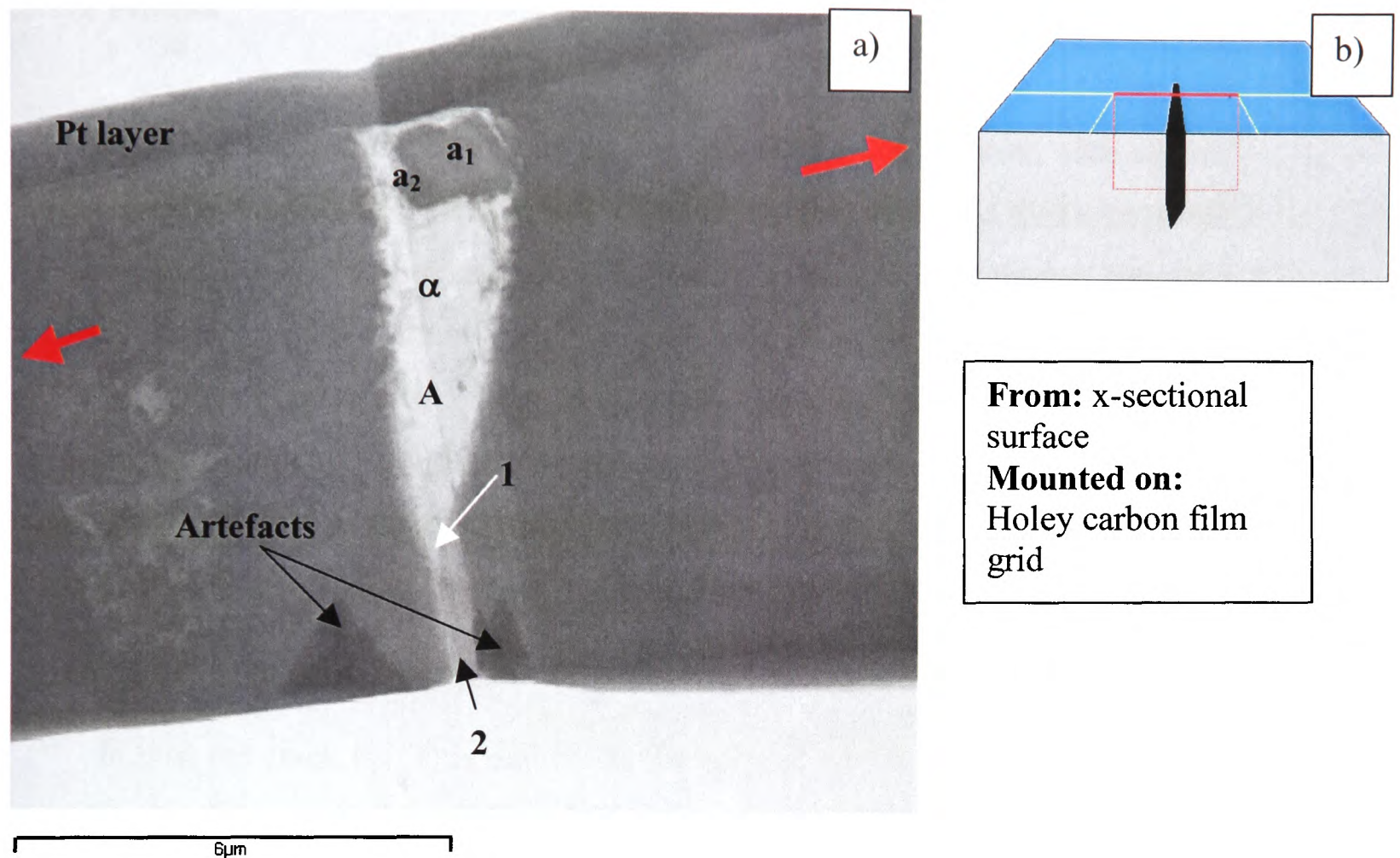


Fig. 8.3.1. a) STEM BF image of sample 3 showing a big blunted crack filled by nanocrystalline NiO plus some particles. The loading direction is indicated by the red arrows (acquired with INCA system in the CM20); b) schematic diagram showing the orientation of the sample.

Fig. 8.3.1a shows a STEM BF image of sample 3, which was prepared from the cross-sectional surface, with the plane of the membrane parallel to the original sample surface and cut at a depth of 1 μm from below surface (Fig. 8.3.1b). It contains a large blunted crack (α) which grew in a grain boundary (A) perpendicular to the loading direction, under mode I load. Crack α blunted in 1 without having reached any triple point. The reason for this might have been that the plastic deformation of the grains released the stress in the area or that grain boundary A was not internally corroded beyond 1. The crack is completely filled by nanocrystalline NiO and it contains a big oxide particle (a_1/a_2) embedded in the oxide. The artefacts shown in the picture are thicker regions which were not completely milled by the FIB. It can also be seen that the right half of the sample is slightly thicker than the left one. Some striations can also be observed below the crack.

8.3.1 Analysis

8.3.1.1 Flanks

The flanks of the crack α showed the typical thin Cr_2O_3 layer, although its thickness was not constant. It seemed that when the crack opened, the Cr_2O_3 layer did not break from the middle but asymmetrically with respect to both flanks. This thin layer was always found in contact with the nanocrystalline NiO as it can be seen in Fig. 8.3.2. It is important to notice the porous nature of the NiO, which would enhance the diffusion of O from the environment inside the crack. The average size of the NiO nanocrystals was found to be around 10 nm.

8.3.1.2 Crack tip area

In this, the crack tip (1) is defined as the point at which the crack is no longer open. Ahead of the crack tip, grain boundary A is attacked, but not opened. This area appears in the sample artificially thin, as it is located just below the crack (feature 2 in Fig. 8.3.1a). In Fig. 8.3.3b, the thin area appears darker in the DF micrograph and the other artefacts (thick regions which were not milled away) appear lighter. Although part of the Cr_2O_3 in the grain boundary was removed while thinning the sample, it still can be seen as light blue in Fig. 8.3.4b. The O EDX map in Fig. 8.3.4a is noisy, although it is still possible to distinguish that the right flank is enriched in O.

8.3.1.3 Particles

Sample 3 contained many different particles embedded in the nanocrystalline NiO that filled the crack, but only the particle labeled **a** was analyzed on detail (Fig. 8.3.5). The rest of particles were supposed to be NiO, NiFe_2O_4 and other Cr-oxides according to their qualitative compositions shown in EDX maps (not shown). Particle **a** has been analyzed by EDX (Fig. 8.3.8) and μD (Figs. 8.3.6 and 7) and it was found to be NiFe_2O_4 (**a**₁) surrounded by crystalline NiO (**a**₂). In Fig. 8.3.6a, particle **a**₁ was orientated with a [110] zone axis parallel to the beam and a μDP acquired. The μDP is indexed in a simulated DP in Fig. 6b. It should be mentioned that even using a small probe for acquiring the μDP , many spots appear superposed, suggesting that the oxide

particle is formed by many crystals in almost parallel orientation. Corresponding data from particle **a₂** is presented in Fig. 8.3.7a. Both particles were perfectly aligned, as both μ DP (Figs. 8.3.7a and 8a) were acquired without tilting the sample using the same camera length, indicating an epitaxial growth of the NiO on the NiFe₂O₄. The faceted nature of the interfaces suggests an edge growth on low energy planes.

The composition of the particle was revealed using EDX mapping and RGB compositions. In the EDX maps of Fig. 8.3.8a it can be seen that the Ni content of the inner particle **a₁** is much lower than for the outer particle **a₂**, consistent with the compositions of the stoichiometric phases. The absence of counts in the oxygen EDX map is explained after checking that the EDX spectra from both particles did not show evidence of a high O peak nor a normal Ni-L peak (Fig. 8.3.9). The Ni-L peak should be similar in height to the Ni-K peak, and this was not the case. This can be explained as an artefact from the X-ray acquisition. The sample was mounted on a Cu-grid which often absorbed low-energy X-rays that did not reach the detector if the orientation of the sample was unfavourable. In this case, the position of the sample on the grid was closer than usual to the Cu grid and it was impossible to improve the shape of the spectra. In Fig. 8.3.8b the Ni rich region from the NiO appears in blue, while the Fe rich region from the core NiFe₂O₄ particle appears in red. In Fig. 8.3.8c the Cr₂O₃ which has formed on the flank of the crack appears in blue.

In order to prove the nature of particle **a**, some EELS spectra were acquired (Fig. 8.3.10). The strong O edges showed that the O peak was indeed absorbed in the EDX maps of Fig. 8.3.9. Neither the spectrum from the NiFe₂O₄ particle (Fig. 8.3.10a) nor the spectrum from the NiO particle (Fig. 8.3.10b) were supposed to have a Cr edge, as observed, although Cr is still present in the particle (as deduced from the small Cr peaks). This is indicating that they contain some Cr in addition to the expected elements.

8.3.2 Main observations

- Mode I loading crack α blunted without reaching a triple point.
- Large duplex NiO/ NiFe₂O₄ particle found embedded in the nanocrystalline NiO.

8.3.3 Sample 3 – Data collection

8.3.3.1 Flanks of the crack

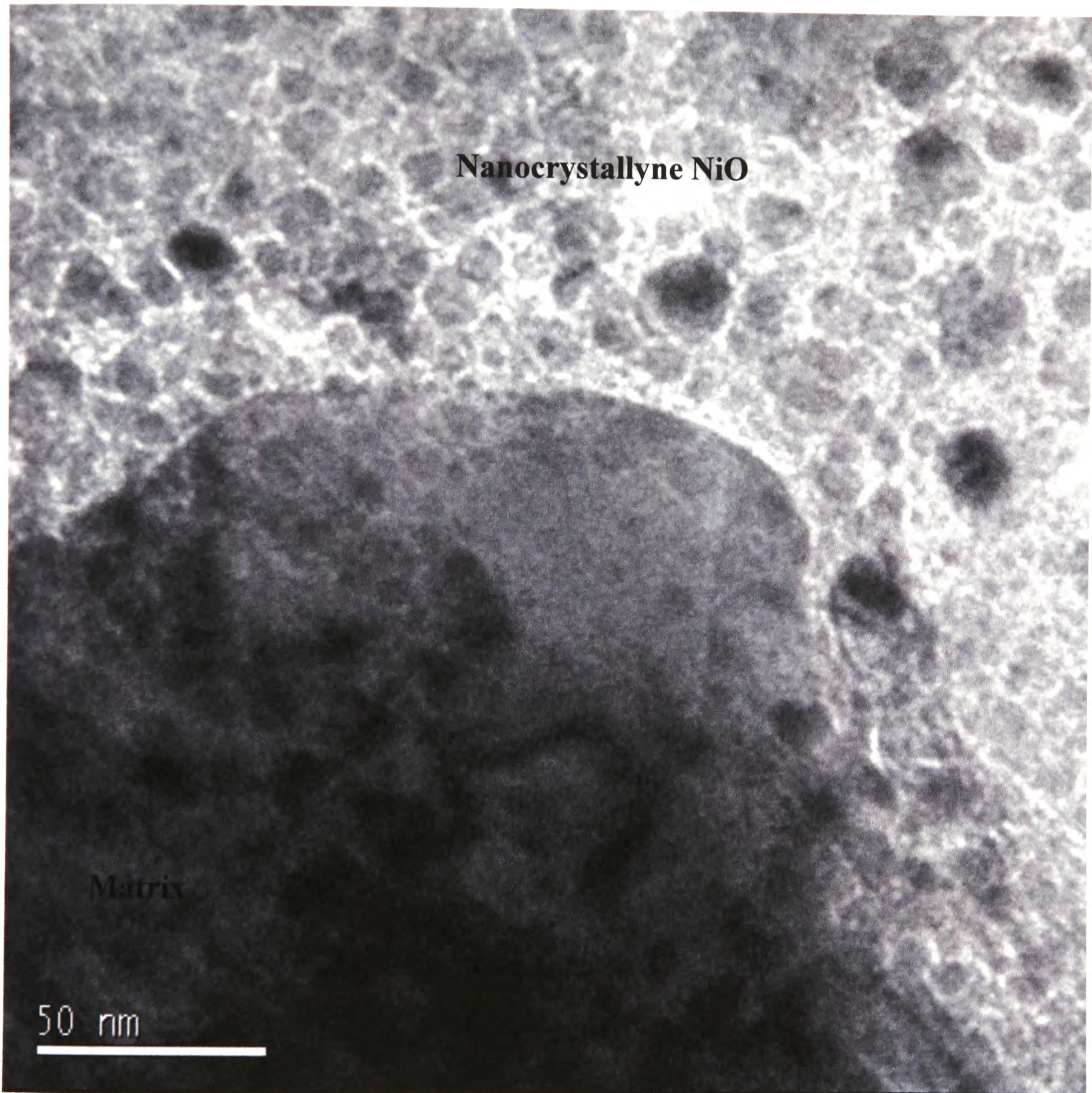


Fig. 8.3.2. TEM BF micrograph showing at a high magnification the nanocrystalline NiO next to the flank of the crack (Acquired with a Multiscan CCD in the 3000F)

8.3.3.2 Crack tip area

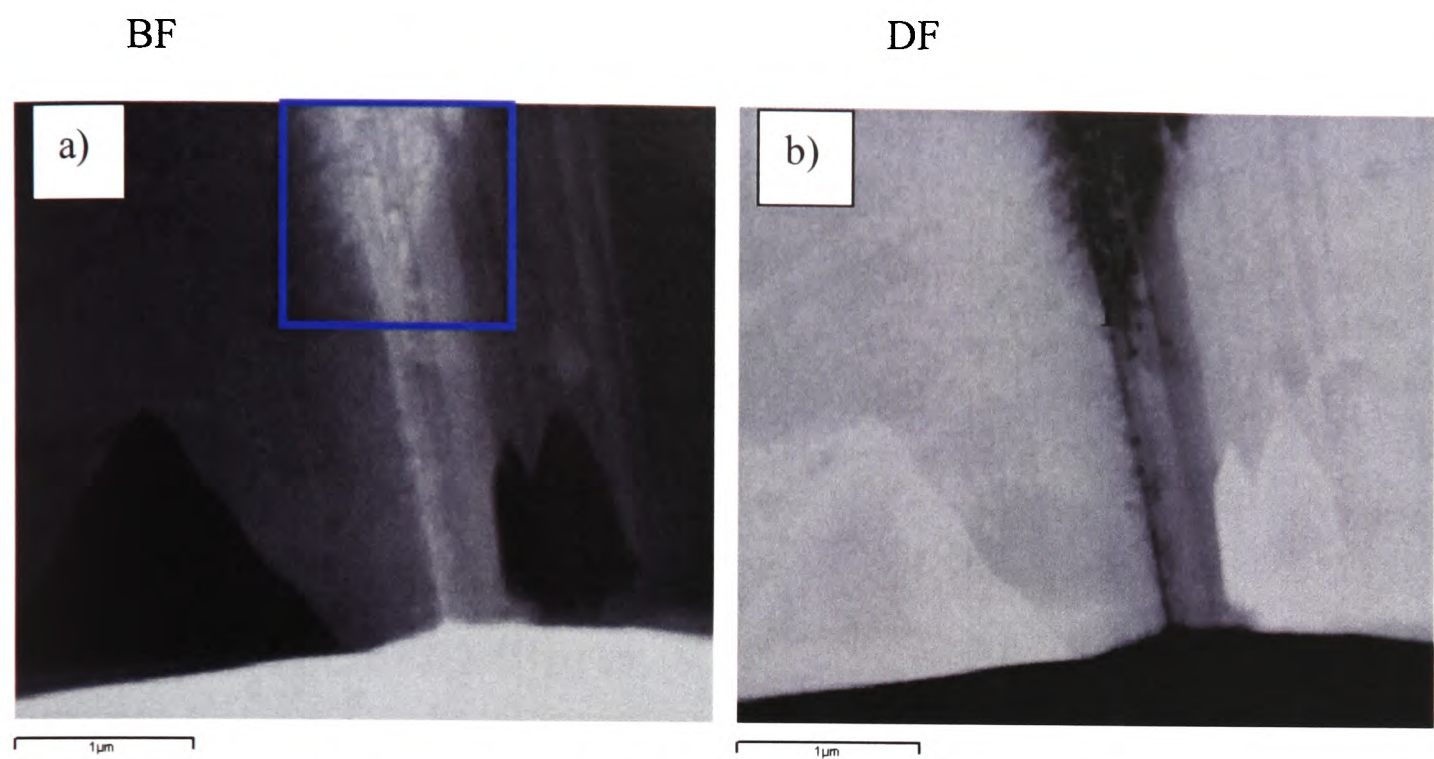


Fig. 8.3.3. STEM BF (a) and DF (b) showing with a blue box the area that has been mapped in Fig. 8.3.4. The feature labelled as 1 indicates the position at which crack α blunted (acquired with the INCA system in the CM20).

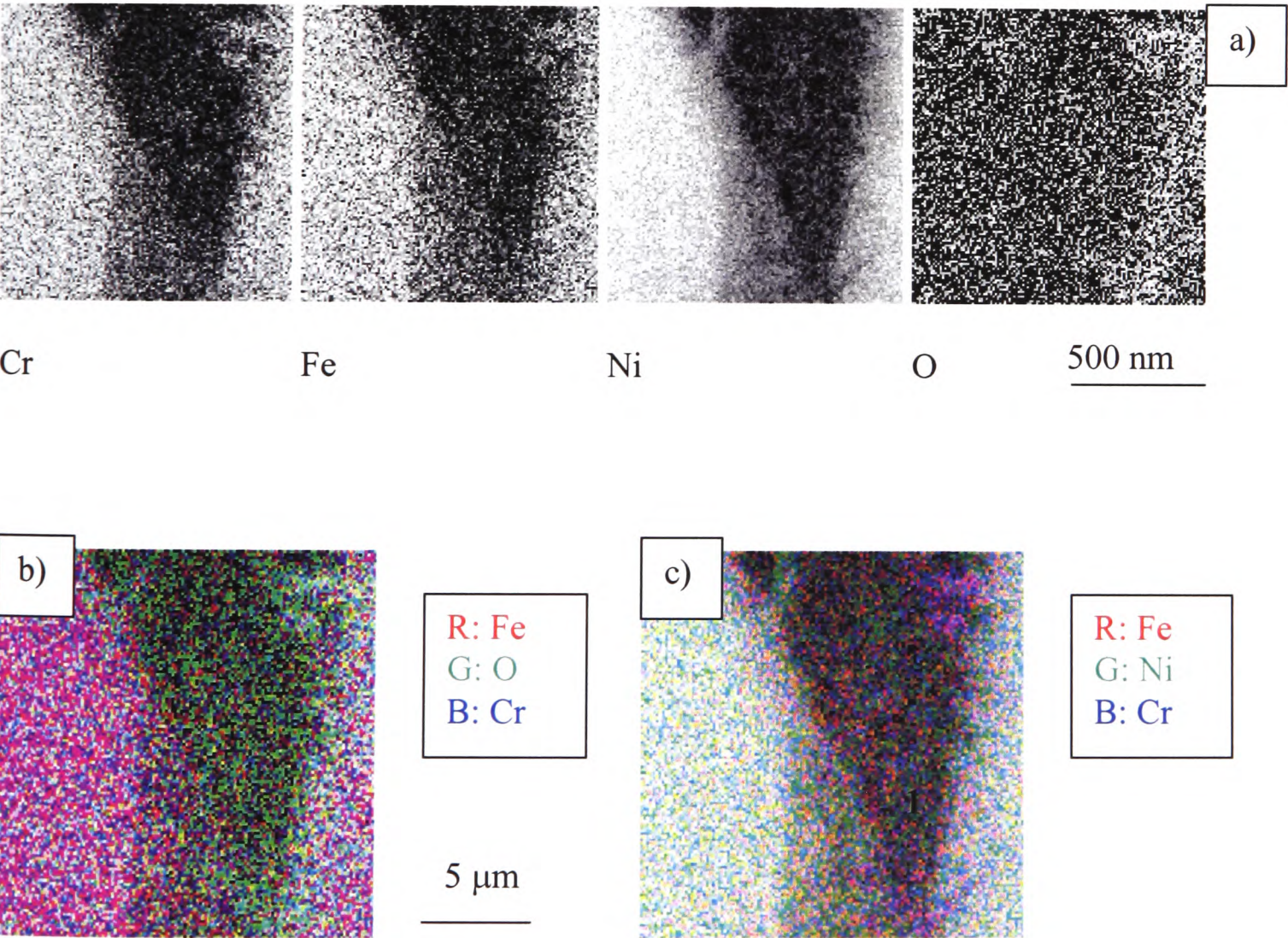


Fig. 8.3.4. a) EDX maps of the crack tip area (1) (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

8.3.3.3 Particles

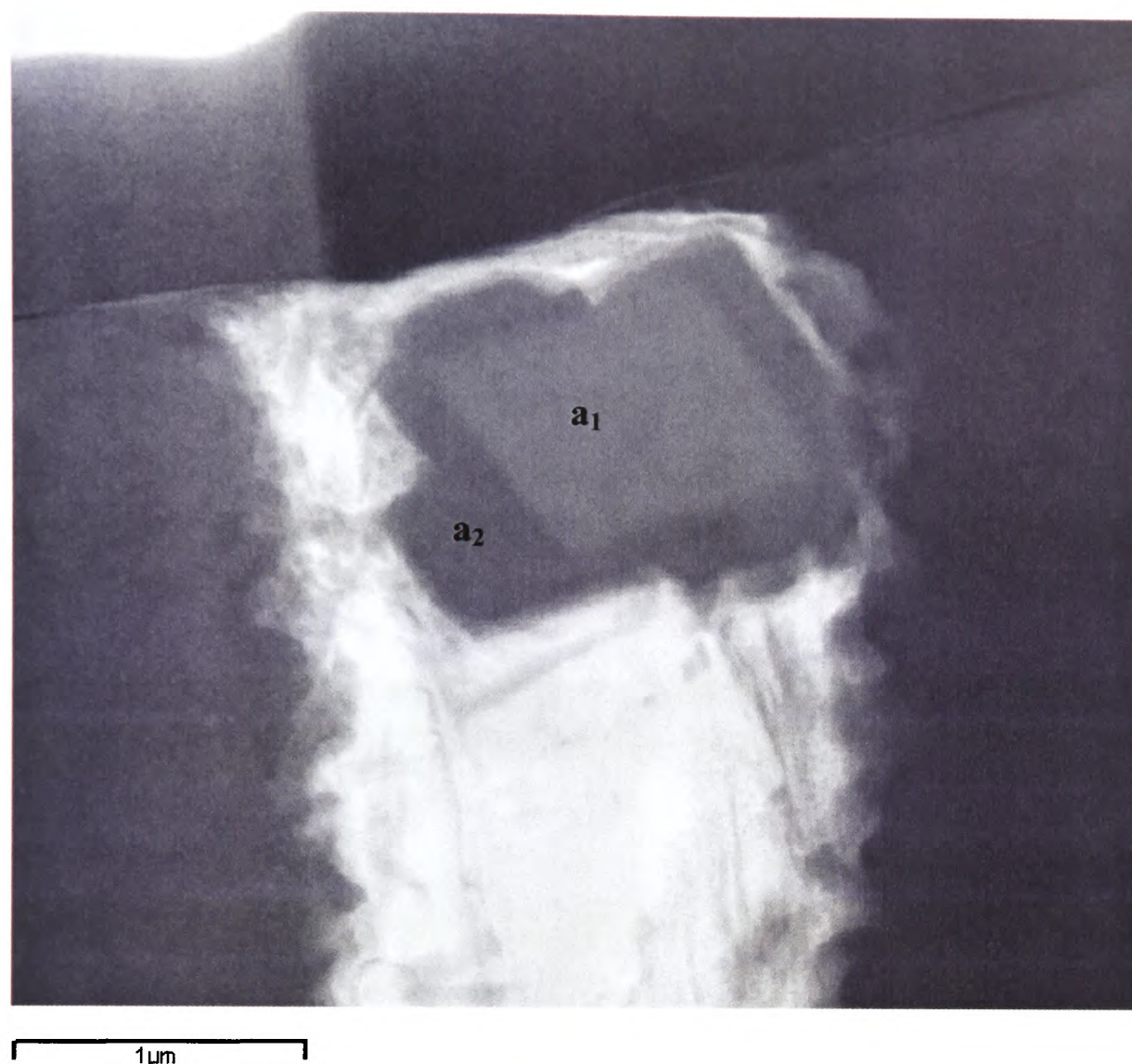


Fig. 8.3.5. STEM BF micrograph showing compound particle “a” embedded in the NiO (acquired with the INCA system in the CM20).

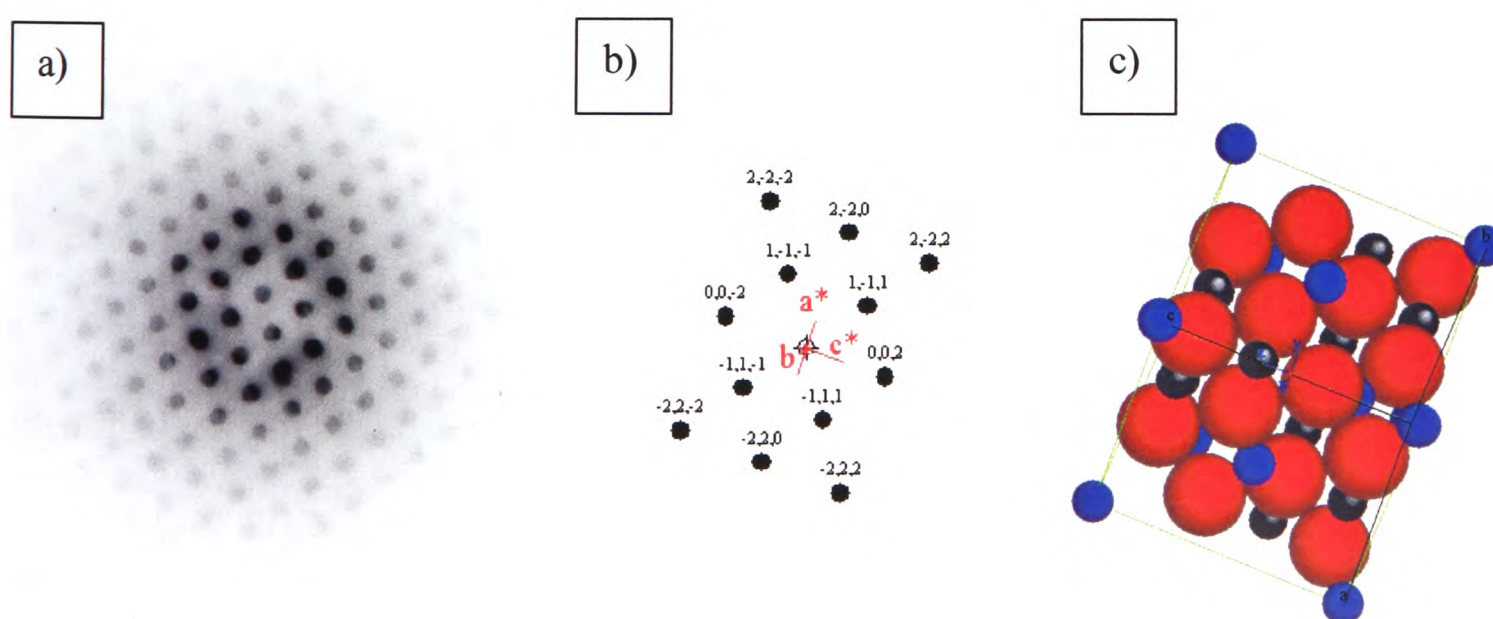


Fig.8.3.6. μ DP of the NiFe₂O₄ particle in a [110] zone axis (a), a simulated DP (b) and a model of the NiFe₂O₄ unit cell (O in red, Ni in blue and Fe in black) in the same orientation (c) (acquired in the CM20).

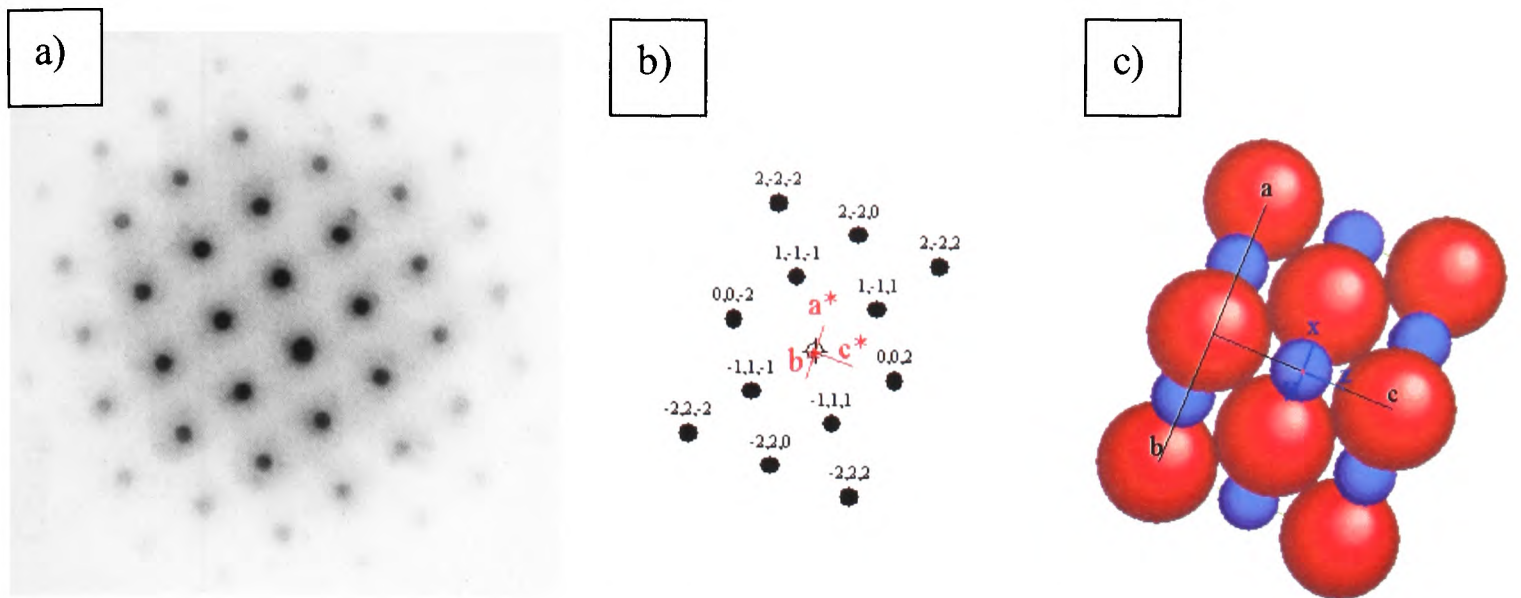


Fig. 8.3.7. μ DP of the NiO particle in a $[110]$ zone axis (a), a simulated DP (b) and a model of the NiO unit cell (O in red and Ni in blue) in the same orientation (c) (acquired in the CM20).

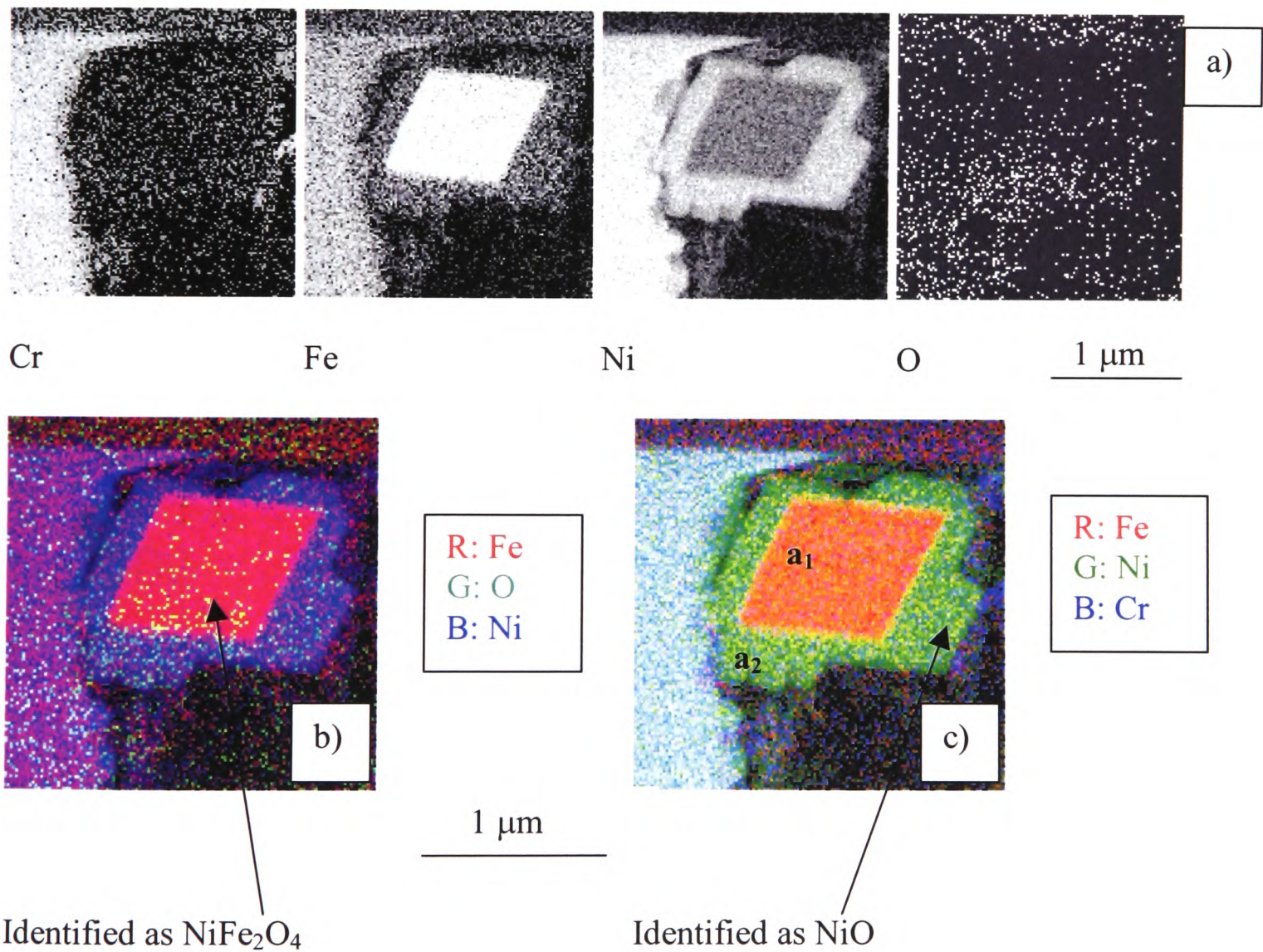


Fig. 8.3.8. a) EDX maps showing the differences in composition of compound particle a_1/a_2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

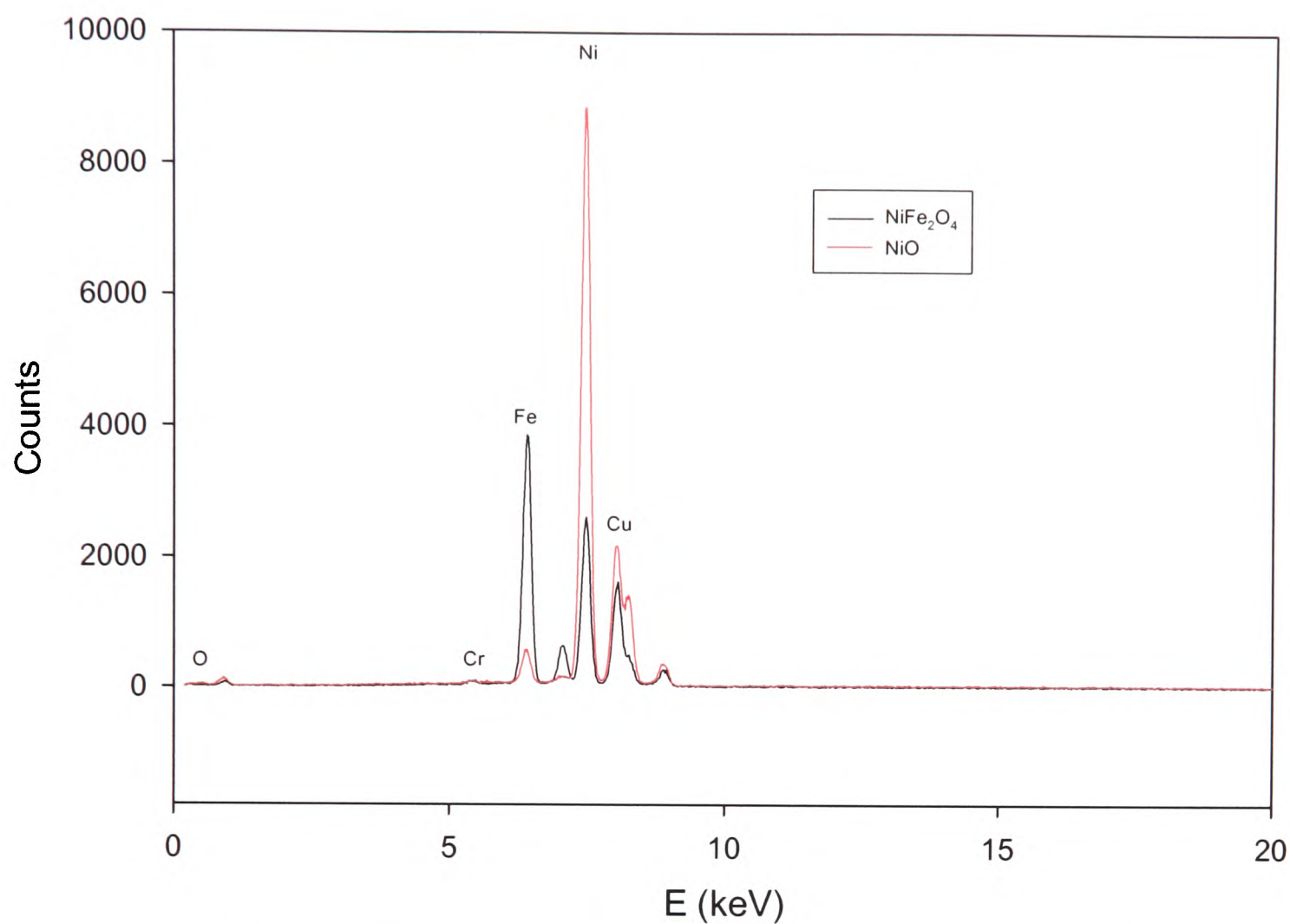
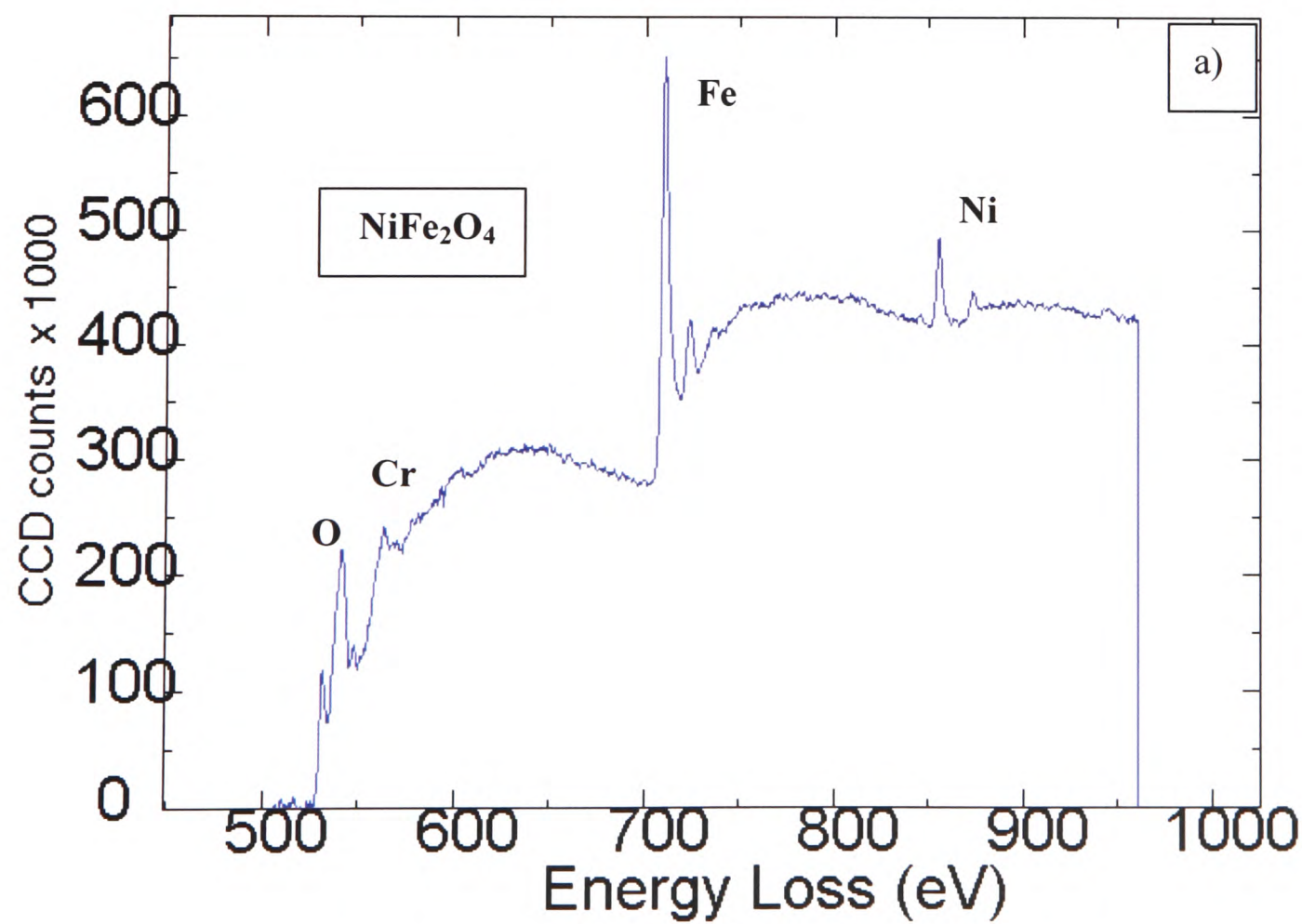


Fig. 8.3.9. EDX spectra from compound particle a_1/a_2 (acquired with the LINK system in the HB501).



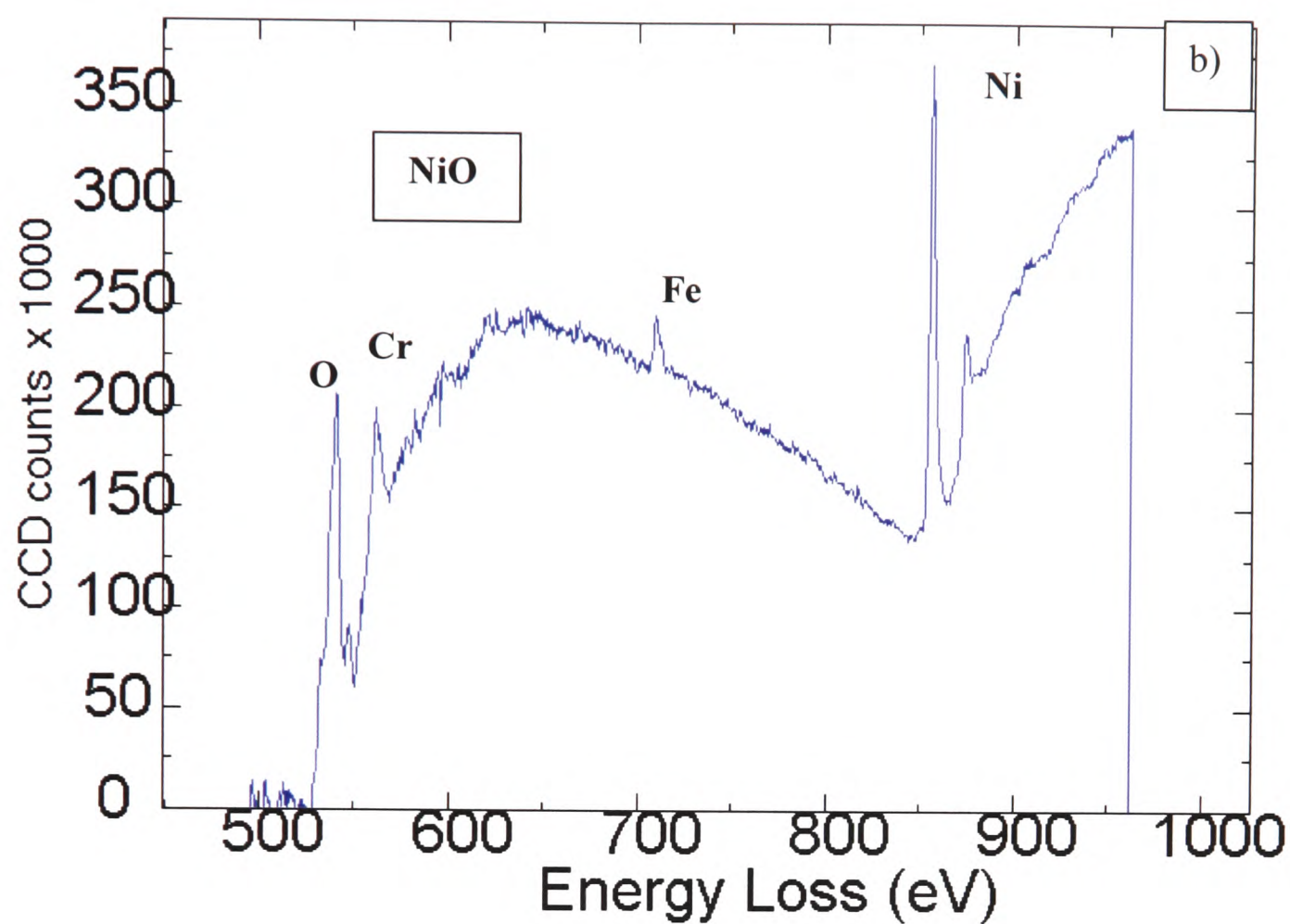


Fig. 8.3.10. EELS spectra from the duplex NiFe_2O_4 (a)/ NiO (b) particle (acquired with the 3000F).

8.4 Sample 4: General observations

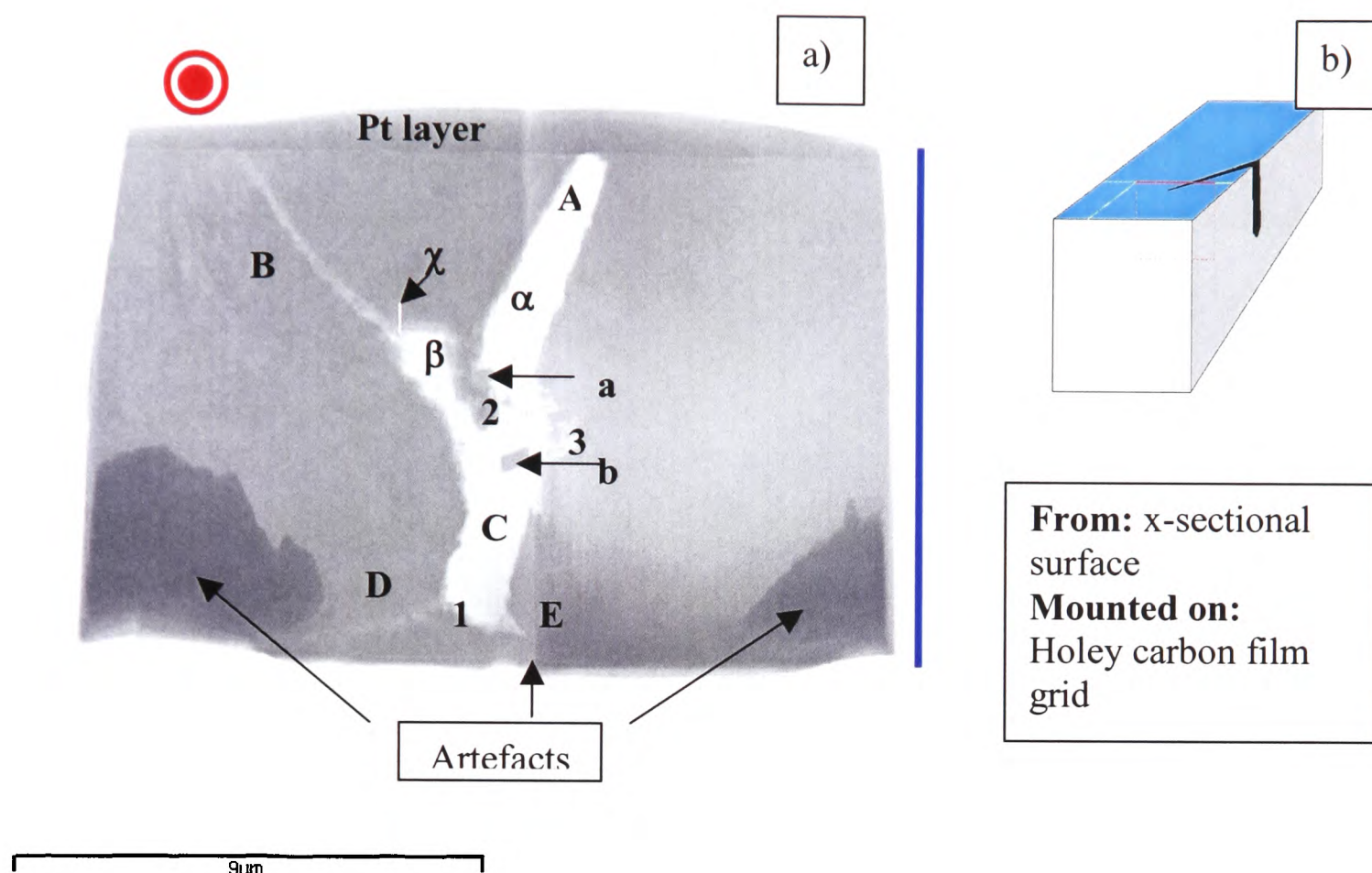


Fig. 8.4.1. a) STEM BF micrograph showing sample 4 after plucking. The loading direction is indicated by the red circle (perpendicular to the plane of the sample). The position of the side of the sample closer to the top surface (in contact with the environment) is indicated in blue (in Fig. 8.4.1b)(acquired with INCA system in the CM20); b) sketch showing the orientation of the crack in the sample.

Fig. 8.4.1a shows a STEM BF micrograph of sample 4, which was prepared perpendicularly to the top surface, from a x-section, and with the sample plane perpendicularly to the loading direction. It has a main crack (α) which formed as a result of the opening of grain boundaries A and C and it blunted at the bottom of the sample when it reached a triple point (1). It is likely that crack β blunted after the triple point (2) and did not succeed in advancing very far along grain boundary B. The reason for this might have been its orientation (not favorable) or because the opening of grain boundaries A and C released the stress in the region. A heavily attacked region was found in this area (3). The attack probably occurred before the opening of the boundary. The two grain boundaries (D and E) after the triple point (1) were also found attacked and Cr_2O_3 formed. χ is a transgranular crack which grew obliquely to grain boundary B, and started in the region where crack β blunted, similar to cracks described by Hipsley². The white line labeled as χ in Fig. 8.4.1a marks the location

of a transgranular crack of low visibility in this image, but revealed later by EDX mapping (similar to those shown in sample 1, Fig. 8.4.2b). Particles **a** and **b** were identified as a duplex NiO/NiFe₂O₄ particles. A high resolution image of particle **b** can be seen in Fig. 8.4.16a with its corresponding FFT (Fig. 8.4.16b) and simulated unit cell (Fig. 8.4.16c) and DP (Fig. 8.4.16d). The artefacts shown in the picture include thicker regions which were not milled uniformly by the FIB and an artificial vertical line due to FIB sample preparation.

8.4.1 Analysis

8.4.1.1 Flanks

The flanks of the crack α contained a thin Cr₂O₃ layer as for the samples described earlier. This layer did not have a constant width and, as can be seen in Fig. 8.4.2a, it has an area (labeled as **3**) which was more intensely corroded than the rest. The EDX qualitative line profiles shown in Figs 2b and 2c, suggest that the phase present in region **3** was Cr₂O₃. This was confirmed by μ D (not shown). This attack was not homogeneous, with the Cr₂O₃ leaving behind Ni-rich “islands” as it advanced into the matrix, as shown by the Ni peaks in Fig. 8.4.2e which correlate with lower Fe and Cr in Figs. 8.4.2b and 2c.

8.4.1.2 Cracks

Fig. 8.4.3 suggests that the crack α blunted on encountering the triple point (**1**) so that grain boundary **C** was attacked but did not open. This result is similar to those obtained for samples 1 and 2. The internally corroded area did not seem to advance linearly, following the grain boundary, but in steps, obliquely to the grain boundary, in the way described by Hippsley ². The artefact shown in Fig. 8.4.3 is an artificial mistakenly “drawn” line during cutting of the bottom of the sample with the FIB.

Fig. 8.4.4 also shows the tip of crack β and the continuation of the attack along grain boundary **B**, including the intragranular crack χ . EDX maps of this area are shown in Fig. 8.4.5a. The O map (Fig. 8.4.5) reveals high O enrichment of the Cr oxide area, and how Fe and particularly Ni (Fig. 8.4.5) have been depleted from the

crack χ area. It is interesting to note that the Cr is not noticeably enriched in the crack area. It might be better to say that it is the only constituent of the matrix that has not been depleted, suggesting that the atomic density of Cr is roughly similar in matrix and oxide. The corresponding RGB compositions in Fig. 8.4.5b very clearly show the Cr_2O_3 in the crack as light green. The presence of the oxide in crack χ as well as on the flanks of crack β was also revealed.

Fig. 8.4.6a shows EDX elemental maps of the crack tip area in crack χ at a higher magnification. They are a good example of how such data allow the estimation of the length of the attack: the O and especially the Ni maps (Fig. 8.4.6a) are the most useful for this. As Cr seems to be not enriched in the crack, its map does not reveal satisfactorily the position of the crack. Note that these maps are qualitative. Fig. 8.4.7 shows an EDX quantitative line profile across crack χ in which the concentration of Cr is clearly enhanced at the crack, as a consequence of the depletion of Ni, when oxygen is not included in the analysis.

Fig. 8.4.8 shows an EDX spectrum from the centre of crack χ acquired within the line profile of Fig. 8.4.8. A higher O peak was expected for this spectrum, but it does not appear for the reason stated earlier, the Ni-L/Ni-K ratio is much smaller than 1, indicating a lot of absorption.

Crack β (Fig. 8.4.9) was also characterized by EDX mapping (Fig. 8.4.10a). The RGB maps in Fig. 8.4.10b and 10c show the diffusion of O along the boundary, but are not good for showing the Cr-oxide, which can be seen better in Fig. 8.4.11. For this reason, another map at a higher magnification was acquired. The presence of O, diffused all along the crack, can be easily seen in the oxygen map in Fig. 8.4.11a. In Fig. 8.4.11c it is now easy to see that the crack is Cr rich, containing some Ni-clusters. Fig 11b shows as light blue the Cr-oxide in the crack and as red the Ni-cluster. Feature 5 in Fig. 8.4.11c was identified as an intragranular attack through a slip band.

An EDX quantitative line profile across attacked grain boundary β was acquired (Fig. 8.4.12). Again, it shows how the crack is enriched in Cr (Fig. 8.4.12c)

and depleted in Ni (Fig. 8.4.12a). The Fe concentration across the crack does not show a big change (Fig. 8.4.16b), although it should be noted that the Fe-depletion on the left flank is due to the formation of a Ni-cluster (see Ni-enrichment in Fig. 8.4.12a), similar to those observed in sample 1. The O could not be quantified by the LINK system. In order to estimate the amount of oxygen diffused along the boundary, an EDX spectrum from the centre of the crack β is shown in Fig. 8.4.13. Again the Ni-L/Ni-K ratio is much smaller than 1, indicating a lot of absorption. This explains the low O counts in Fig. 8.4.13. However, the presence of the O and Cr-oxide is revealed clearly in the EELS spectrum (Fig. 8.4.14) acquired from the same area as the EDX spectrum from Fig. 8.4.13. In this spectrum the Fe and Ni edges are extremely small, showing that it is basically Cr-oxide (Cr_2O_3). An EELS spectrum from the matrix was acquired (Fig. 8.4.15) in a neighboring area to show that the O-K edge has disappeared and the Ni-L₂₃/Cr-L₂₃ edge ratio has increased significantly. It must be noted that the ratio of the L₂₃ edge cross sections favors Cr. Roughly equal number of Cr:Fe:Ni atoms will produce peaks/edges with an intensity ratio of 4:2:1. The exact values vary mainly with EHT and collection angle. In Fig. 8.4.15, Cr/Ni $\approx$ 1 and so the Ni concentration is approximately 4 times that of Cr, which is roughly correct for the nominal matrix composition.

In Fig. 8.4.16, a HR image of particle **g** together with its FFT is shown to illustrate the quality of the FIB samples.

8.4.2 Main observations

- All 5 boundaries contained in the sample were attacked. Two of them were opened (**A** and **C**).
- One intragranular crack was found close to triple point **2**.

8.4.3 Sample 4 – Data collection

8.4.3.1 Flanks

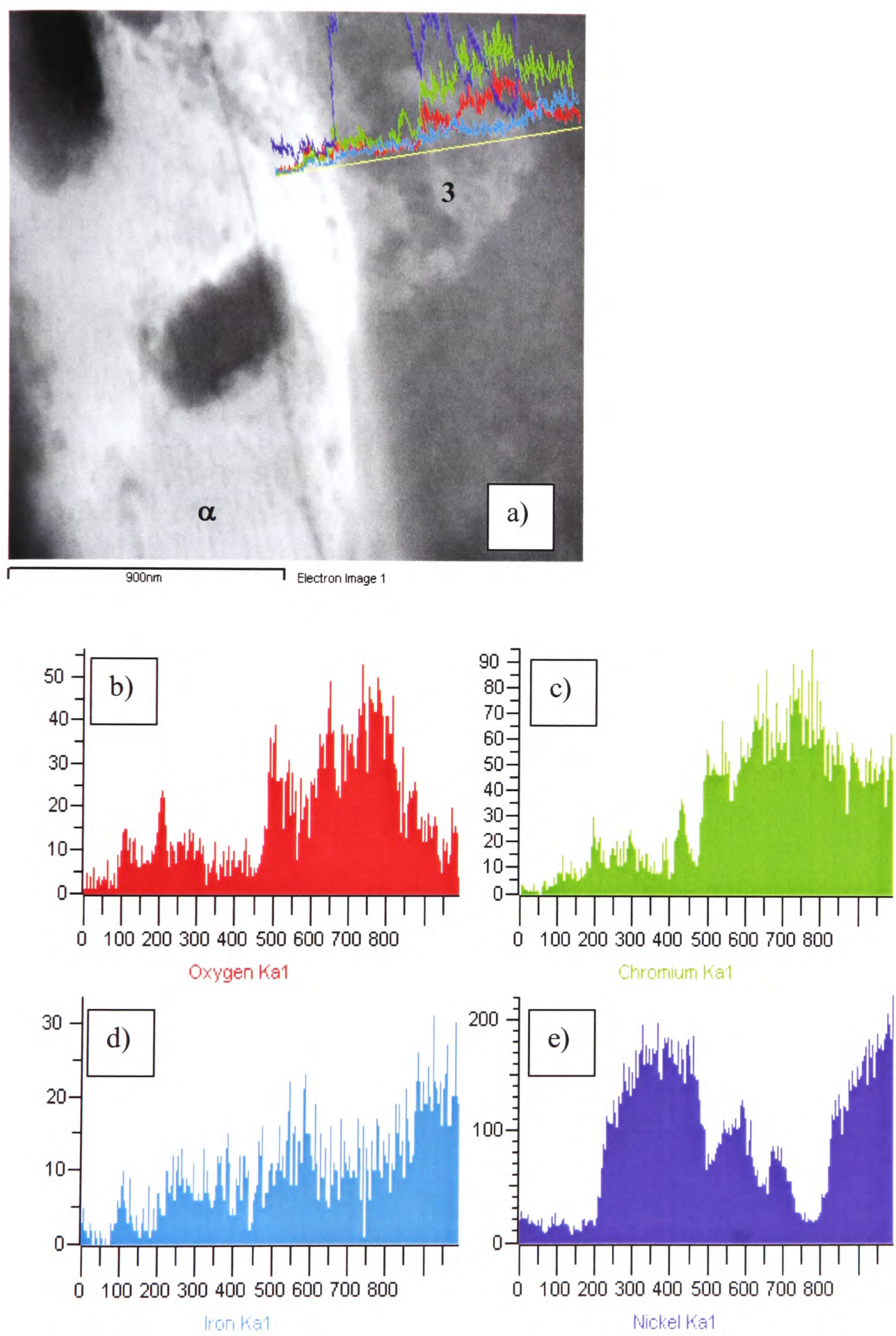


Fig. 8.4.2. EDX qualitative line profile showing an attacked area with Cr_2O_3 (labelled as 3) on the right flank of crack α (acquired with the INCA system in the CM20).

8.4.3.2 Cracks

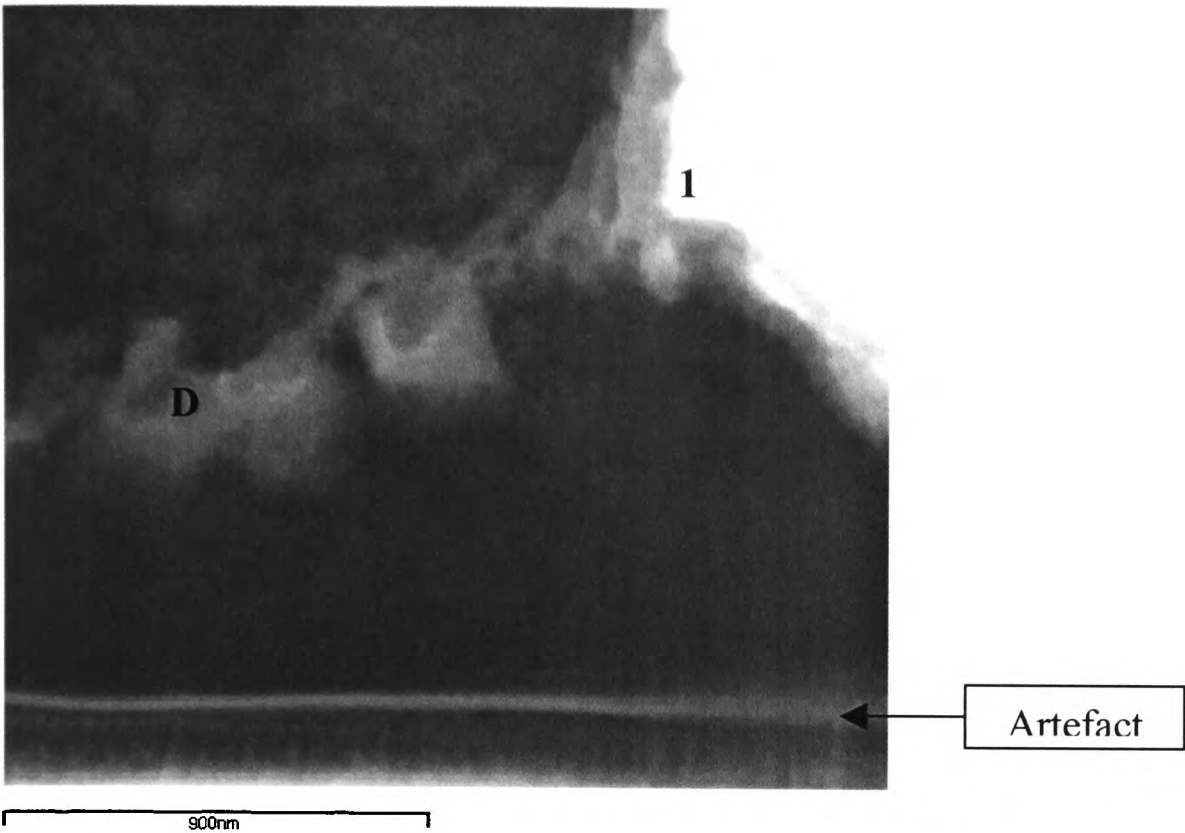


Fig. 8.4.3. STEM BF micrograph showing details of the attack of grain boundary *D* in the triple point area (*1*) (acquired with the INCA system in the CM20).

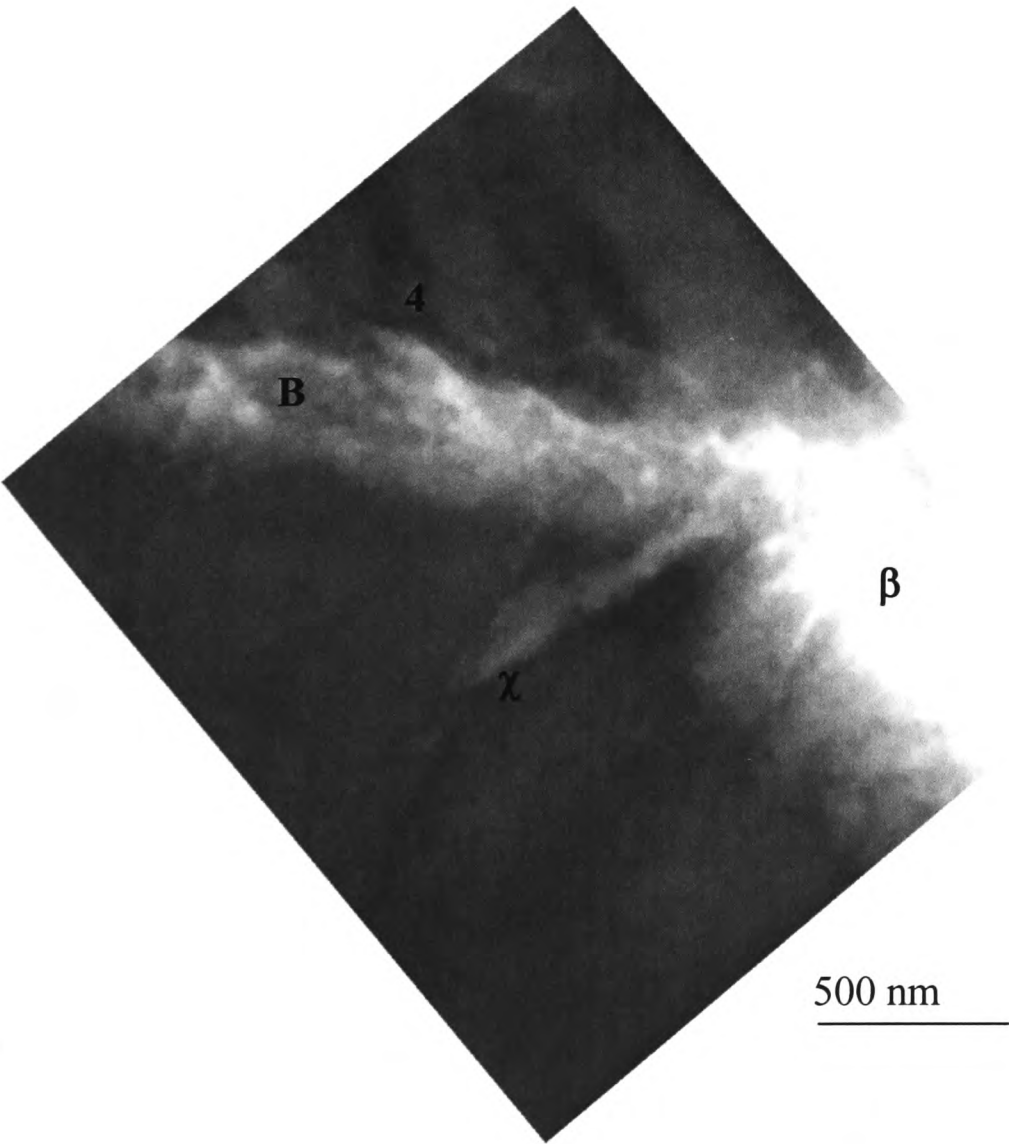


Fig. 8.4.4. STEM BF micrograph showing crack *χ* (acquired with the INCA system in the CM20).

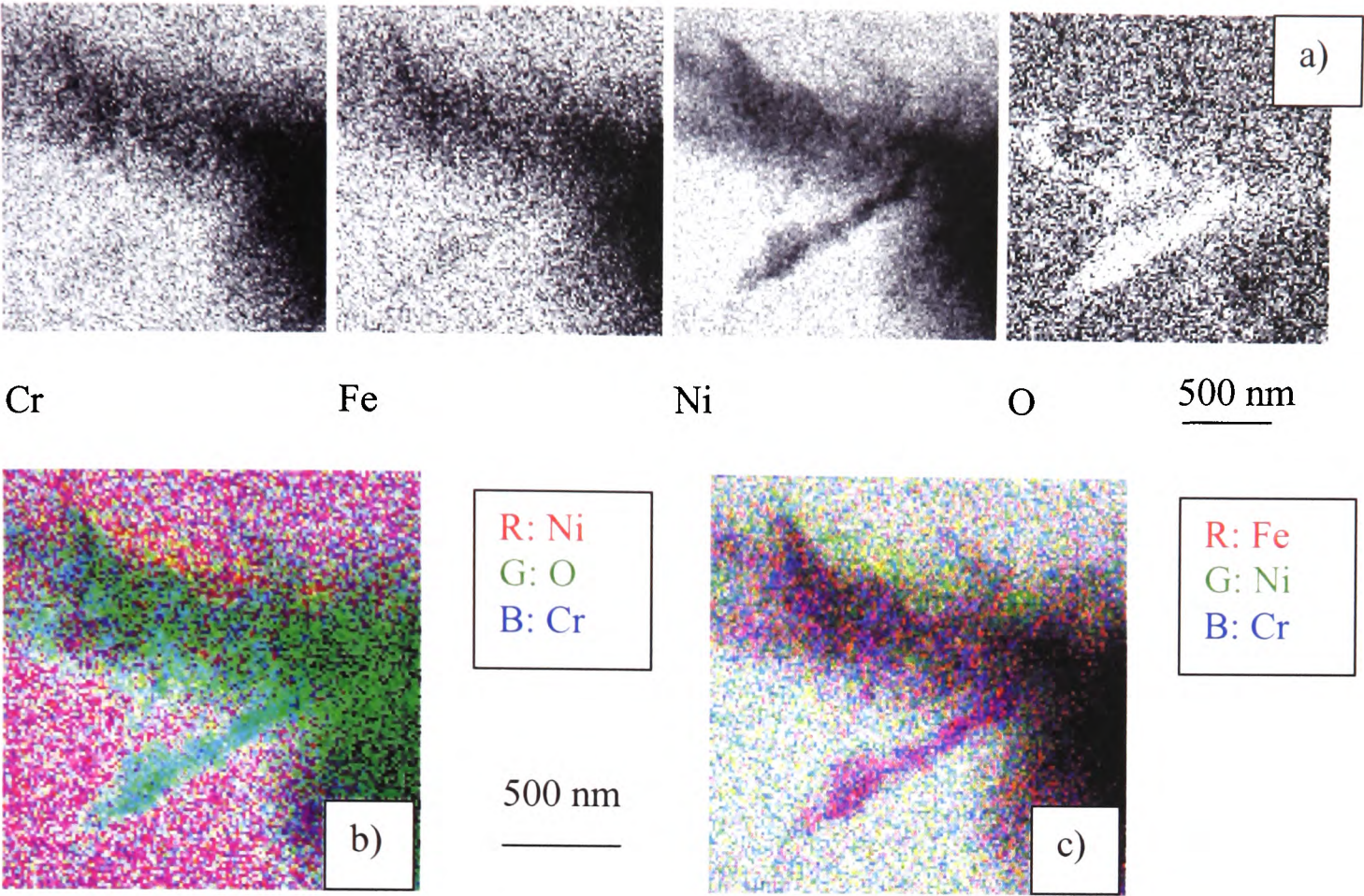


Fig. 8.4.5. a) EDX maps of the crack χ area (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

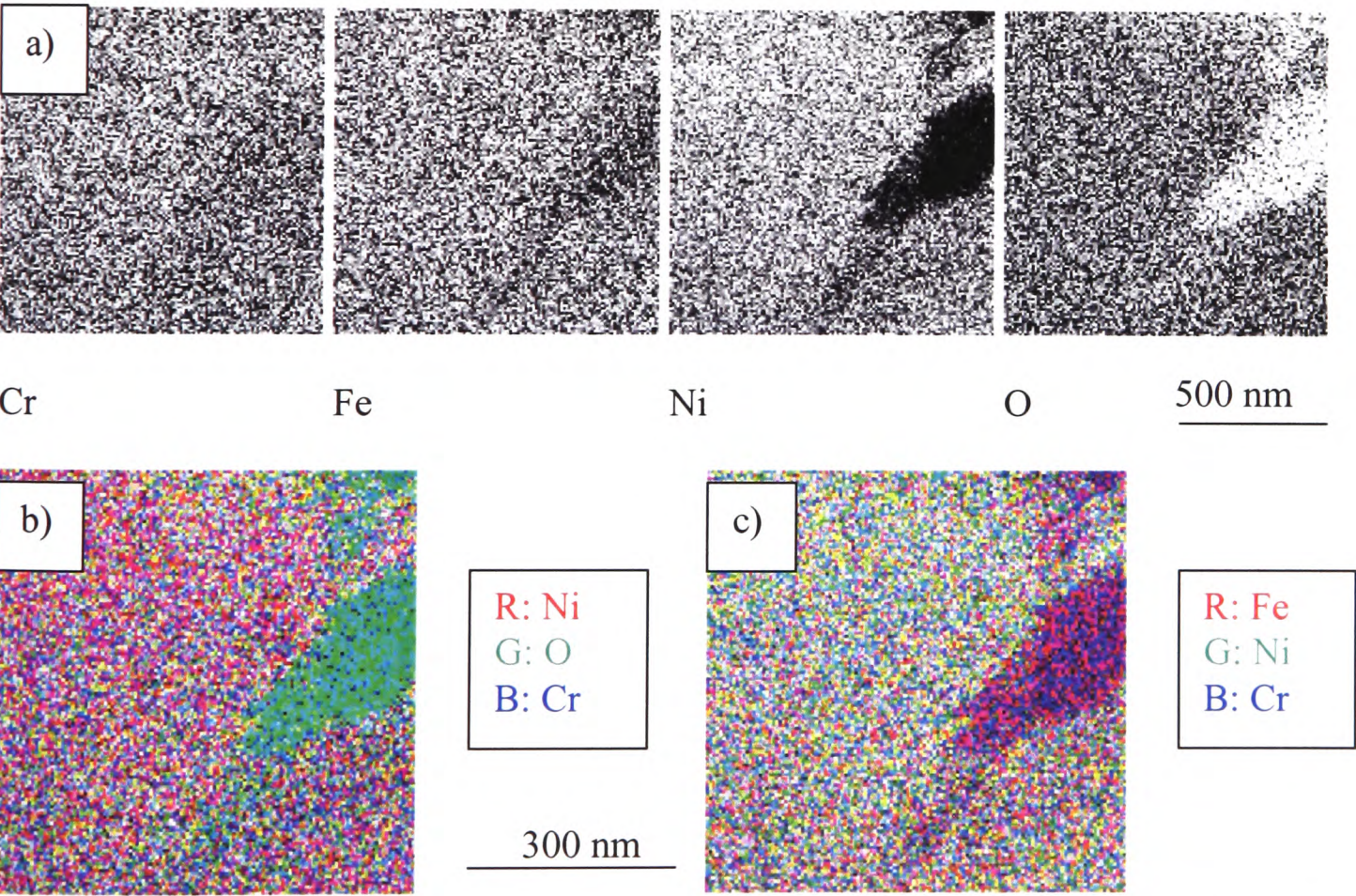


Fig. 8.4.6. a) EDX maps of the tip of crack χ area (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

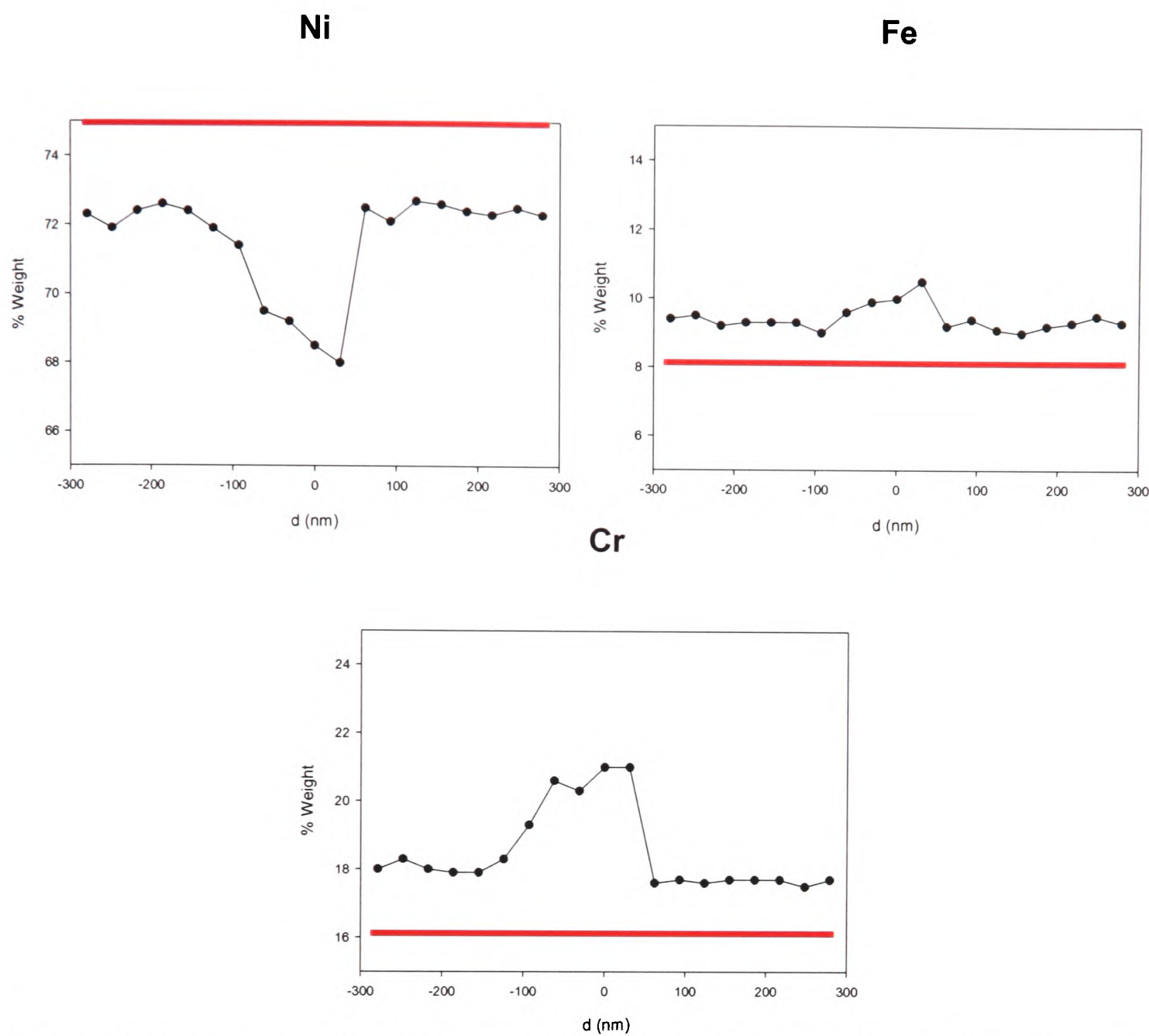


Fig. 8.4.7. EDX compositional line profile across the intragranular crack χ . For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red line represents the nominal composition of the alloy (acquired with the LINK system in the HB501).

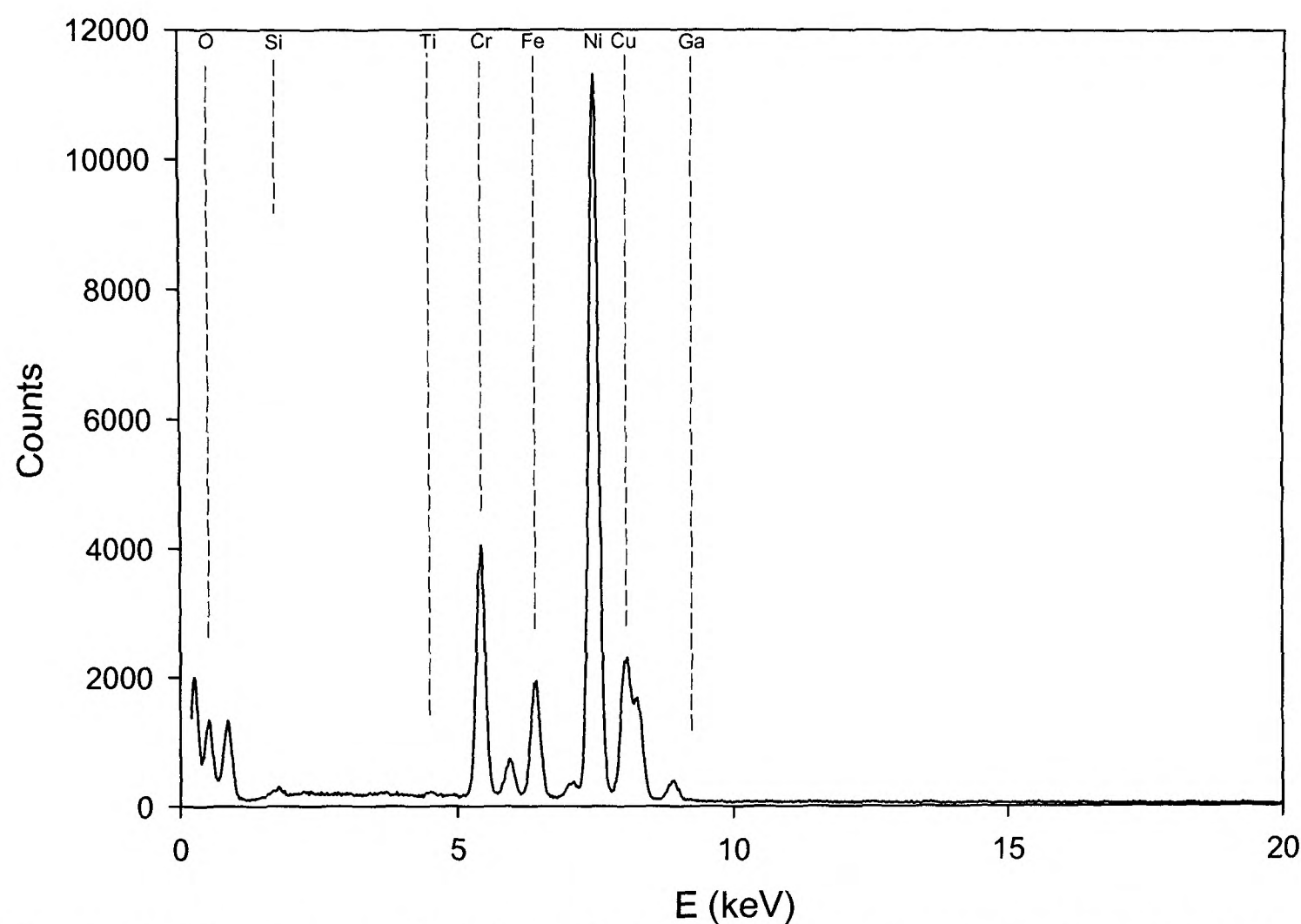


Fig. 8.4.8. EDX spectrum from the oxide in the intragranular crack χ (acquired with the LINK system in the HB501)

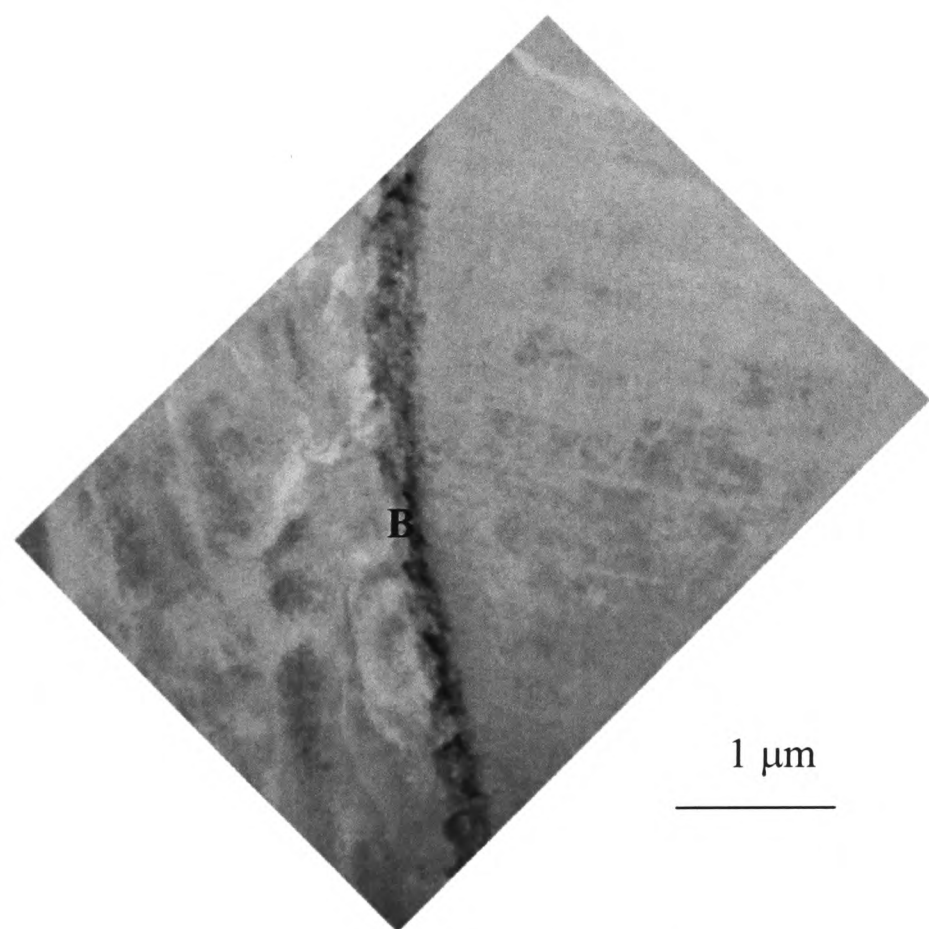


Fig. 8.4.9. STEM DF micrograph showing the attacked grain boundary **B** (acquired with the INCA system in the CM20).

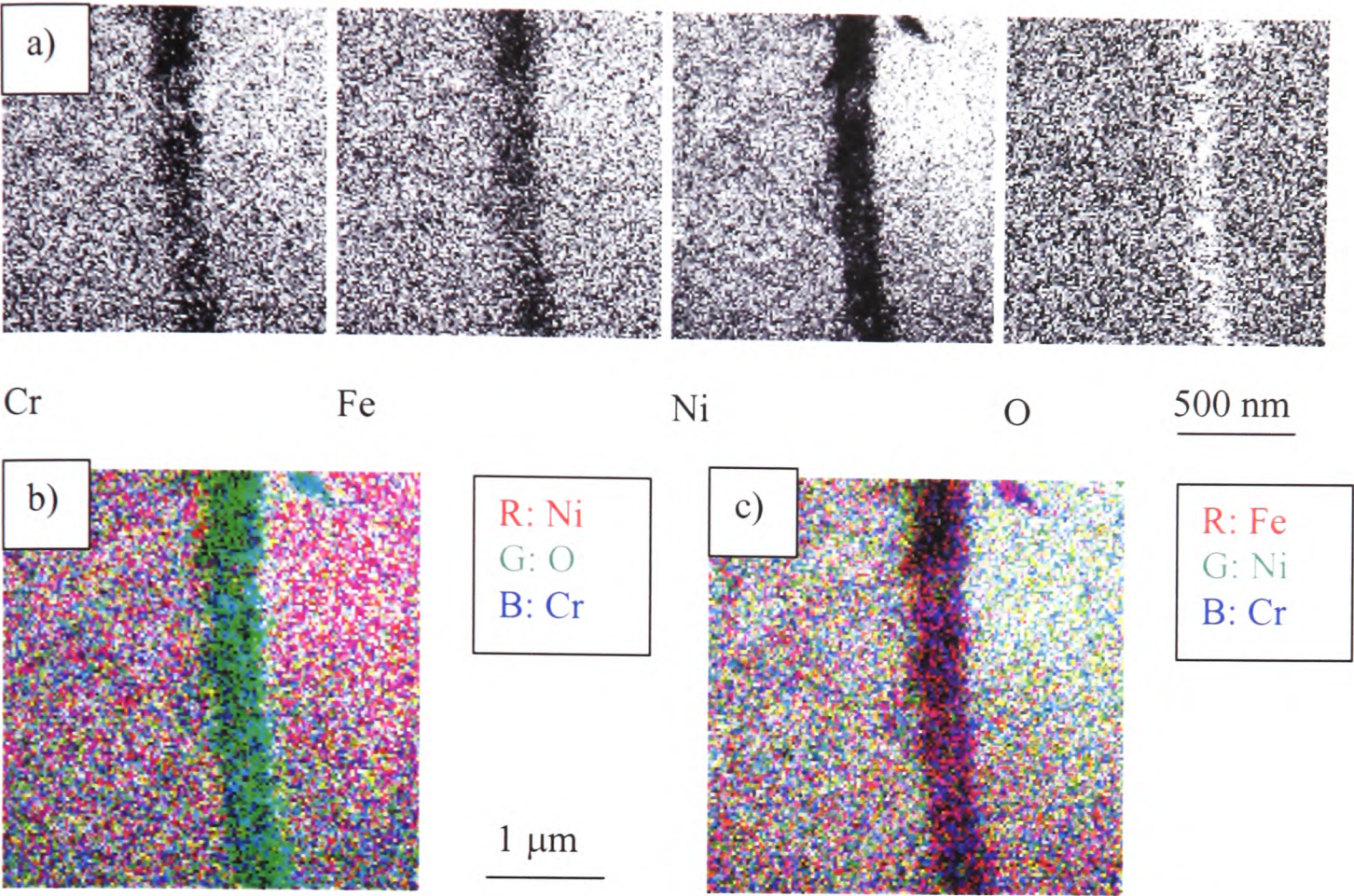


Fig. 8.4.10. a) EDX maps from grain boundary **B** (acquired with the LINK system in the HB501), b) and c) RGB composition of images.

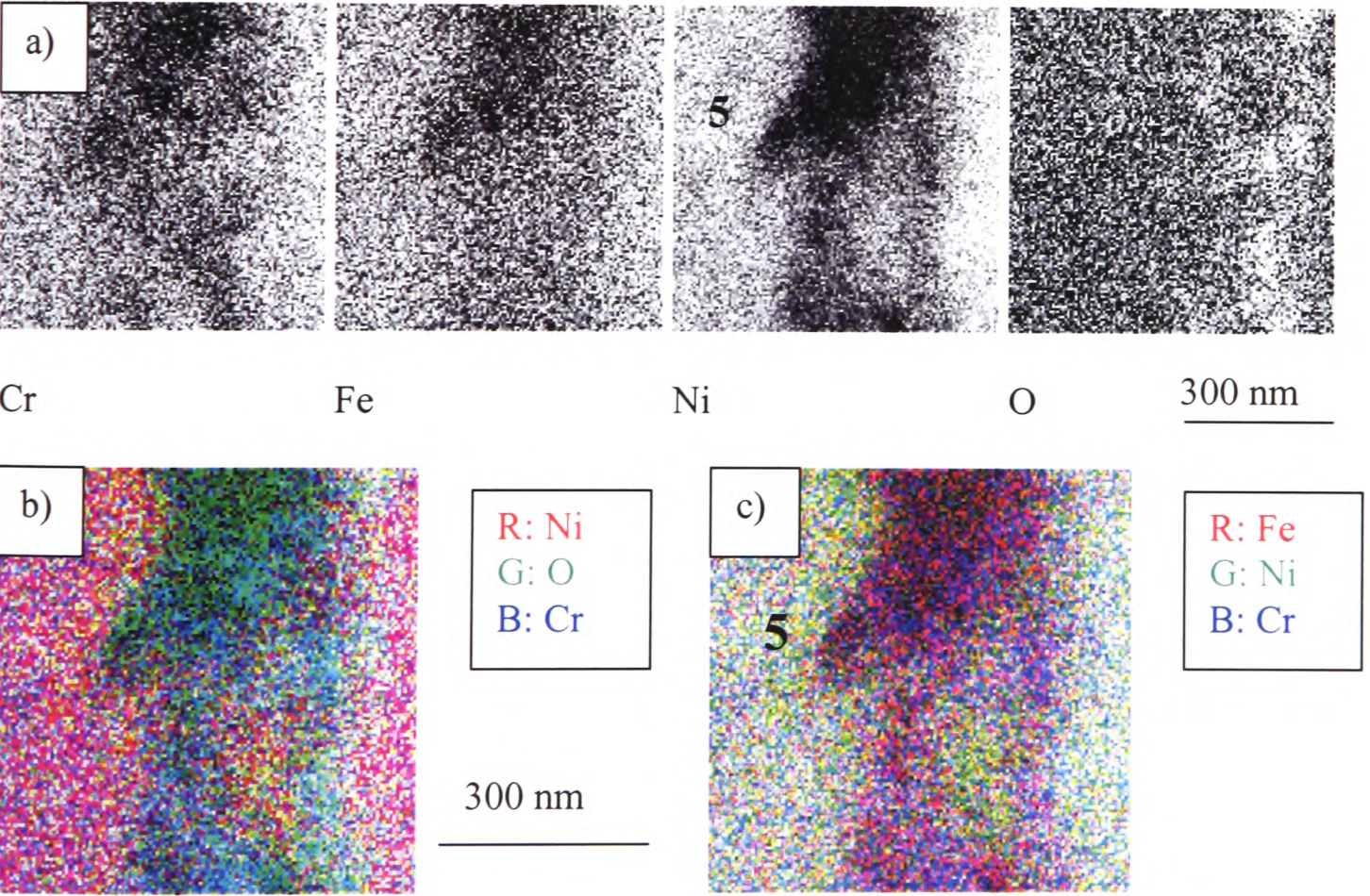


Fig. 8.4.11. a) EDX maps from grain boundary **B** at a higher magnification (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

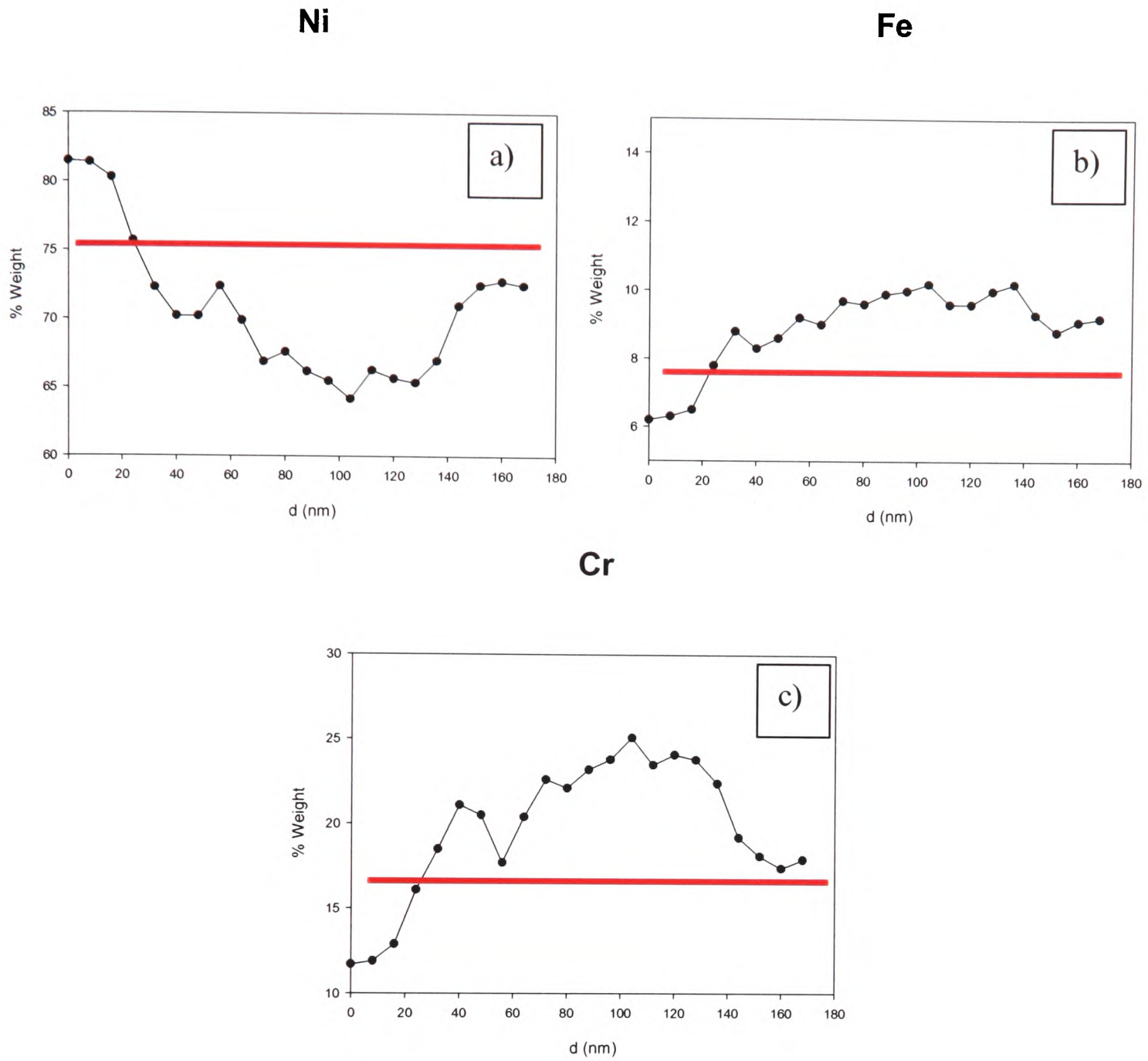


Fig. 8.4.12. EDX compositional line profile across grain boundary **B**. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.2$, $\sigma(\% \text{ wt. Cr}) = 0.3$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.2$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red lines indicate the nominal composition (acquired with the LINK system in the HB501).

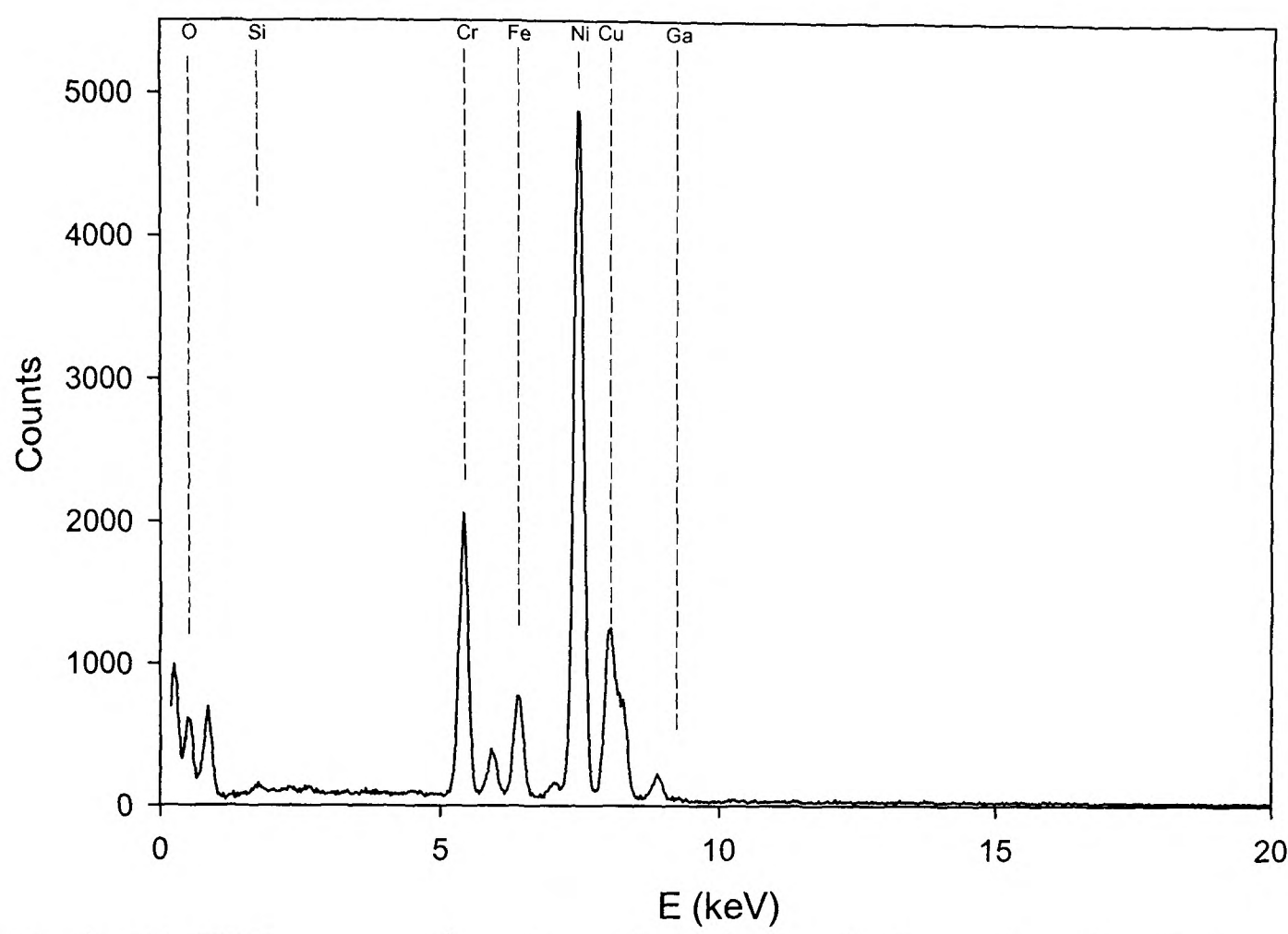


Fig. 8.4.13. EDX spectrum from the oxide in the attacked grain boundary **B** (acquired with the LINK system in the HB501)

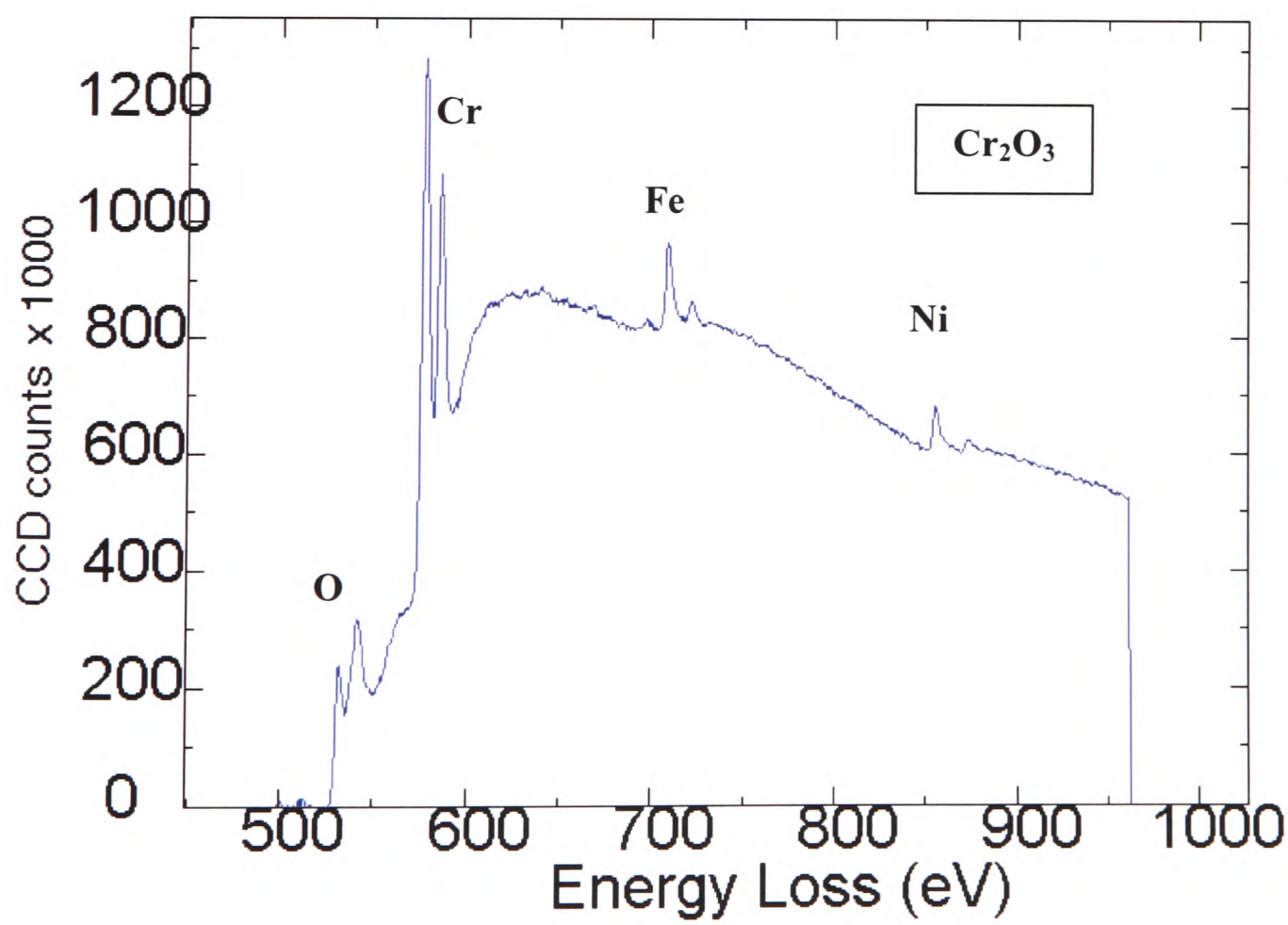


Fig. 8.4.14. EELS spectra from the Cr₂O₃ in grain boundary **B** (acquired with the 3000F)

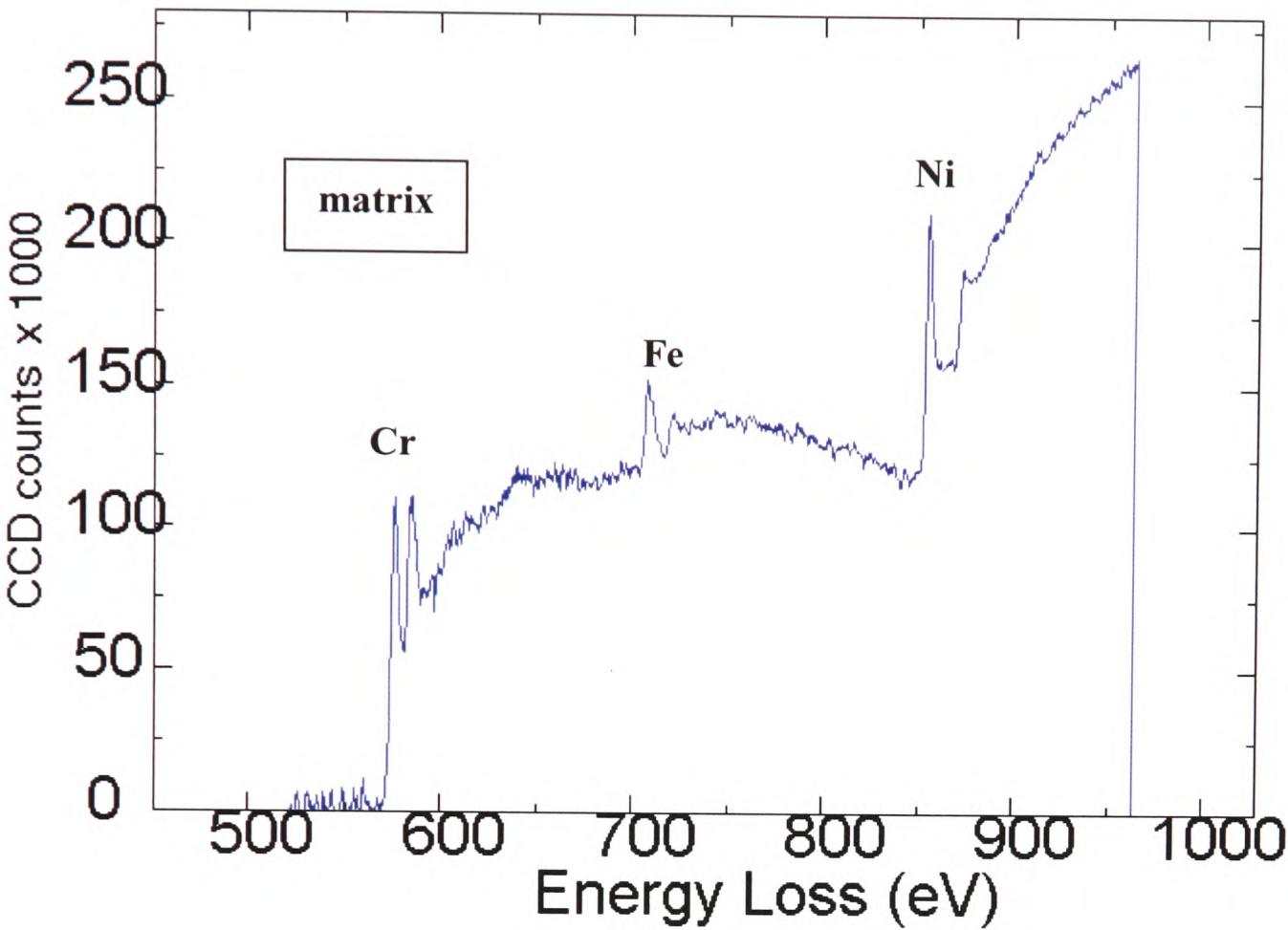


Fig. 8.4.15. EELS spectrum from the matrix (acquired with the 3000F).

8.4.3.3 Particles

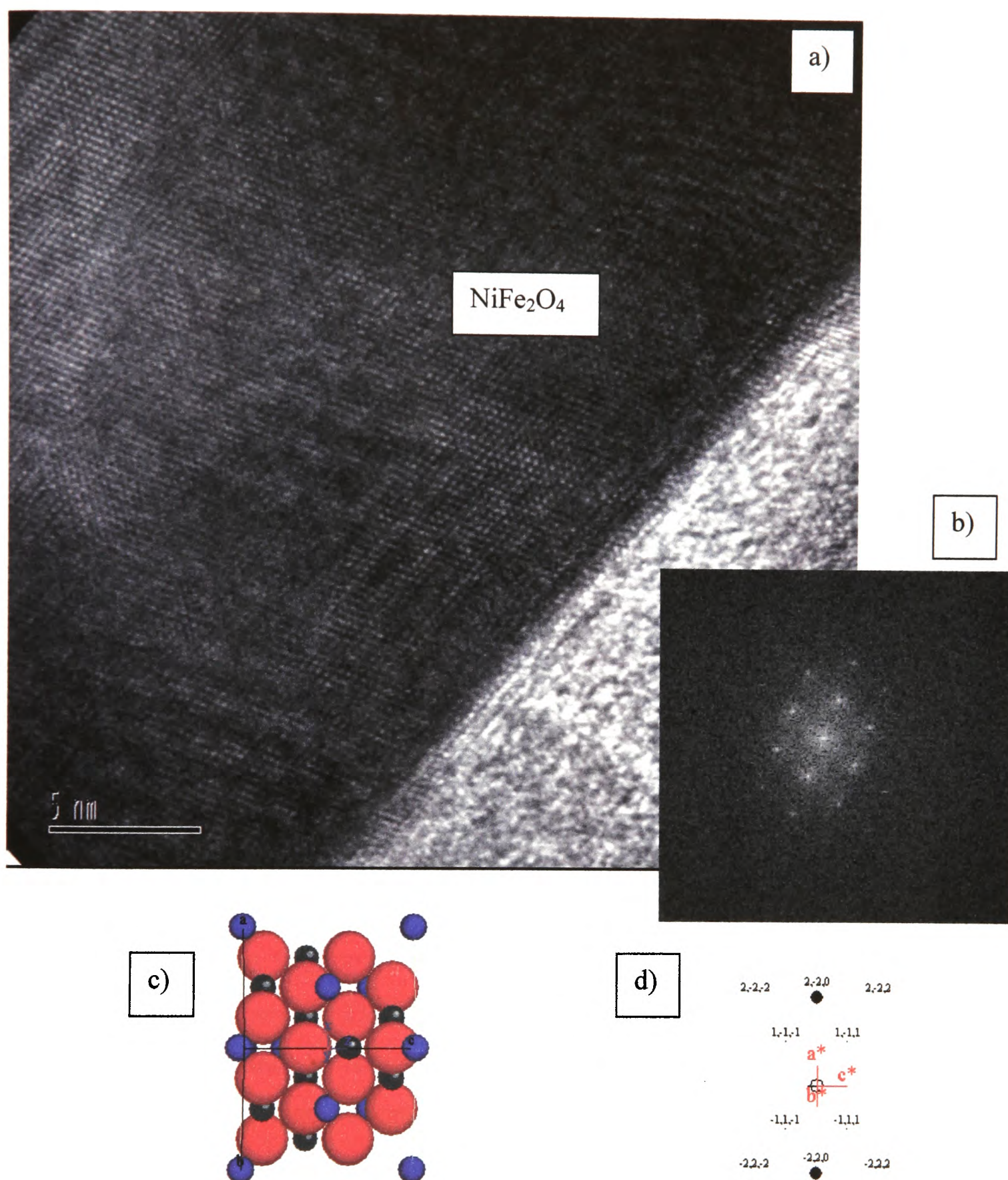


Fig. 8.4.16 a) HR micrograph showing particle **g** (NiFe_2O_4) in a $[110]$ zone axis, b) shows a FFT of the particle, in which the $[110]$ spots can be seen clearly (Images acquired with the 3000F and processed with Gatan Digital NiFe_2O_4 in Micrograph), c) shows a simulation of a NiFe_2O_4 unit cell in a $[110]$ zone axis (Ni atoms in blue, Fe in black and O in red) and d) its simulated DP.

8.5 Sample 5: General observations

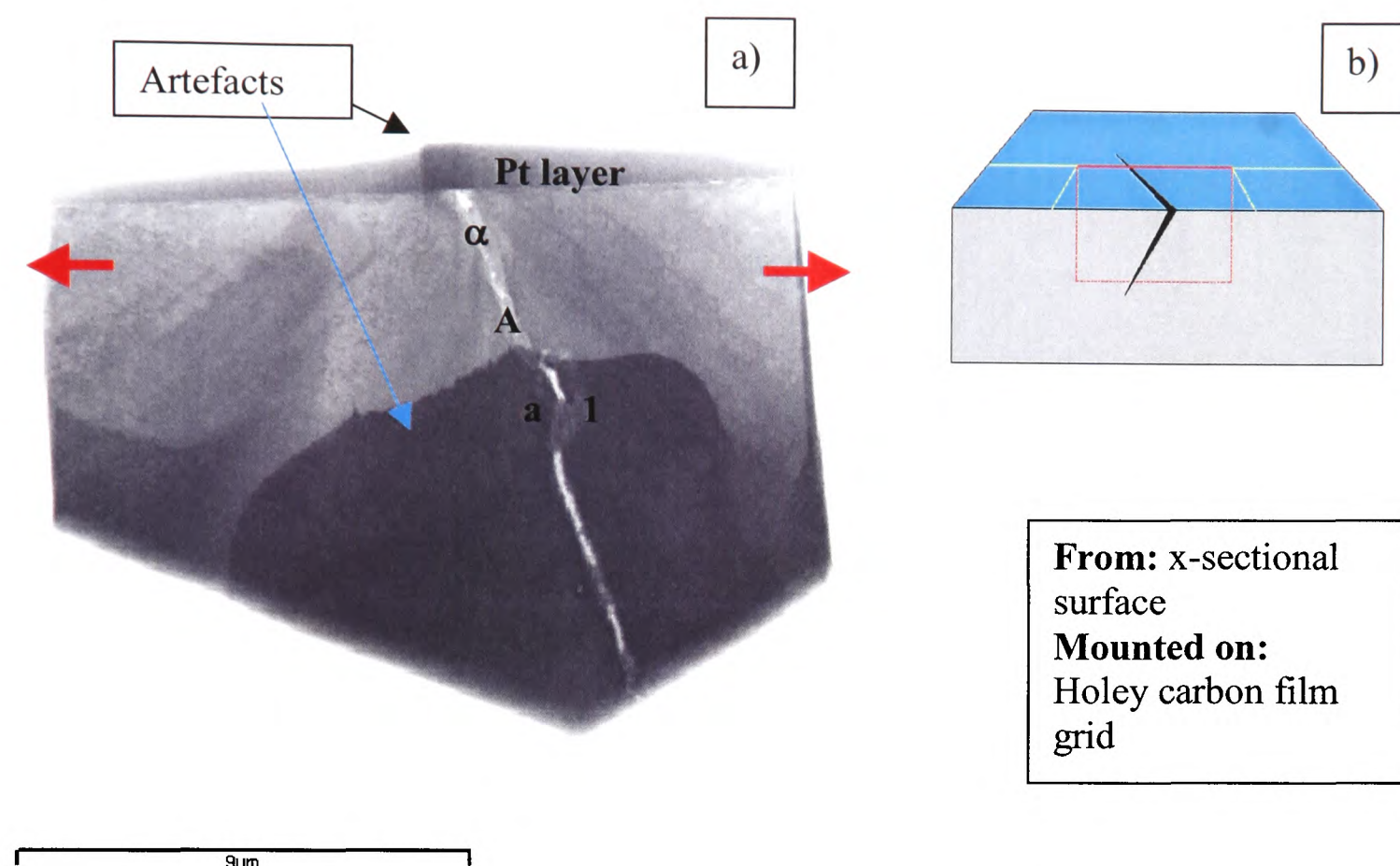


Fig. 8.5.1. a) STEM BF micrograph showing sample 5 after plucking. The loading direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) sketch showing the orientation of the sample.

Sample 5 (Fig. 8.5.1a) was prepared from a x-sectional polished surface (in blue in Fig. 8.5.1b), at 6 μm below the top surface (in grey in Fig. 8.5.1b). It had a long crack (α) which has grown oblique to the loading direction, attacking and opening grain boundary A. Crack α was found to be filled with homogeneous nanocrystalline NiO and the flanks of the crack were rich in Cr_2O_3 . However, the most interesting observation was the remains by the flanks of the crack of what appear to have been intergranular Cr-carbides. Most of them had been severely attacked and almost completely dissolved, but at least one of them (a) was able to divert the attack around it. Thus, when the crack opened, it did not follow the original plane of grain boundary A at position 1.

The sample contains some artefacts that require explanation. The first and most obvious one is the strange shape of the sample (not rectangular). This was due to the orientation of the grains contained in the sample, which were quite different. While the right one was in a favorable orientation for milling, the left one was much

“harder” to mill, so the trench did not have a homogeneous depth and, when cutting the bottom, it was found that re-deposited material made a straight cut impossible. Also, the right grain had to be thinned for a longer time (for the same reason), and this is why an artificial vertical line appears in the centre of the sample (Fig. 8.5.1). The last artefact is the artificially thick region at the bottom of the sample, which is due to an unfinished thinning in the FIB.

8.5.1 Analysis

8.5.1.1 Flanks

The left flank of crack α was studied using an EDX quantitative line profile (Fig. 8.5.2). The quantitative results are not complete: as for other samples O could not be included in the analysis. The sample showed the presence of a thin Cr_2O_3 layer of thickness 20 nm and a progressive enrichment of Cr close to the edge caused by the dissolution of a Cr-carbide in a neighboring area (Fig. 8.5.2c). The Ni concentration decreased towards the edge but showing a peak (Fig. 8.5.2a), which suggested that when the Cr_2O_3 layer broke and the crack opened, most of it stayed in the right flank. It can also be seen that the composition of the three elements in the matrix reaches the nominal composition of the alloy.

8.5.1.2 Cracks

Fig. 8.5.3 shows a STEM DF micrograph at the orientation of the sample which was used to acquire some of the EDX maps (Fig. 8.5.3a). With these maps, the presence of the carbides next to the boundary is revealed. In Fig. 3b, the NiO inside the crack appears as a mixture of yellow and green. There are two kinds of Cr-rich regions. The bottom one is light blue, indicating the presence of oxygen, but the top one is not oxidized and it is highly depleted in Ni and Fe, as can be seen in the EDX maps in Fig. 8.5.3a. It remains unclear if the attacked region at the bottom was originally a carbide.

In Fig. 8.5.4b, in another region of the crack, it can be seen how the Cr-oxide (light blue) “invades” the crack region, and no NiO is found for a few hundreds of nm along the crack. In Fig. 8.5.4a Ni and O maps reveal the magnitude of the attack. The presence of well-defined clusters of Cr-oxide in the surface, in comparison with the inhomogeneous attack of other samples (e.g. Sample 4, feature 3 in Fig. 8.5.2a) suggest again that the grain boundary was decorated with carbides before the attack.

An interesting feature can be seen in Fig. 8.5.5, in which the sample has been rotated to show the crack vertically. Apart from the usual Cr_2O_3 layer which is mostly in the right flank, with some rests in the left (appearing as light blue in Fig. 8.5.5b), an almost pure-Ni layer was found in the left flank of the crack. This Ni might have been rejected from the formation of Cr_2O_3 . It is possible that when the crack opened and the Cr_2O_3 layer broke, the remaining Cr_2O_3 in the left flank (can be better seen in the Cr map of Fig. 8.5.5a) was enough to protect or slow down the dissolution of Ni into NiO, as pure Ni is not stable under the $[\text{O}^{2-}]$ in the environment.

8.5.2 Main observations

- The presence of an intergranular Cr-carbide diverted the attack.

8.5.3 Sample 5 – Data collection

8.5.3.1 Flanks

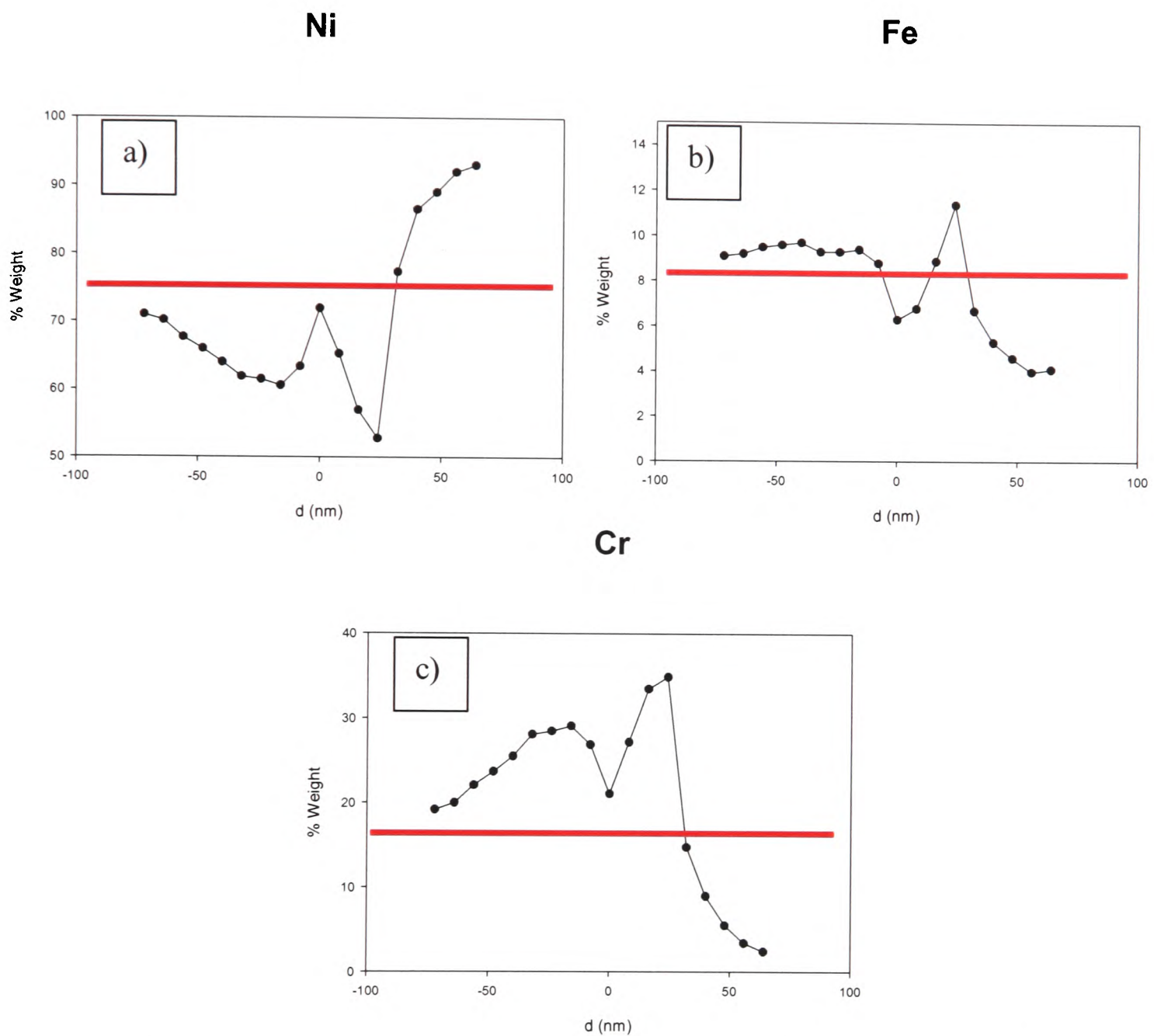


Fig. 8.5.2. EDX compositional line profiles across the left flank of the crack. Negative values of d represent the matrix and $d = 0$ the interface with the NiO. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$ (acquired with the LINK system in the HB501). The red lines represent the nominal compositions of the alloy.

8.5.3.2 Crack

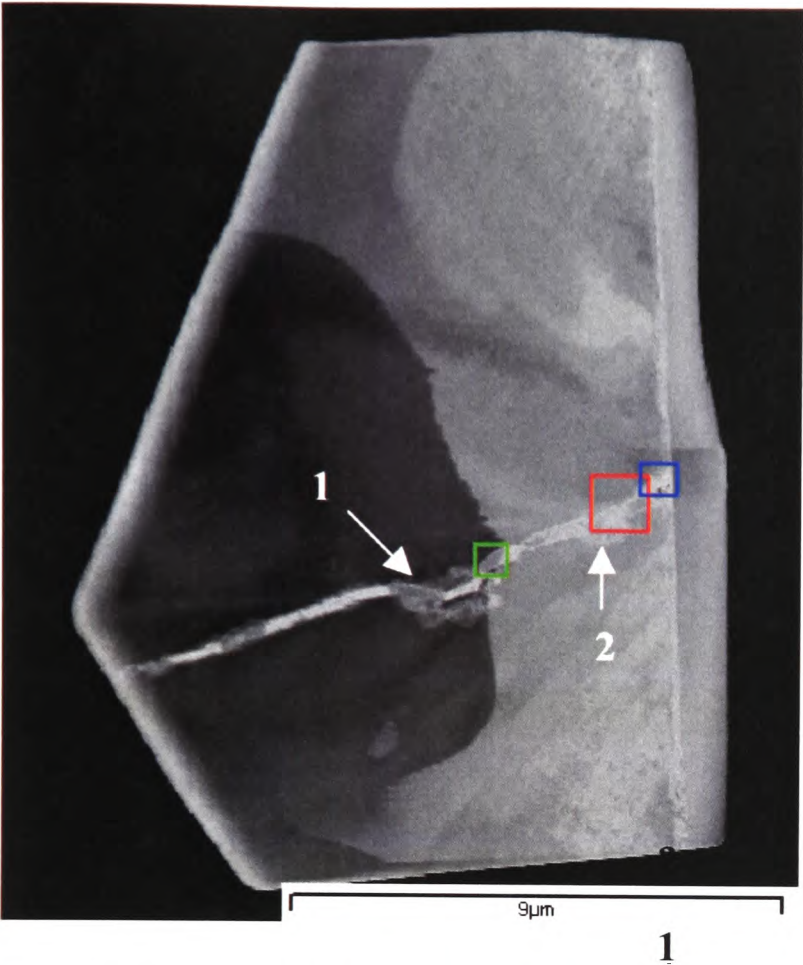


Fig. 8.5.2. STEM DF micrograph in which the compositional mappings areas have been marked by colour boxes (acquired with the INCA system in the CM20).

Zone 

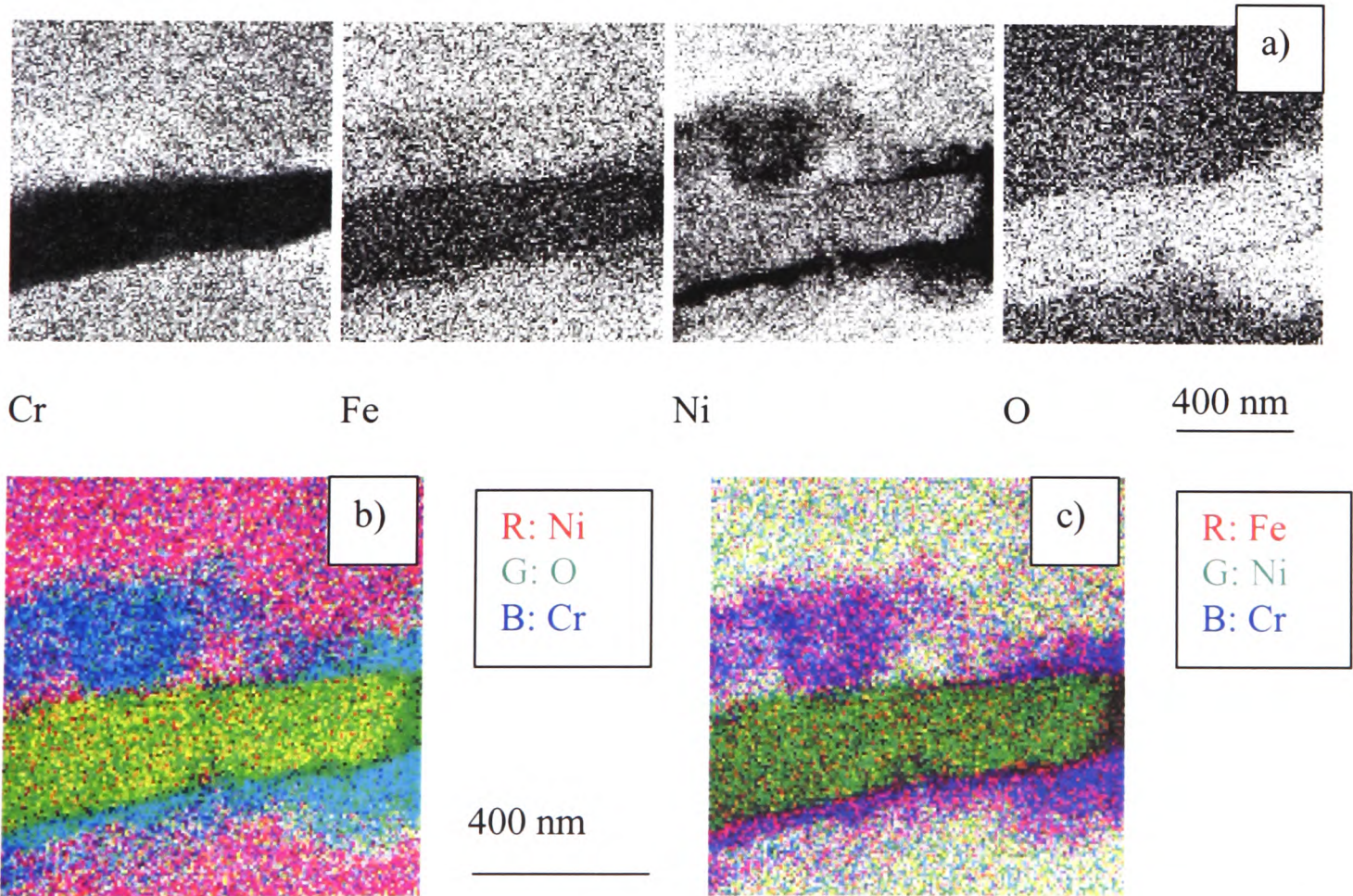


Fig. 8.5.3. a) EDX maps from the area boxed in red in Fig. 2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

Zone

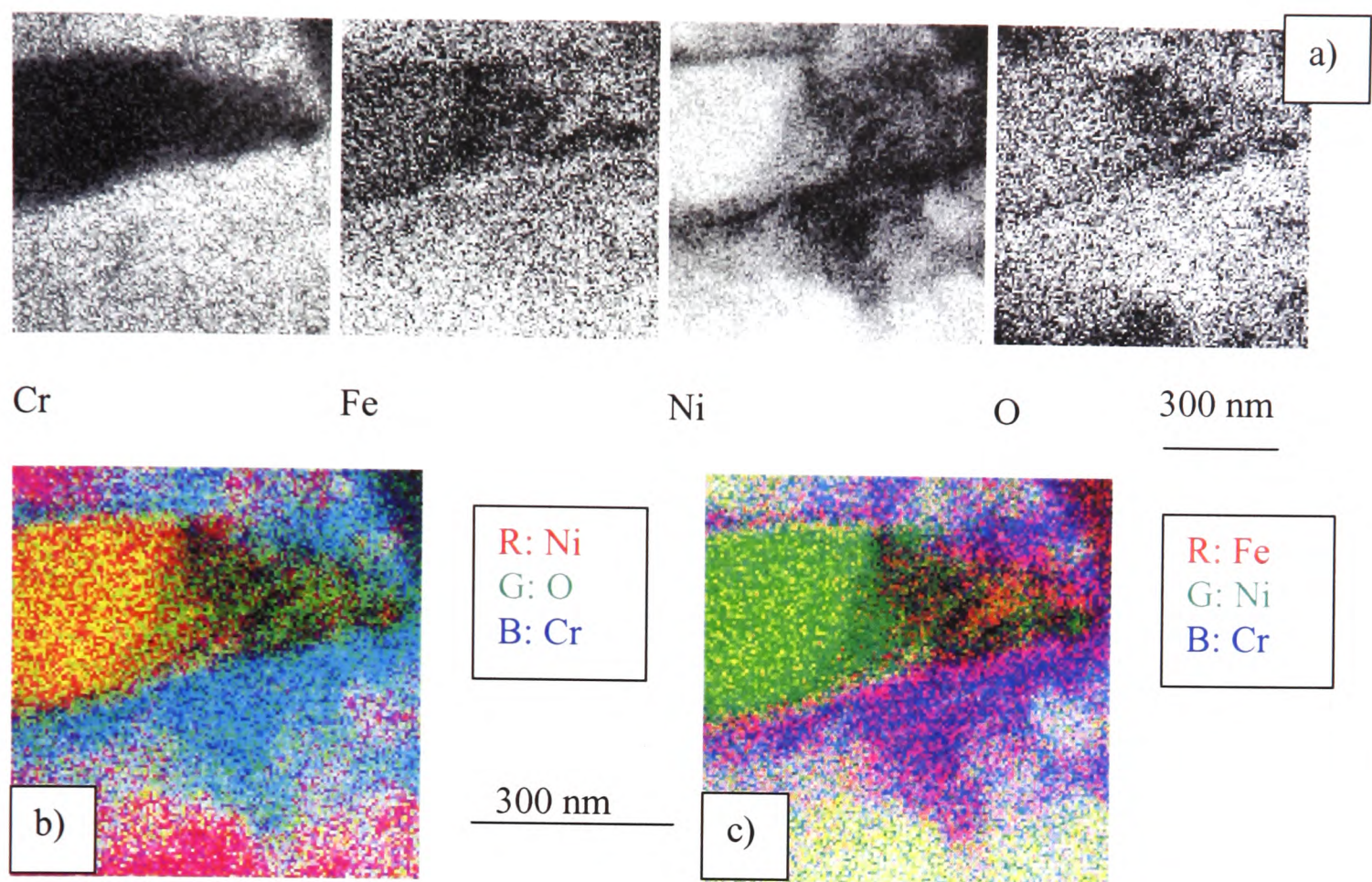


Fig. 8.5.4. a) EDX maps from the area boxed in blue in Fig. 2(acquired with the LINK system in the HB501); b) and c) RGB composition of images.

Zone (Rotated to show the crack vertically)

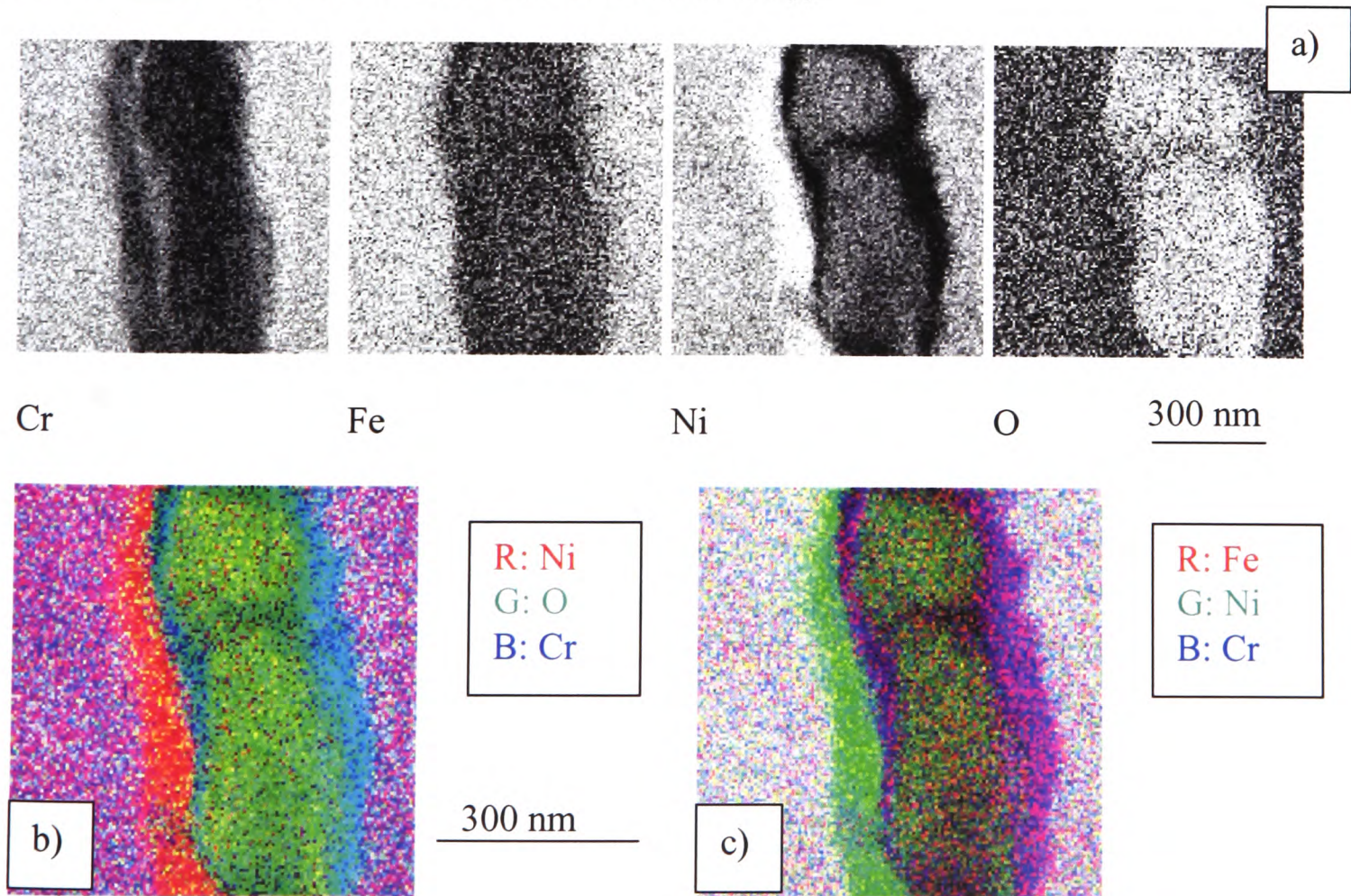


Fig. 8.5.5. a) EDX maps from the area boxed in green in Fig. 2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

8.6 Sample 6: General observations

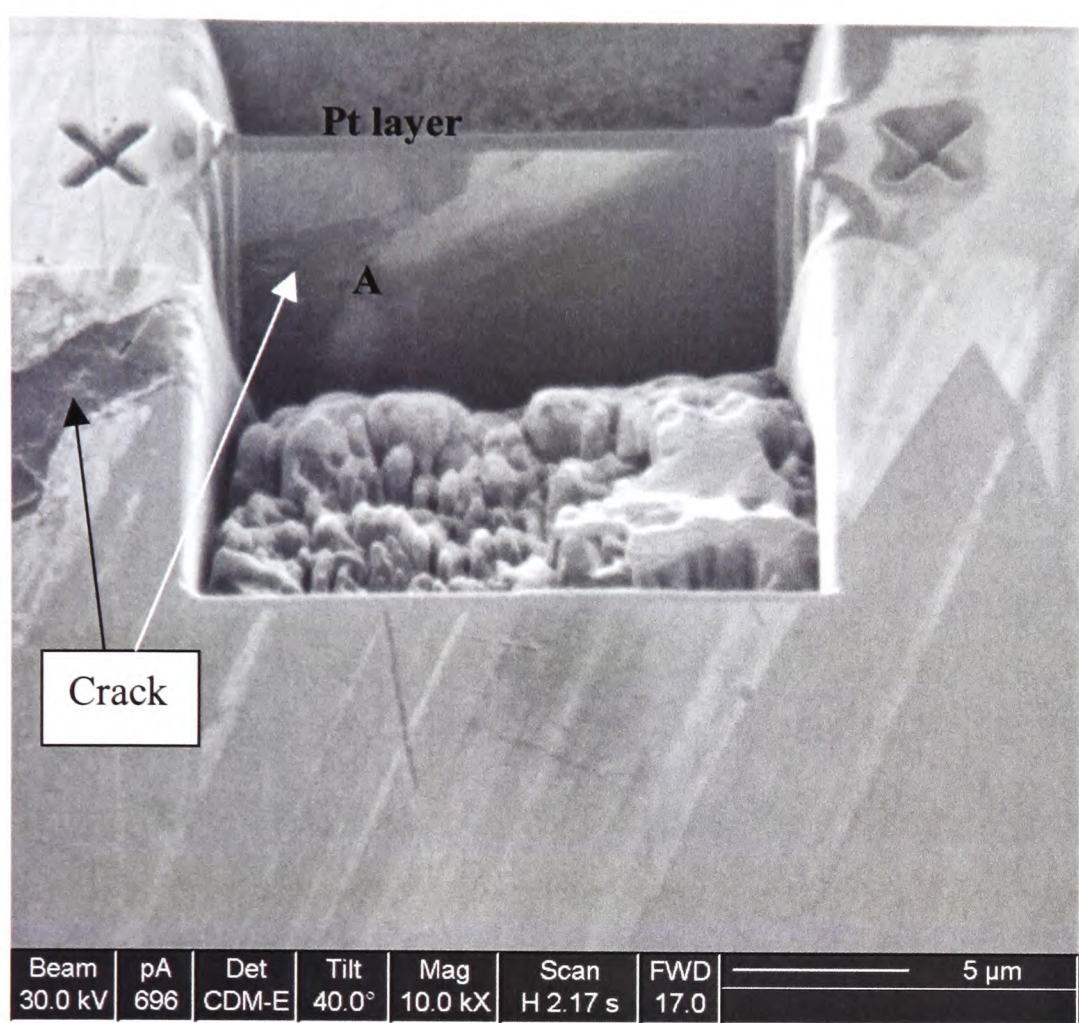


Fig. 8.6.1. FIB SE micrograph showing sample 6 before cutting and plucking.

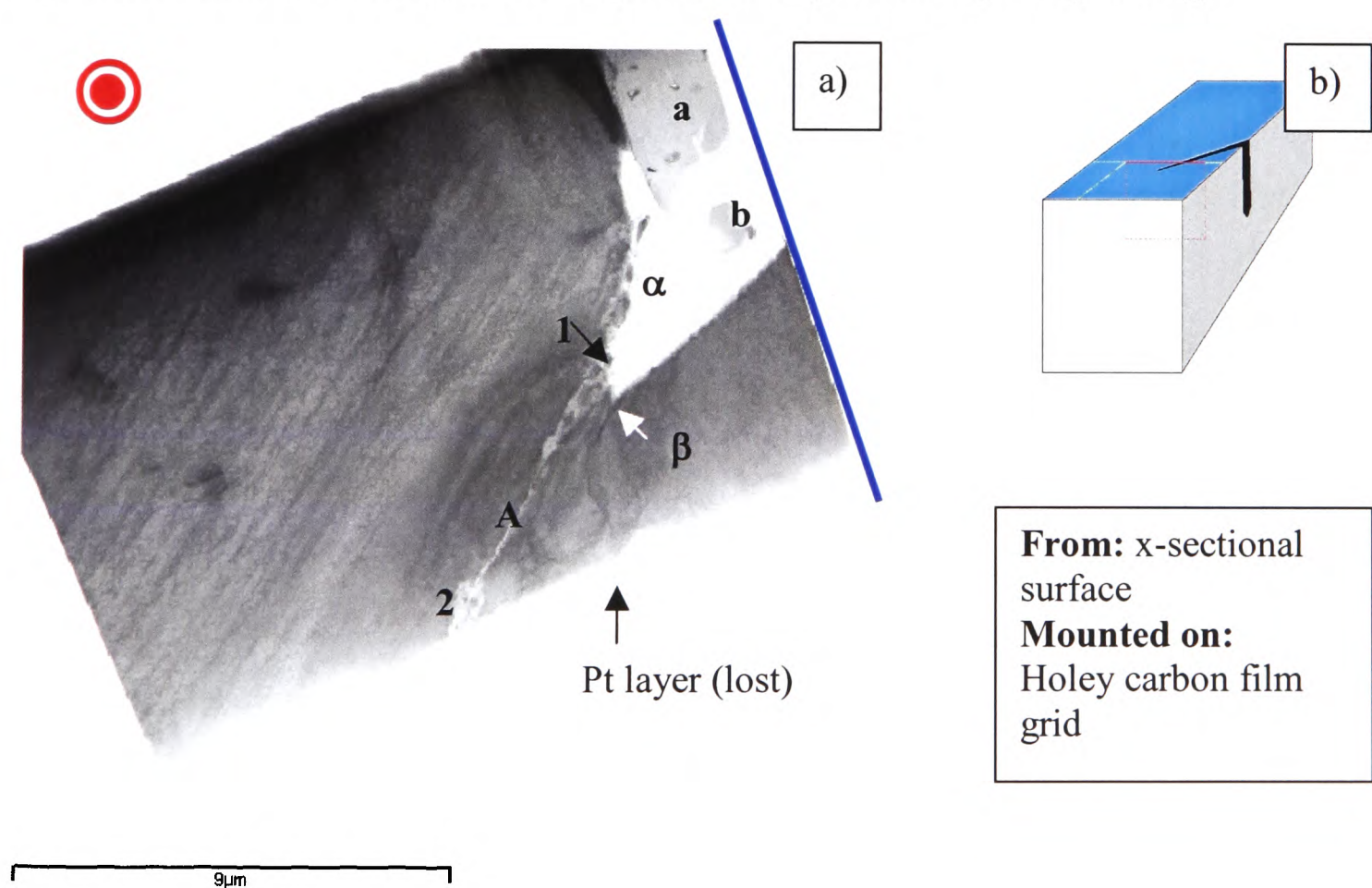


Fig. 8.6.2. a) STEM BF micrograph showing sample 6 after plucking. The direction of the loading is indicated by the red circle(perpendicular to the sample). The position of the top surface (in contact with the environment) is indicated in blue (acquired with the INCA system in the CM20); b) sketch showing the orientation of the sample.

In Fig. 8.6.1, an SE FIB image of Sample 6 is shown. In this image, the position of the crack which is intersected by the sample is arrowed. The sample is shown at a late stage of preparation, prior to final thinning, cutting and plucking. A BF STEM image of the sample after plucking is shown in Fig. 8.6.2a. As can be seen in Fig. 8.6.2b, sample 6 was sectioned perpendicular to the top surface, from a x-sectional surface which was previously polished and with an orientation perpendicular to the loading direction. It has a main crack α which has opened grain boundary A until it blunts at position 1. After that point, at which grain boundary A probably changed its direction, the attack continued but the grain boundary was not in direct contact with the environment. The grain on the right of the sample has been attacked intragranularly (β) through a slip band.

The sample appears artificially thick at the bottom (top in the picture), which is one of the typical artefacts when using the FIB for TEM sample preparation. It has also lost the protective Pt layer during the final steps of the thinning. Despite this, no other loss of material from the crack region is evident.

8.6.1 Analysis

8.6.1.1 Flanks

The “upper” flank (as oriented in Fig. 8.6.2) was analyzed using a qualitative line profile (not shown). A thin Cr_2O_3 layer (of around 50 nm) was found between the matrix and the nanocrystalline NiO.

In Fig. 8.6.3, the “lower” flank of crack α is analyzed. As can be seen in Fig. 8.6.3a, the qualitative EDX line profile intersects particle c next to the flank. Moving from the matrix towards the interface (right to left in the profile), an oxygen rich layer is found centred at 650 nm (Fig. 8.6.3b), which corresponds to a Ni-depleted (Cr-enriched) region (Fig. 8.6.3e), so it is a Cr-oxide (Cr_2O_3 was later confirmed by μD). Then, at $d = 500$ nm in Fig. 8.6.3e, a Ni-rich region is observed which coincides with a low-count region in Cr, Fe and O, suggesting the presence of a Ni-cluster which is dissolving into NiO in contact with the porous NiO in the crack. Next, a Cr-oxide region is found again and finally particle c. An EDX spectrum acquired from particle

c (shown in Fig. 8.6.4) revealed a very high O peak, and mainly Ni and Cr. The quantification of the spectrum is shown in Table 1:

Element	Weight%	Atomic%
O	40.49	70.80
Cr	10.10	5.44
Fe	9.41	4.71
Ni	39.99	19.05

Table 1: Quantitative results from particle c.

Hence, it is very likely that particle c is an spinel Ni oxide (although this has not been confirmed) which had been transferred from the top surface oxide layers.

The GIF was also used to acquired elemental maps from the flank of the crack. The area chosen was located on the lower flank of the crack, as shown in Fig. 8.6.5. The artefact noted in the picture is contrast from the holey carbon film underneath the sample. In the compositional maps of Fig. 8.6.6, it can be seen that a Cr₂O₃ layer has formed, rejecting Ni which accumulates in clusters (Figs. 8.6.5 and 6c). The Cr and O rich regions in Figs 6a and 6d correspond to the Cr₂O₃. An RGB composition is shown in Fig. 8.6.8e to help with the identification of the layers. The Ni-rich clusters (red) and Cr₂O₃ (blue-green) are clearly revealed, with the matrix (purple) in the lower left corner.

8.6.1.2 Cracks

The crack tip of crack α will be defined as the point at which the flanks of grain boundary A stop being in contact with the environment. Thus, the position labelled as 1 in Fig. 8.6.7 has been chosen. This area also includes the intragranular crack β, which grew very close to the position labelled 1 (see Fig. 8.6.7).

Crack β was found to occur along a low-angle sub-boundary which was found to be orientated in a {111} plane (Fig. 8.6.8a). This sub-boundary had a maximum misorientation of 7° at the entrance of the crack, where the two μDP shown in Fig.

8.6.8b were acquired, which gradually decreased to zero after a distance of approximately 1 μm . After this distance, the sub-boundary disappears into the grain.

This area was studied using EDX mapping and μD . In Fig. 8.6.9a, compositional EDX maps of the crack tip area are shown. It is easy to see that the attacked region extends beyond the plane of grain boundary A into the matrix. There seems to be clear Ni and Fe depletion which correlates with areas of high O content (Fig. 8.6.9a). The Cr intensity also seems to be smaller in the attacked region, although later studies revealed that Cr_2O_3 formed in the grain boundary. The RGB composition in Fig. 8.6.9b reveals the existence of Ni-clusters (green), which have also been found in previous samples. Fig. 8.6.9b shows the Cr-oxide in light blue. The tip of crack β appears enriched in Cr, as can be seen in Fig. 8.6.9c (in blue), suggesting that the tip of crack β was also attacked.

In Fig. 8.6.9, the area ahead of the crack tip of crack α was analyzed. Similar features to those found in Fig. 8.6.9 were found. In the EDX maps of Fig. 8.6.10a, the boundary was found to be depleted in Ni and Fe (although not so strongly). The Cr content also appears to be lower, according to the EDX map, but the RGB composition in Fig. 8.6.10b shows that Cr-oxide formed in the boundary (light blue). Fig. 8.6.10c again shows the formation of Ni-clusters (in green).

A qualitative EDX line profile was acquired across grain boundary A at a position shown by the yellow line in Fig. 8.6.11a. The results show some interesting features. The Ni, as expected, appeared depleted in the grain boundary region, in a strip of around 100 nm (Fig. 8.6.11d). The same behaviour was observed for the Fe (Fig. 8.6.11c), although to a lesser extent. This area correlated with an O-rich area of the same width and at the same position (Fig. 8.6.11e). The chromium profile did not exhibit any change across the grain boundary region (Fig. 8.6.11b). Assuming a constant thickness, as confirmed by some GIF thickness maps (acquired with the 3000F), this means that the Cr content did not change substantially in the grain boundary area after the attack. Only the Ni and the Fe atoms diffused and depleted the area. The enrichment of O is expected, as it diffused along the boundary causing the oxidation of Cr.

A quantitative EDX line profile was also acquired in the same area (Fig. 8.6.12). For the quantification, a constant thickness was assumed and the O was not included. The results showed an overall Ni depletion of around 25% (Fig. 8.6.12a), with a slight enrichment close to the left side of the boundary (probably caused by the formation of a Ni-cluster). The iron appeared enriched in the grain boundary (Fig. 8.6.12b), but taking into account the observations from the EDX qualitative profile (Fig. 8.6.11c) it is suggested that the number of Fe atoms decreased in the area. As the same happened to the Ni but to a greater extent, the Fe content exhibits an enhancement (Fig. 8.6.12b). The same happened to the Cr, which appeared clearly enriched at the grain boundary (Fig. 8.6.12c).

Moving along grain boundary A from the crack tip (labelled as 1 in Fig. 8.6.2a and 7) to the lower edge of the sample (in Fig. 8.6.2a), a heavily attacked area was found (feature 2 in Figs. 8.6.2a and 13). In this area, the width of the attack changed from ~100 to 500 nm. A possible explanation could be the proximity of a bigger crack which was connected to grain boundary A beyond the edge of the sample, or the dissolution of an intergranular Cr-carbide. EDX maps were acquired in the area, as shown in Fig. 8.6.14a, and apart from the usual Ni and Fe depletions, the most interesting feature is a clear increase in the Cr counts in the attacked region. As stated above, the signal from the Cr was not clearly enhanced along the boundary, but now the tendency changed. RGB compositions in Figs. 8.6.14b and 14c clearly show the formation of Cr-oxide (Cr_2O_3 , confirmed by SADP, not shown) which appears as light blue in Fig. 8.6.14b and the Cr-enrichment of the attacked region (in blue in Fig. 8.6.14c).

A TEM BF micrograph of the same area (Fig. 8.6.15), taken with the left grain in a [110] zone axis and hence black in the image, revealed that the attack left some “islands” and did not extend uniformly into the matrix. These islands appear as black in the picture (features 3 and 4), indicating that they are part of the left grain, which was tilted to a zone axis. The area boxed in white in Fig. 8.6.15, is shown in focus and underfocussed in Fig. 8.6.16 in order to reveal the nanoporous structure of the oxide. In Fig. 8.6.16a the image is in focus and the nanopores cannot be seen easily. In Fig. 8.6.16b the image was underfocussed by 700nm and the nanopores were revealed (the

“Fresnel contrast” technique was described in Chapter 3). The artefact arrowed is the edge of a hole in the supporting carbon film.

8.6.1.3 Particles

Particle **a** (in Fig. 8.6.2a) was identified as a large NiO monocrystal. Particle **b** (Fig. 8.6.2a and 17) showed a very complex structure. The EDX elemental maps (Fig. 8.6.18a) revealed that it had a Fe-oxide core with two Si-oxide inclusions. The particle also seemed to be covered by a thin Ni layer, as can be seen in the Ni map. The RGB compositions of Figs. 8.6.18b,c,d and e, shows the different phases clearly.

8.6.2 Main observations

- An intragranular crack was found.
- The presence of nanopores was confirmed.
- The crack which grew under mode I loading blunted before reaching a triple point.

8.6.3 Sample 6 – Data collection

8.6.3.1 Flanks

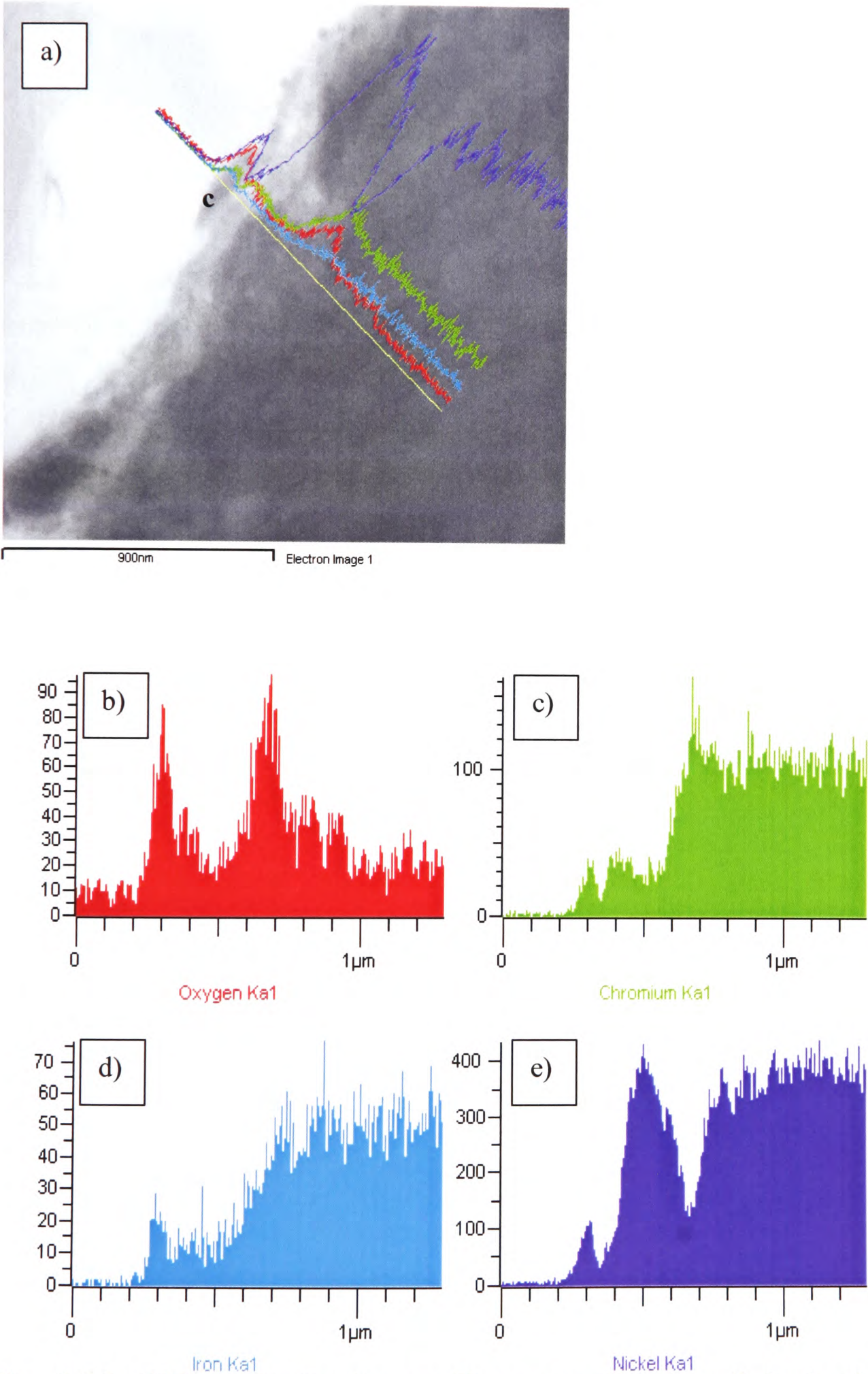


Fig. 8.6.3. EDX qualitative line profile across the “lower” flank of the crack (acquired with the INCA system in the CM20)

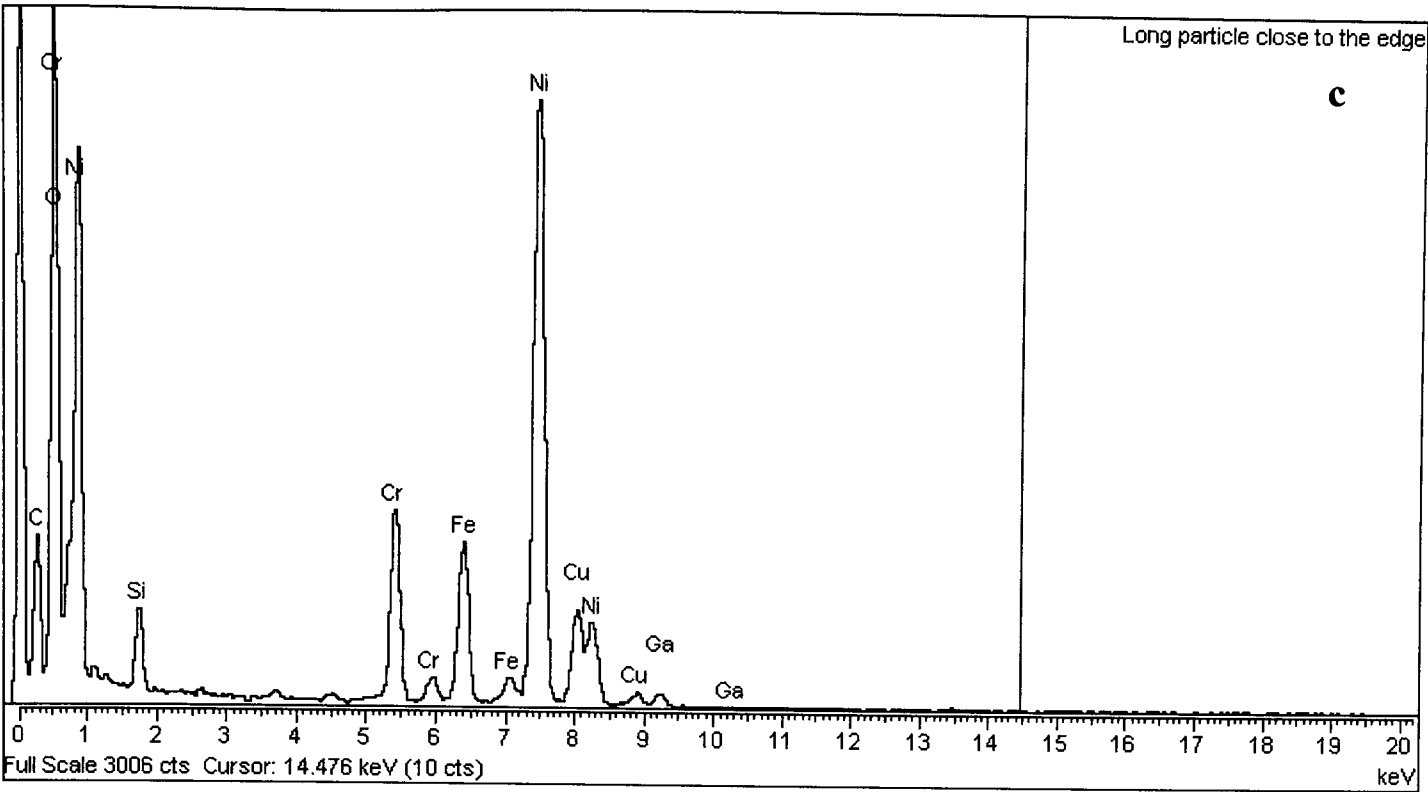


Fig. 8.6.4. EDX spectrum from particle *c* (acquired with the INCA system in the CM20).

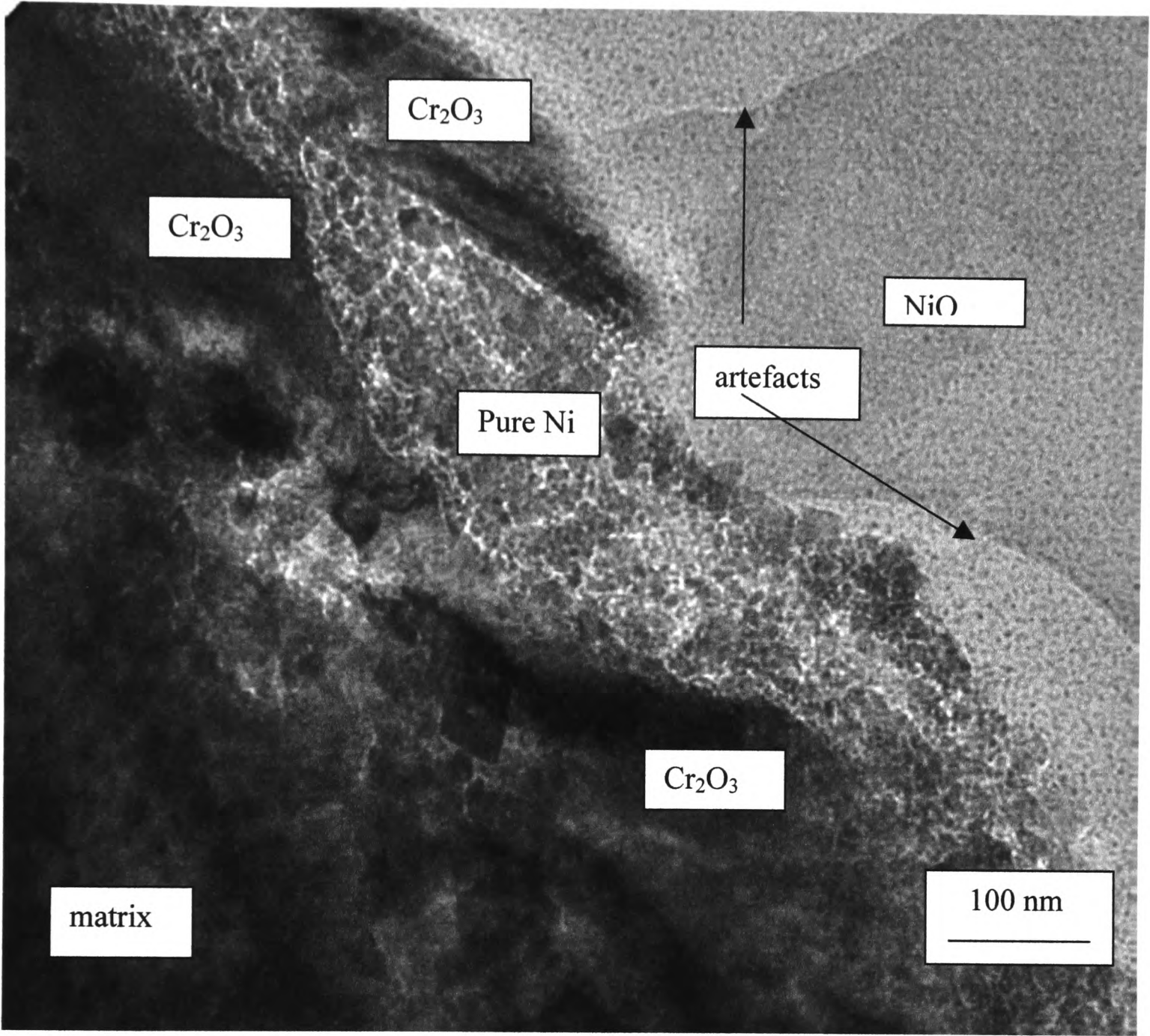
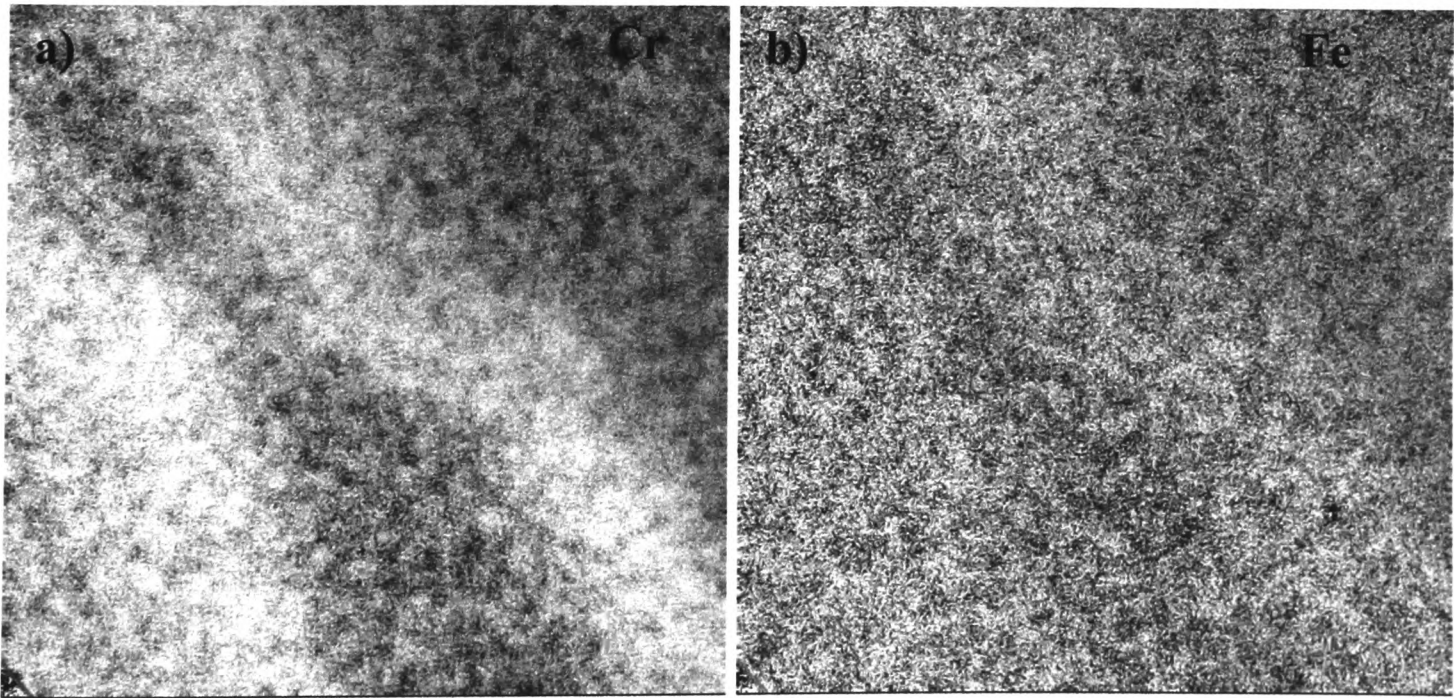


Fig. 8.6.5. TEM BF micrograph showing the oxides layers on the flank of the blunt crack in sample 8 (Acquired with a multiscan CCD in the 3000F)



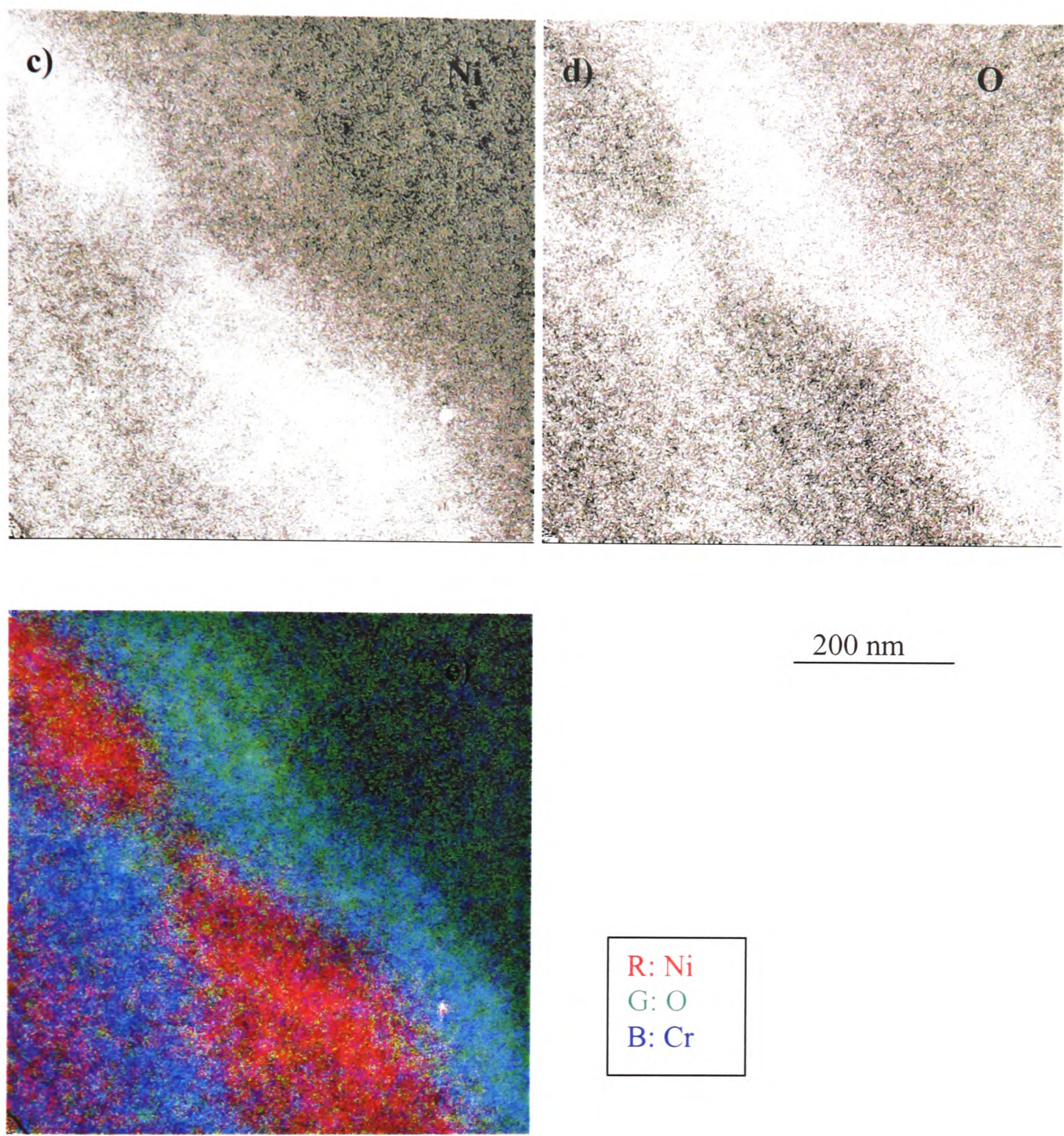


Fig 8.6.6. GIF maps (a,b,c,d) from the area shown in Fig. 8.6.5 and RGB composition (e) (acquired with the GIF in the 3000F).

8.6.3.2 Cracks

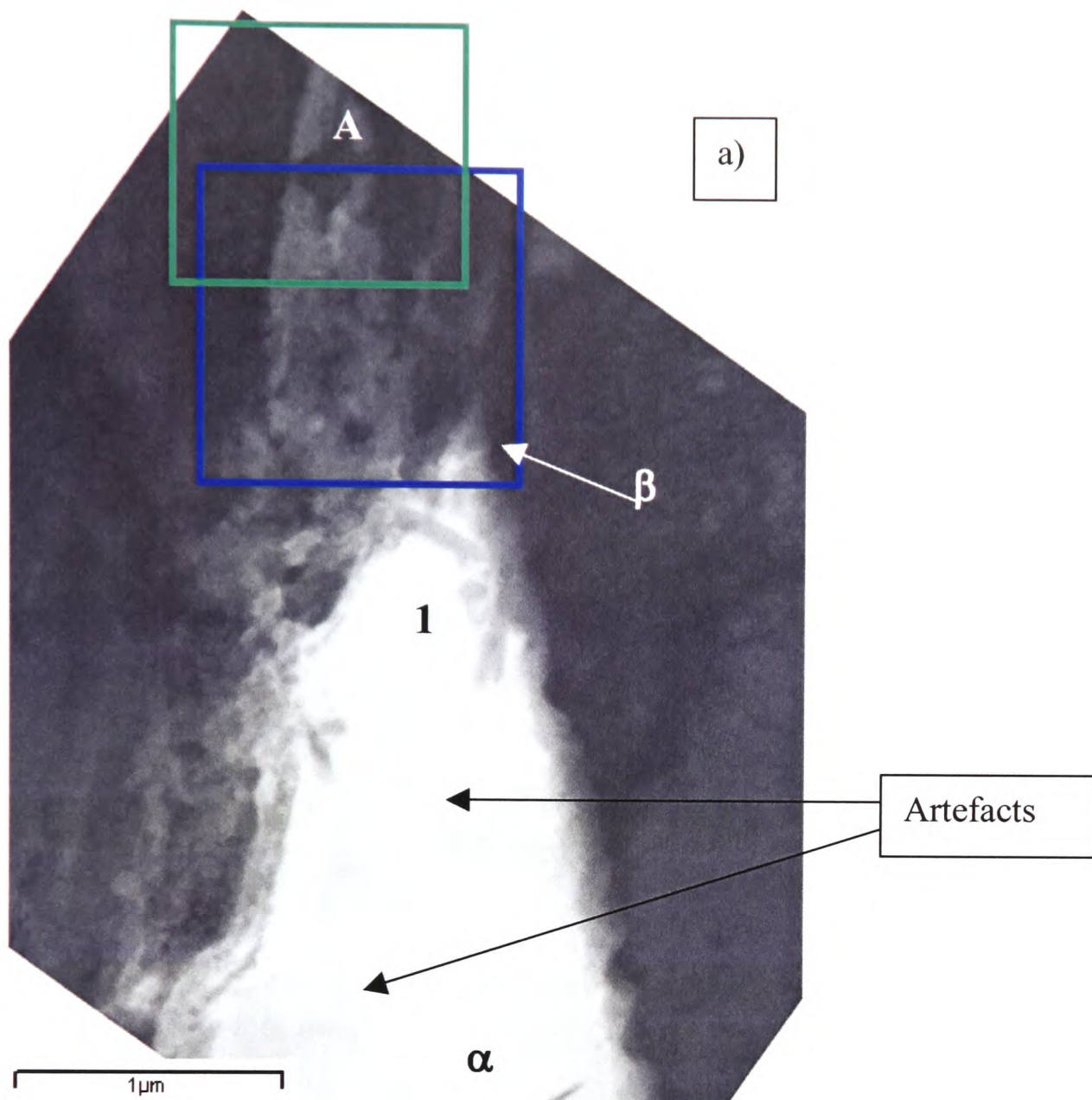


Fig. 8.6.7 STEM BF micrograph in which the compositional map areas have been marked by coloured boxes (acquired with the INCA system in the CM20).

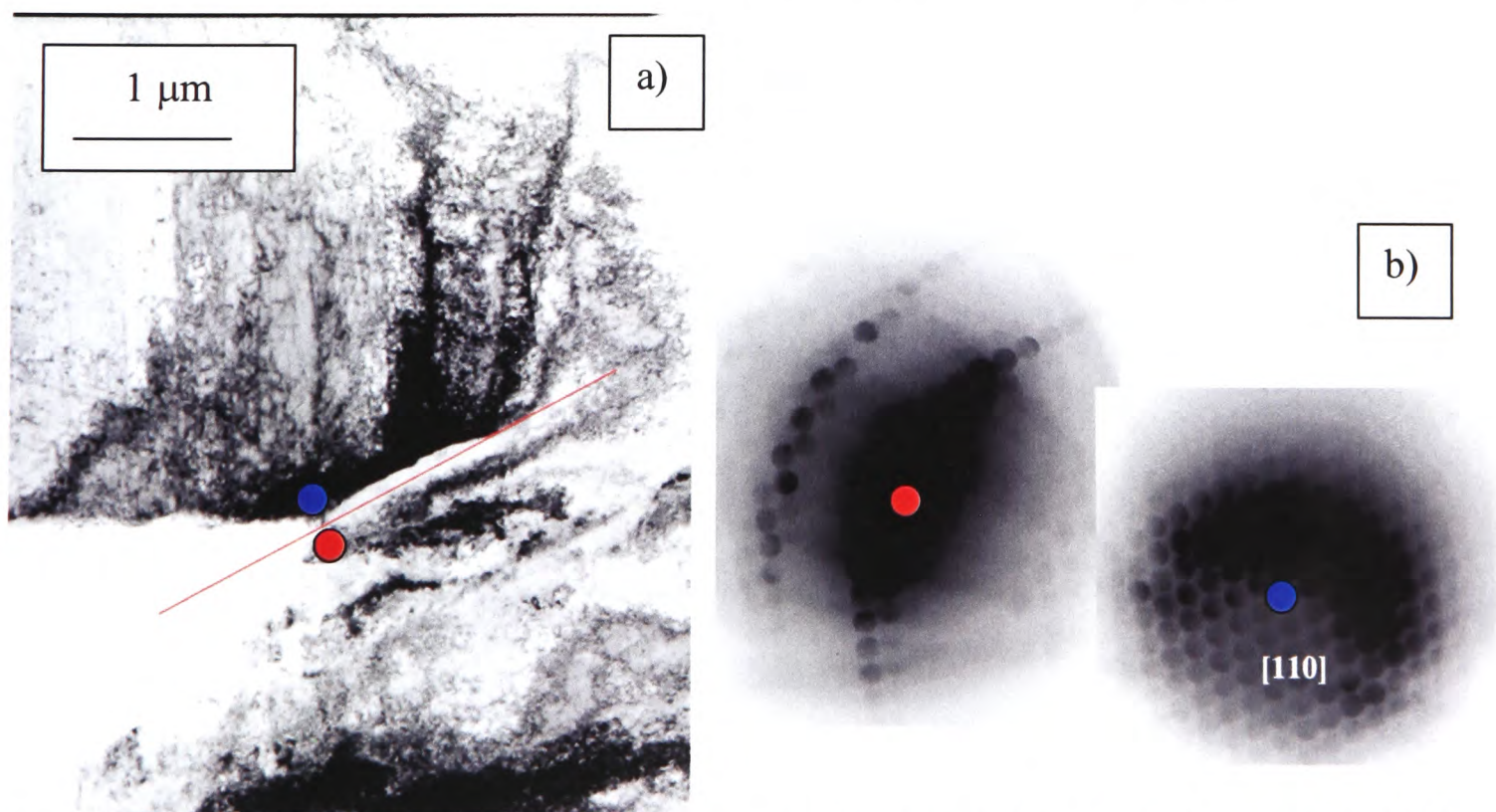


Fig. 8.6.8 a) TEM BF micrograph showing crack β and the orientation of the $\{111\}$ planes (red line); b) μ DPs acquired at the positions indicated by the red and blue spots showing a misorientation of 7° (acquired with the CM20).

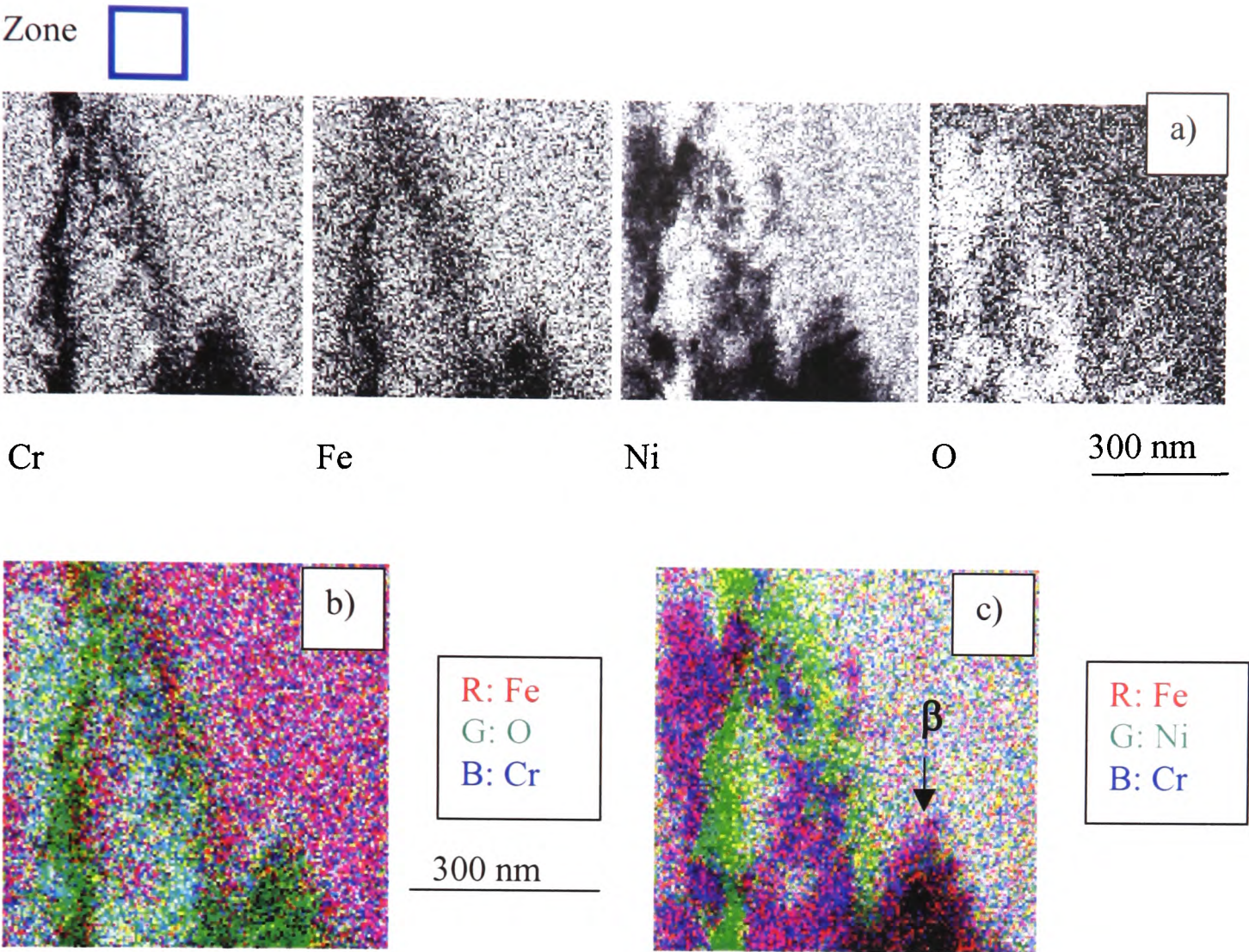


Fig. 8.6.9. a) EDX maps from the area under the blue box in Fig. 8.6.7 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

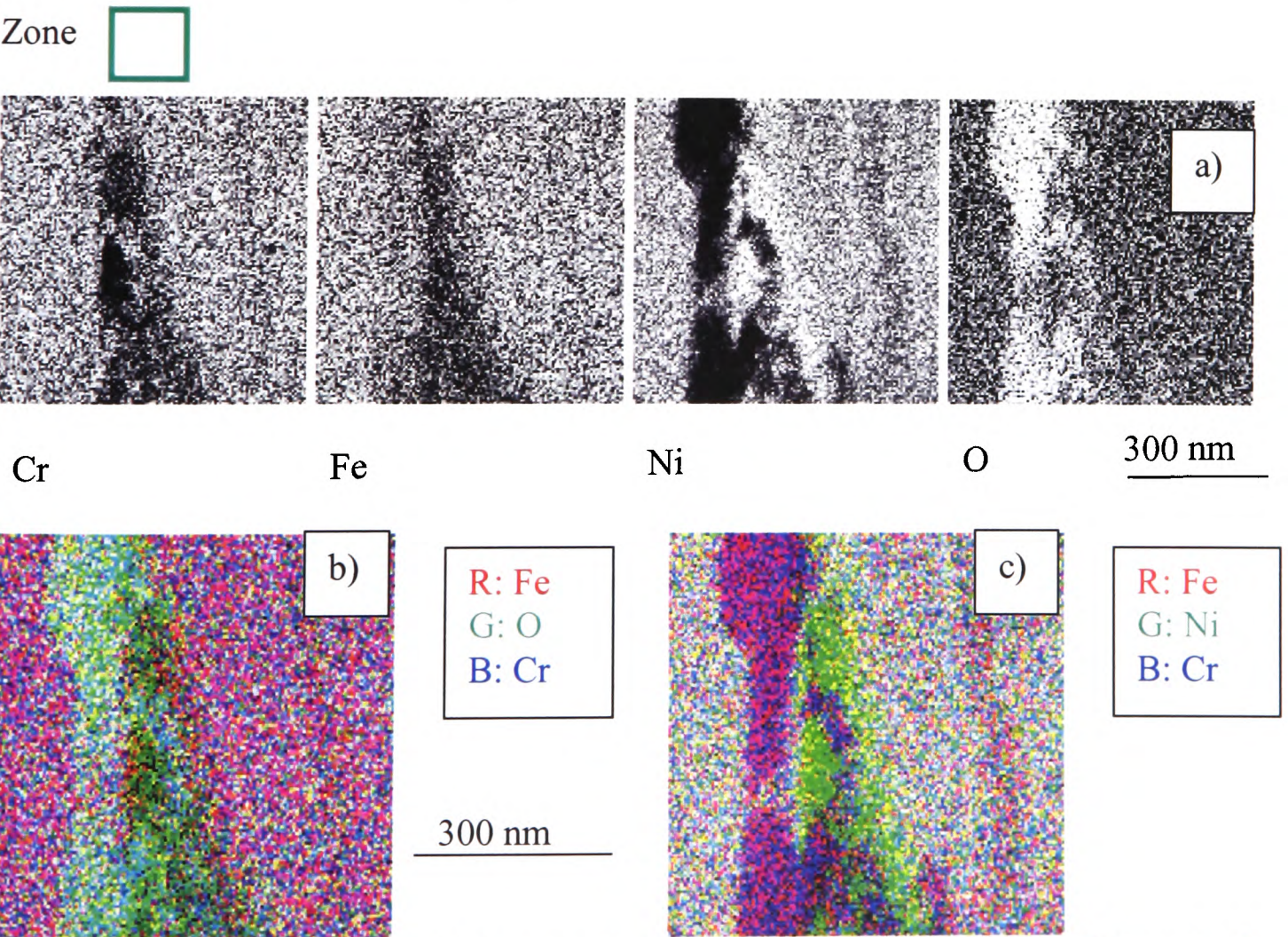


Fig. 8.6.10. a) EDX maps from the area under the green box in Fig. 8.6.7 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

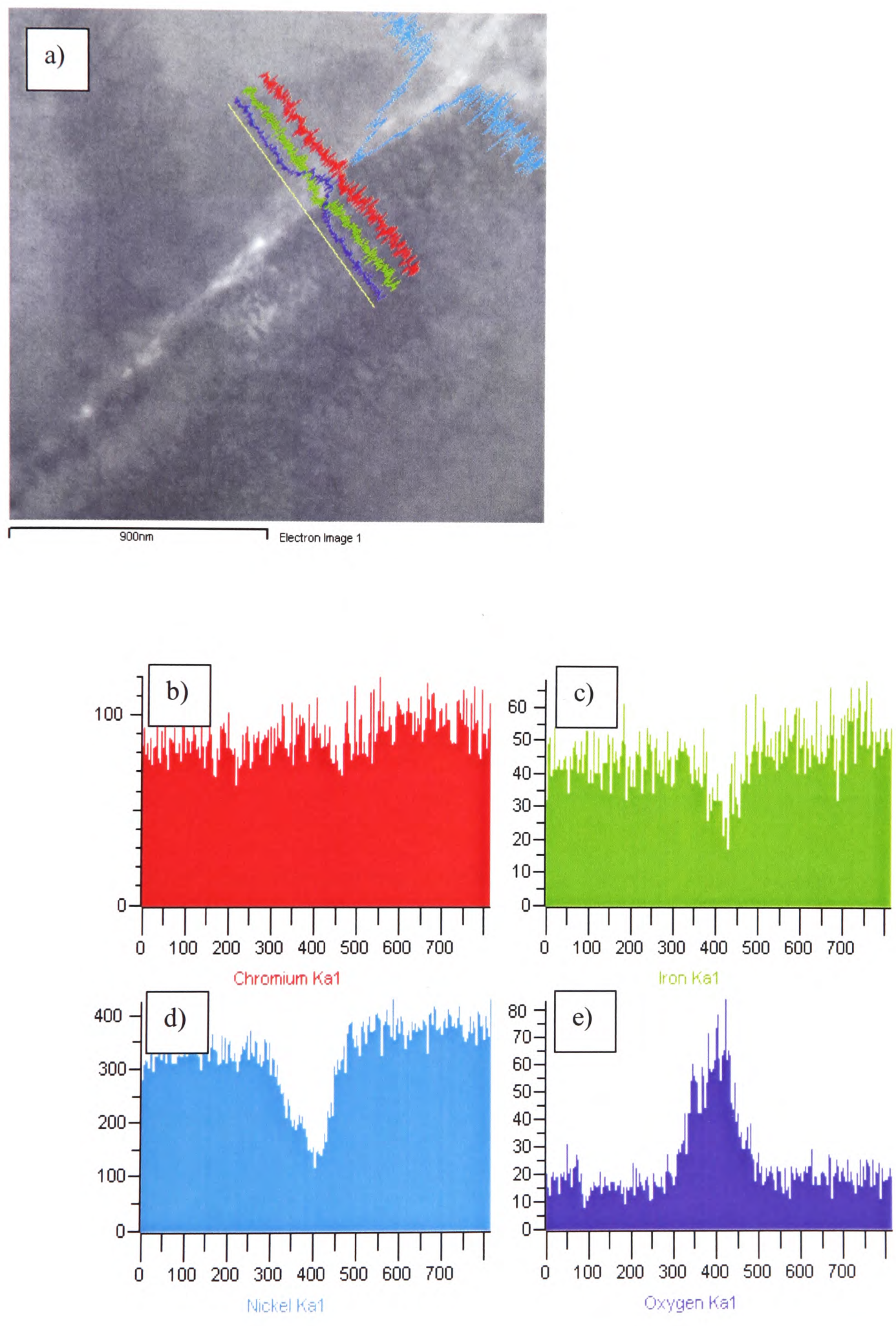


Fig. 8.6.11. EDX qualitative line profile across grain boundary A (acquired with the INCA system in the CM20).

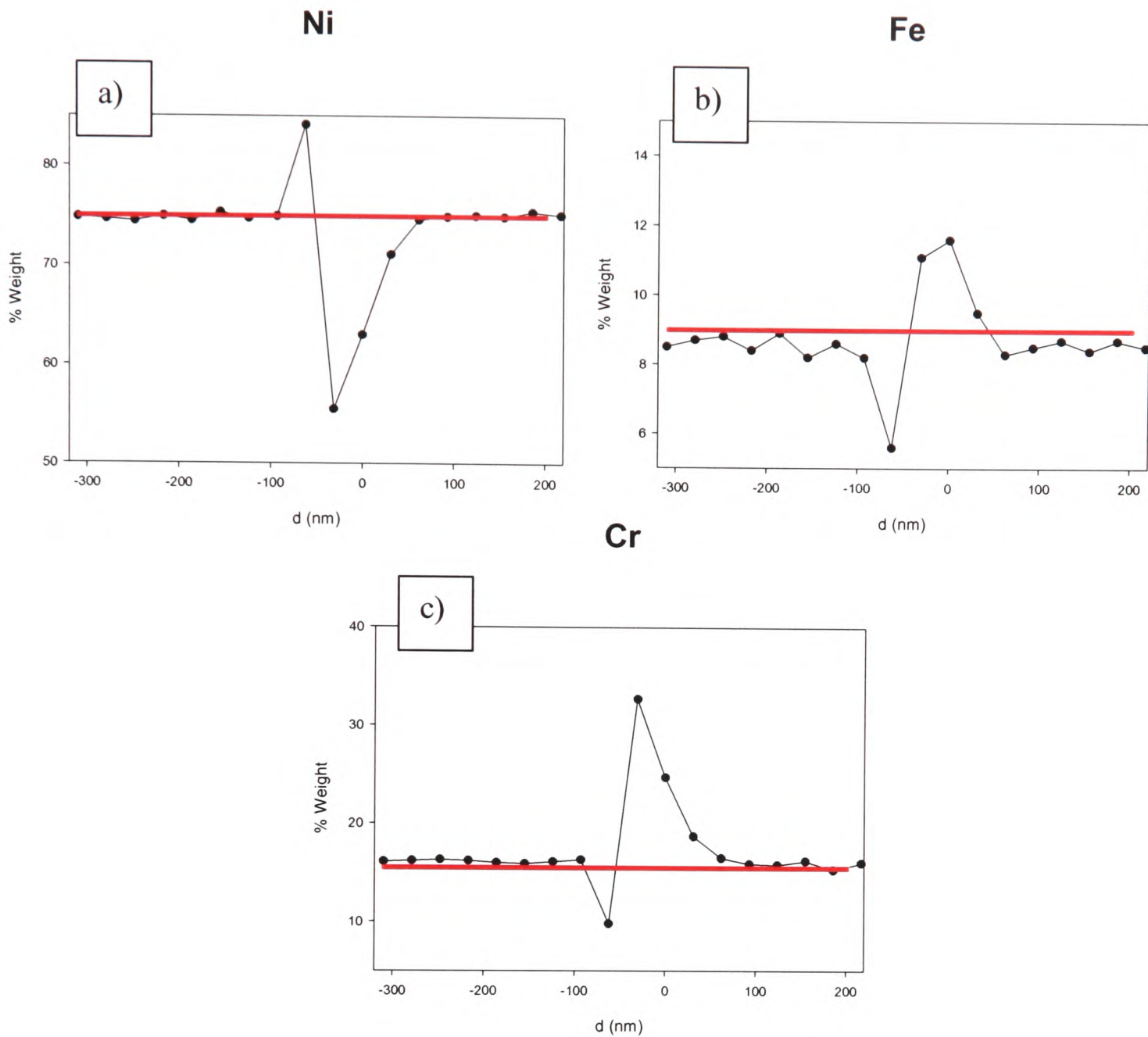


Fig. 8.6.12. EDX compositional line profile across attacked grain boundary A. Note that O has not been included in the quantification. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.7$, $\sigma(\% \text{ wt. Fe}) = 0.3$, $\sigma(\% \text{ wt. Cr}) = 0.4$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.6$, $\sigma(\% \text{ wt. Fe}) = 0.2$, $\sigma(\% \text{ wt. Cr}) = 0.2$ (acquired with the LINK system in the HB501). The nominal composition of the alloy is indicated by the red lines.

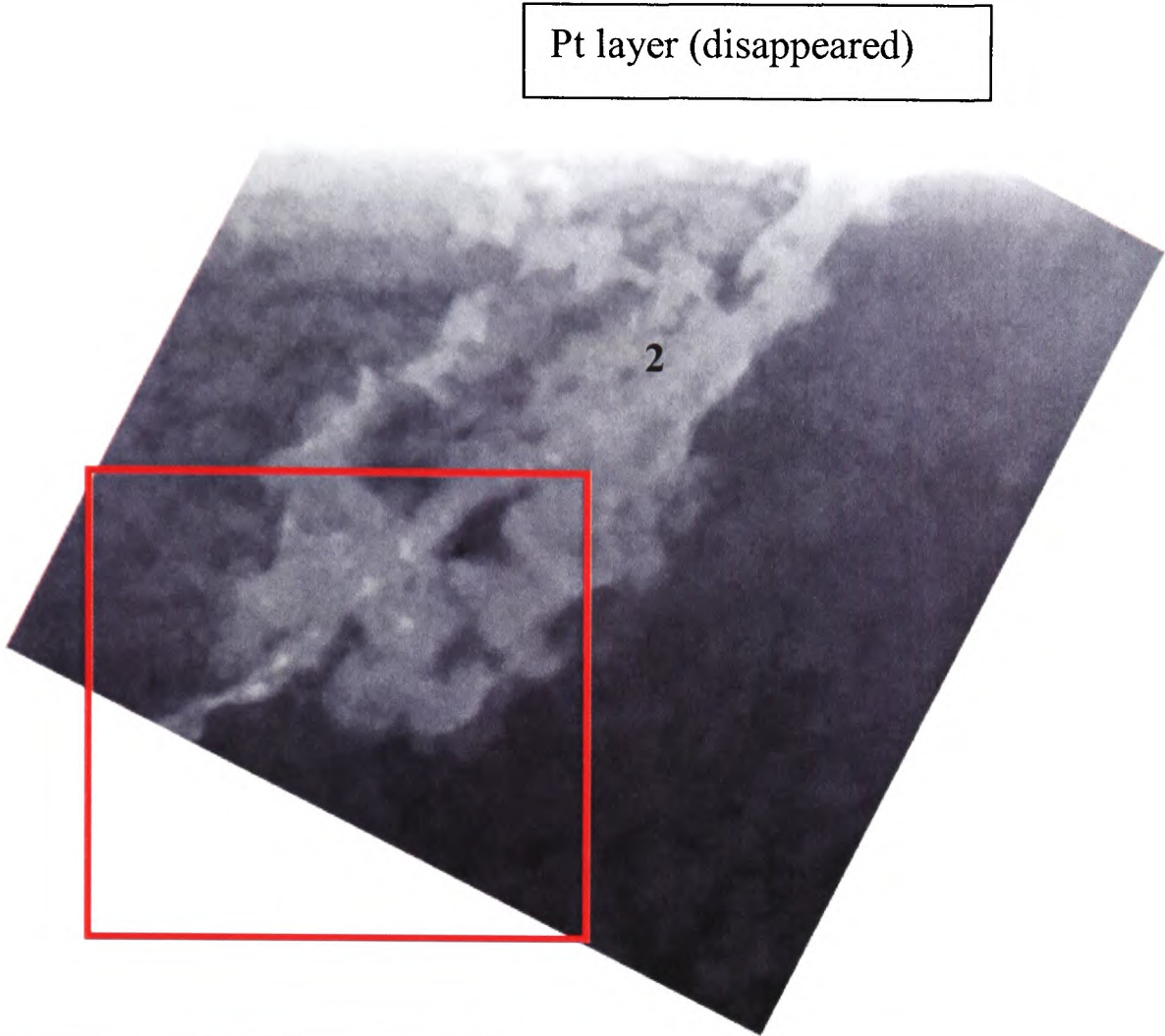


Fig. 8.6.13. STEM BF micrograph showing the attacked grain boundary *A* intersecting the top of the sample (where there was originally a Pt layer) (acquired with the INCA system in the CM20).

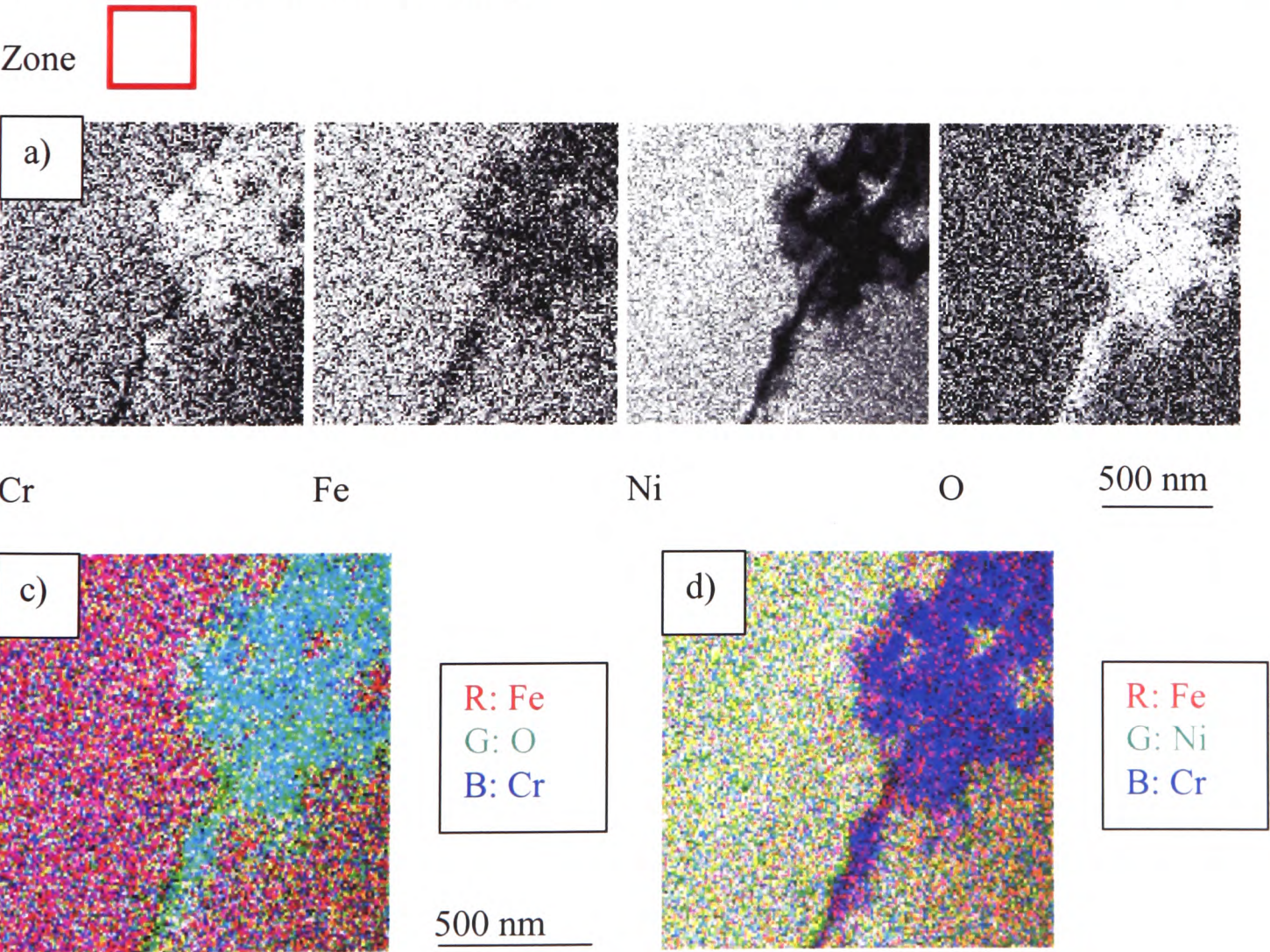


Fig. 8.6.14. a) EDX maps from the area under the red box in Fig. 8.6.13 (acquired with the LINK system in the HB501); b) and c) RGB composition images.

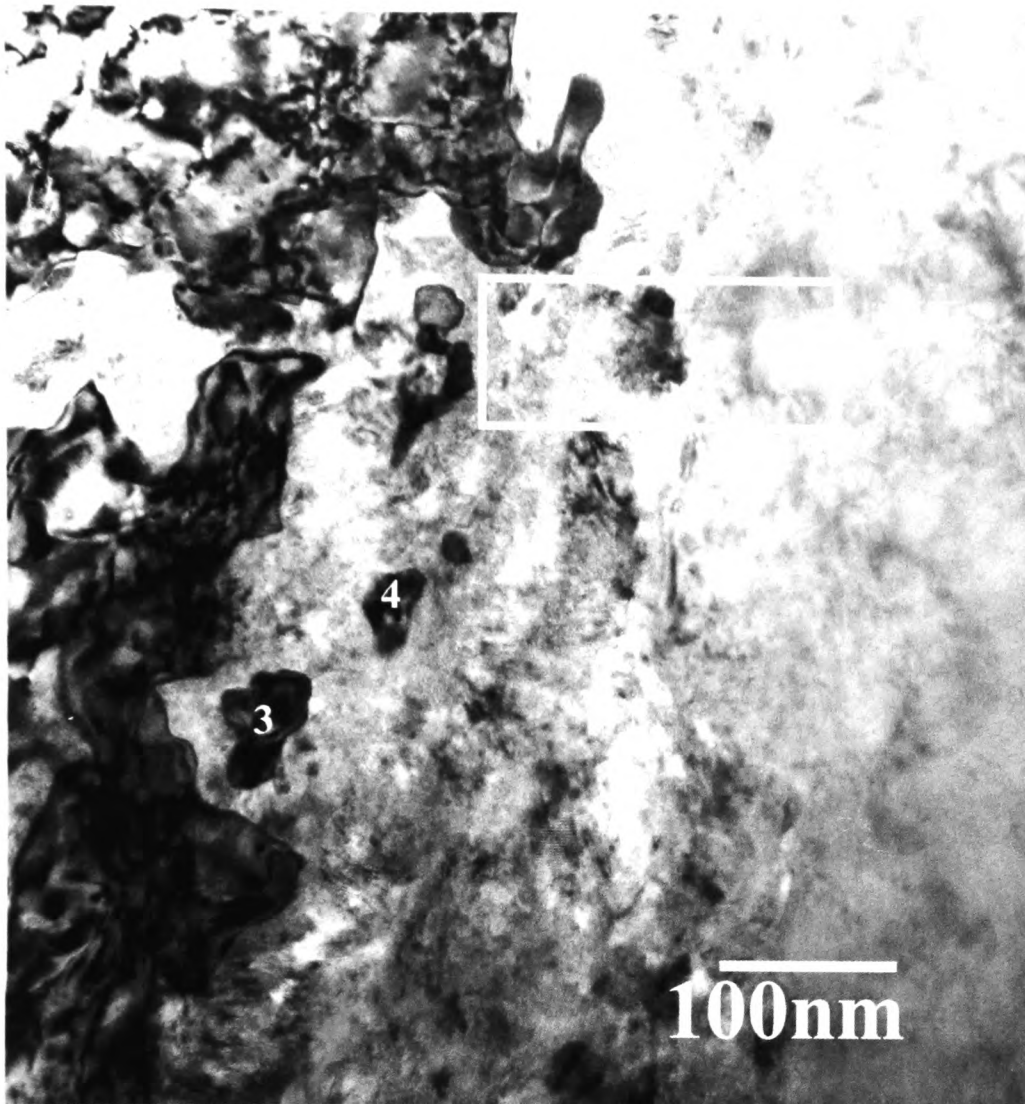


Fig. 8.6.15. TEM BF micrograph showing the grain on the left in a zone-axis (dark) and the attacked grain boundary with Cr_2O_3 . The picture was taken in focus (acquired with the CM20).

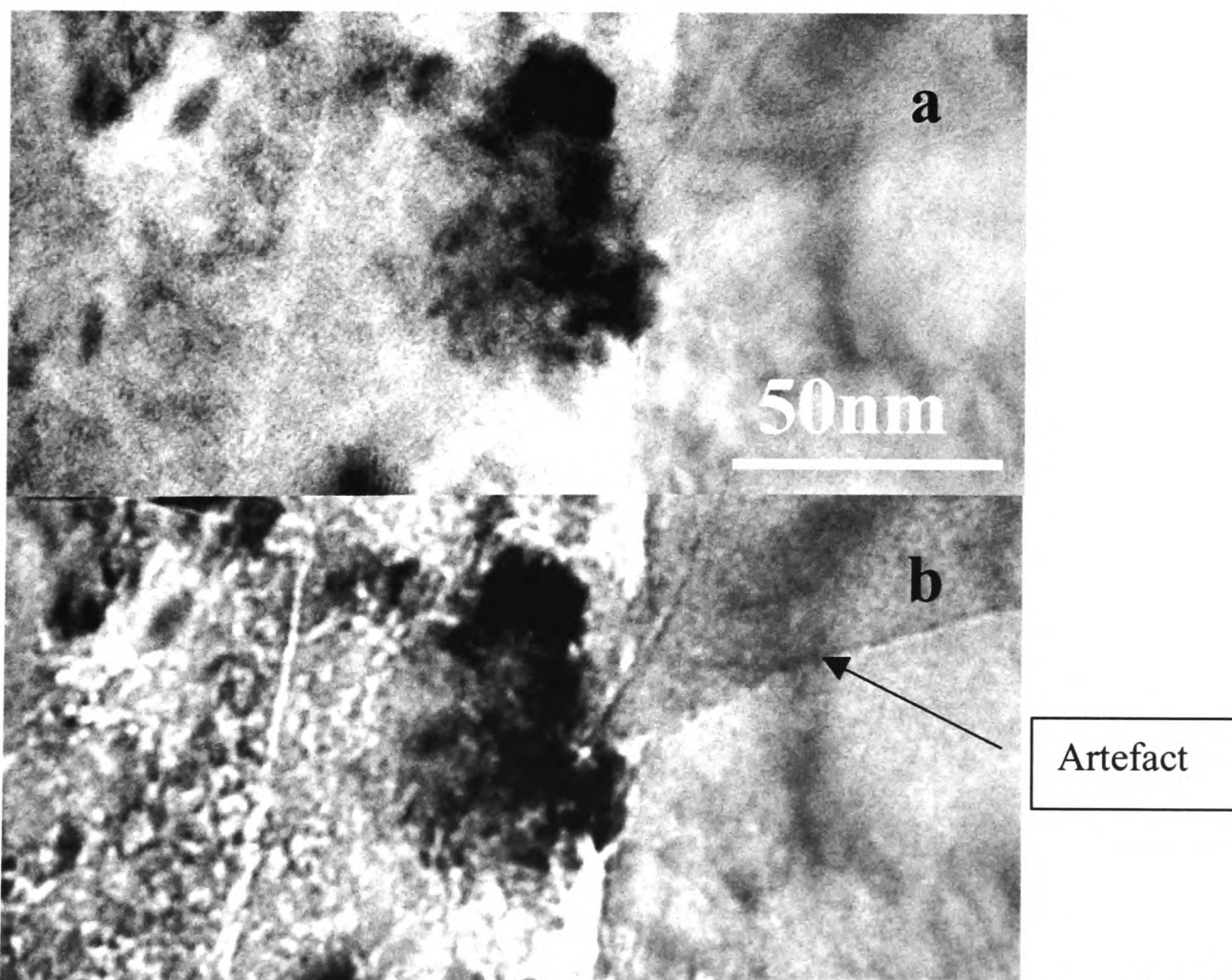


Fig. 8.6.16. TEM BF micrographs showing the area boxed in the previous figure in focus (a) and underfocussed with $\Delta f = -700 \text{ nm}$ (b) (acquired with the CM20)

8.6.3.3 Particles

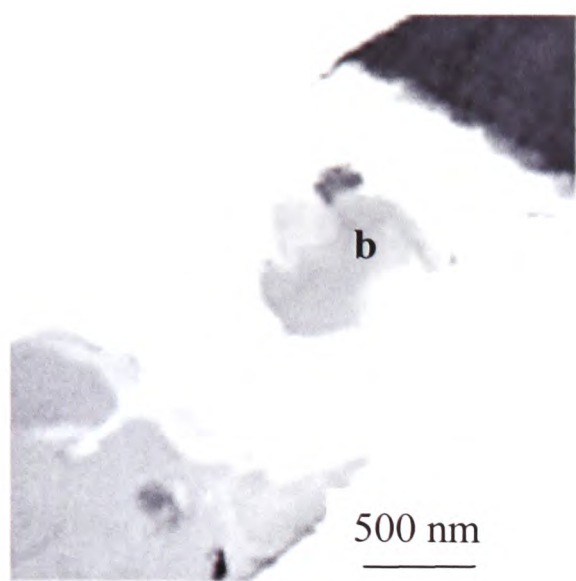
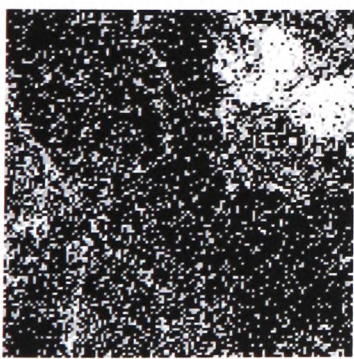
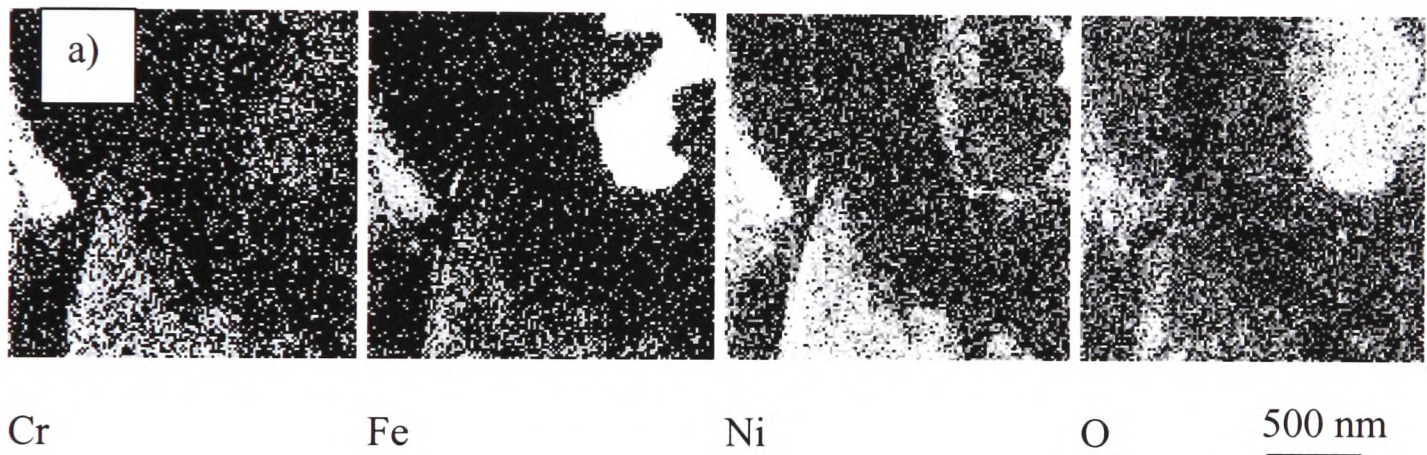
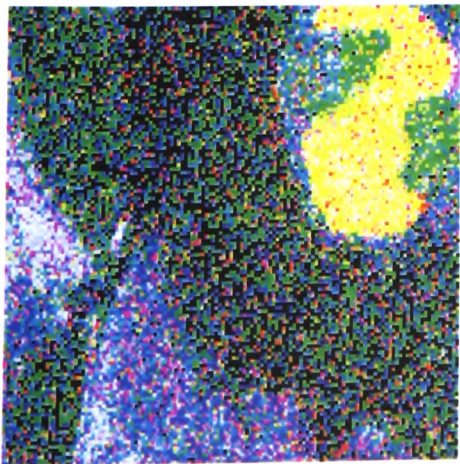


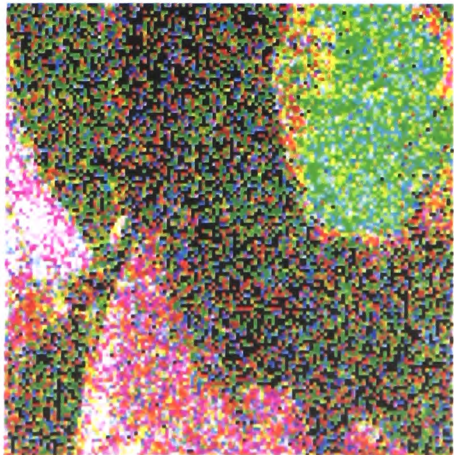
Fig. 8.6.17. STEM BF micrograph showing a “strange” particle (b) embedded in the nanocrystalline NiO (acquired with the INCA system in the CM20).



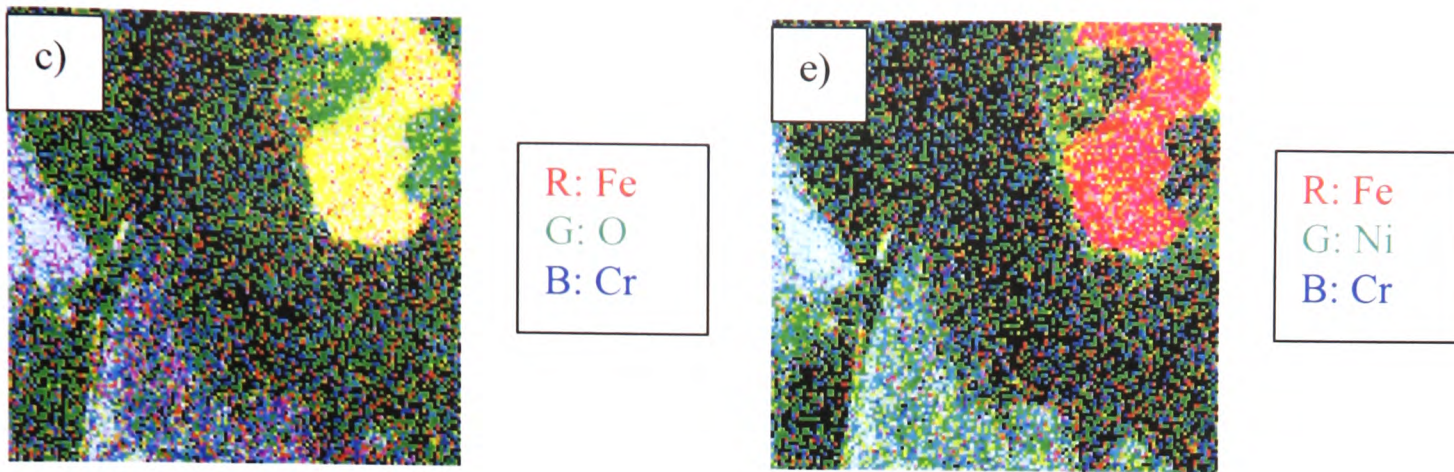
Si



R: Fe
G: O
B: Ni



R: Ni
G: O
B: Cr



*Fig. 8.6.18. a) EDX maps from particle **b** and surroundings (acquired with the LINK system in the HB501); b) and c) RGB compositions of images.*

8.7 Sample 7: General observations

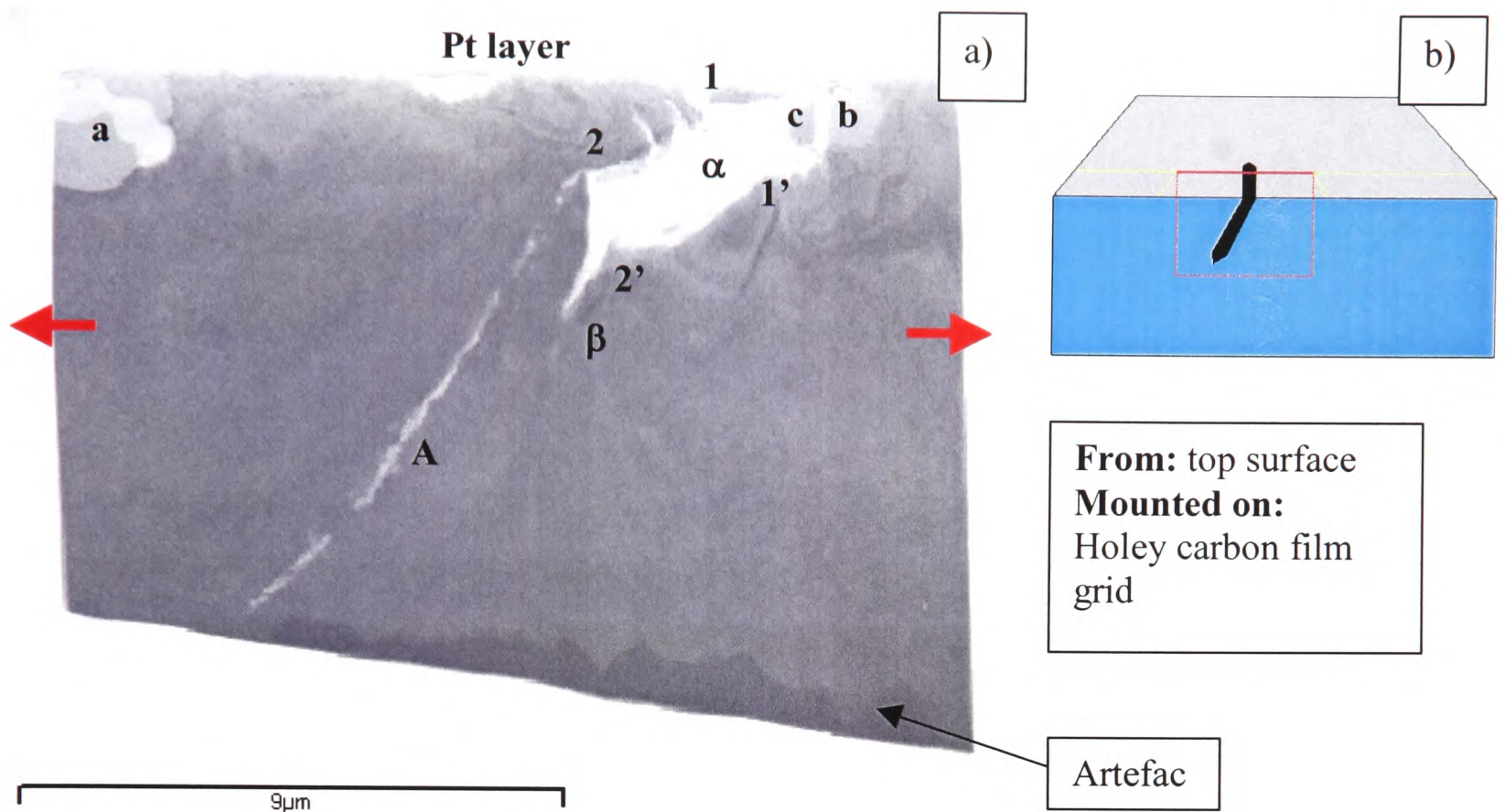


Fig. 8.7.1. a) STEM BF micrograph showing sample 7 after plucking. The loading direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) Sketch showing the orientation of the sample.

Sample 7 (Fig. 8.7.1a) was prepared from the top surface (in grey in Fig. 8.7.1b) and it contained a blunt crack (α) which continued propagating along grain boundary (A). The blunted crack seems to have opened abruptly (as features 1-1' and 2-2' match on both flanks), and as a consequence of this, many intragranular cracks developed in the sample, β being the most obvious. This sample also contained some inclusions that have also been characterized as a Ti-Mg particle (a) and TiN (b), . Particle c was identified as NiO. Such inclusions have been seen in many samples analyzed, especially those prepared directly from the top surface. The artefact arrowed in Fig. 8.7.1 is an artificially thick region which was not milled away properly during the final steps of the FIB sample preparation.

8.7.1 Analysis

8.7.1.1 Flanks

The flanks of crack α contained the same features as other blunted cracks described previously: a thin Cr_2O_3 layer (of the order of 50 nm) separating the matrix from the nanocrystalline NiO.

8.7.1.2 Cracks

Fig. 8.7.2 shows the cracks and all the areas that have been mapped using EDX. The first of these areas appears boxed in red and contains two intragranular cracks (χ and δ). These cracks were found to contain Cr_2O_3 layers on the flanks similar to those found in intergranular cracks. The EDX maps of Fig. 8.7.3a show that these cracks are only filled by NiO. Cr_2O_3 layers are evident only on their flanks, as can be seen in Fig. 8.7.3b (in light blue). The Cr-rich layer also extended to the flanks of crack α , as can be seen in Fig. 8.7.3c.

The large intragranular crack β also had a Cr-oxide layer on its flanks and at its tip (Fig. 8.7.4a). This Cr-oxide layer was of thickness about 50 nm (light blue in Fig. 8.7.4b). Considerable diffusion of O was found on the right flank of crack β and ahead of the crack tip of crack β as can be seen in the O map in Fig. 8.7.4a. A qualitative EDX line profile was acquired ahead of the crack tip, across the slip band that followed crack β , as can be seen in Fig. 8.7.5a. Again, the number of counts from the Cr (Fig. 8.7.5b) remained constant across the attacked zone, while the number of counts from the Ni (Fig. 8.7.5d) decreased considerably. At the slip band line, the O counts (Fig. 8.7.5e) increased, suggesting diffusion of O along the slip plane and rejection of Ni.

In Fig. 8.7.6 the region at the beginning on the attack of grain boundary A is analyzed (outlined by the purple box in Fig. 8.7.2). It can be seen that the flanks of crack α have a Cr_2O_3 layer (light blue in Fig. 8.7.6b) and that the Ni clusters have formed along the boundary (in red in Fig. 8.7.6b). However, the oxygen seemed to dissolve these Ni clusters, breaking through them and diffusing along the whole

boundary, as can be seen in Fig. 8.7.6b (oxygen in green). Although it is difficult to appreciate in the EDX maps (Fig. 8.7.6a), Cr_2O_3 filled all the Ni-depleted regions.

In Fig. 8.7.7, grain boundary A is examined at a higher magnification, in an area with a Ni-cluster (under the blue box in Fig. 8.7.2). The EDX maps in Fig. 8.7.7a reveal that the Ni appears to be rejecting the Fe to the right. In Fig. 8.7.7b the Cr-oxide layer is distinguishable (in light-blue) from the thinner Cr_2O_3 in the central region very rich in oxygen (green). In Fig. 8.7.7b, it can be also be seen that only the Cr occurs together with oxygen, the Ni-rich regions being completely O-free.

The Ni-cluster shown in Fig. 8.7.8, an enlargement of the region at the purple box in Fig. 8.7.2, has been analyzed using EELS (Fig. 8.7.9). In the EELS spectrum, only the Ni edge area is shown, as no other elements were detected in the analysis.

8.7.1.3 Particles

In Fig. 8.7.10a, particle **a** can be seen in detail. Its compositional analysis revealed that it was an inclusion, containing Ti, Mg and S. Fig. 8.7.10e shows that it is basically a Ti inclusion with 2 inclusions of Mg-oxide (Figs. 8.7.10b and 10c). On the left flank, the particle is enriched in sulfur (Fig. 8.7.10d).

In Fig. 8.7.11, the areas chosen for the EDX maps of particles **b** and **c** are boxed. The EDX shown in Fig. 8.7.12a from the area boxed in red in Fig. 8.7.11 revealed that particle **b** is a Ti-rich inclusion. These maps could also suggest that the particle is a Ti oxide, but later quantitative EDX analysis showed that it was a TiN particle. The reason why the particle appeared rich in O in the EDX map is the proximity of the K peaks of O and N. The window used for the O map probably detected counts from the N peak. In Fig. 8.7.12d we can see how the surroundings of the particle have been attacked and the formation of Cr_2O_3 (in light blue) has rejected Ni (in red).

Particle **c** was analyzed using EDX maps (Fig. 8.7.13). Its orange (Ni+O) colour in Fig. 8.7.13b, indicated that it was a NiO monocrystal (confirmed by μD), similar to the outer part found surrounding the NiFe_2O_4 duplex particles. It can also be

seen how the flank of the crack shown at the bottom of the maps has been attacked and has a Cr-oxide layer (as light blue in Fig. 8.7.13b).

TiN inclusions have been found regularly in the matrix (intragranularly), although not usually as big as particle **b**. NiO particles have been also found inside the blunt crack, embedded in the nanocrystalline NiO. EDX spectrum were acquired from both particles. The quantification is shown in Table 1:

Spectrum	N	O	Ti	Cr	Fe	Ni	Total
Particle b	47.78		51.21	1.01			100.00
Particle c		58.38		0.36	1.64	39.63	100.00
Oxide around particle b		67.92		21.56	3.53	6.99	100.00
Oxide in the crack flank		67.62		22.68	3.42	6.28	100.00

Table 1: Quantitative results from particles **b** and **c** and neighbouring oxides. All results in Atomic Percent

A smaller particle close to the flank of crack α (particle **d**) has been also analyzed (Fig. 8.7.14). Particle **d** was almost round, had a diameter of 20 nm and was found almost touching the flank of the crack. Other smaller particles were also found around it, but were not identified.

Several elemental GIF maps (Fig. 8.7.15) were acquired in the region shown in Fig. 8.7.14. An EELS spectrum acquired from the particle (Fig. 8.7.16) revealed that the major enrichments were Cr, Ni and O, suggesting that the particle was a Ni-Cr spinel (probably NiCr_2O_4) with some Fe.

8.7.2 Main observations

- 1 μm long intragranular crack found after an intergranular crack blunted with high-O diffusion associated.
- Two large inclusions found in the sample.

8.7.3 Sample 7 – Data collection

8.7.3.1 Cracks

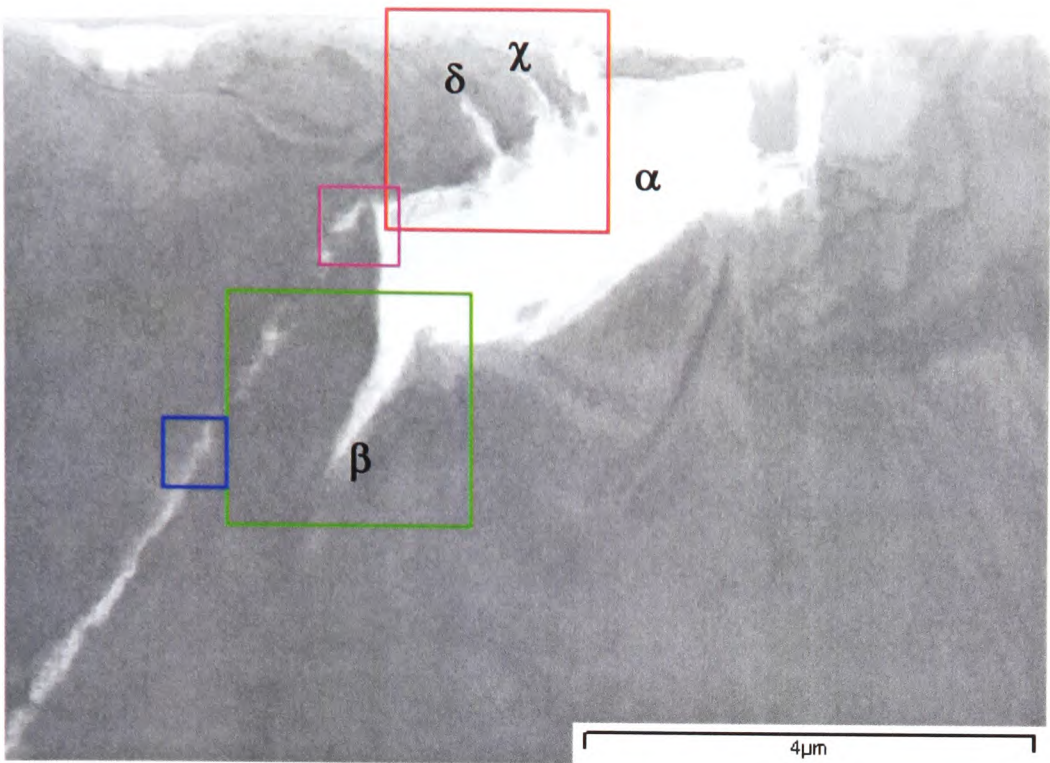
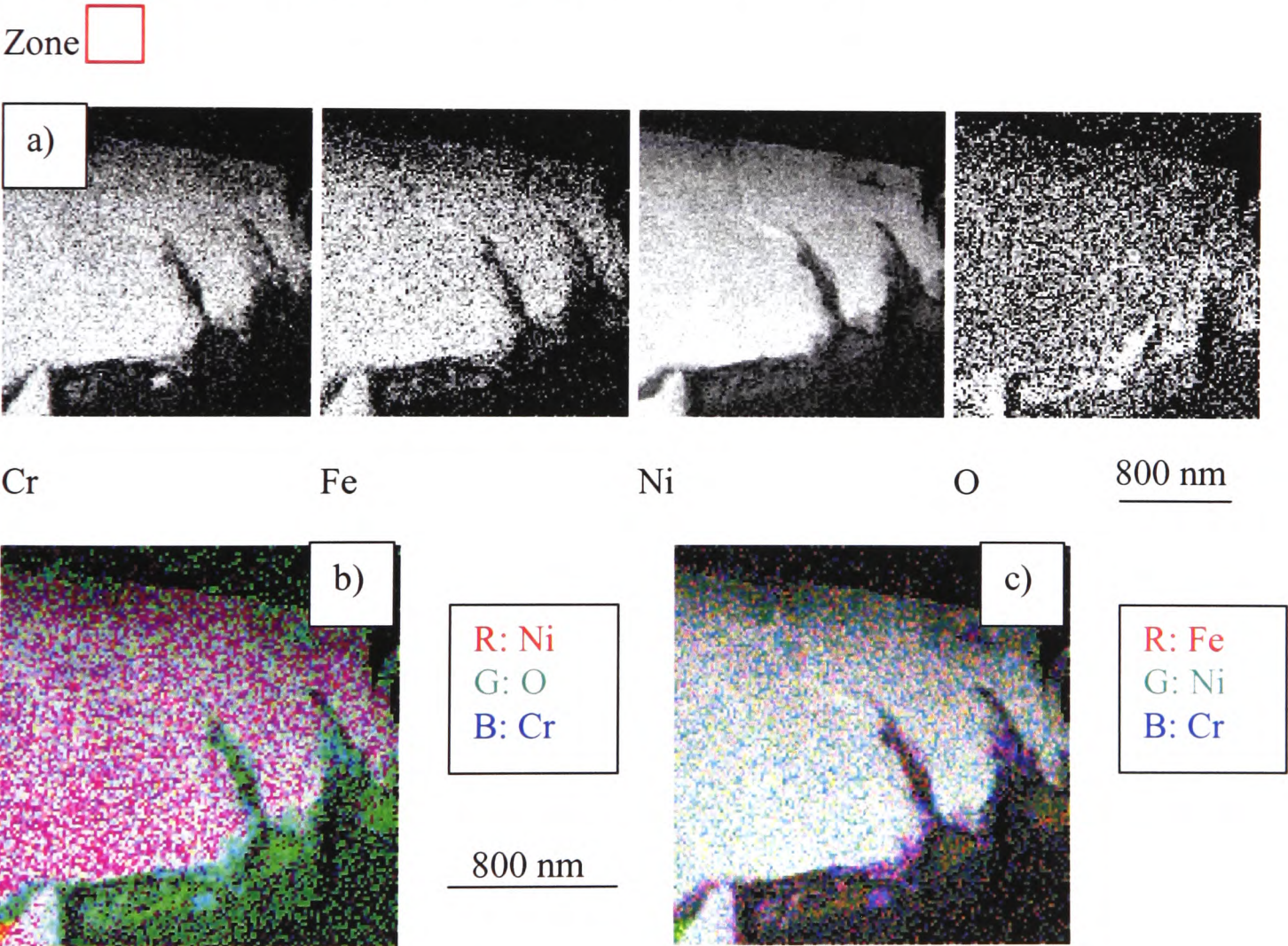


Fig. 8.7.2. STEM BF micrograph showing the areas with coloured boxes chosen for EDX mapping (acquired with the INCA system in the CM20).



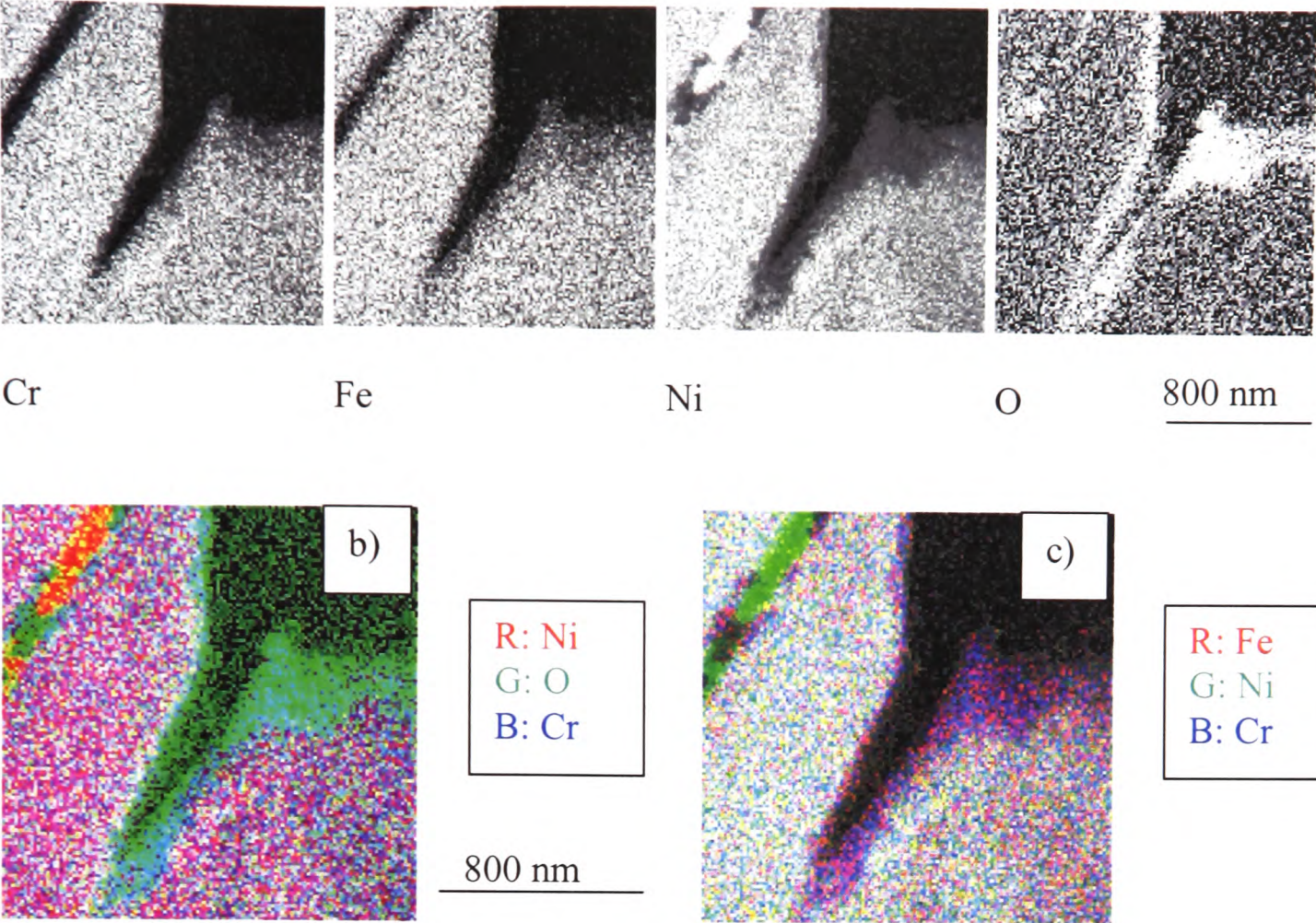
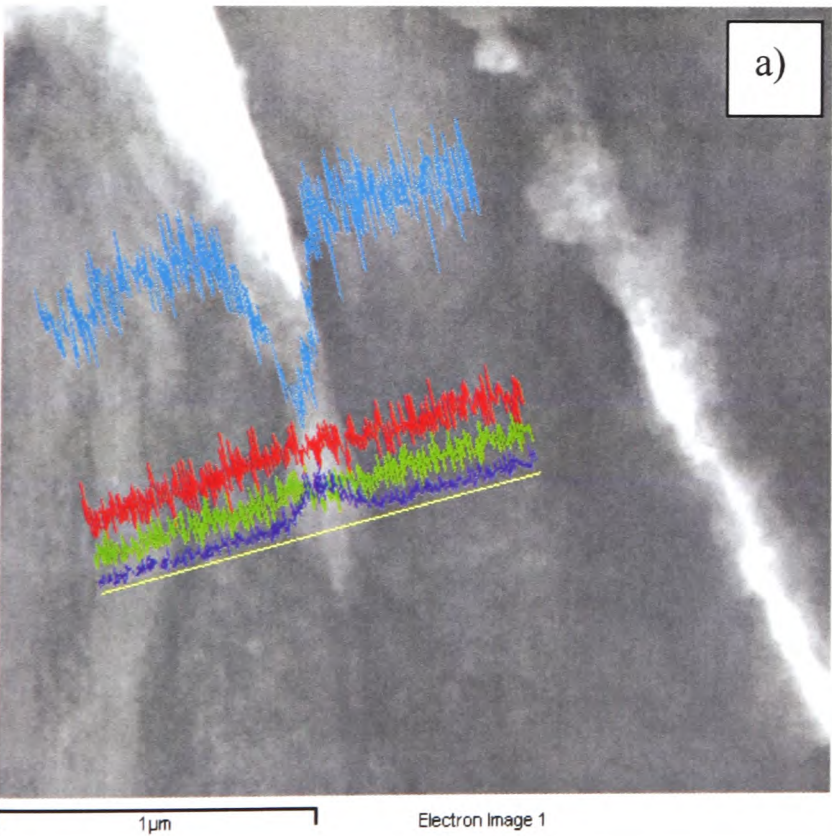


Fig. 8.7.4. a) EDX maps from the area under the green box in Fig. 2 (acquired with the LINK system in the HB501), b) and c) RGB composition of images.



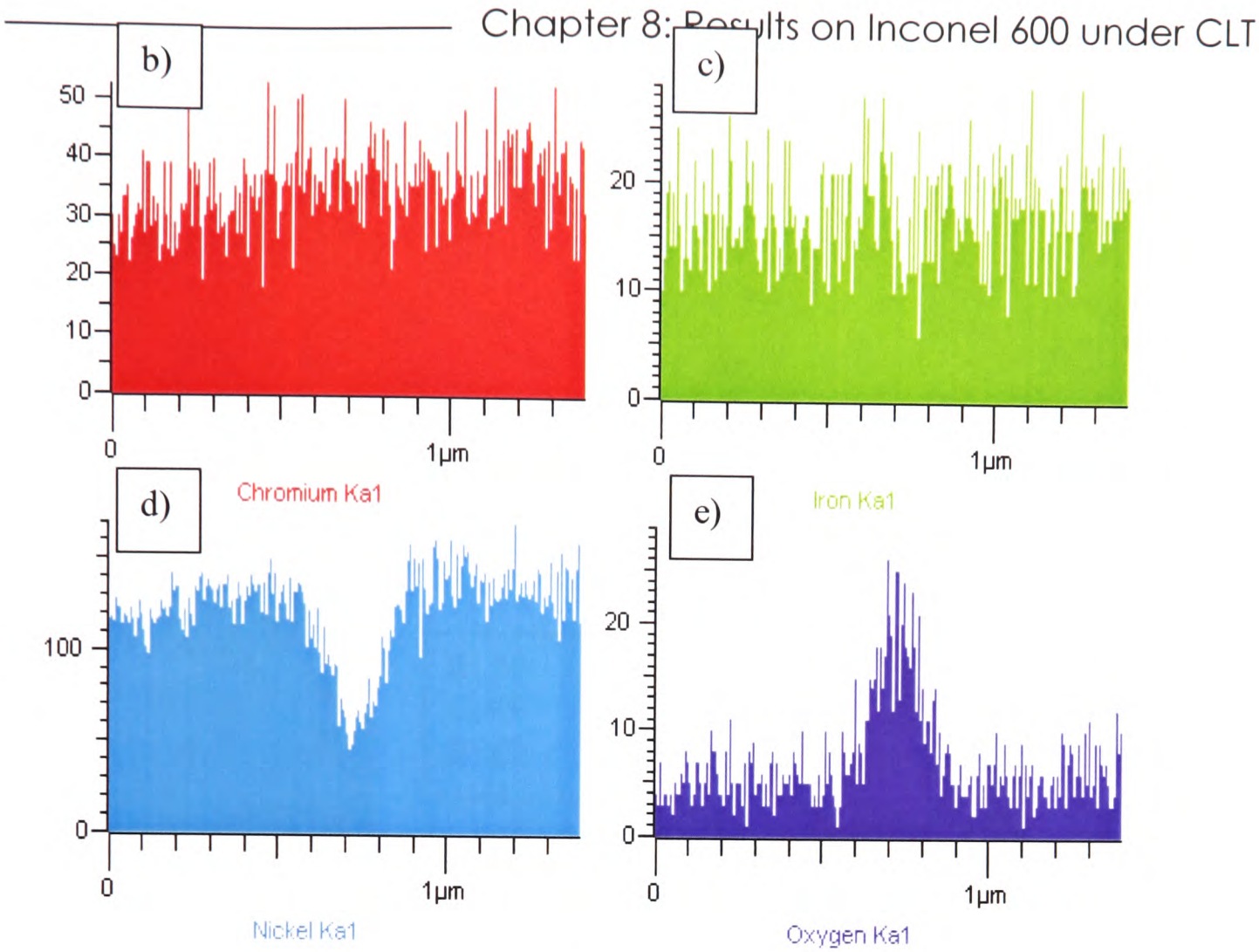


Fig. 8.7.5. EDX qualitative line profile across the intragranular crack β (acquired with the INCA system in the CM20).

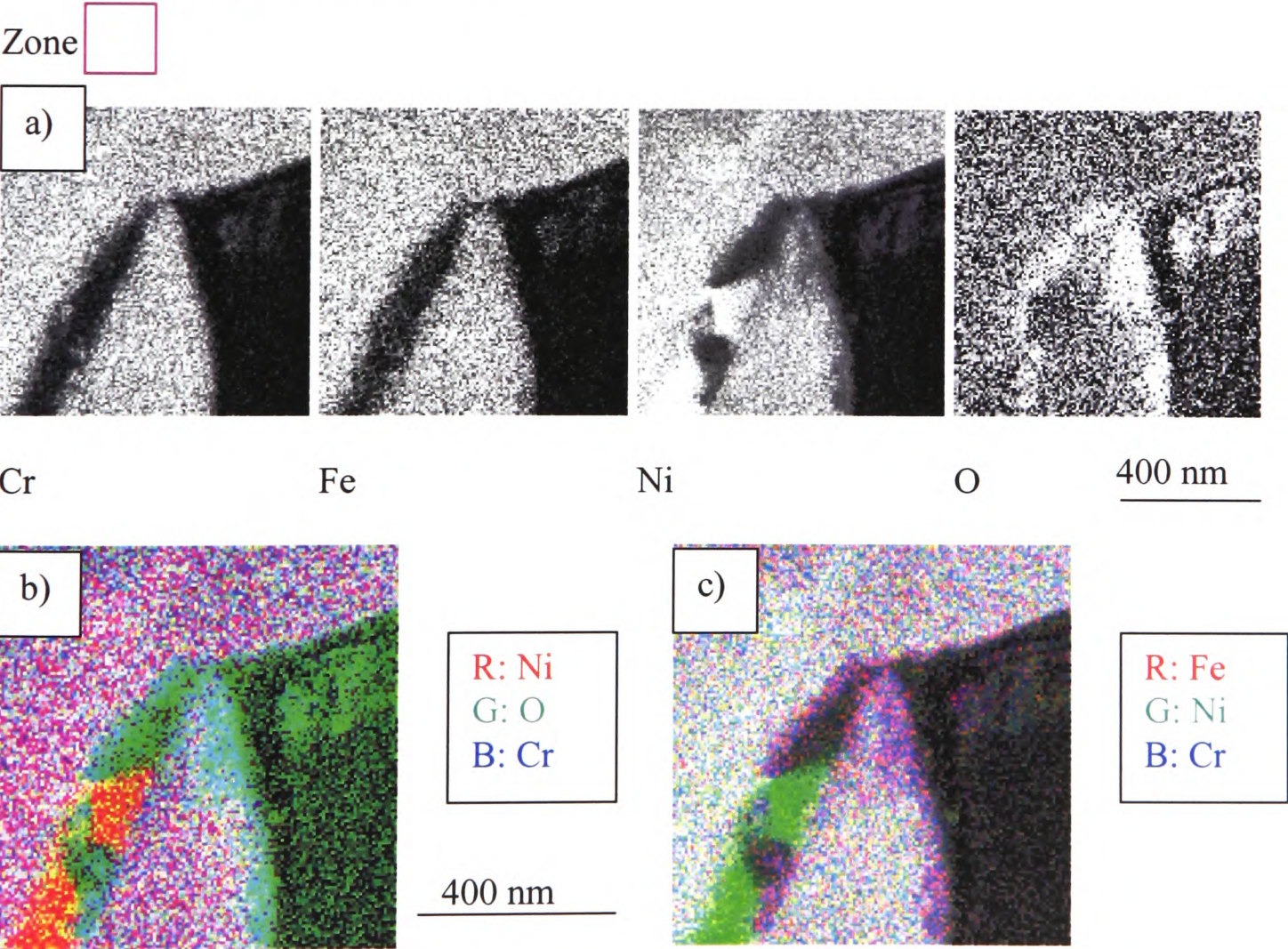


Fig. 8.7.6. a) EDX maps from the area under the purple box in Fig. 2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

Zone

a)

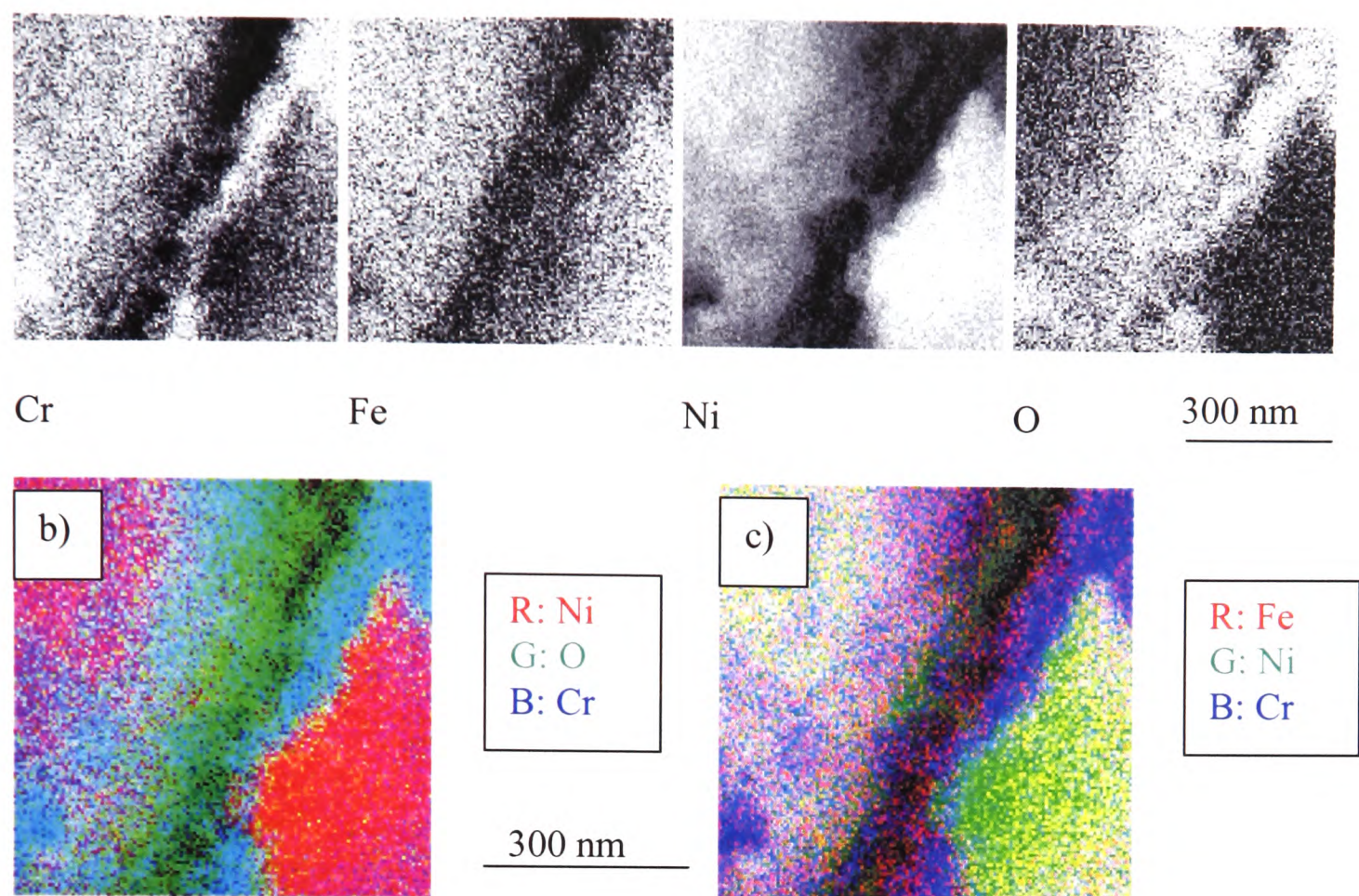


Fig. 8.7.7. a) EDX maps from the area under the blue box in Fig. 2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

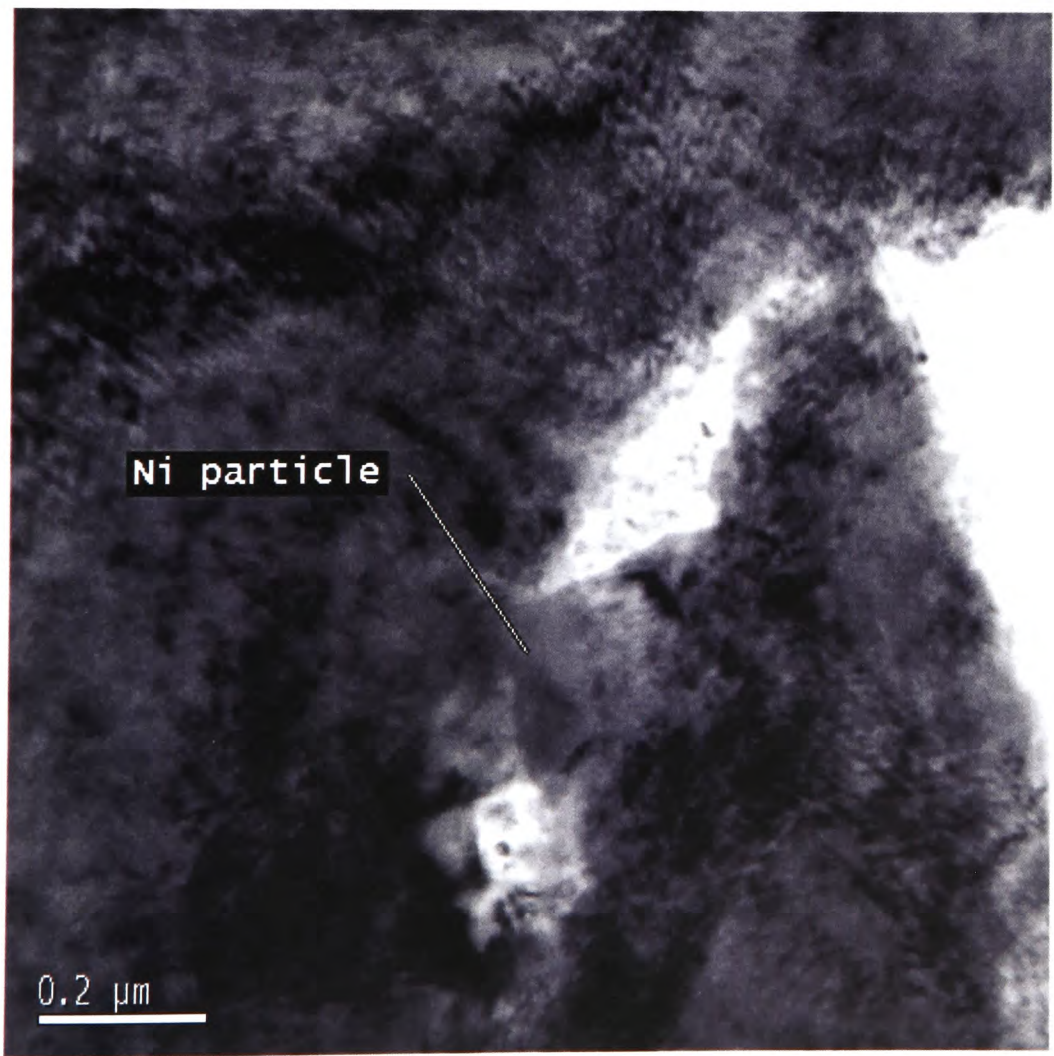


Fig. 8.7.8. TEM BF micrograph showing a Ni cluster close to the entrance of grain boundary A (acquired with a multiscan CCD camera in the 3000F).

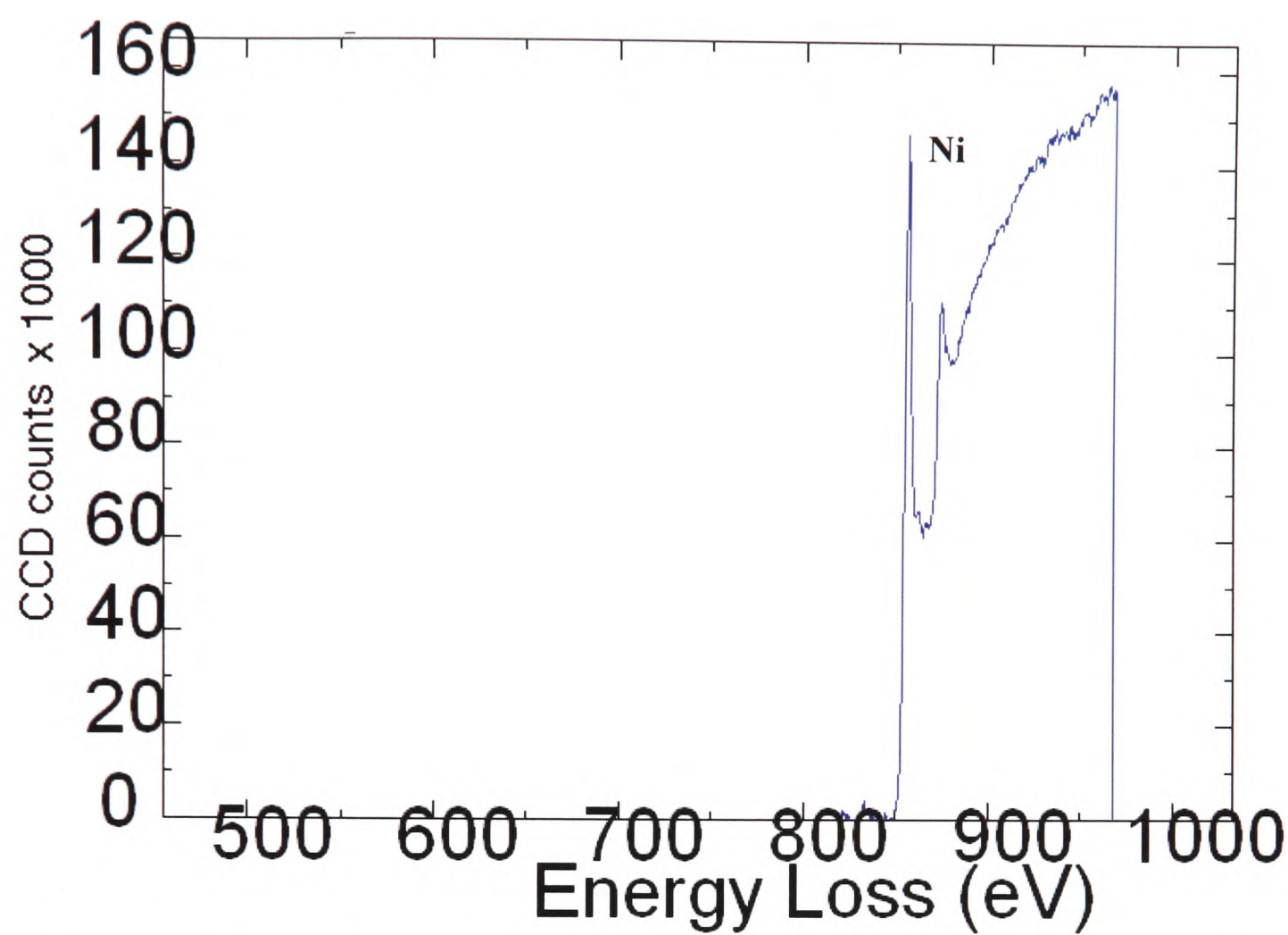


Fig. 8.7.9. EELS spectrum from a Ni particle in grain boundary A. (acquired with the 3000F).

8.7.3.2 Particles

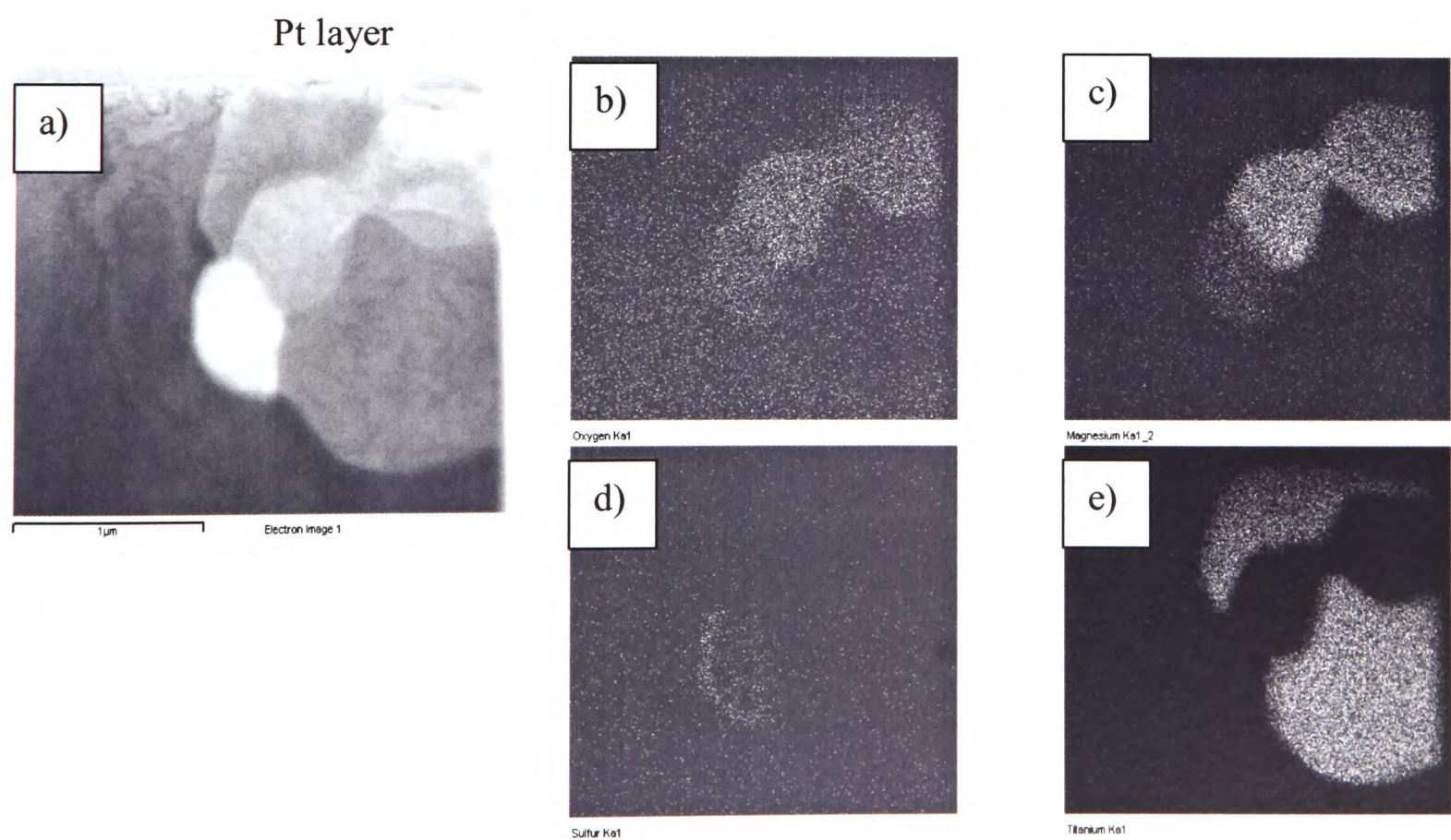


Fig. 8.7.10. a) STEM BF micrograph showing particle a and b),c),d),e) EDX maps from the particle (acquired with the INCA system in the CM20).

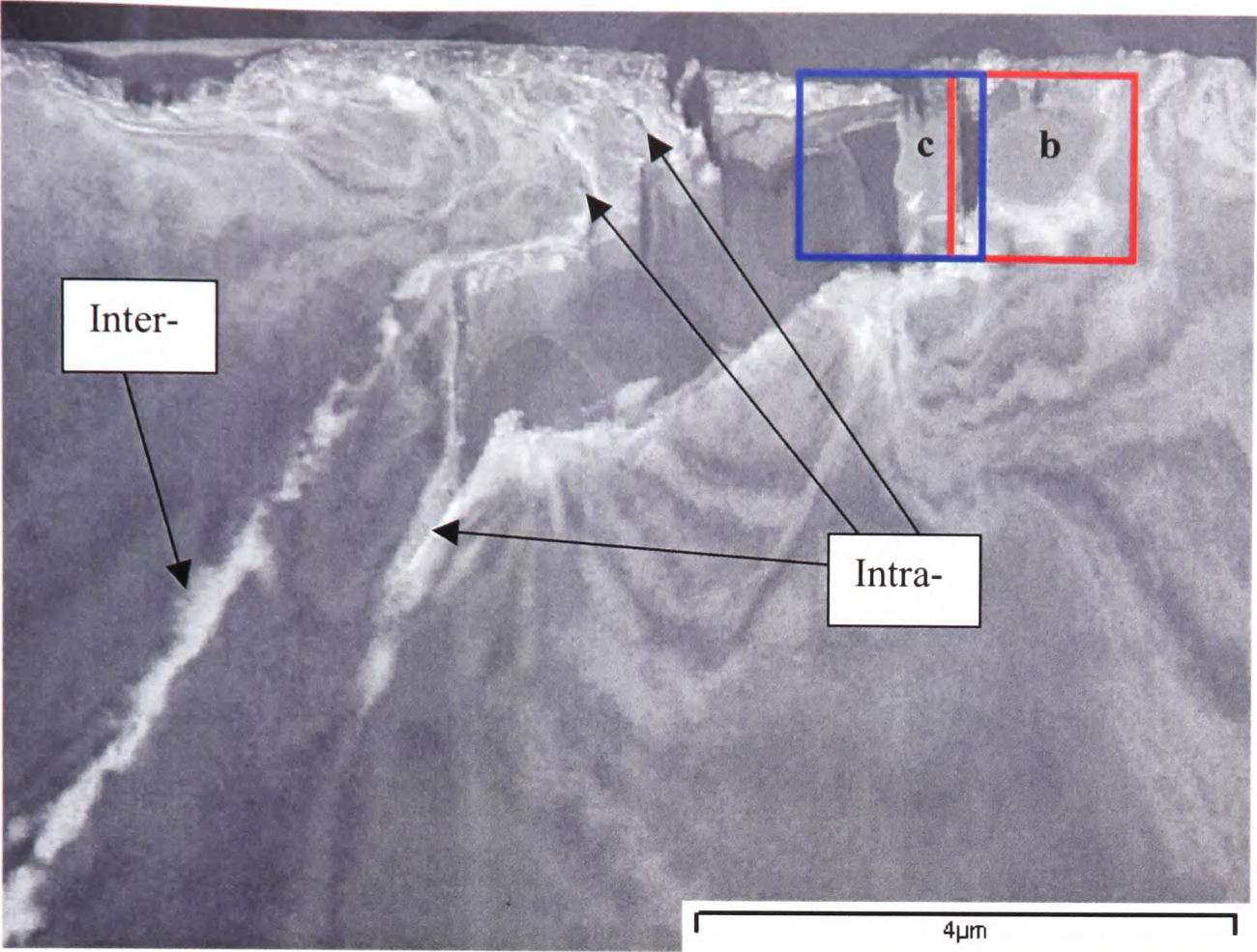
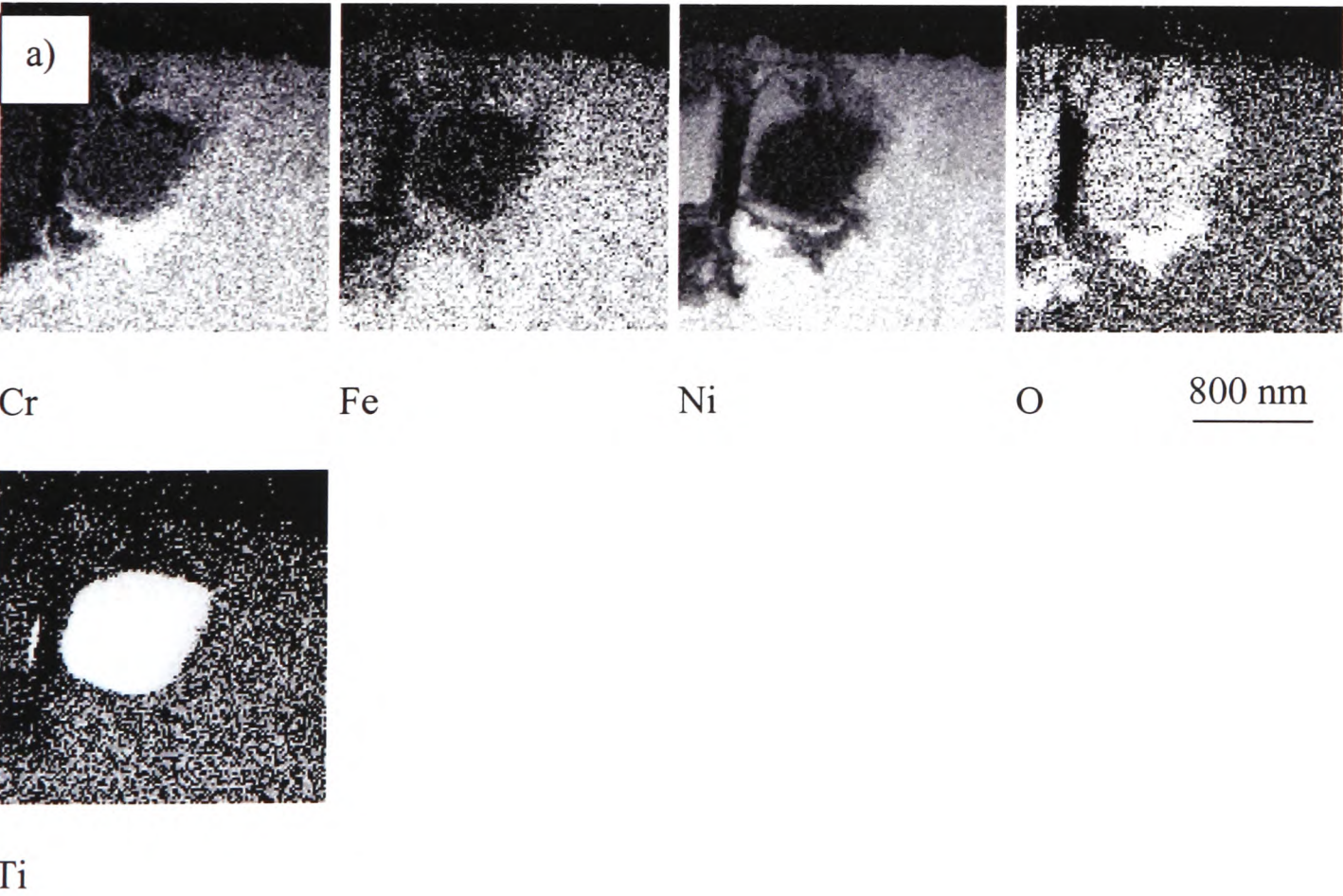


Fig. 8.7.11. STEM DF micrograph showing details of the inter and intragranular attack and the particles *b* and *c* (acquired with the INCA system in the CM20).

Zone 



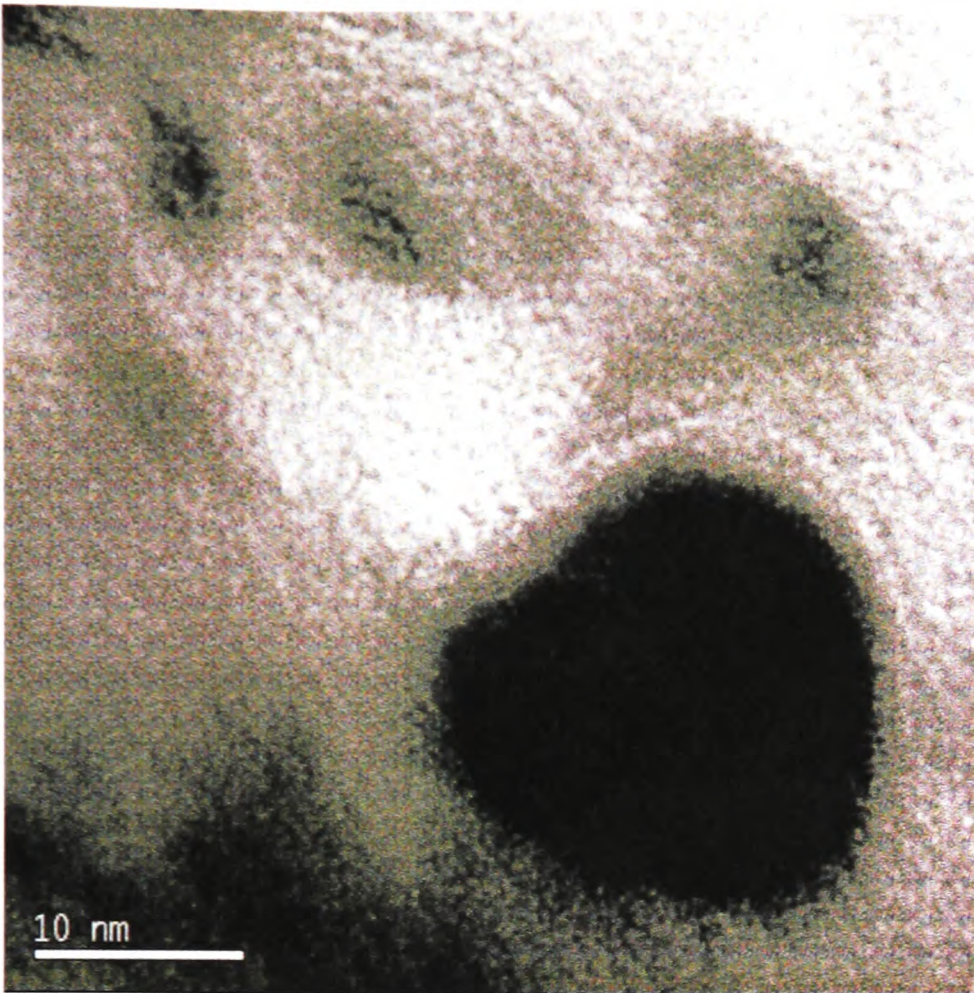
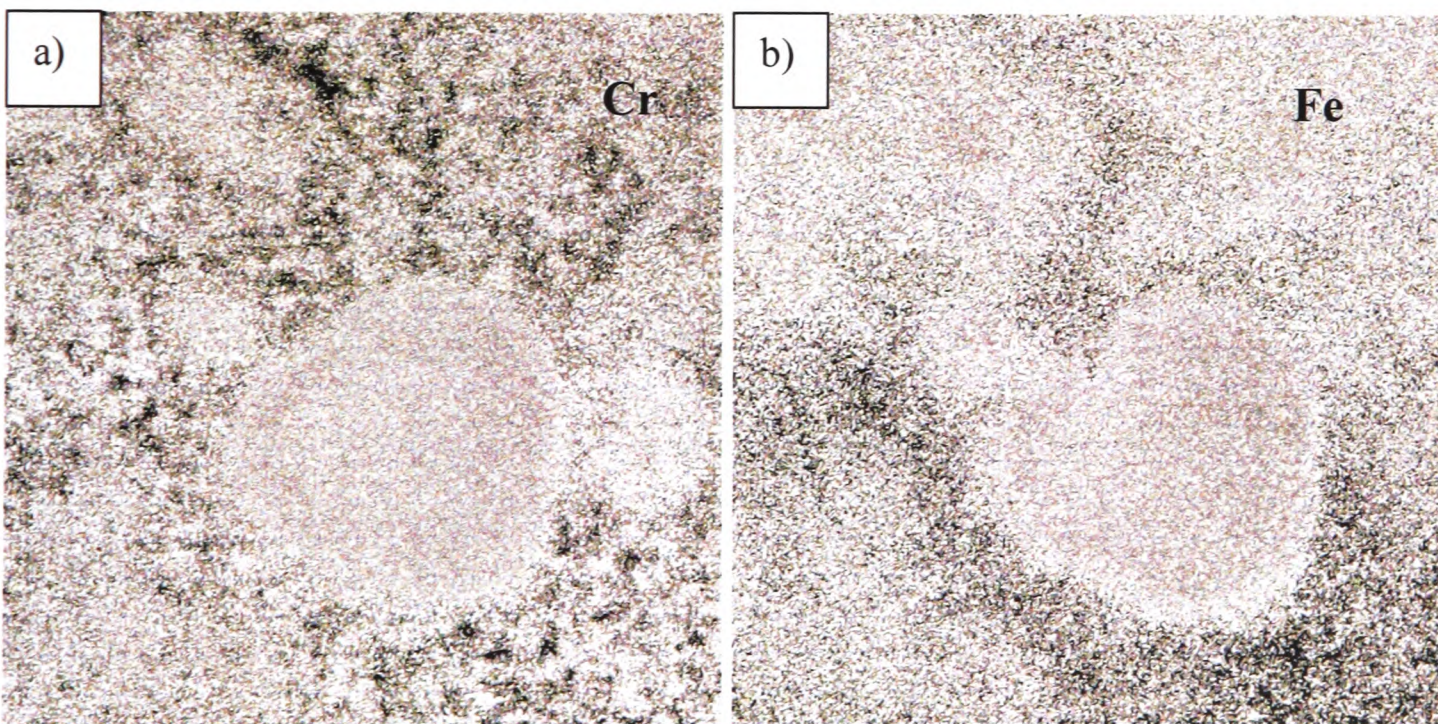
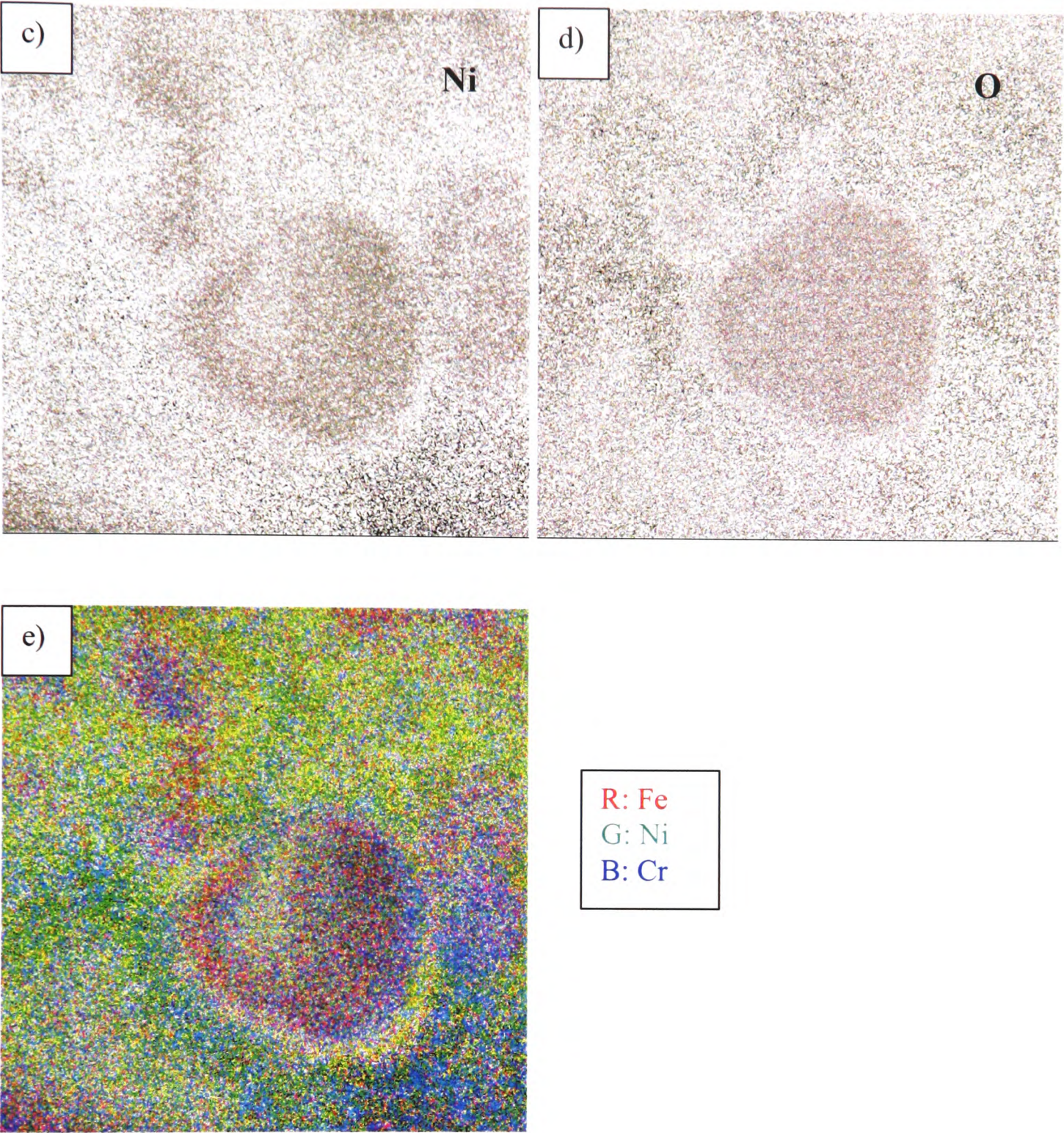


Fig. 8.7.14. TEM BF micrograph showing the edge of crack α and. particle d (acquired using a multiscan CCD camera in the 3000F).





*Fig. 8.7.15. GIF maps of particle **d** and surroundings (acquired with the 3000F).*

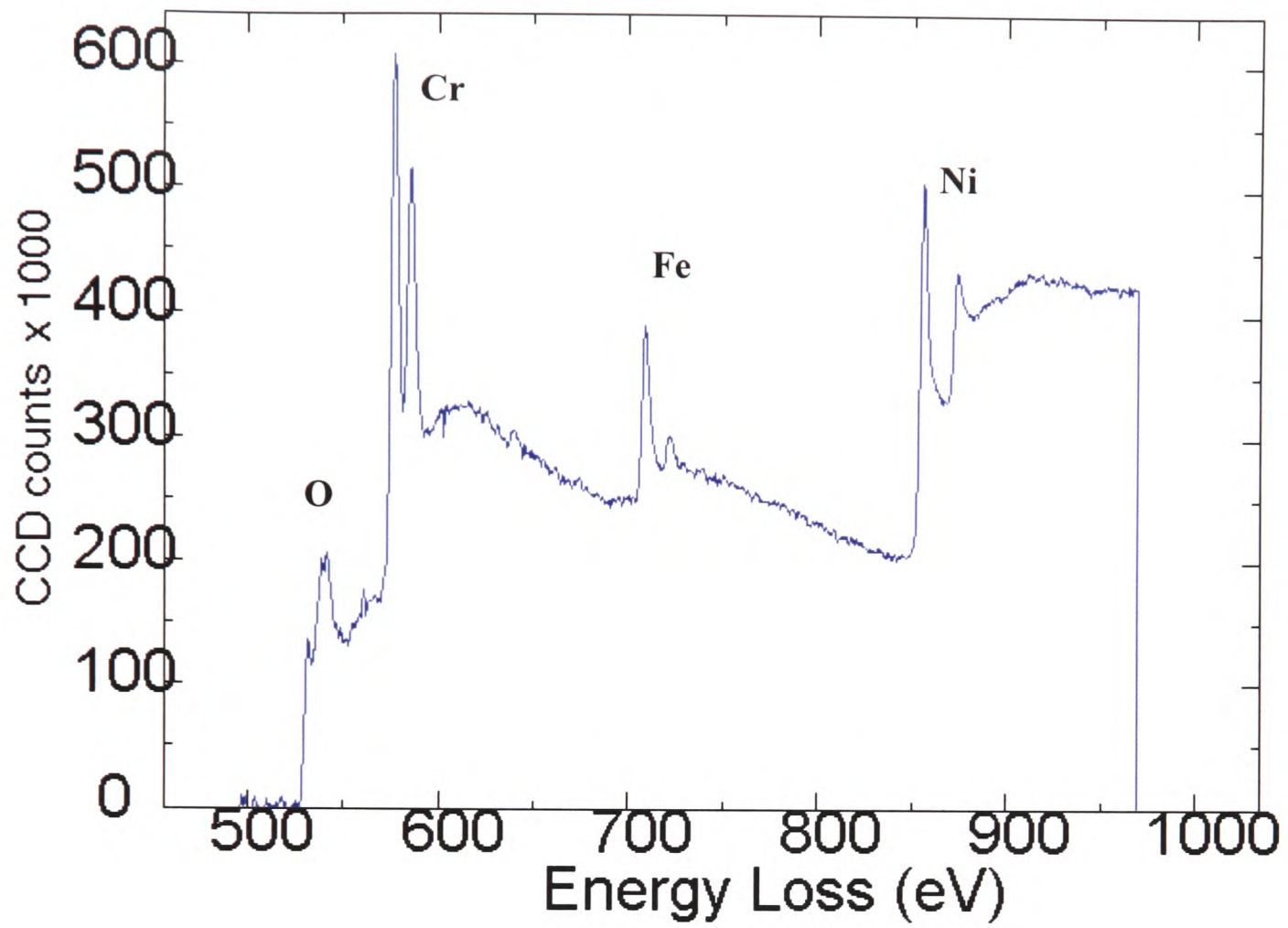


Fig. 8.7.16. EELS spectrum from particle *d* (acquired with the 3000F).

8.8 Sample 8: General observations

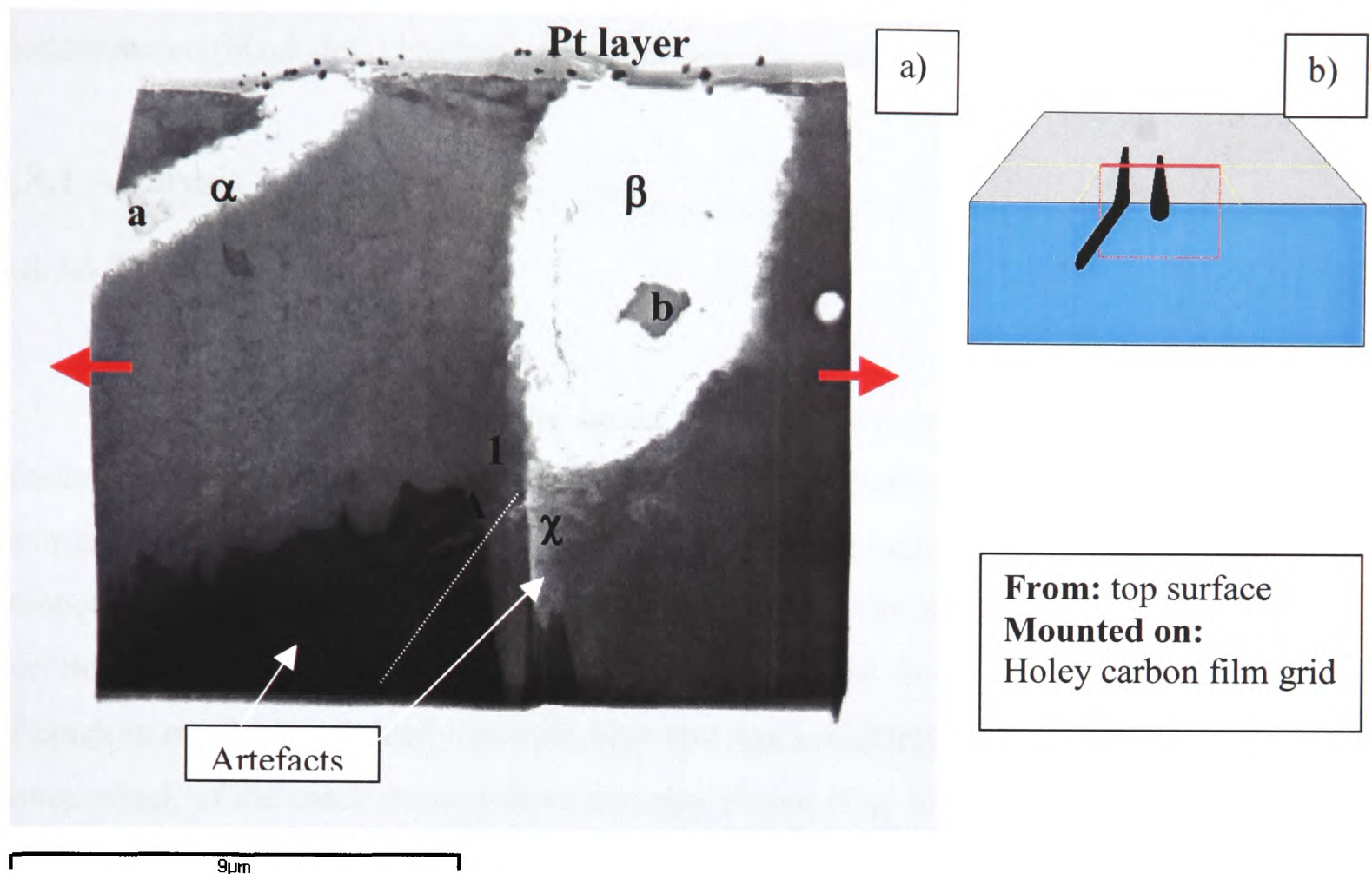


Fig. 8.8.1. a) STEM BF micrograph showing sample 8 after plucking. The loading direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) Sketch showing the orientation of the sample.

Sample 8 (Fig. 8.8.1a) was prepared in the FIB from the top surface (grey in Fig. 8.8.1b), so one of the cracks (β) is fully contained in the sample. Crack β blunted when grain boundary A changed its orientation at 1, probably because it could not continue advancing under pure Mode I loading. A transgranular crack (χ) was observed at the bottom of crack β and it is believed that appeared as a consequence of the stress generated by the arresting of crack β . Two large particles were found embedded in the nanocrystalline NiO of the cracks: particle **a** was found to be CaCO_3 and particle **b** a duplex NiO/ NiFe_2O_4 particle.

There are three artefacts in this sample that should be mentioned. Two of them are due to FIB sample preparation. The first consisted of an artificially thicker region at the bottom of the sample (in later figures this can be seen more clearly, e.g. Fig. 8.8.14). The second is below the blunt crack, and consists of an artificially thinner region due to the different milling rates of the oxide in the crack and the matrix. This

last artefact could have masked the transgranular crack χ , but fortunately, the presence of Cr-oxide in the EDX mappings reveals its position. Thirdly, some contamination (black dots) has been deposited near the platinum layer.

8.8.1 Analysis

8.8.1.1 Flanks: Crack α

Crack α maintained its oxide layers intact, as they were preserved by the nanocrystalline NiO that filled the crack and by the protective Pt layer during FIB sample preparation. EDX and GIF mapping revealed the complexity of the oxides and compounds formed. EDX maps in Fig. 8.8.3a show that the flank of the crack was depleted in Ni and enriched in O and Cr. In Fig. 8.8.3b, the Cr-oxide of the top flank of crack α can be seen clearly as light blue and has a width of around 100nm. The bottom flank of the crack showed more complex phases (Fig. 8.8.4), including almost pure Cr particles, not seen in other previous samples. These “pure-Cr” particles were found to be remains of a dissolved Cr-carbide present in the grain boundary before the attack. In Fig. 8.8.4b we can see that the Cr-rich particles are only oxidized partially (as light blue). The separation between the Cr and the Ni is total, as revealed by Fig. 8.8.4c and the EDX maps (Fig. 8.8.4a). The EDX maps also reveal how the Fe seemed to be correlated with the Ni, not with the Cr. Almost no O enrichment was observed. This is somewhat surprising, as this flank of the crack was exposed to the environment when the grain boundary opened and the nanocrystalline NiO and other “foreign” particles (e.g. particle **b**) entered. The absence of O is shown in the EDX spectrum from the Ni-rich area (Fig. 8.8.7), although is more evident in the spectrum from the Cr-rich particle (Fig. 8.8.8).

These spectra were quantified, including O, to give the results shown in Table 1, confirming that Cr and Ni are almost pure on the flank:

Spectrum	O	Ti	Cr	Fe	Ni	Total
Ni particle at the tip (on the edge)			5.24	10.85	83.91	100.00
High Cr particle before the Ni particle			94.24		5.76	100.00

Table 1: Quantification of the particles in the lower flank of crack α . All results in Weight Percent. Carbon was not included in the quantification.

Some EELS spectra and GIF maps were also acquired from this area. In Fig. 8.8.7, the area is shown prior to the analysis and positions **A** and **B** are marked. The particle in position **A** (Fig. 8.8.8a) was found to be half Cr-rich without traces of oxygen and half FeNi_2O_4 , as can be seen in the GIF maps (Figs. 8.8.8b, 8c, 8d, 8e). Figs. 8.8.8b and 8d clearly show that Cr and Ni are separated in the particle. Fig. 8.8.8c show some traces of Fe in the top half. The upper half of particle **A** was identified as FeNi_2O_4 using μD (Fig. 8.8.9a) and the lower half as the remains of a Cr_7C_3 Cr-carbide (as revealed by the high carbon peak in the EDX spectrum showed in Fig. 8.8.6 and the μDP in Fig. 8.8.9c).

8.8.1.2 Flanks: Crack β

The left top flank of crack β was analyzed (Fig. 8.8.10), detecting a Cr-oxide (Cr_2O_3) layer of width around 50 nm. Fig. 8.8.11b revealed that apart from the Cr-oxide layer (light blue) at the flank, there were other Cr-rich particles inside the matrix. These particles were slightly enriched in O, as can be seen in the EDX maps of Fig. 8.8.11a. The proximity of the top surface (in contact with the environment) suggests that some internal oxidation has occurred.

A qualitative EDX line profile across the left flank (Fig. 8.8.12a) reveals that apart from the Cr-oxide layer at the flank of the crack, there is another Cr-rich region (Fig. 8.8.12b) which suggests internal oxidation. This second region does not show such a high oxygen peak as the first oxide layer, but it clearly contains O (Fig. 8.8.12e).

The quantitative analysis of the Cr-rich layer (shown in Table 2) plus μD (not shown) revealed it as Cr_2O_3 :

Element	Weight%
O K	32.82
Cr K	43.29
Fe K	6.62
Ni K	17.26
Totals	100.00

Table 2: Quantitative results from the Cr-rich layer on the left flank of crack β .

The right flank was also analyzed (results not shown), obtaining similar results.

8.8.1.3 Crack β

Crack β was found to be completely filled by nanocrystalline NiO. An EELS spectrum from this oxide is shown in Fig. 8.8.13.

The tip of crack β , where it blunted, showed a small intragranular crack (χ) and a heavily attacked area, with a high density of Cr-rich oxides (Fig. 8.8.14). In Fig. 8.8.15b we can see how although the presence of the grain boundary **A** on the right of the map might facilitate the attack, the dimensions of the Cr-rich region are much bigger and wider suggesting that an intragranular crack has developed (χ). In Fig. 8.8.15b, the Cr-oxide appears as light blue and the rejected Ni as red.

Fig. 8.8.16a shows the changes in composition in the area within the orange box in Fig. 8.8.14, which is the continuation of grain boundary **A**. In Fig. 8.8.16a it is possible to see how the Ni and Fe are correlated in most of the area. The formation of Cr-oxide (light blue) is clear in Fig. 8.8.16b. The maps of Fig. 8.8.16a suggest that grain boundary **A** has been heavily attacked after the blunting of crack β and that it could even be considered that it has opened slightly. In Fig. 8.8.16a the end of the attack (especially in the O map) in grain boundary **A** is visible, There also seem to be Cr-carbides present (blue round spots in Figs. 8.8.16b and 16c). Note the presence of an artefact in this area, as the thicker region that was not properly removed with the FIB appears more intense in the maps.

8.8.1.4 Particles

Particle **a** (Fig. 8.8.1a) had a length of almost 1 μm and was found embedded in the NiO of crack α . It was identified as CaCO_3 using μD (not shown).

Particle **b** (Fig. 8.8.17) was identified as another $\text{NiO}(\mathbf{b}_2)$ / NiFe_2O_4 ($\mathbf{b}_1$) duplex particle, as it can be seen in the EDX maps in Fig. 8.8.18a. In Fig. 8.8.18b, the external NiO appears as light blue (green+blue) and the inner particle almost white, as all three elements in the RGB composition are present. In Fig. 8.8.18e, some Cr-rich particles appear next to the particle (in blue). The EDX maps (Fig. 8.8.18a) reveal the differences in intensity between the Ni in the inner NiFe_2O_4 particle (less intense) and the outer NiO particle (more intense). The inverse applies for the Fe, although its content in the NiO is minimal. Similar duplex particles have been also found in Samples 1, 3 and 4, always embedded in the nanocrystalline NiO.

EELS analyses were also performed on the NiO ($\mathbf{b}_2$) and the NiFe_2O_4 ($\mathbf{b}_1$) compound particle. The results are shown in Fig. 8.8.19 for the NiO and in Fig. 8.8.20 for the NiFe_2O_4 . It is interesting to observe the differences between an EELS spectrum from the nanocrystalline NiO that filled the opened cracks (Fig. 8.8.19) and the NiO monocrystal (Fig. 8.8.30). In the first case, the O edge is much higher, suggesting that there is more oxygen than expected. This oxygen could be in excess at the pores and grain boundaries. The EELS spectrum from the NiFe_2O_4 particle (Fig. 8.8.31) is consistent with the composition from the particle: Assuming an atomic ratio of 2:1 for Fe:Ni and a factor of 2 greater sensitivity to Fe, the Fe:Ni ratio in edge intensity would be 4:1, as observed. μD analysis was performed to confirm the identity of the particles.

8.8.2 Main observations

- Remains of Cr-carbides were found in the flank of the crack. They did not oxidize.
- An intragranular crack was found after an opened intergranular crack blunted at a triple point. This attack was preferred over grain boundary attack.

8.8.3 Sample 8 – Data collection

8.8.3.1 Flanks: Crack α

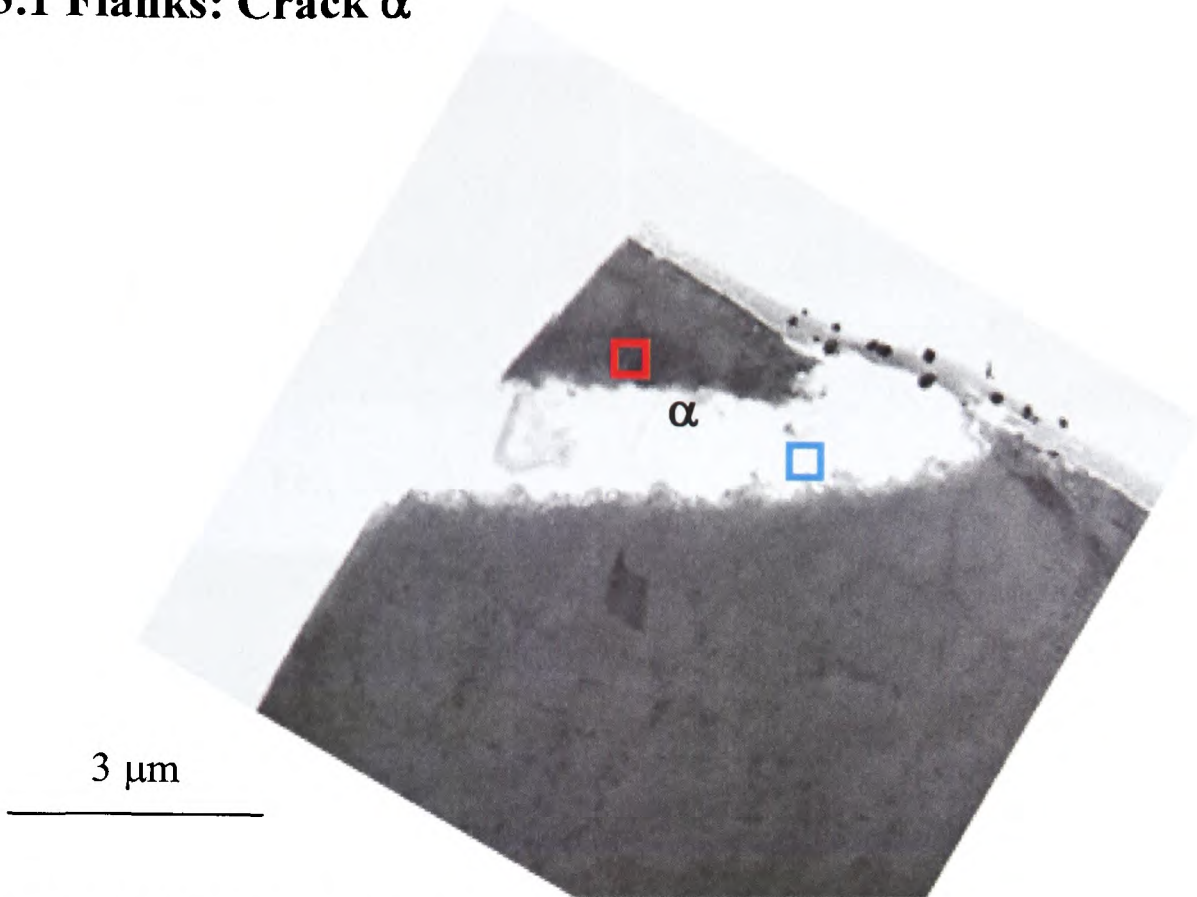


Fig. 8.8.2. STEM BF micrograph showing details of crack α and the areas chosen for EDX mapping (acquired with the INCA system in the CM20).

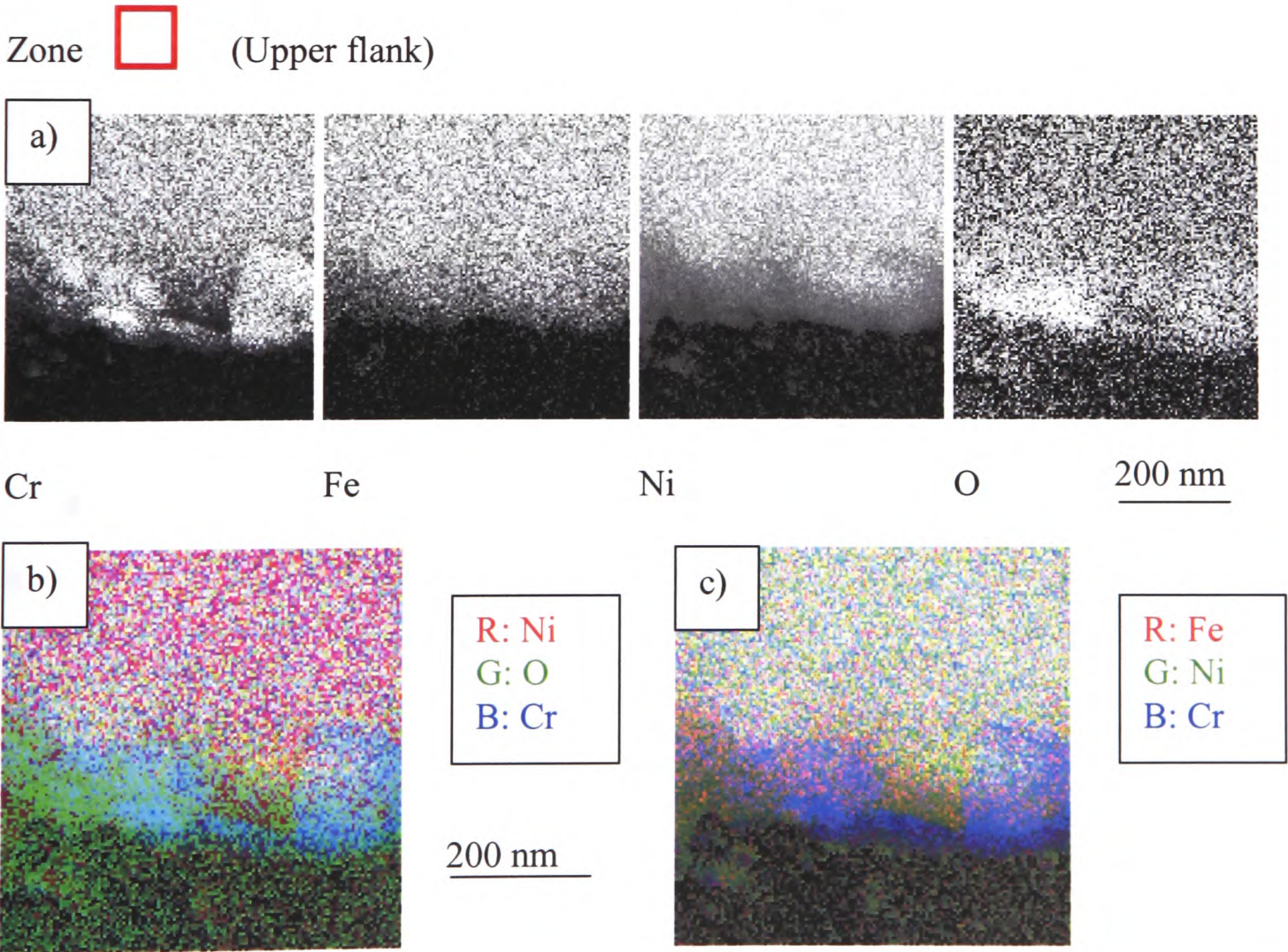


Fig. 8.8.3. a) EDX maps from the area under the red box in Fig. 8.8.2 (acquired with the LINK system in the HB501); b) and c) RGB compositions of images.

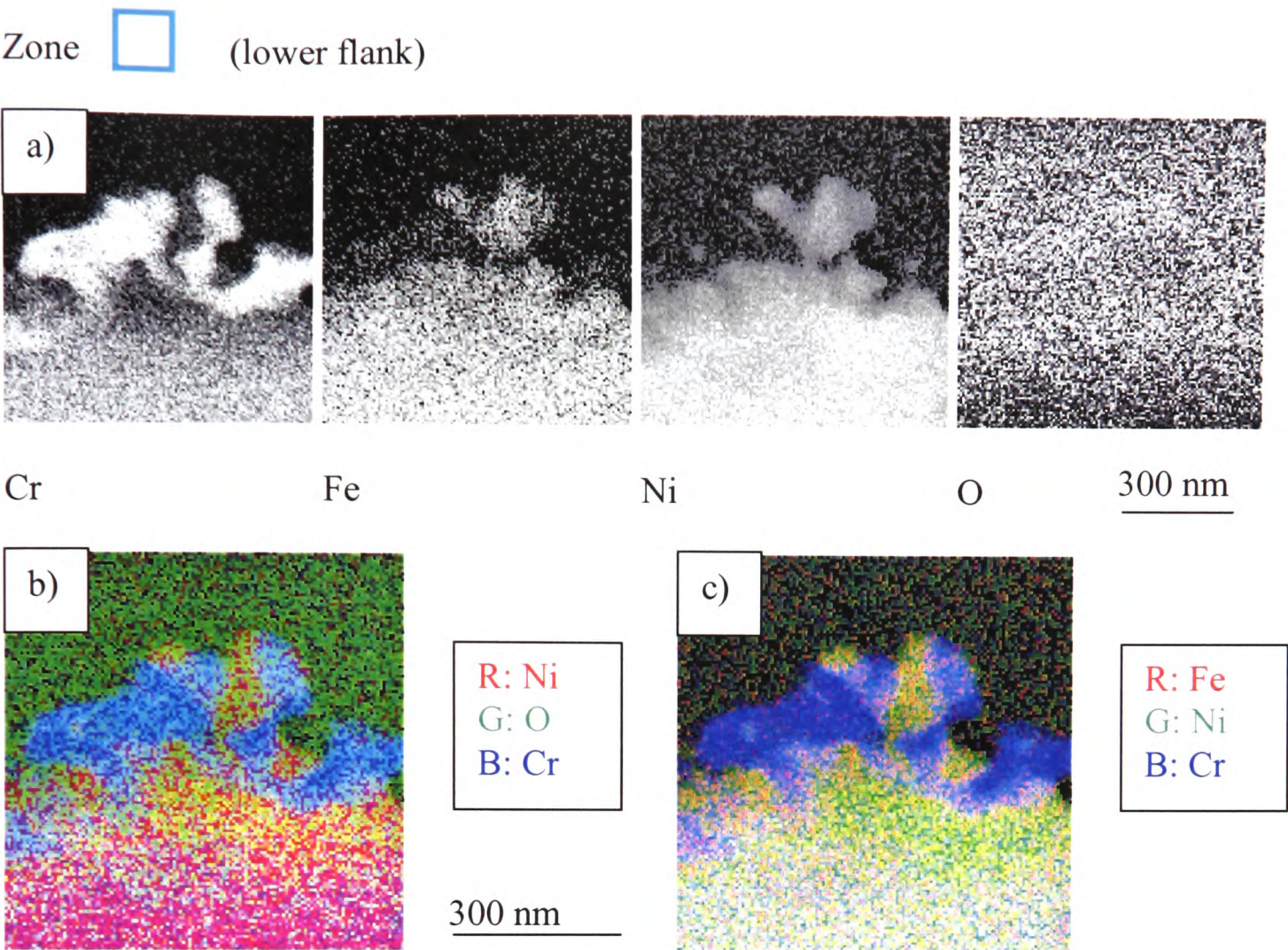


Fig. 8.8.4. a) EDX maps from the area under the blue box in Fig. 8.8.2 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

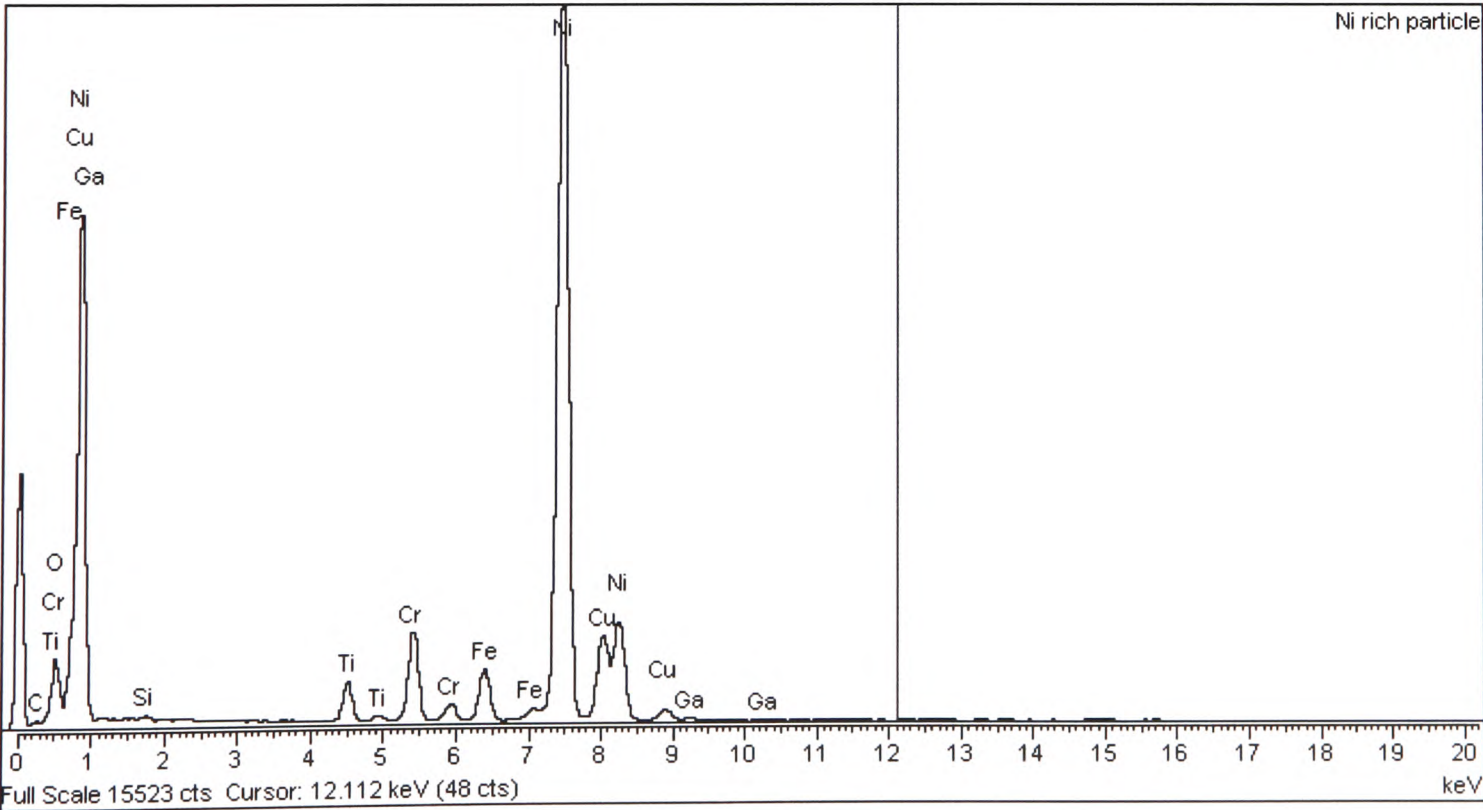


Fig. 8.8.5. EDX spectrum from a Ni-rich particle on the bottom flank of crack α (acquired with the INCA system in the CM20).

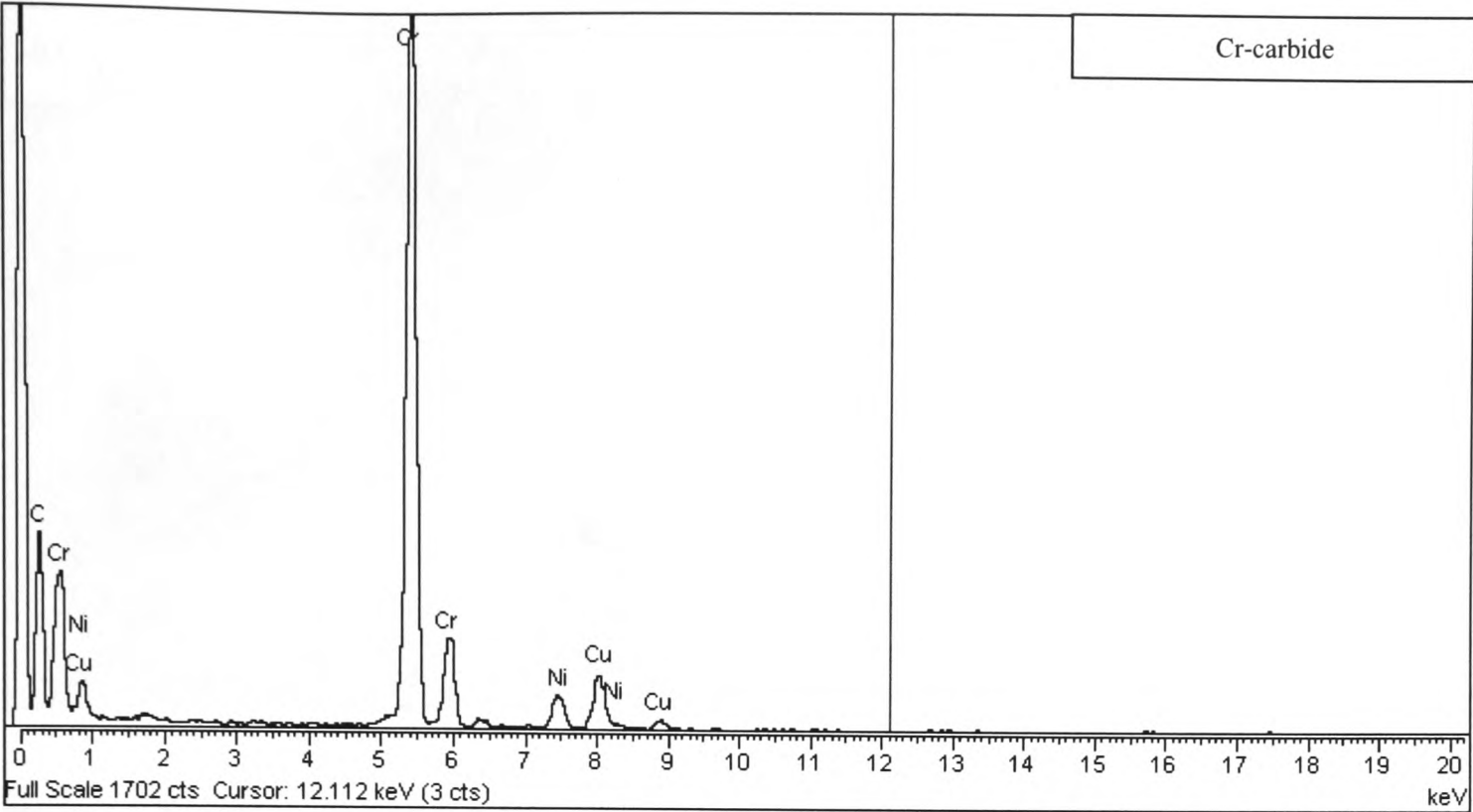


Fig. 8.8.6. EDX spectrum from a Cr-carbide on the bottom flank of crack α (acquired with the INCA system in the CM20).

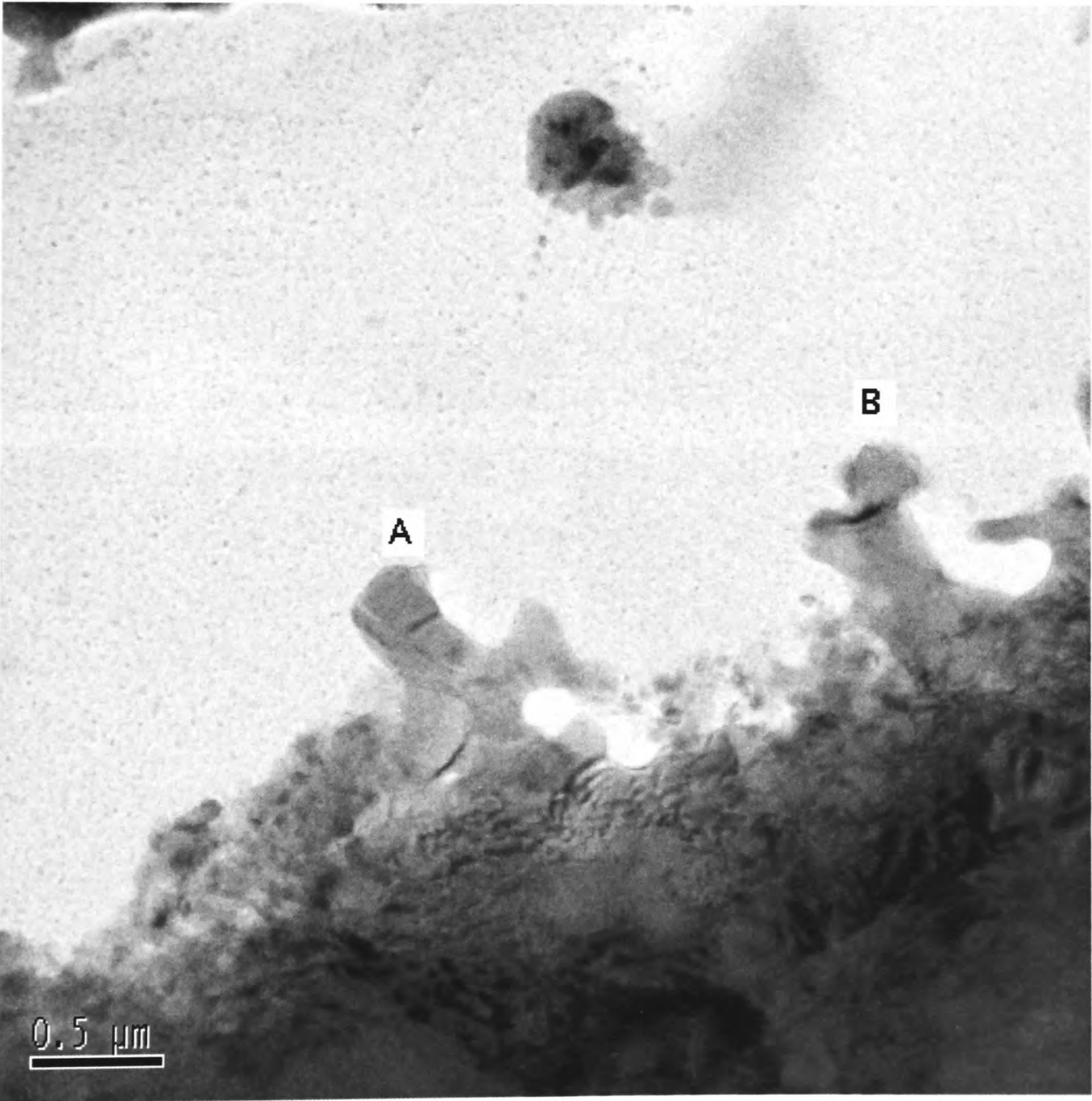


Fig. 8.8.7. TEM BF micrograph showing details of the microstructure of the bottom flank of crack α (acquired with a multiscan CCD in the 3000F).

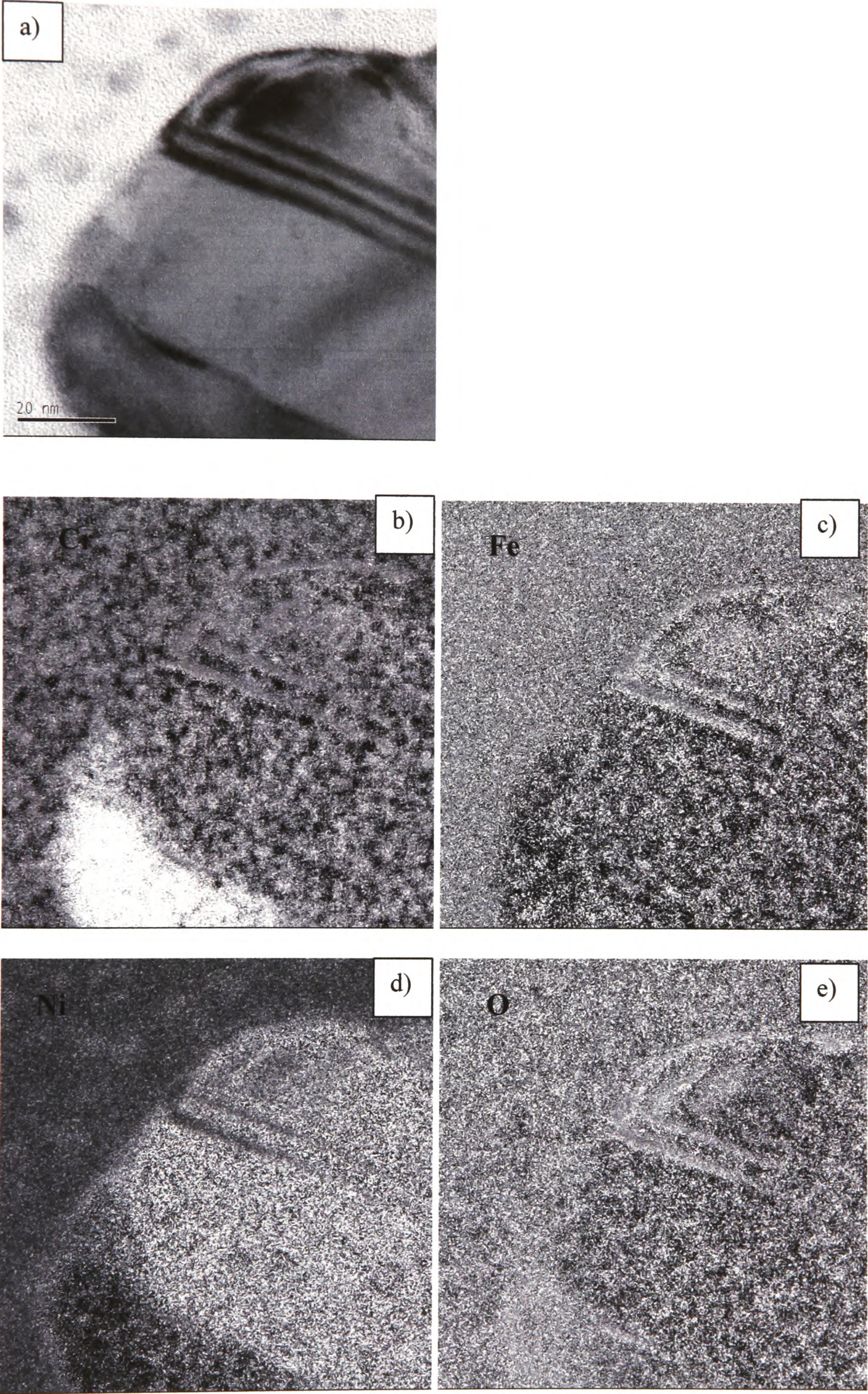


Fig. 8.8.8. a) TEM BF micrograph showing the top half of particle A; b), c), d) and e) GIF maps (acquired with a multiscan CCD in the 3000F).

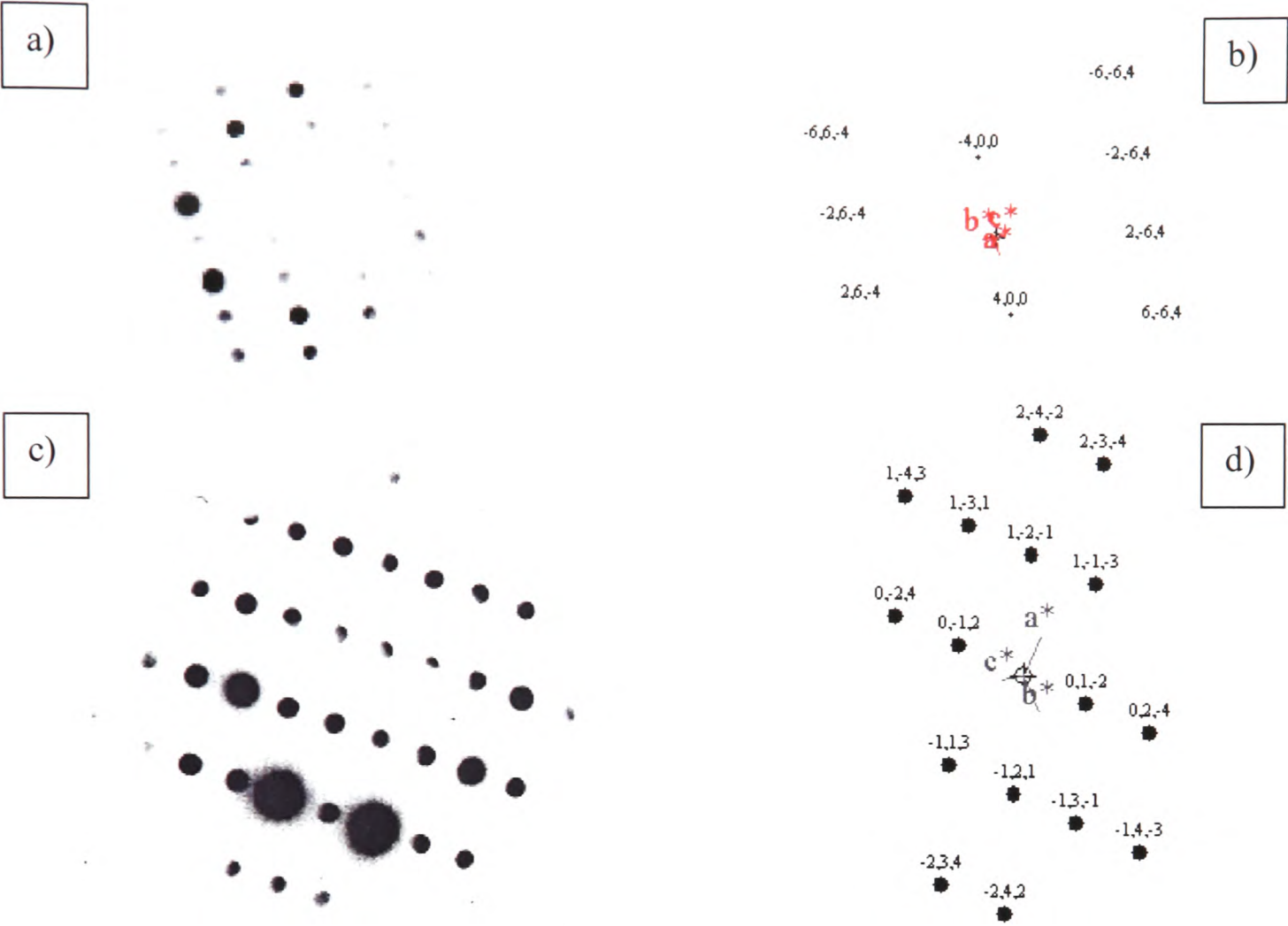


Fig. 8.8.9. a) μ DP of the upper half of particle A, b) simulated DP of FeNi_2O_4 in a $[023]$ zone axis, c) μ DP of the lower half of particle A and d) simulated DP of a Cr_7C_3 carbide in a $[521]$ zone axis (acquired with the CM20).

8.8.3.2 Flanks: Crack β

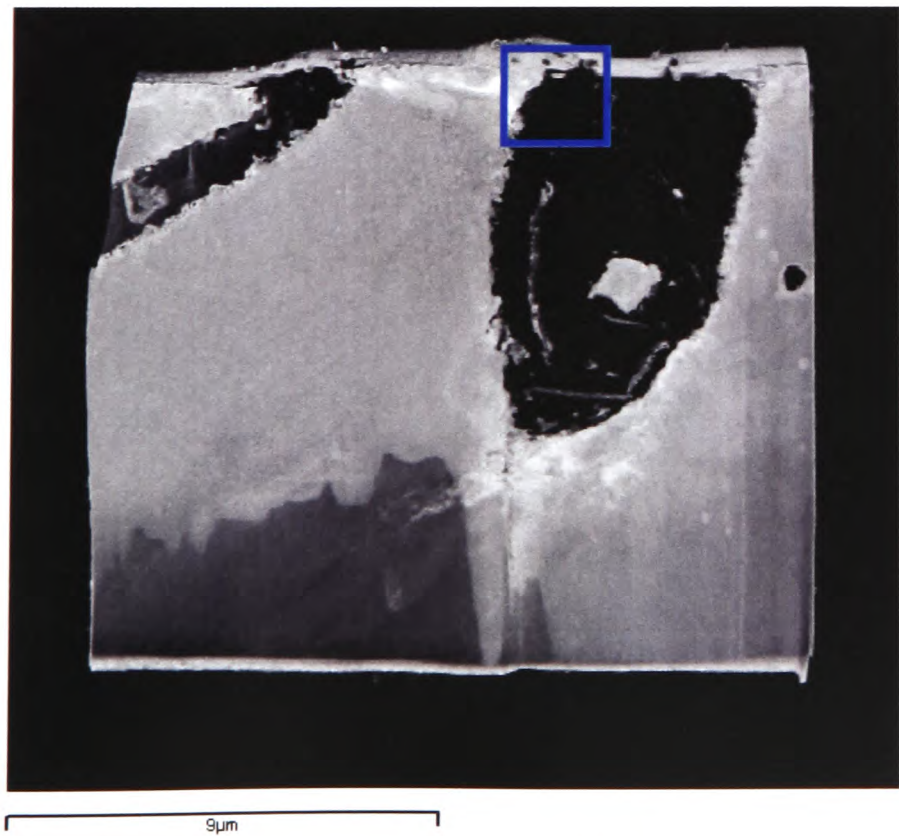


Fig. 8.8.10. STEM DF micrograph of sample 8 showing the area chosen to analyze the flank of crack β (acquired with the INCA system in the CM20)

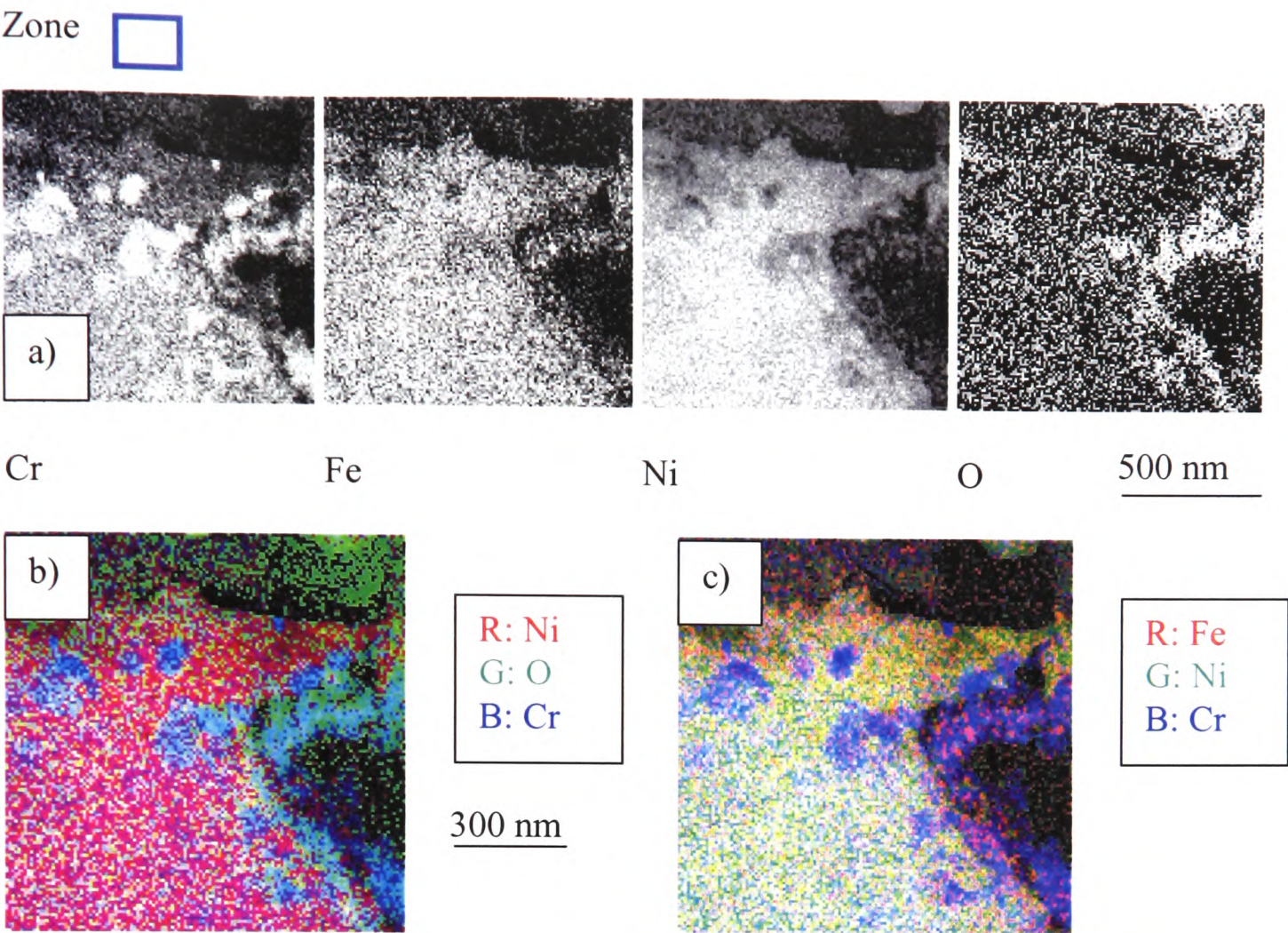
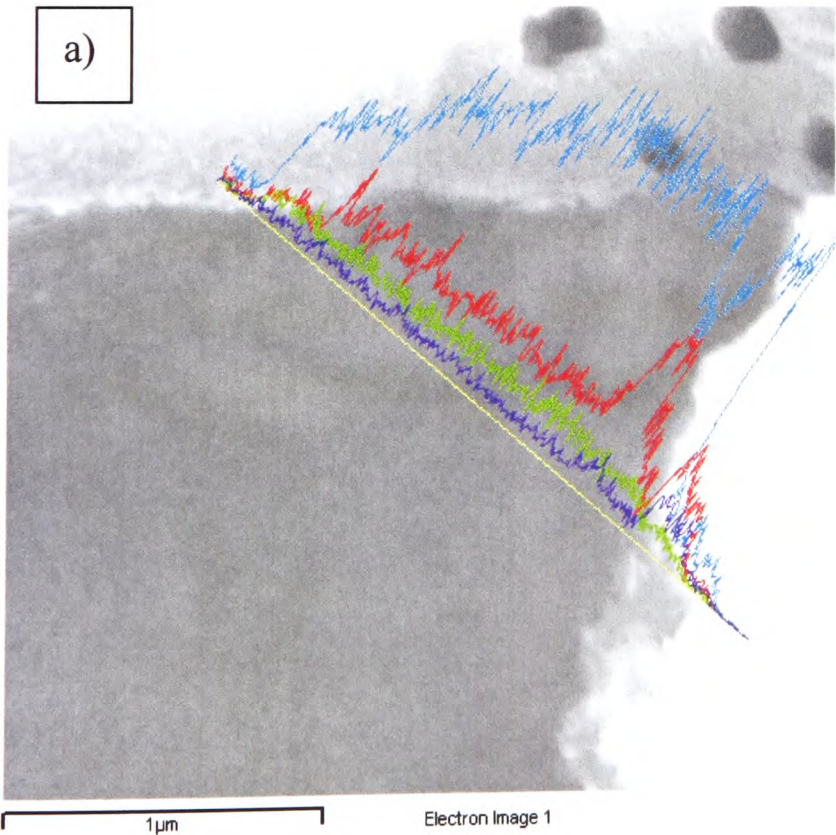


Fig. 8.8.11. EDX maps from the area under the blue box in Fig. 8.8.10 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.



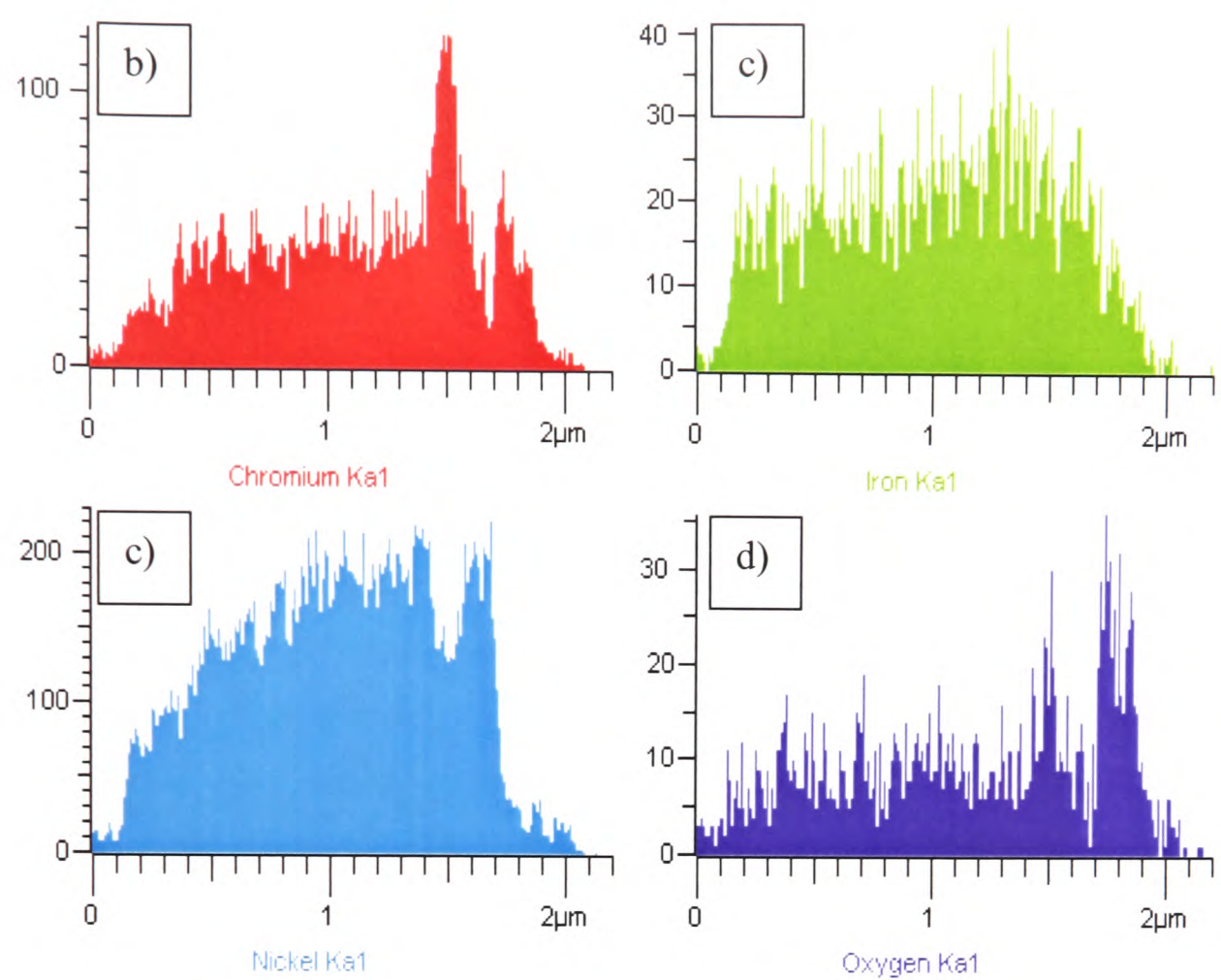


Fig. 8.8.12. EDX qualitative line profile across the left flank of crack β (acquired with the INCA system in the CM20).

8.8.3.3 Crack β

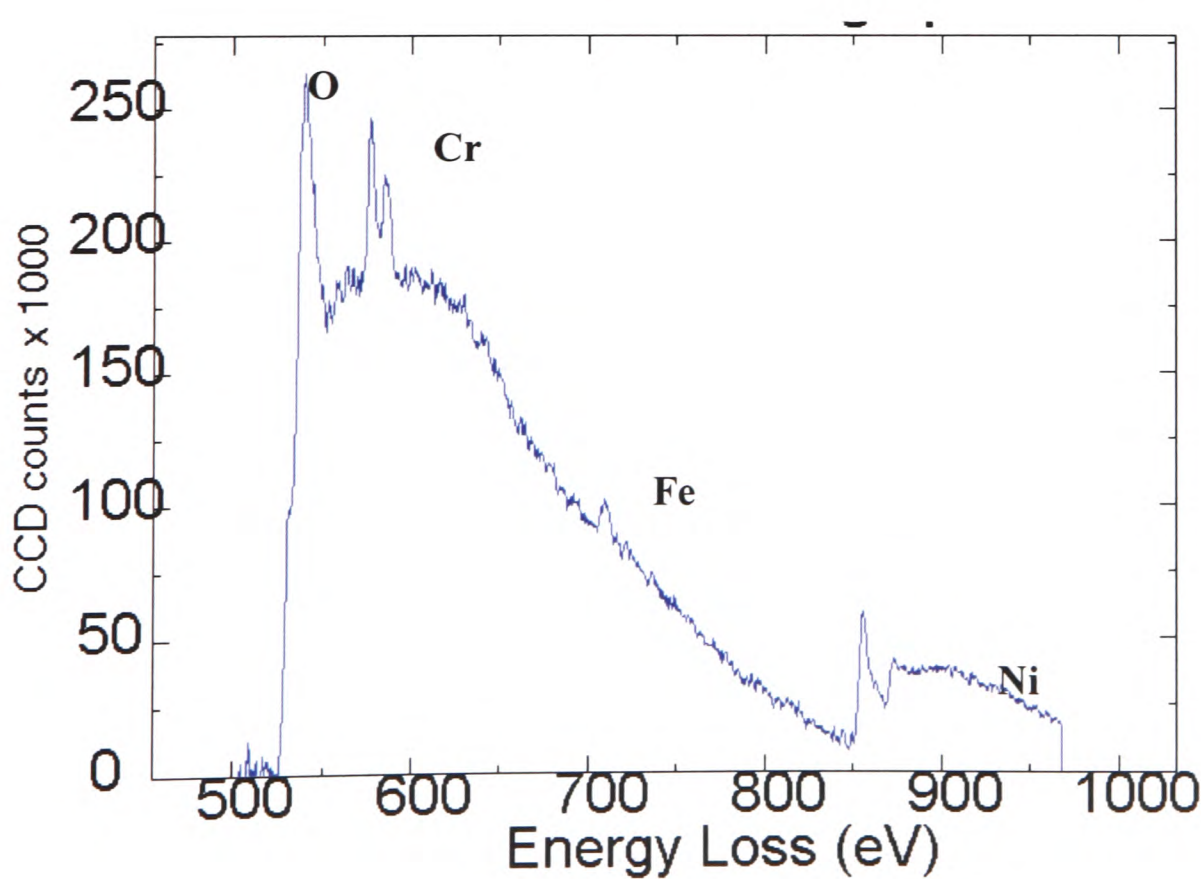


Fig. 8.8.13. EELS mapping from the nanocrystalline NiO in crack β (acquired with the 3000F).

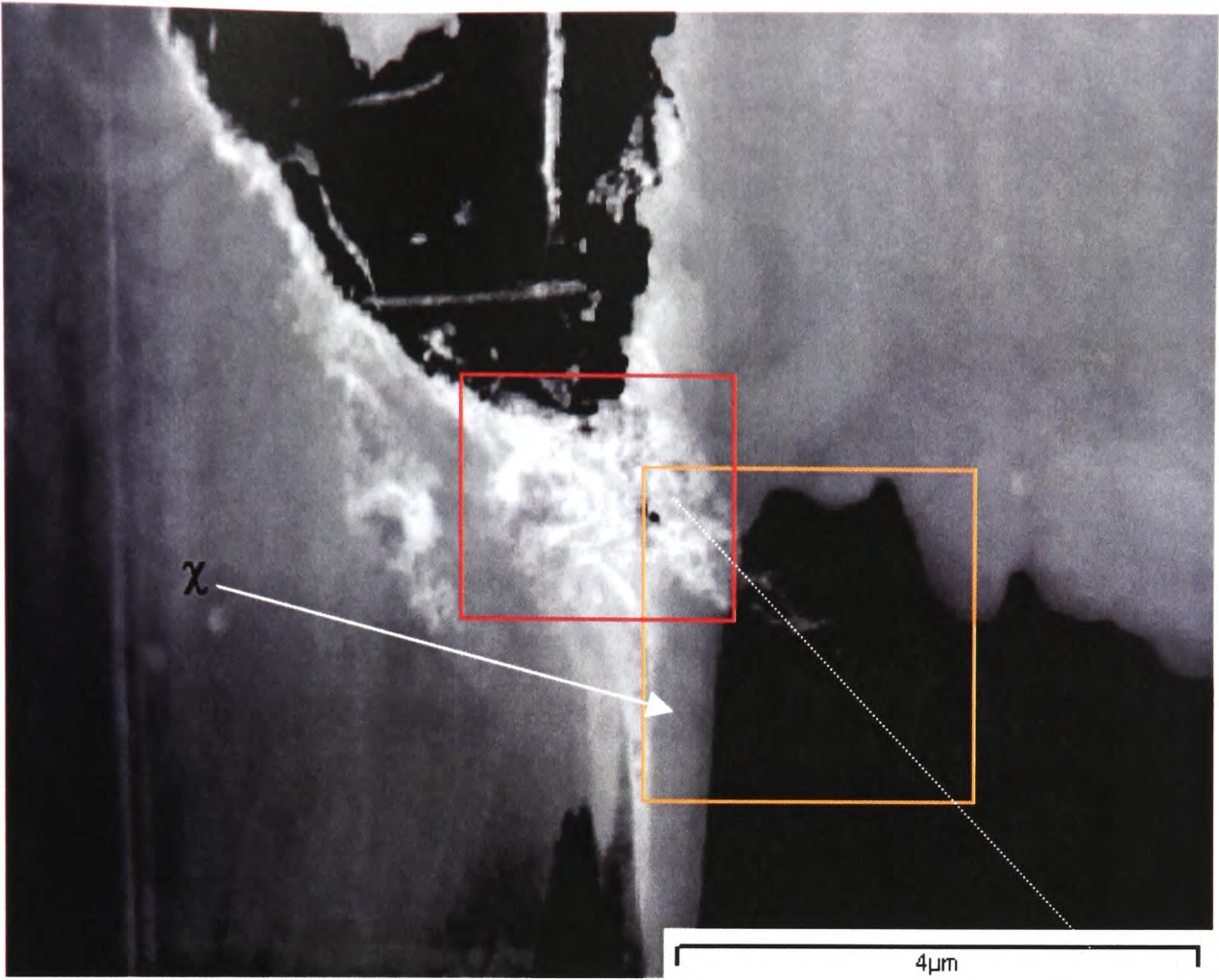


Fig. 8.8.14. STEM DF micrograph showing the different areas chosen for EDX mapping at the bottom of crack β . Note that this image is inverted vertically respect to Fig. 8.8.1 (acquired with the CM20).

Zone 

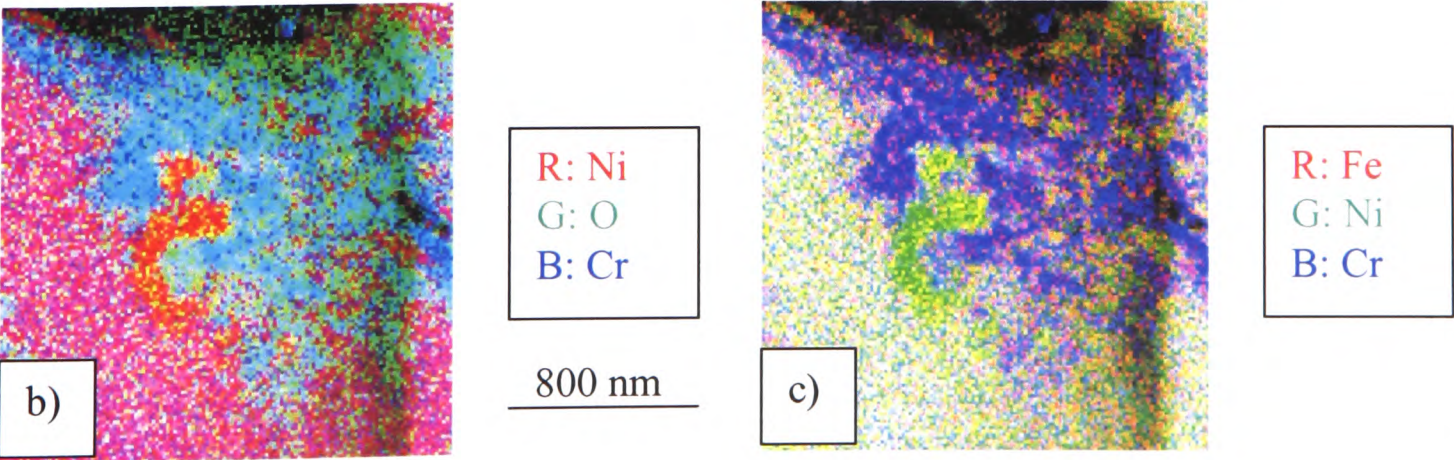
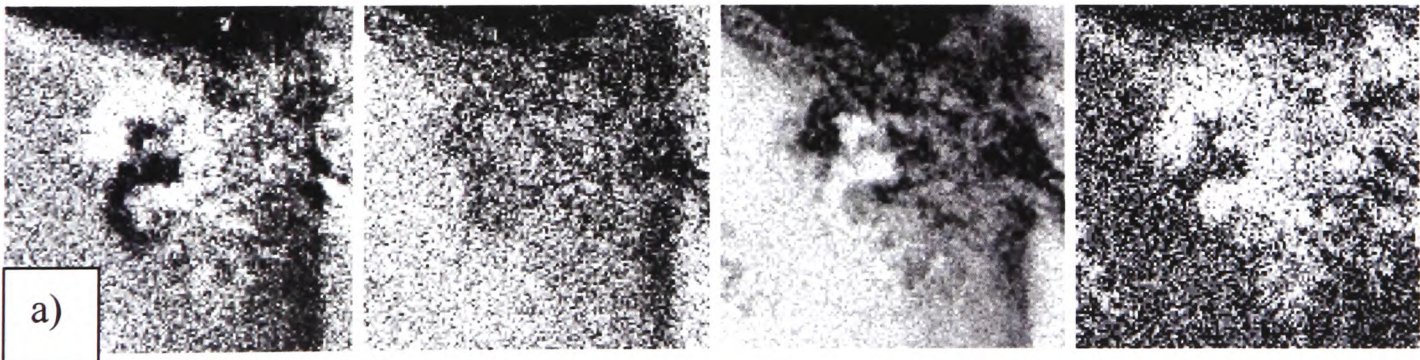


Fig. 8.8.15. a) EDX maps from the area under the red box in Fig. 14 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

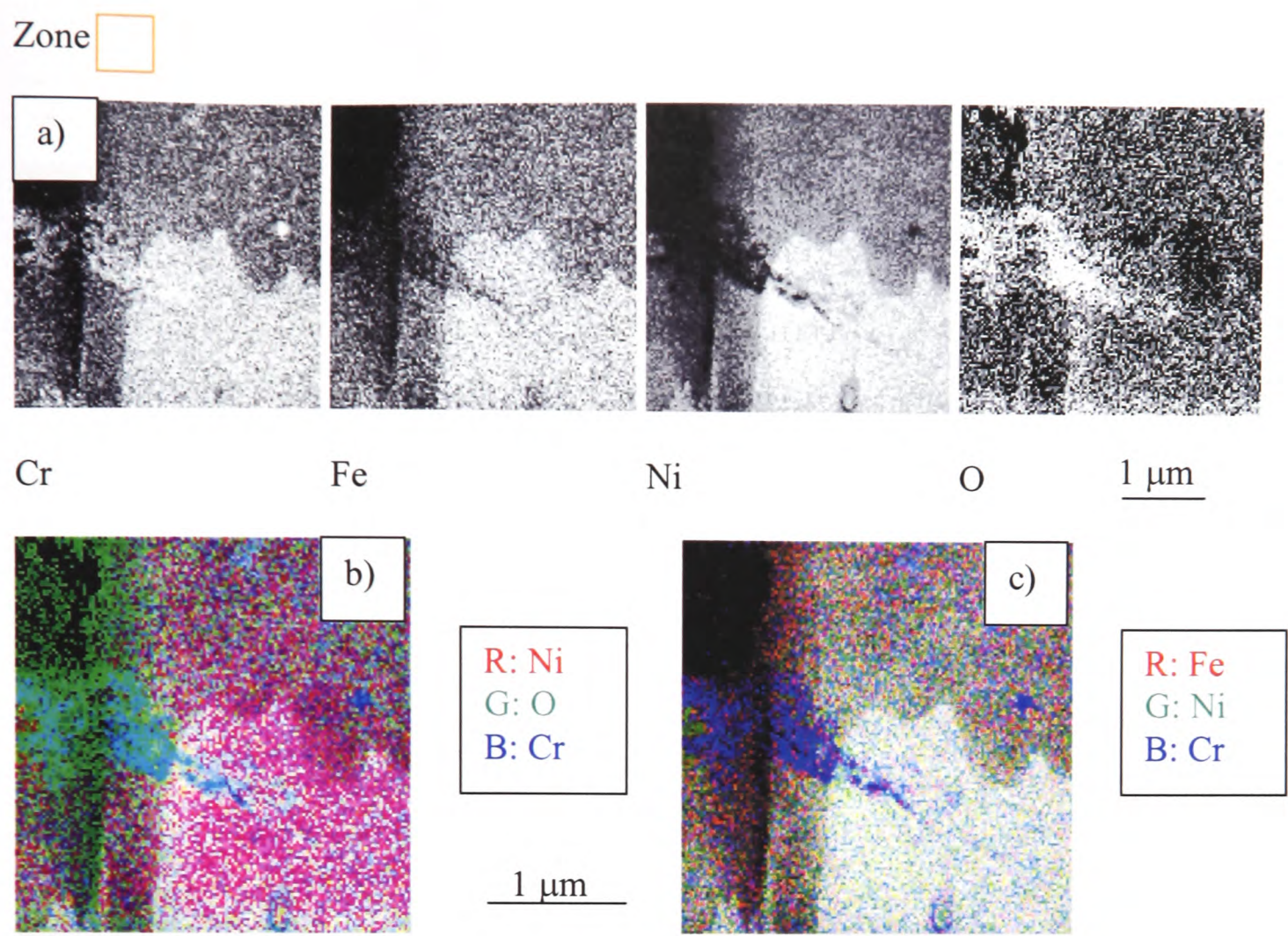


Fig. 8.8.16. a) EDX maps from the area under the orange box in Fig. 20 (acquired with the LINK system in the HB501); b) and c) RGB composition of images.

8.8.3.4 Particles

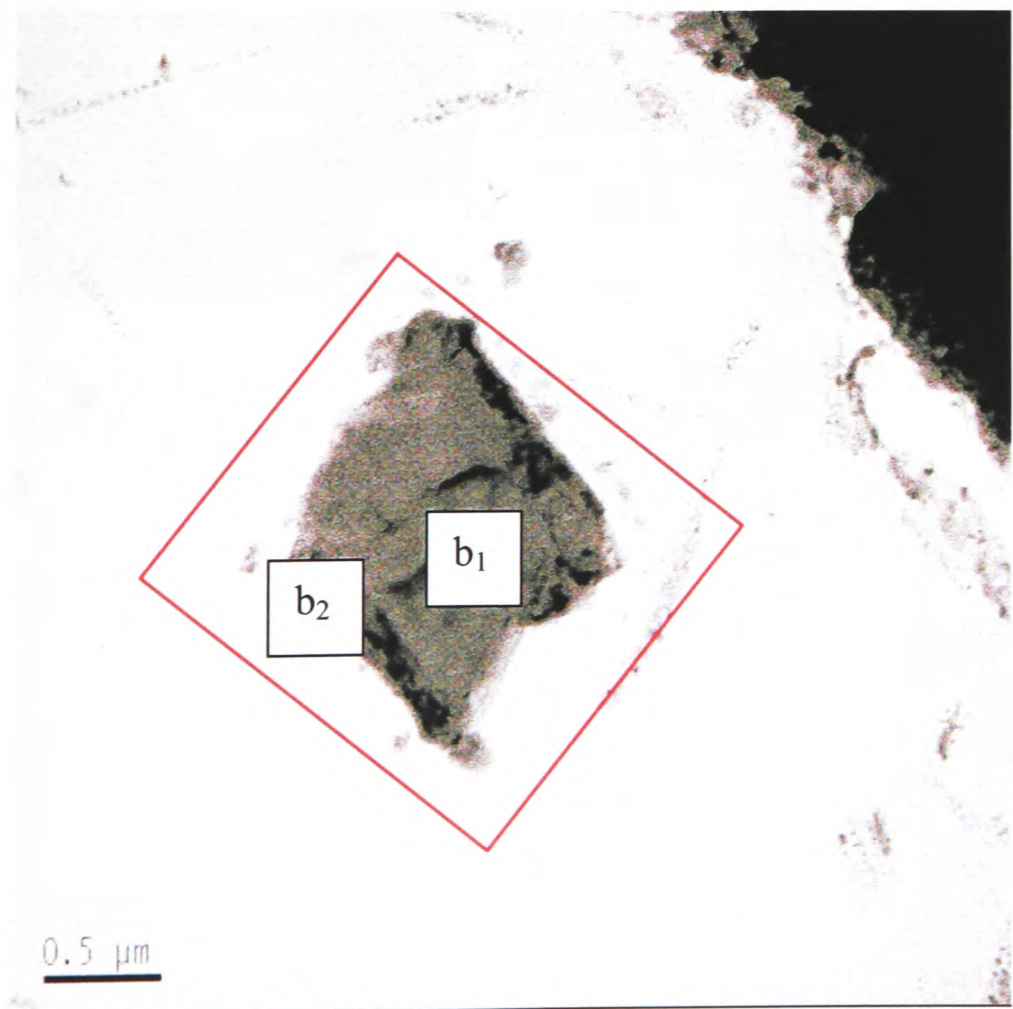


Fig. 8.8.17. TEM BF image of particle **b** (acquired with the 3000F).

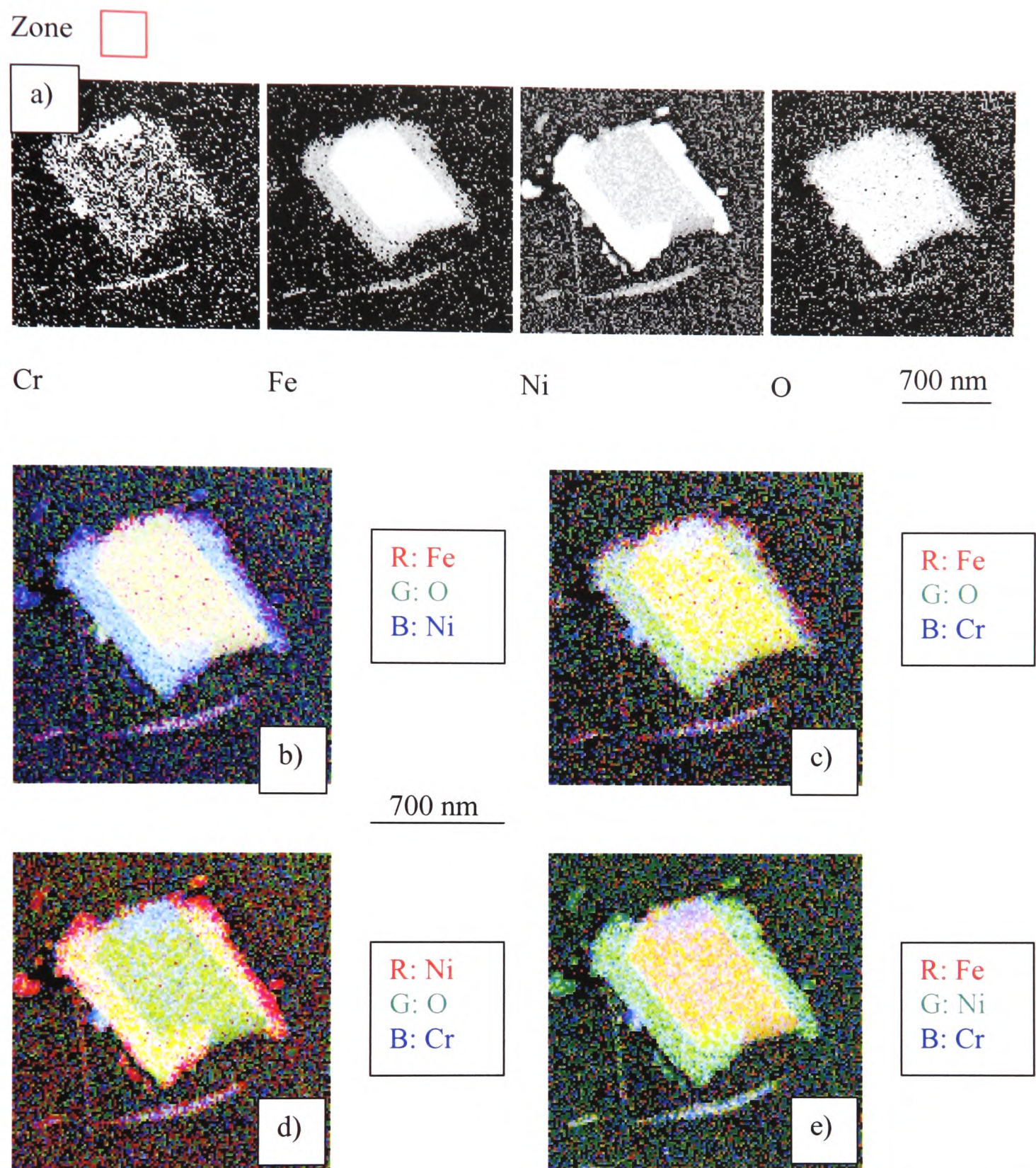


Fig. 8.8.18. a) EDX maps from the area under the red box in Fig. 8.8.27 (acquired with the LINK system in the HB501); b), c), d) and e) RGB composition of images.

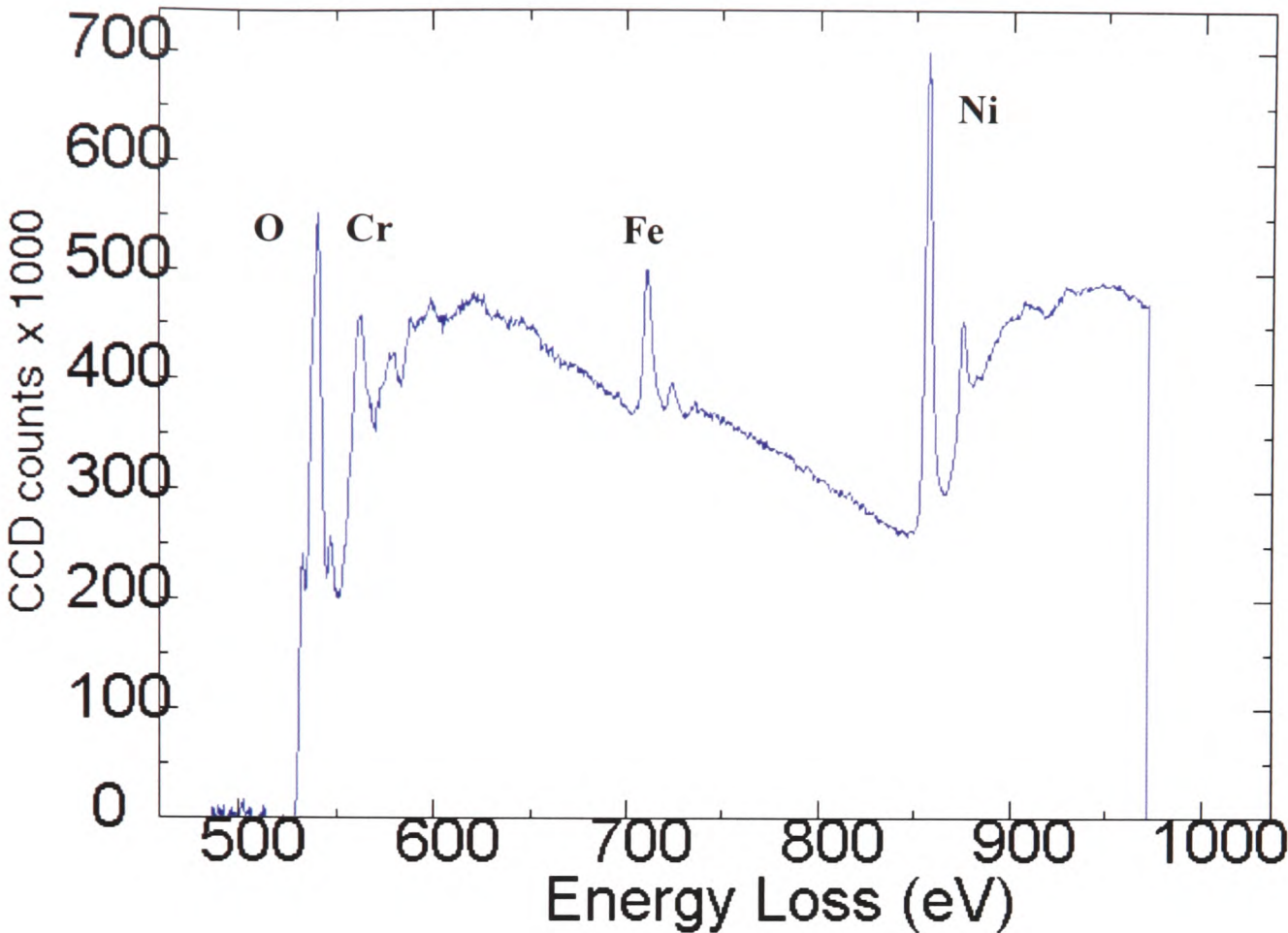


Fig. 8.8.19. EELS spectrum from the NiO (b₂) (acquired with the 3000F).

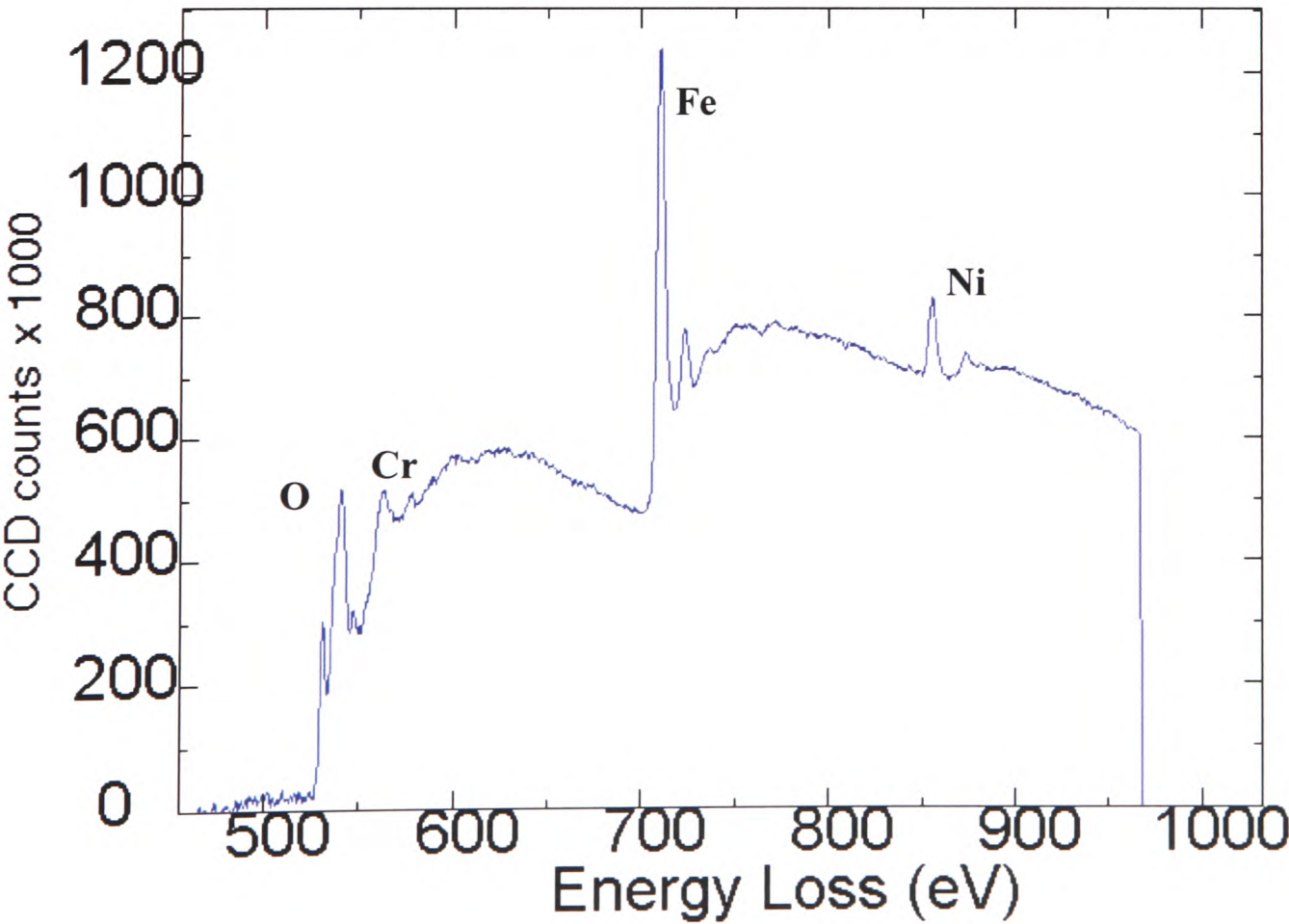


Fig. 8.8.20. EELS spectrum from the NiFe₂O₄ (b₁) (acquired with the 3000F).

8.9 Sample 9: General observations

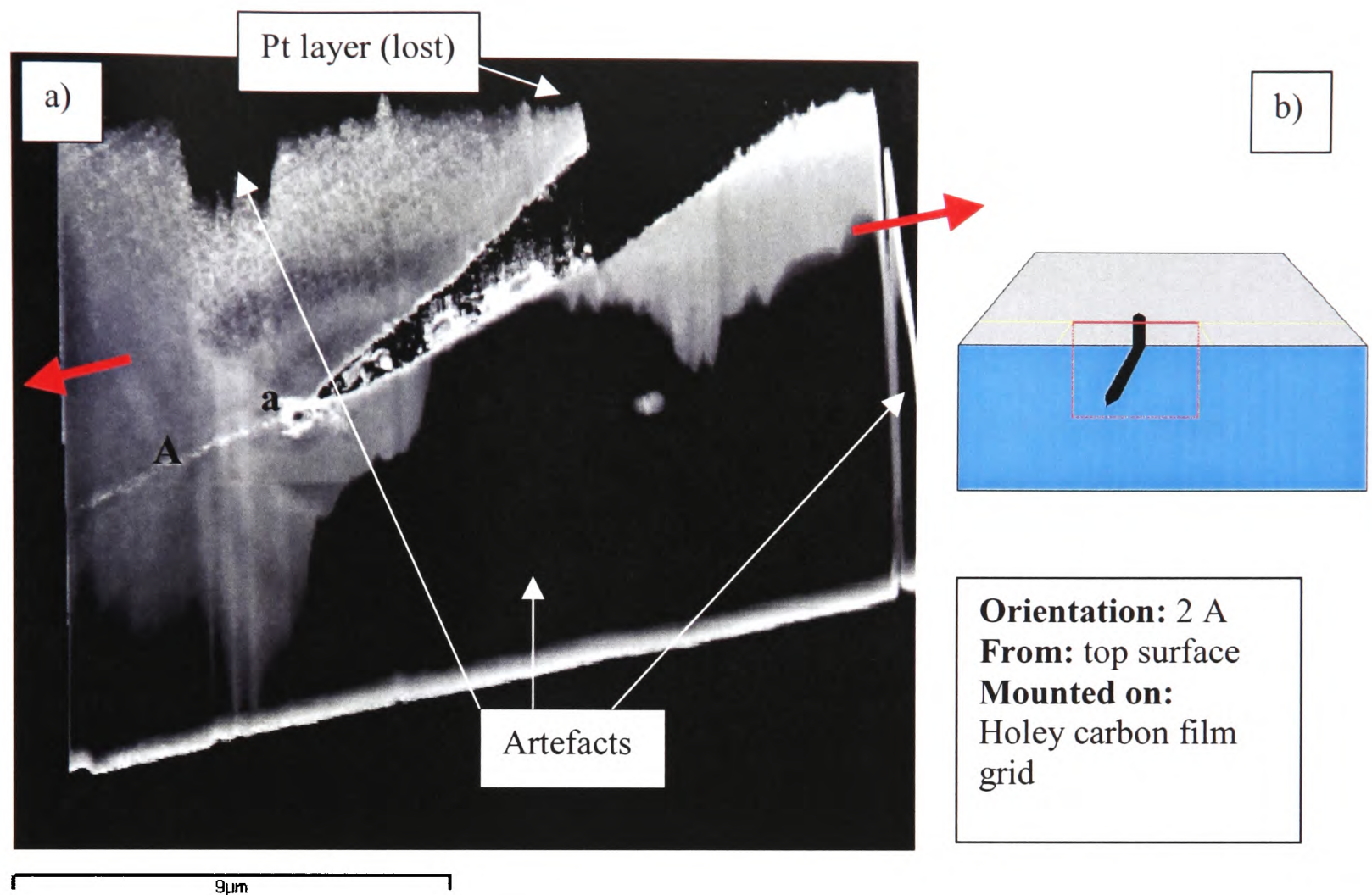


Fig. 8.9.1. a) STEM DF micrograph showing sample 9 after plucking. The loading direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) sketch showing the orientation of the sample.

Sample 9 (Fig. 8.9.1a) was prepared directly from the top surface (in blue in Fig. 8.9.1b), in an orientation perpendicular to the loading direction. It fully contains crack α , which blunted after opening along grain boundary A until it reached particle a. The attack through grain boundary A continued beyond the dimensions of the sample. The reason for the blunting might be the presence of a particle (a) or a change in orientation of the plane of the grain boundary which cannot be observed or determined from a 2-dimensional sample. The artefacts arrowed in the figure are a thicker region at the bottom (which appears darker) which was not properly milled with the FIB and an unfinished cut on the right which appears as a straight vertical line. Also, due to non-ideal FIB sample preparation, the Pt layer was lost as well as part of the top of the sample.

The whole crack α was filled by nanocrystalline NiO (Fig. 8.9.2a). EDX maps revealed the presence of many Cr-rich particles (Fig. 8.9.2b) embedded in the

nanocrystalline NiO, as well as some Ni-rich particles (Fig. 8.9.2d). Only the upper flank of the crack had a thick Cr-oxide layer (Fig. 8.9.2b and 2f). This might indicate that when the crack opened abruptly, the Cr-oxide remained mostly on the top layer. The different corrosion products found inside the crack, embedded in the NiO, also support the hypothesis of the abrupt opening. In the titanium map (Fig. 8.9.2e) it is also possible to see an intragranular TiN particle (bottom left corner).

The qualitative EDX line profile shown in Fig. 8.9.3 confirms that the lower flank has a Cr-oxide layer. The Cr-content (Fig. 8.9.3b) remained constant across the flank, but the Ni-depleted region (Fig. 8.9.3d) correlated with the enrichment in O (Fig. 8.9.3e). The width of the Cr-oxide is around 200nm.

In Fig. 8.9.4, the sample has been rotated relative to Fig. 8.9.2 and the difference between both flanks can be observed better. Fig. 8.9.4c shows how all the internal corrosion took place on the “left” flank (bottom in the previous micrographs), as the flank is depleted in Ni. These depleted regions correlate with the Fe (Fig. 8.9.4d) depleted regions and anticorrelate with the O (Fig. 8.9.4e) and Cr (Fig. 8.9.4b), indicating the nature of the attack.

The EDX maps of Fig. 8.9.6 (b, c, d and e) indicate that the Cr particles rejected Ni when they formed, as their positions correlate with dark areas in the Ni map. It is not clear that they are oxidized and could have the same nature as the Cr-rich particles in Sample 8 (which were believed to originate from intergranular Cr-carbides). In the RGB maps (Fig. 5f), it is easy to see the transition between the matrix (purple) and the nanocrystalline NiO (dark green) at the flank of crack α . The presence of nanoparticles of Cr-rich nanoparticles (blue in Fig. 8.9.5g) of the order of 10 nm in size was already reported in Sample 8.

8.9.1 Analysis

8.9.1.1 Crack tip

The crack tip of crack α coincided with the position of an intergranular Ti particle (a) (Fig. 8.9.6a). This particle might have changed the diffusion rate of oxygen along the boundary and represented an obstacle strong enough to locally

retard the advance of the crack. The big Ni cluster (arrowed in Fig. 8.9.6f) found in the position where the Ti particle was seems to have been formed as nickel was rejected from the formation of Cr_2O_3 in the grain boundary ahead of the opened crack. The Cr-oxide has advanced following oblique paths to the grain boundary (light blue in Fig. 8.9.6g and O map in Fig. 8.9.6b), in what could be considered an intragranular crack (features **1** and **1'** in Figs. 8.9.6g and 6b). The nature of these intragranular attacks is reminiscent of those mentioned by Hipsley for Ni-Al alloys ². He suggested that at the crack tip, the oxygen would diffuse preferentially along the grain boundary ahead of the crack tip and the regions of high dislocation density on either side. The pair of intrusions observed in this sample (**1** and **1'**) were also predicted. It is interesting to remark that in intrusion **1** the oxygen seems to have diffused beyond the Cr-rich and Ni-depleted region.

It can also be observed how the “intensity” of the attack seems to have decreased immediately beyond the Ti particle (O and Ni map in Figs. 8.9.6b and 6f), although it recovers after 1 μm . This might be due to the 2-dimensional nature of the attack. Oxygen diffuses two-dimensionally along the boundary plane. Locally, diffusion may be inhibited by the particle, but occurs normally at other positions on the plane, and so the particle is by-passed.

In Fig. 8.9.7a, the area ahead of the crack tip is studied. It can be seen that the intensity of the attack increased beyond position **2** (arrowed in Fig. 8.9.7f). In Fig. 8.9.7g the Cr_2O_3 appears as light blue, although some high-O concentration areas (in green) can be seen which do not correlate with the Cr-rich areas (Fig. 8.9.7b and 7d), suggesting that a high diffusion of O had occurred.

A quantitative line profile was performed across the grain boundary A to estimate the width of the attack (Fig. 8.9.8). It was found to be of the order of 200 nm on the image.

8.9.2 Main observations

- The intergranular crack blunted after reaching a Ti particle. This particle slowed down the attack in the neighboring area.
- The Ti particle diverted the direction of the attack into the matrix. Intragranular inclusions with a high-O content were observed.

8.9.3 Sample 9 – Data collection

8.9.3.1 Flanks

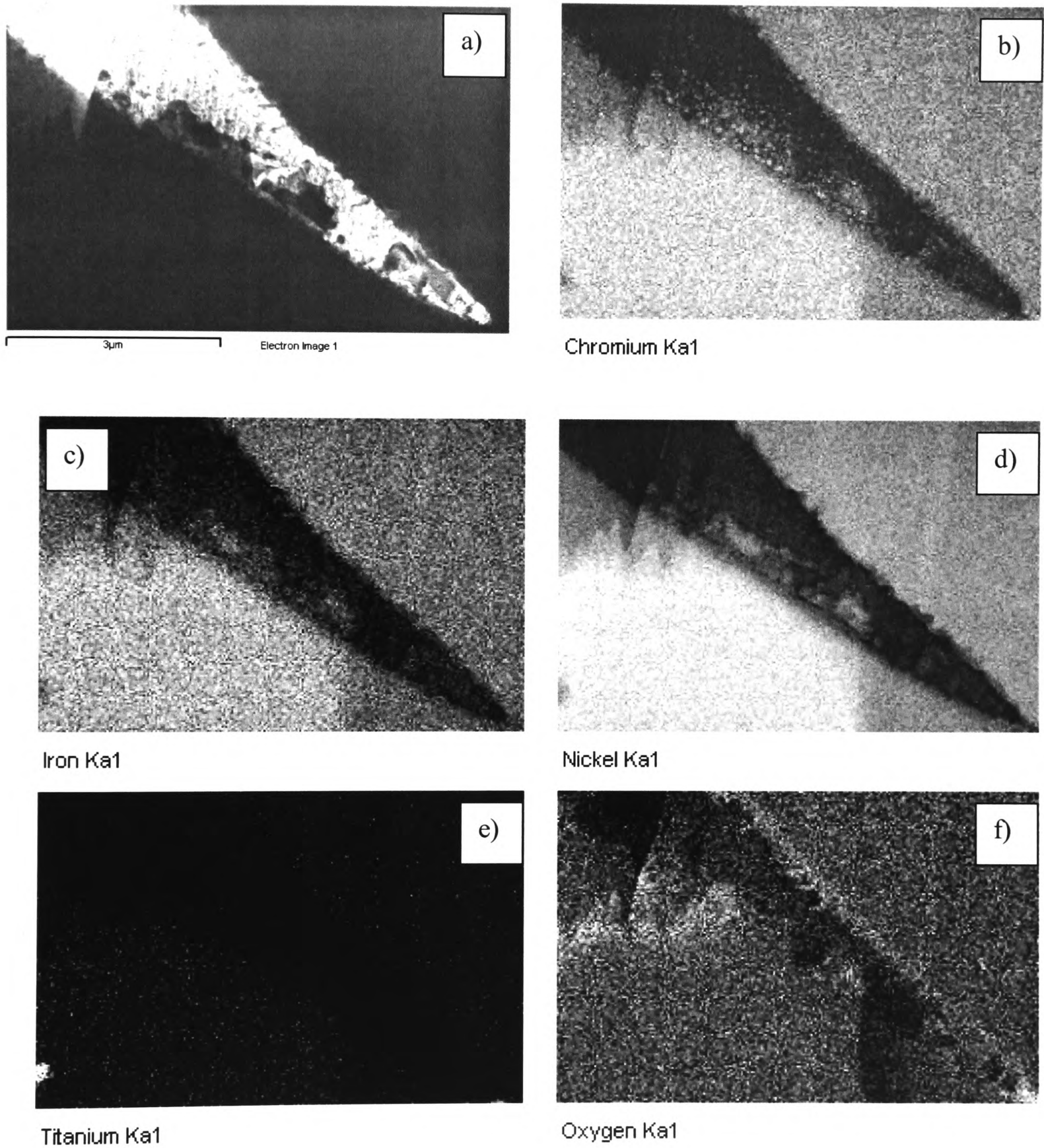


Fig. 8.9.2. a) STEM BF micrograph and b), c), d), e), f) EDX maps showing crack α (acquired with the INCA system in the HB-501).

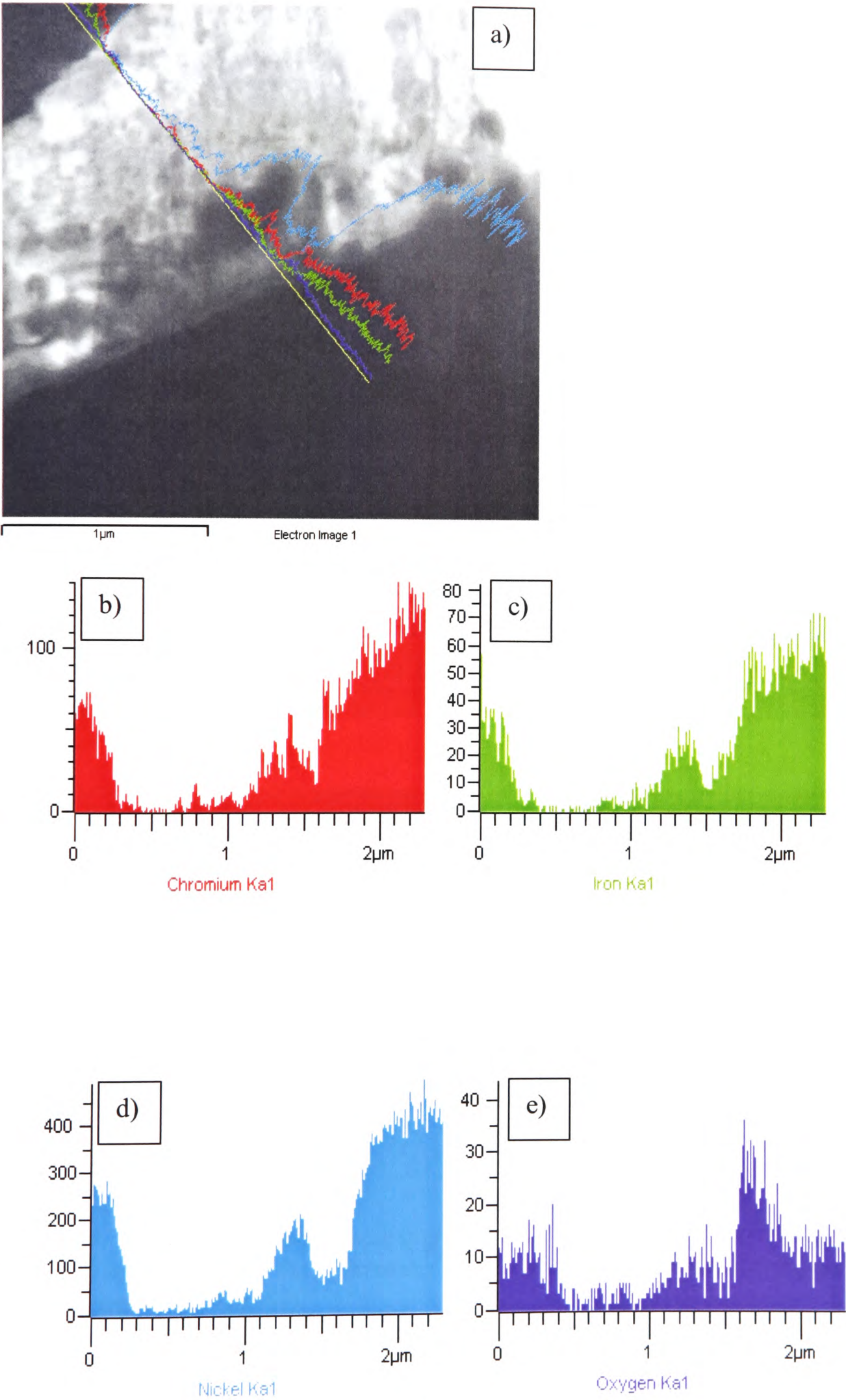


Fig. 8.9.3. EDX qualitative line profile across the lower flank of crack α (acquired with the INCA system in the CM20).

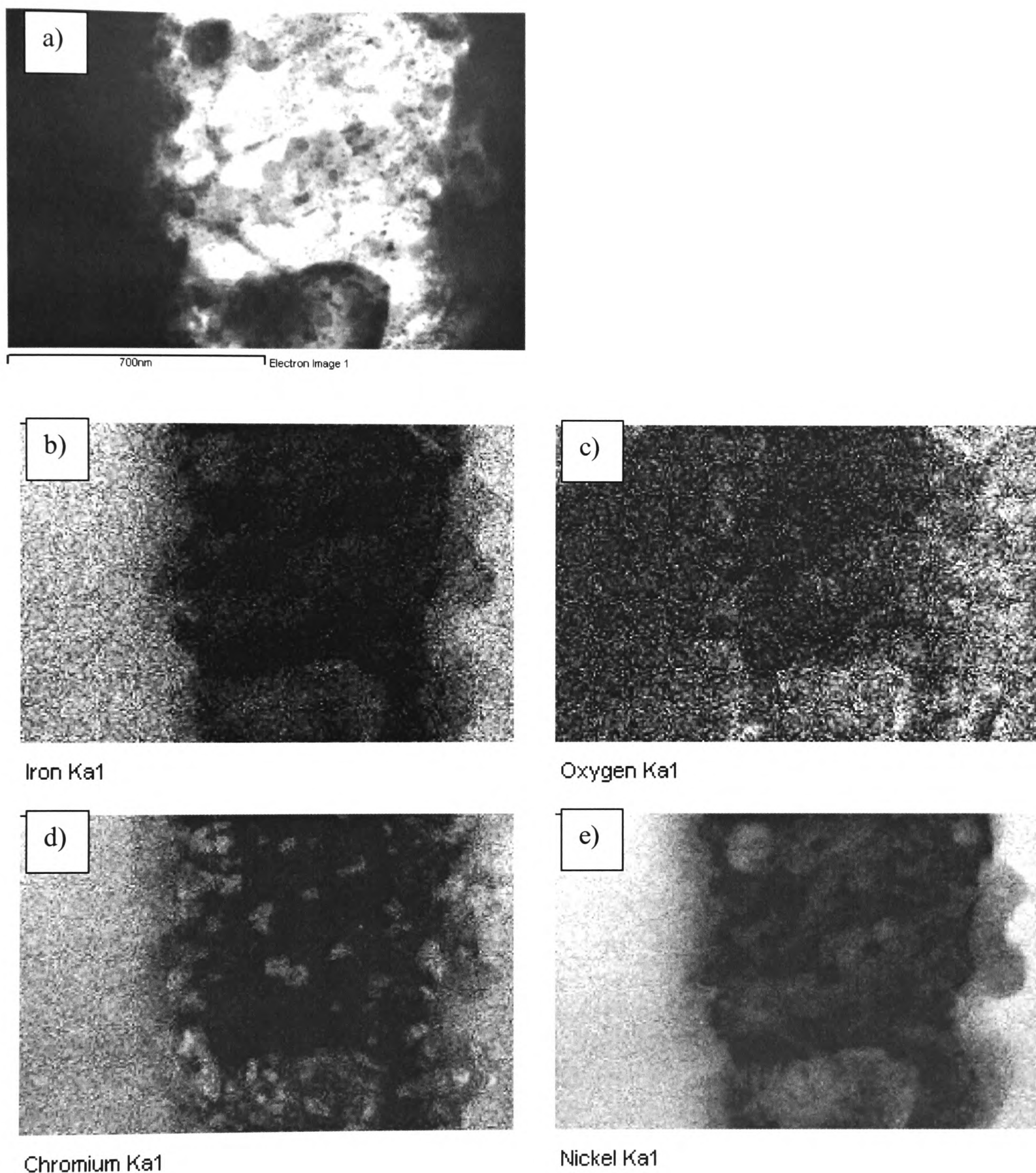


Fig. 8.9.4. a) STEM BF micrograph and b), c), d), e) EDX maps of crack α orientated vertically in order to see the differences in the attack in both flanks (acquired with the INCA system in the HB501).

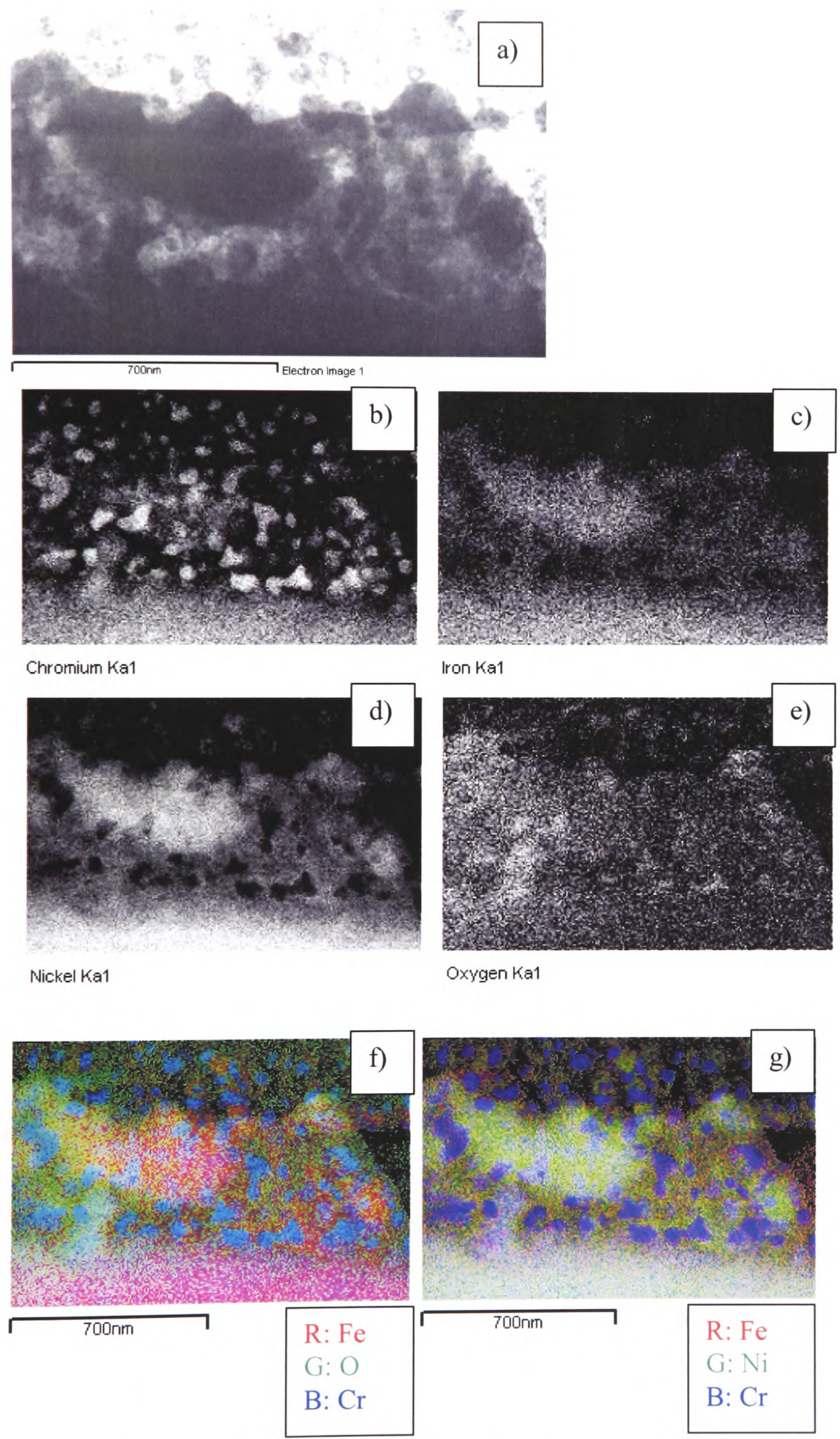


Fig. 8.9.5. a) STEM BF micrograph from the “bottom” flank of crack α and b), c), d), e) EDX maps (acquired with the INCA system in the HB501); f), g) RGB composition of images.

8.9.3.2 Crack tip

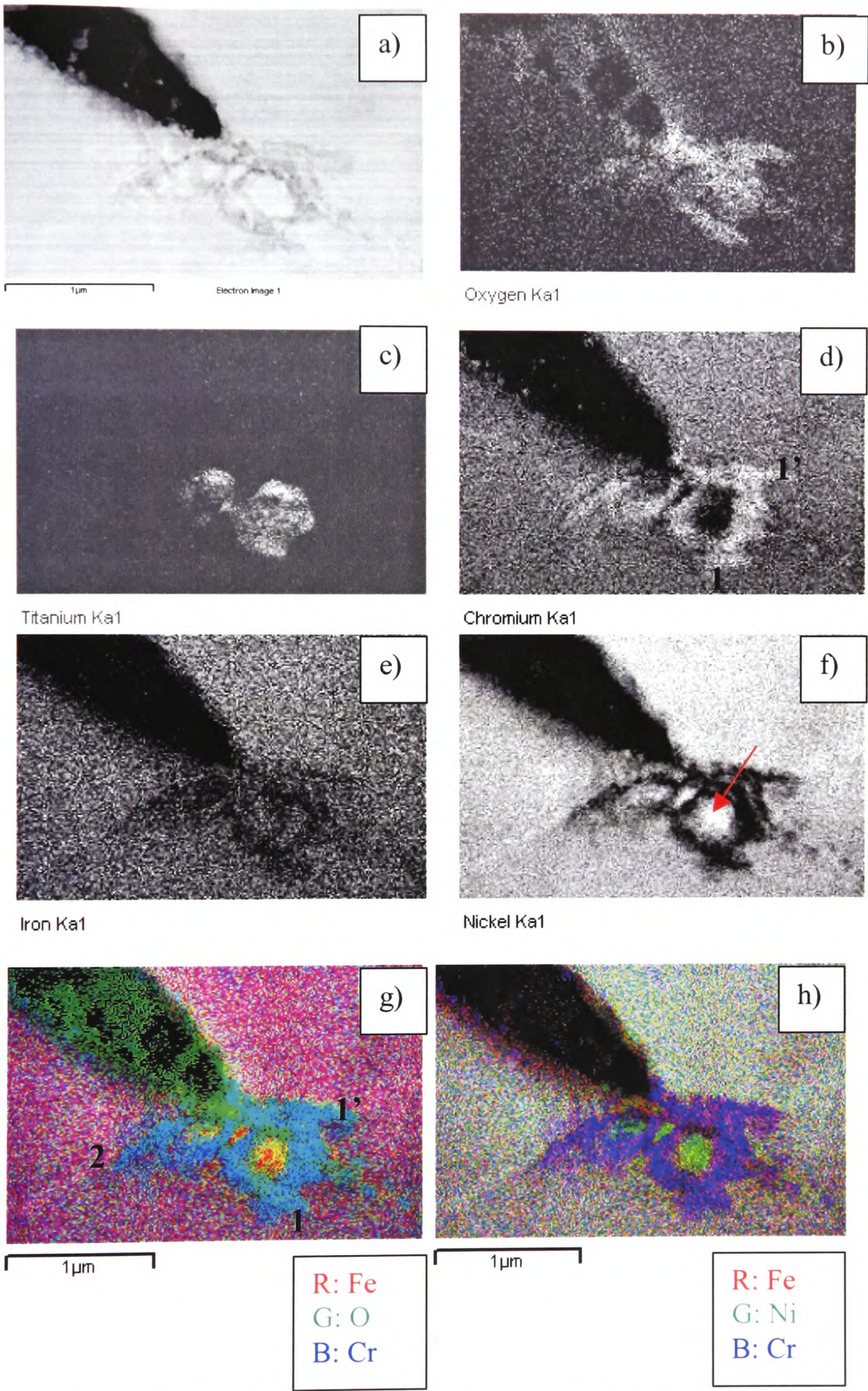


Fig. 8.9.6. a) STEM DF micrograph showing the tip of crack α ; b), c), d), e), f) EDX maps; g) and h) RGB composition of images (acquired with the INCA system in the HB501).

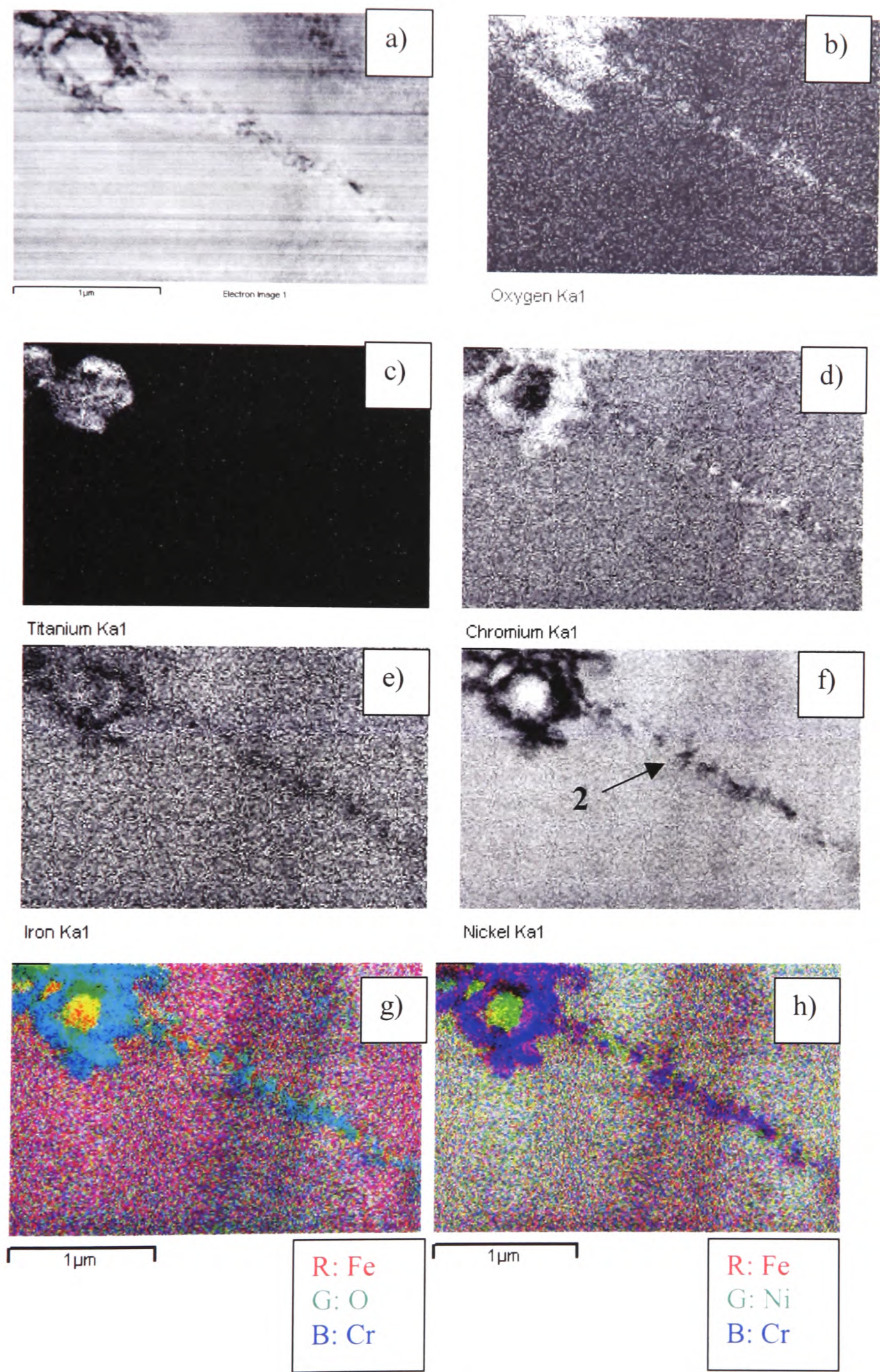


Fig. 8.9.7. a) STEM DF micrograph showing grain boundary A after the Ti particle ; b), c), d), e), f) EDX maps; g) and h) RGB composition of images (acquired with the INCA system in the HB501).

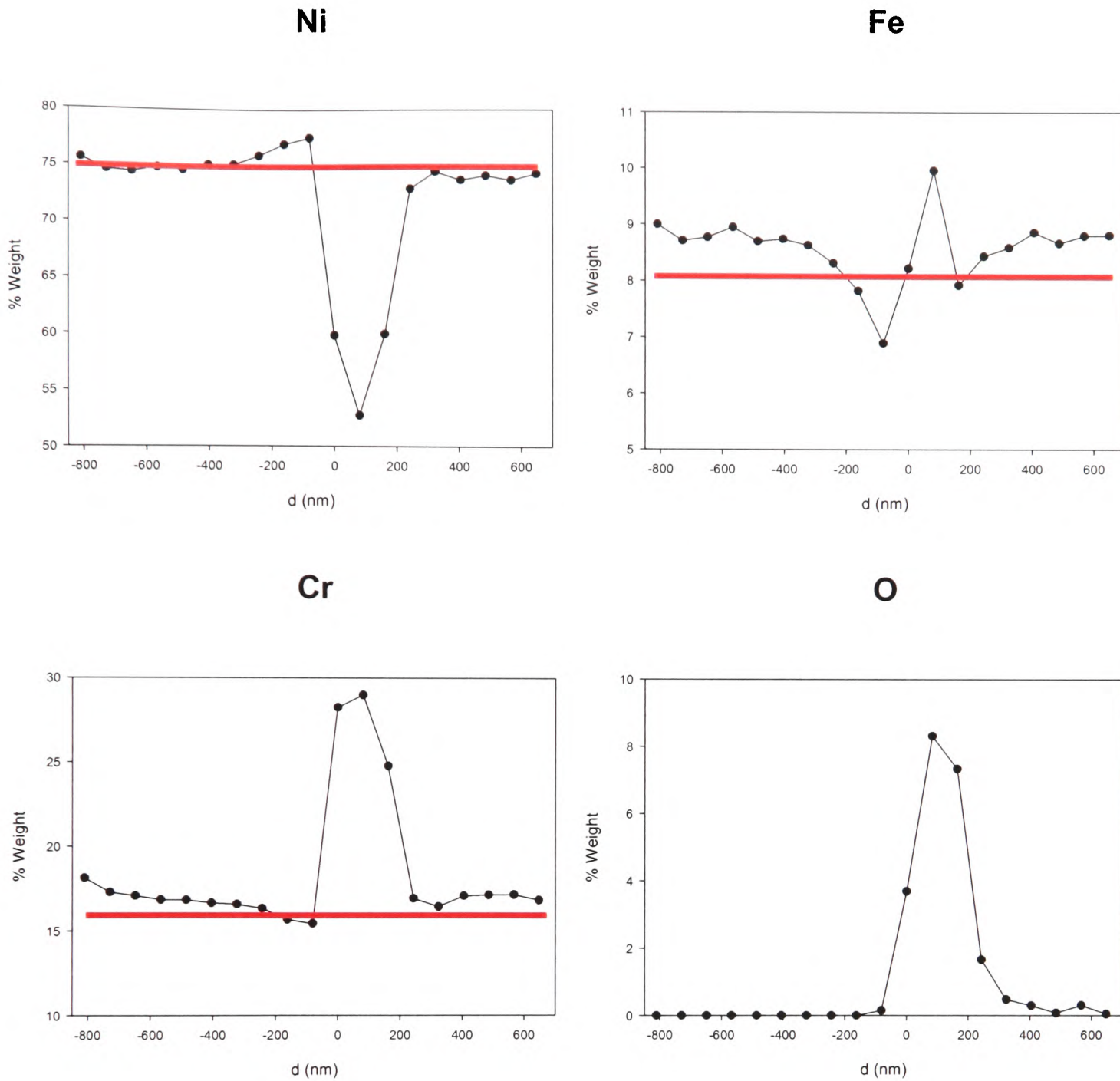


Fig. 8.9.8. EDX quantitative line profile across grain boundary B. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. (acquired with the INCA system in the HB501). The red lines indicate the nominal composition of the alloy.

8.10 Sample 10 – Uncracked: General observations

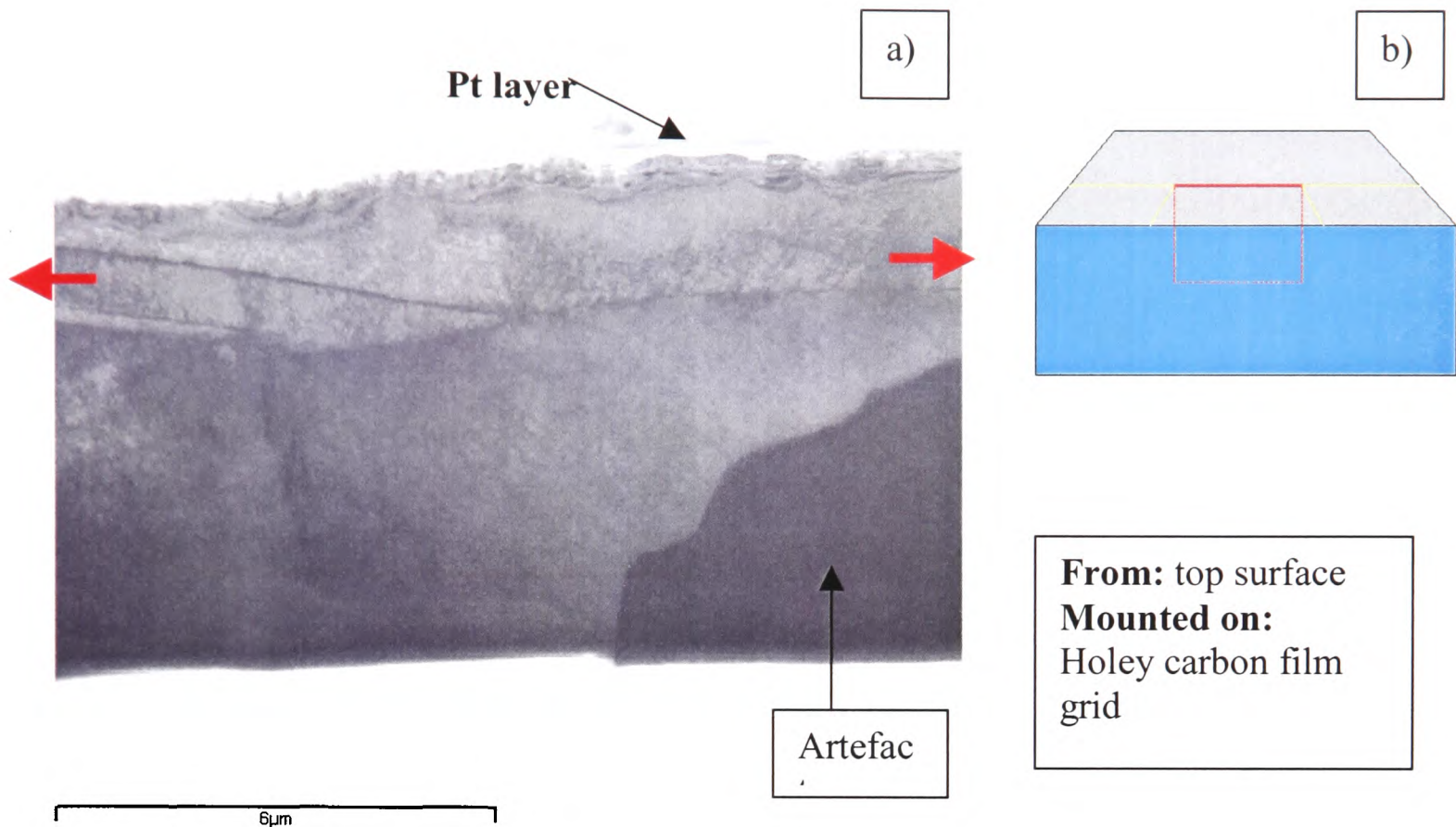


Fig. 8.10.1. a) STEM BF micrograph showing sample 9 after plucking. The strain direction is indicated by the red arrows (acquired with the INCA system in the CM20); b) Sketch showing the orientation of the sample.

Sample 10 (Fig. 8.10.1a) was prepared from the top surface (in grey in Fig. 8.10.1b) in order to study the superficial oxide layers. However, it was found that the thick scales found elsewhere^{1; 3; 4} were missing. This indicated that due to sample handling, polishing, etc after testing, these oxide layers were lost. However, the remaining layers were analyzed and the results are shown in Fig. 8.10.2. The x axis in Figs. 8.10.2a,b,c represents the distance from the edge of the sample. The first layer was a Ni-rich layer of approx. 20 nm (Fig. 8.10.2a). Next, a Cr-rich (Fig. 8.10.2c) of approx. 30 nm was found and finally the matrix. The Cr-enrichment might be associated with increased Fe, but the Fe data was too noisy to be certain. As the LINK system could not quantify the O, the quantification is not expected to give exact results. This would explain the differences between the nominal composition of the alloy and the measured data, although the region analyzed is close enough to the environment (and only 200 nm in depth) to exhibit the Ni depletion and the Cr-enrichment shown in Fig. 8.10.2. An EDX spectrum from the Cr-rich layer is shown in Fig. 8.10.3, to prove that it was an oxide. The relative height of the Cr-L peak in

comparison to the Cr-K $_{\alpha}$ peak is too high to arise only from the Cr, indicating the presence of O.

The artefact region noted in Fig. 8.10.1 is an artificially thick region which was not thinned properly in the FIB.

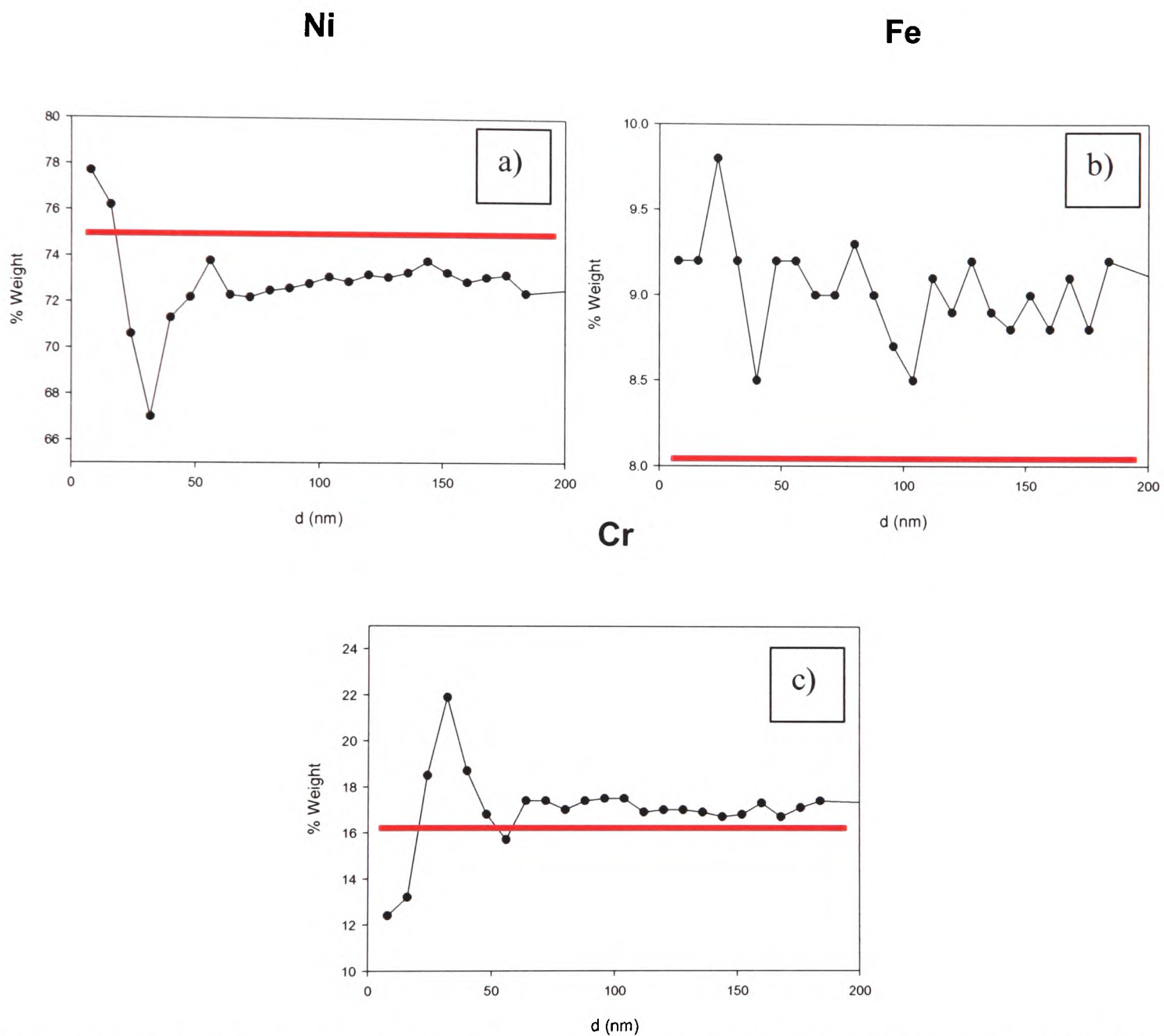


Fig. 8.10.2. EDX compositional line profile across the top surface edge. For the oxide: $\sigma(\% \text{ wt. Ni}) = 1.4$, $\sigma(\% \text{ wt. Fe}) = 0.4$, $\sigma(\% \text{ wt. Cr}) = 0.4$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.7$, $\sigma(\% \text{ wt. Fe}) = 0.3$, $\sigma(\% \text{ wt. Cr}) = 0.3$. (acquired with the LINK system in the HB501). The red lines represent the nominal composition of the alloy.

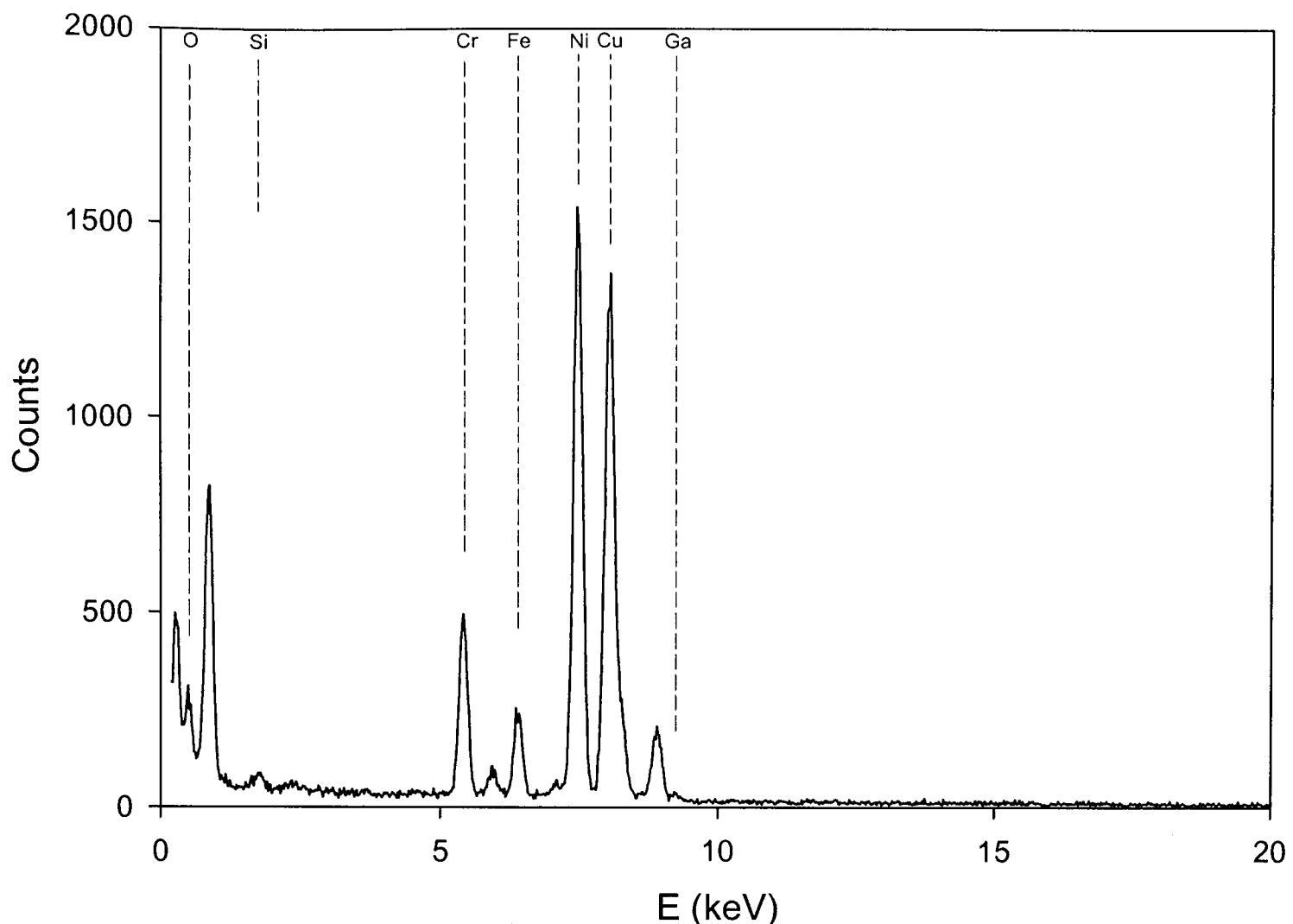


Fig. 8.10.3. EDX spectrum of the Cr-rich layer at the surface of the sample (acquired with the LINK system HB501).

8.10.1 Main observations

- Some oxide layers seem to be missing.
- Cr-oxide observed close to the top surface

8.11 References

1. Combrade, P., Cayla, O., et al. (1988) Environmental degradation of materials in nuclear power systems.
2. Hipsley, C. A. and DeVan, J. H. (1989) Acta Metallurgica 37(5), 1485.
3. Miglin, B., Sarver, L., et al. (1988). Proceedings of the Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors. 535
4. Moulin, G., Huntz, A. M., et al. (1989) Materials-Science-&-Engineering-A- (Structural-Materials:-Properties,-Microstructure-and-Processing). vol.A120-121; 15 Nov. 1989;p.221-8.

Chapter 9:

Results on Alloy 600 under slow strain rate test

9.1 Introduction

In order to compare with a Constant Load Test, samples of Alloy 600 under Slow Strain Testing have been analysed.

The conditions of these tests have been already described in Chapter 5 (Section 5.2.5). All the samples analysed showed similar results, so only sample (6LA) will be described in detail. Its composition was:

Sample 6LA: C: 0.0063, Si: 0.35, Mn: 0.36, P: 0.009, S: 0.002, Ni: 74.86, Cr: 16.12, Fe: balance.

FIB was used to prepare the samples, in a similar way to the Constant Load samples.

9.2 Sample 6LA

Sample 6LA showed sharper and longer cracks than the Constant Load samples, as can be seen in Figs. 9.1 a) and b). The horizontal lines are an artefact from the image acquisition software.

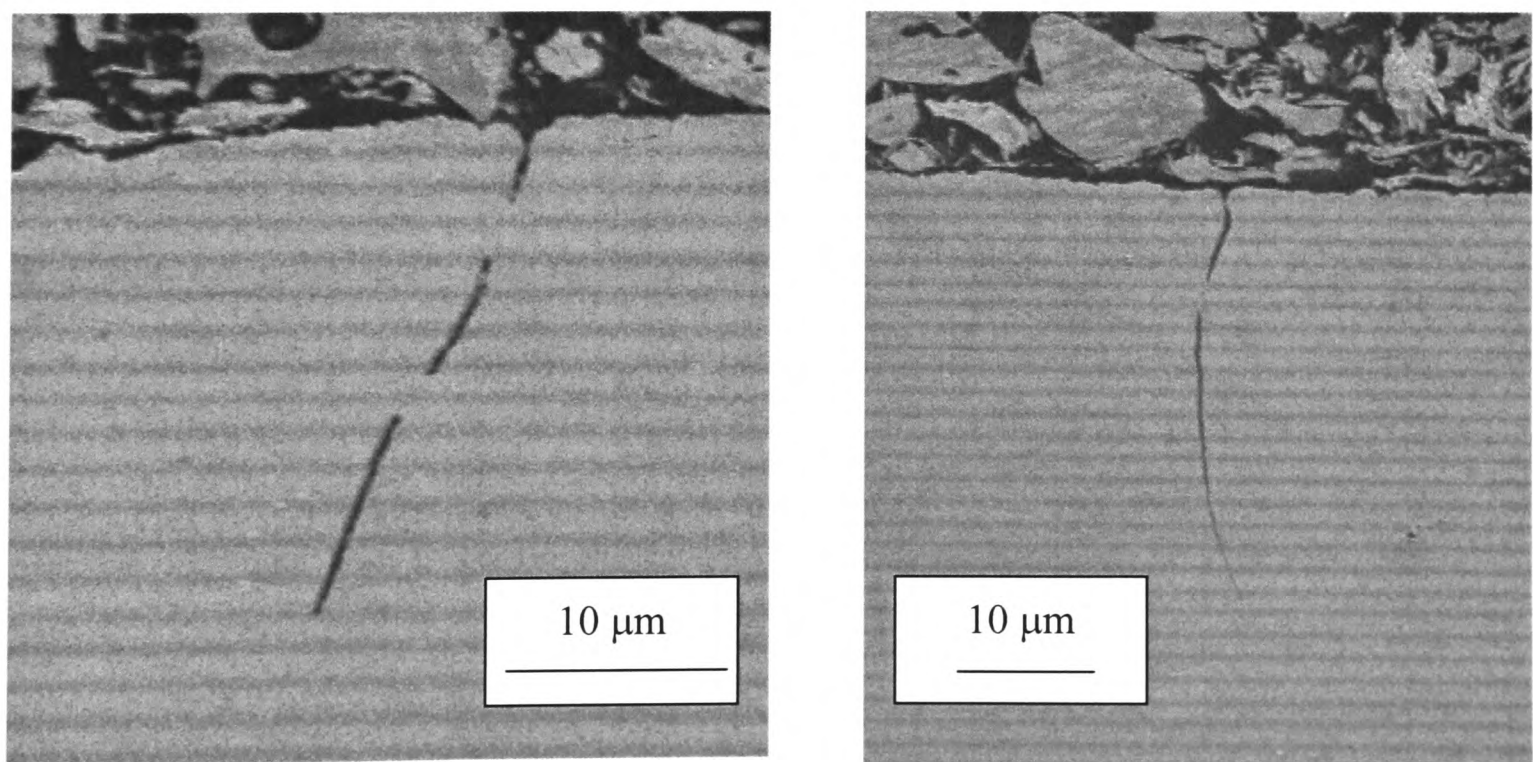


Fig. 9.1 a),b) FIB SE micrograph showing stress corrosion cracks in a x-sectional view. The sample was mounted on bakelite, which can be seen on the upper part of the image.

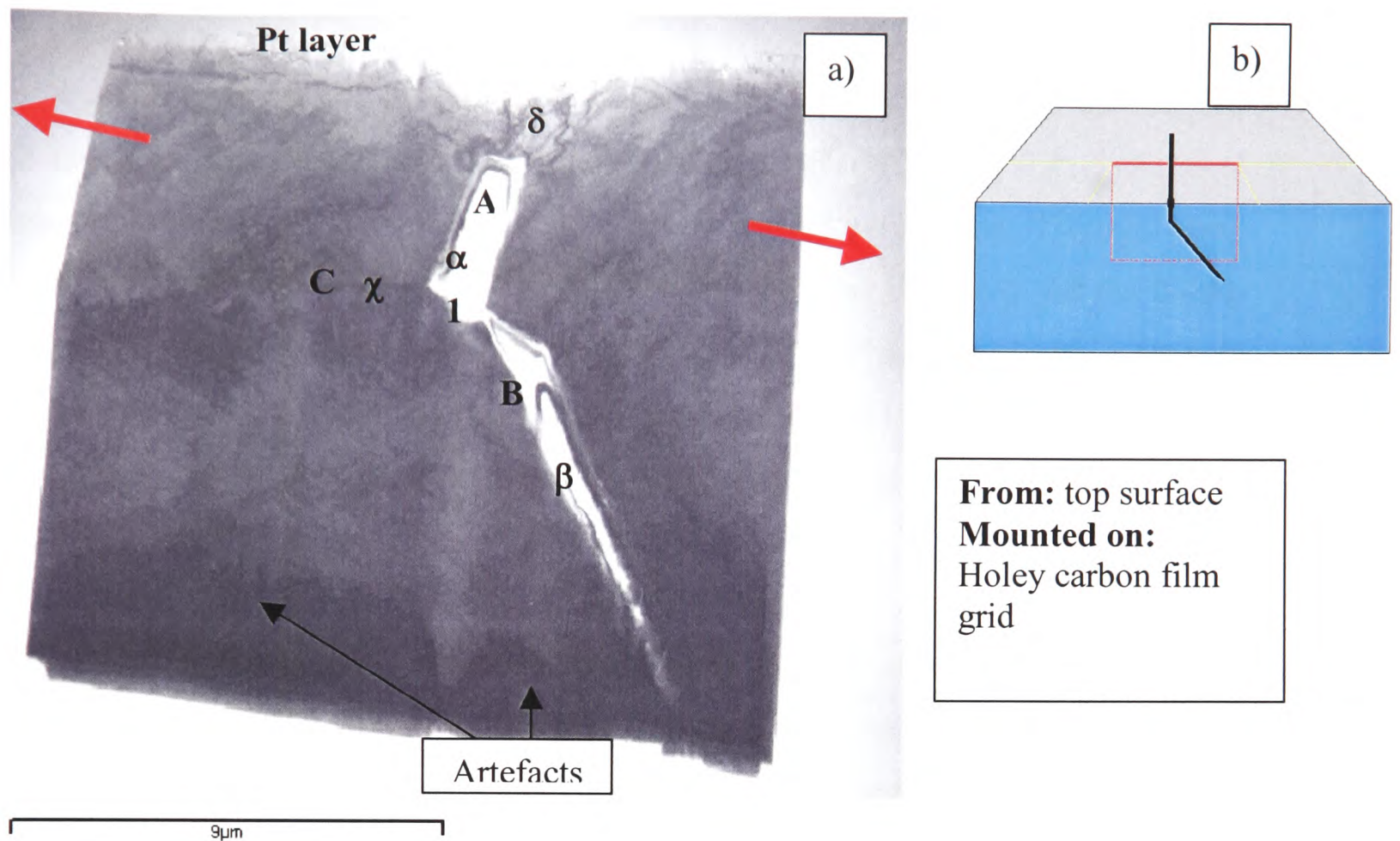


Fig. 9.2. a) STEM BF micrograph showing sample 6LA after plucking. The loading direction is indicated by the red arrows (acquired with INCA system in the CM20); b) sketch showing the orientation of the crack in the sample.

Fig. 9.2a shows a STEM BF micrograph of sample 6LA, which was prepared from the top surface and with the sample plane parallel to the loading direction. It has two main cracks (α and β) which have attacked grain boundaries **A** and **B**, respectively. At the triple point (labeled **1** in Fig. 9.2a), boundary **C** is also attacked and a small crack (γ) can be seen at higher magnification in Fig. 9.3. At the upper part of the sample, another crack (δ) was discovered, along grain boundary **A**.

The sample has some artefacts due to FIB sample preparation. Some thicker regions can be seen at the bottom of the sample (arrowed in Fig. 9.2a) and part of the protective Pt layer plus a small part of the sample has been lost during the final thinning.

9.2.1 Analysis

Both cracks α and β seem to have filled with nanocrystalline NiO although it has not been preserved completely. Several holes (arrowed in Fig. 9.3) have been observed which might have been caused by FIB sample preparation. Through these holes, as an artefact, the C supporting film can be observed (Fig. 9.3). All the flanks analyzed had a thin Cr-oxide layer between the nanocrystalline NiO and the matrix. It should also be noted that reciprocal features can be observed in each flank. In Fig. 9.3 they have been labeled as 2-2' and 3-3'. This suggests that the boundaries were opened abruptly.

In Fig. 9.4, crack χ is shown at a higher magnification, together with the positions of the two EDX compositional line profiles acquired. The “blue” line profile was acquired along the attacked boundary, carefully choosing the position of the spots so that they were in the attacked region. This line profile revealed that the depth of the attack was ~ 200 nm (Fig. 9.5). It can also be seen that the depletion in Ni (Fig. 9.5a) anticorrelates with the enrichment in O (Fig. 9.5d). The position at which the O concentration in the boundary falls to zero is coincident with the position at which the Ni concentration returns to the nominal value of the alloy. The Fe concentration (Fig. 9.5b) seems to be stable along the boundary while Cr (Fig. 9.5.c) is enriched wherever there is O enrichment, indicating the presence of a Cr-oxide. Fig. 9.6 shows the results of the “red” line profile, across the attacked grain boundary. At a depth of ~ 120 nm, the width of the attack can be defined by the width of the Ni-depleted area or the width of the O-enriched area. In both cases a value of ~ 40 nm is obtained.

The upper part of crack α , including crack δ , is shown in Fig. 9.7. In the BF image (Fig. 9.7a) crack δ and the Ni particle are hardly distinguishable. The DF image, acquired with the annular dark field detector in the STEM (HB501), is more useful, as the contrast is mostly controlled by differences in atomic number, Z . Crack δ is depleted in Ni, and enriched in O (lower Z) so it appears darker. The Ni particle also appears lighter than the matrix.

An EDX quantitative line profile was acquired across crack δ revealing a Ni depletion of $\sim 20\text{nm}$, although a small Ni enrichment is also observed on the left flank (Fig. 9.8a). The crack is filled by Cr-oxide, as shown by Figs. 9.8c and d, and probably Cr_2O_3 although this was not confirmed. A qualitative EDX map was acquired in the lower region of crack δ (Fig. 9.9a) and confirmed what the line profile had already revealed: the crack is depleted in Ni (Fig. 9.9d) and filled by Cr-oxide (Figs. 9.9b and e).

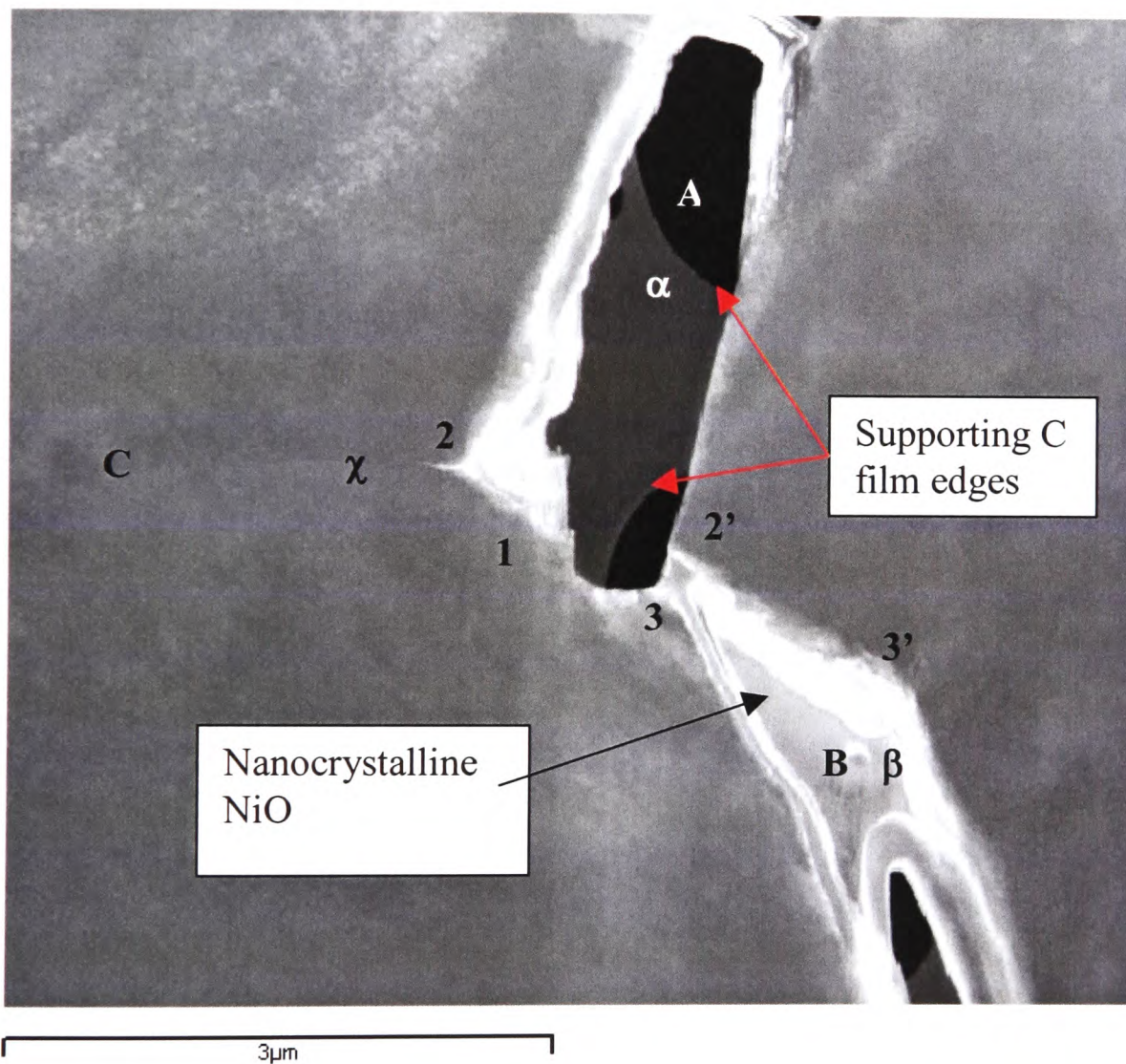


Fig. 9.3 STEM DF micrograph showing the region of the triple point (1) at a higher magnification (acquired with the CM20).

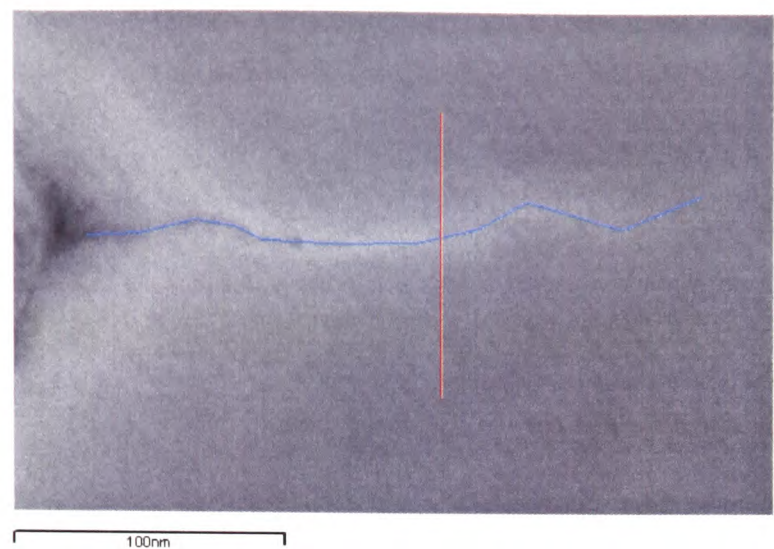


Fig. 9.4 STEM DF micrograph showing crack χ and the positions of the two line profiles (acquired with the HB501).

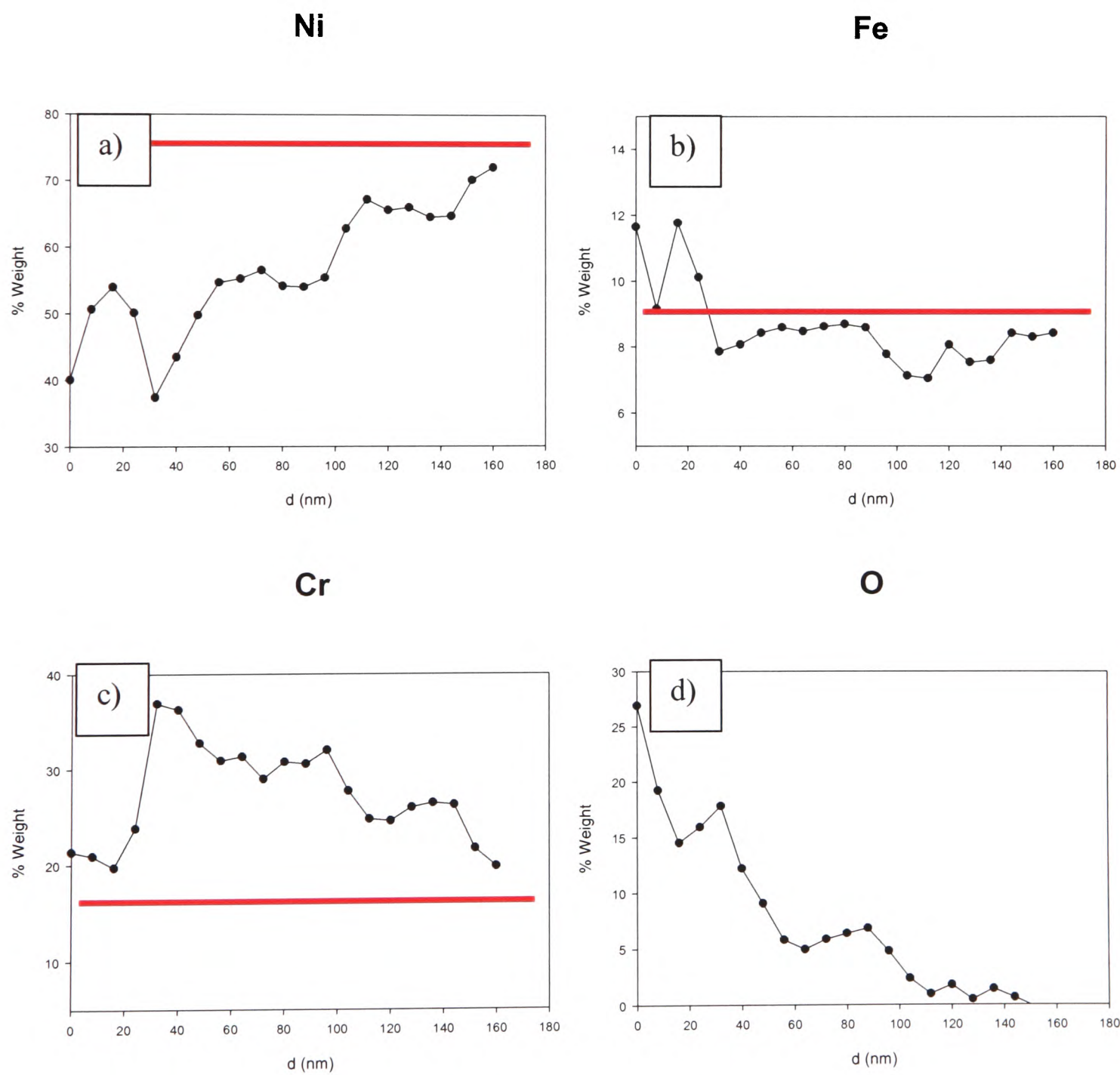


Fig. 9.5 EDX quantitative line profile along the blue line in Fig. 9.4. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red line represents the nominal composition of the alloy (acquired with the INCA system in the HB501).

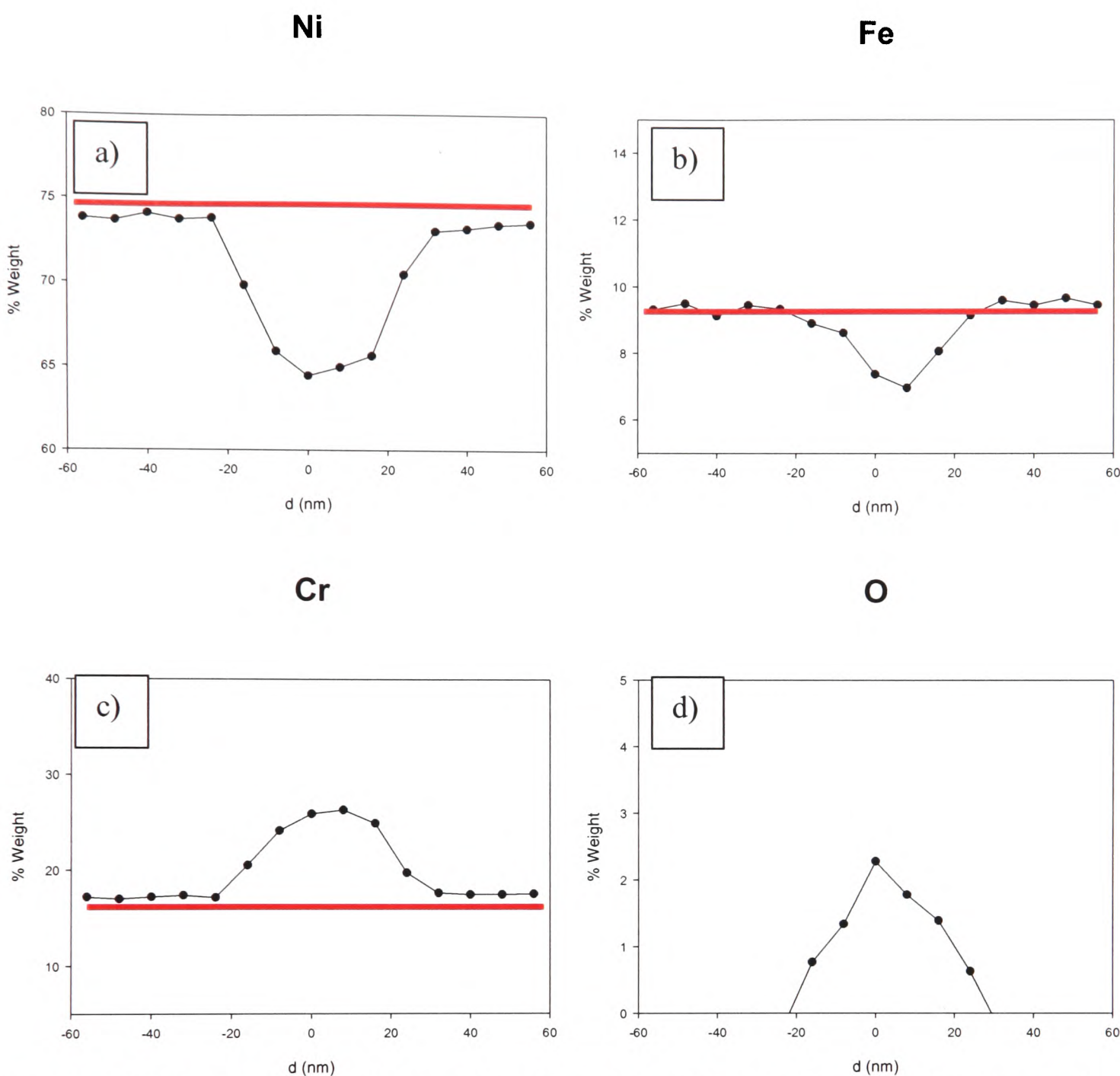


Fig. 9.6 EDX quantitative line profile along the red line in Fig. 9.4. For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.3$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red line represents the nominal composition of the alloy (acquired with the INCA system in the HB501).

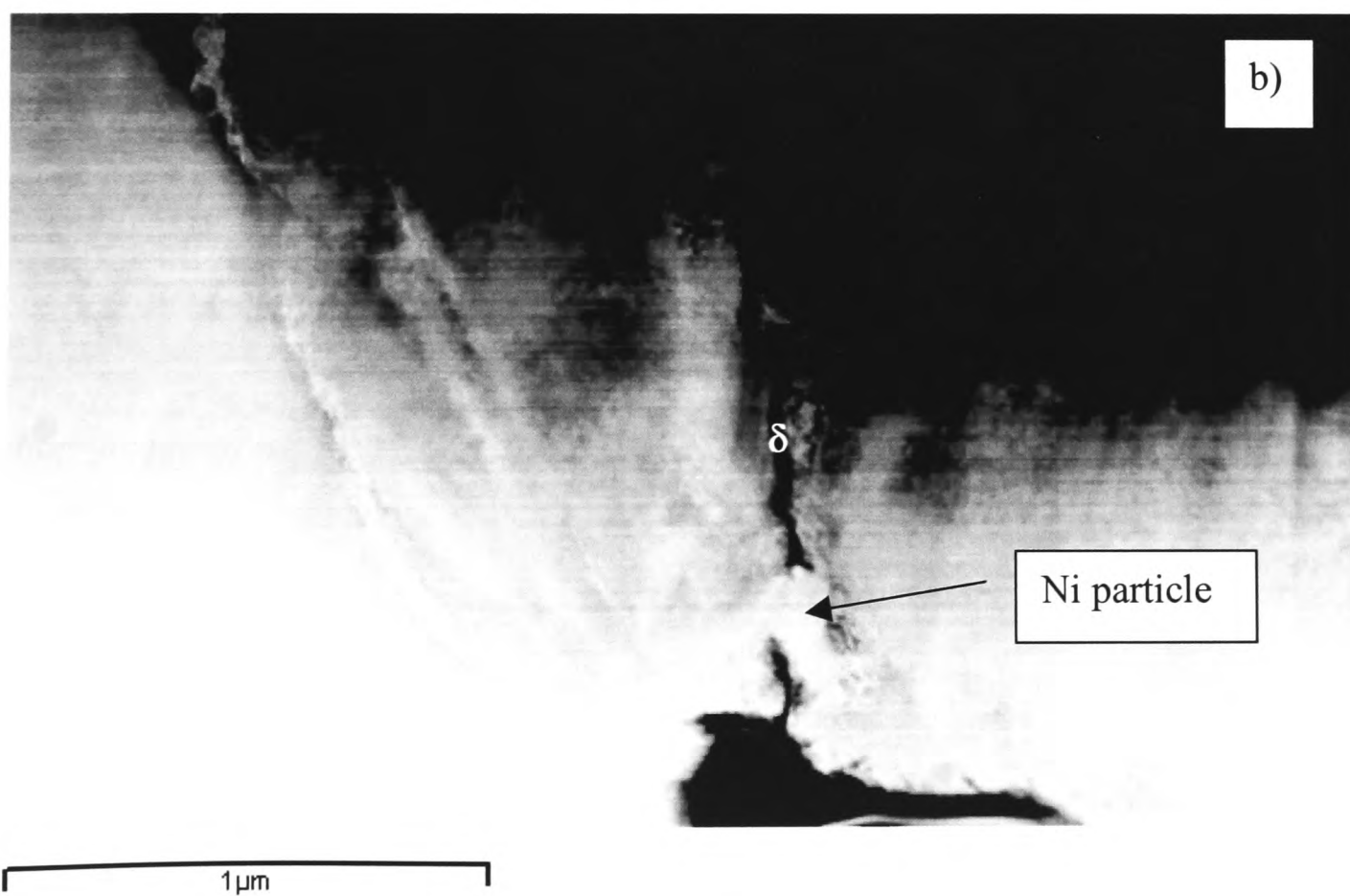
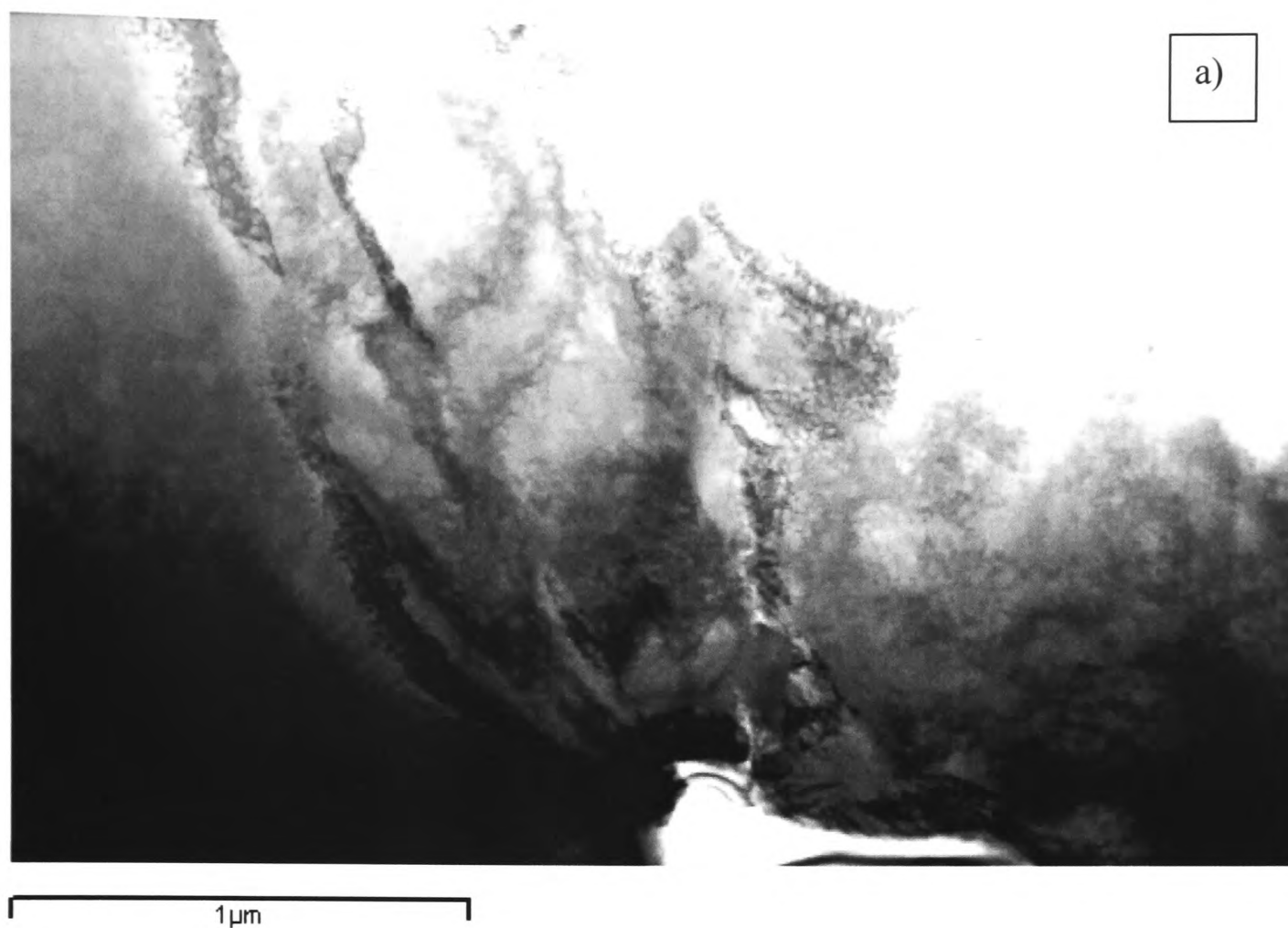


Fig. 9.7 a) STEM BF image of the area containing crack δ ; b) STEM DF image of the same area (acquired with the INCA system in the HB501).

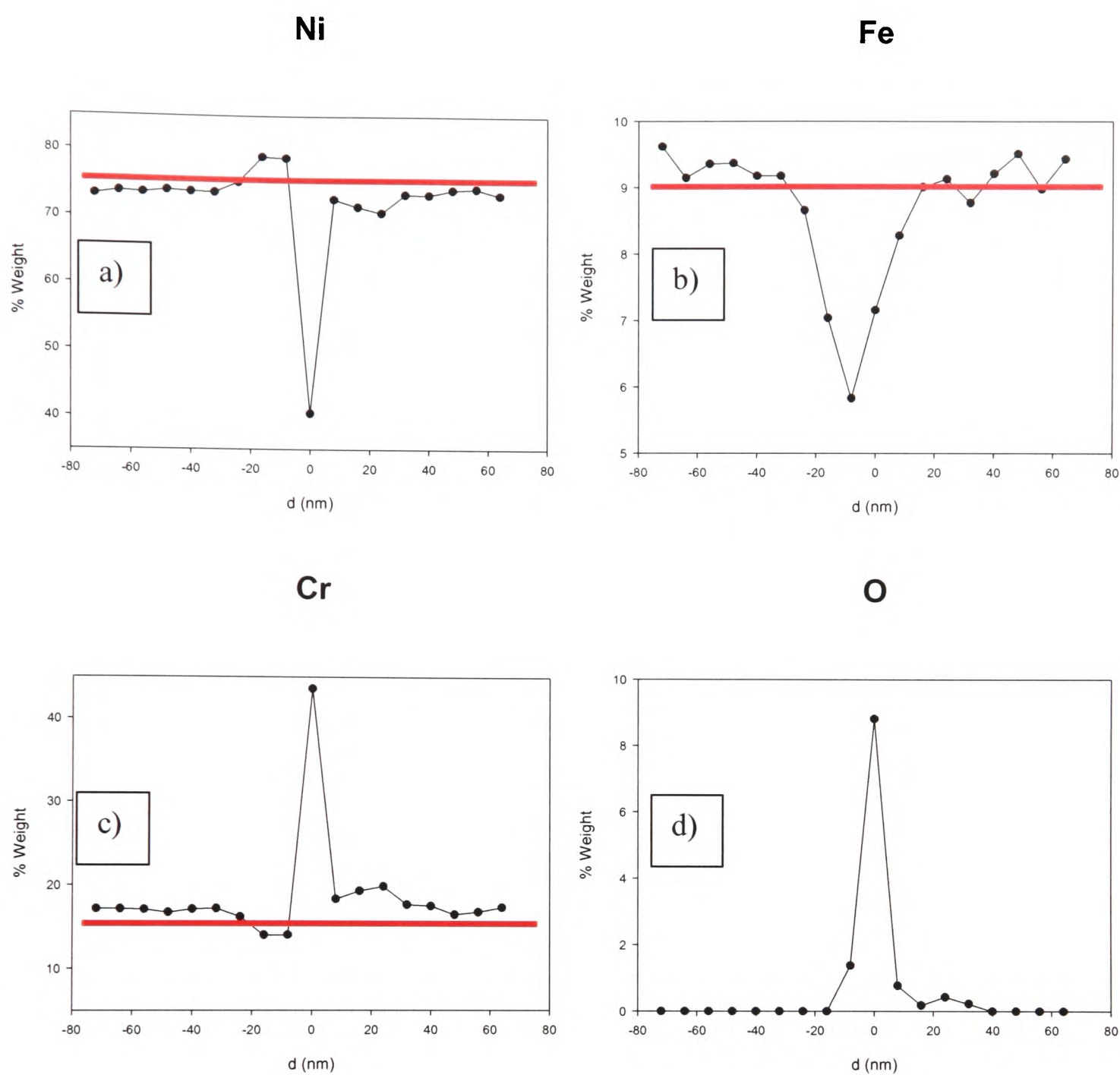


Fig. 9.8 EDX quantitative line profile across crack δ . For the oxide: $\sigma(\% \text{ wt. Ni}) = 0.3$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. For the matrix: $\sigma(\% \text{ wt. Ni}) = 0.4$, $\sigma(\% \text{ wt. Fe}) = 0.1$, $\sigma(\% \text{ wt. Cr}) = 0.2$. The red line represents the nominal composition of the alloy (acquired with the INCA system in the HB501).

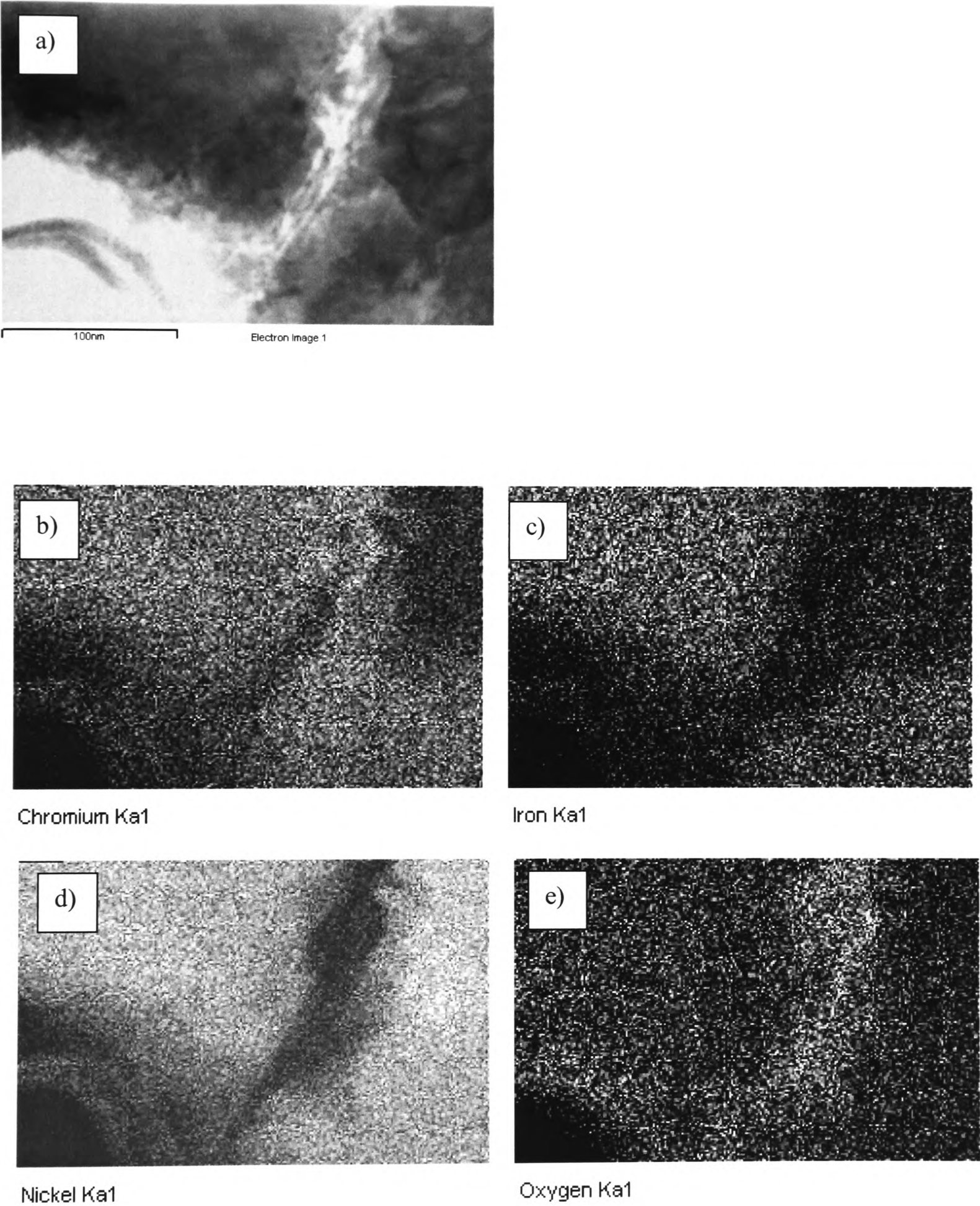


Fig. 9.9 a) STEM BF image; b),c),d) and e) EDX compositional maps from the “lower” part of crack δ (acquired with the INCA system in the HB501).

Chapter 10:

Discussion

10.1 Introduction

The discussion will be focused mainly on the Alloy 600 sample under CLT, as it provided most of the results shown in this thesis. The results acquired from the other samples and materials will be compared to those of the CLT Alloy 600.

10.2 Sample preparation

The choice of a technique for the TEM sample preparation was not easy. At the time this project started (Oct. 99), no references were found in the open literature to a reliable technique which would allow the observation of SC cracks with a length of microns. That is why an evaluation of the available techniques was performed, finding that only Ion Beam Thinning (IBT) and Focused Ion Beam (FIB) could give the precision required. Both techniques were used in the way described in Chapter 4 and evaluated. FIB was chosen rather than the PIPS (IBT) for preparing TEM samples containing shallow cracks. The main reasons for this choice were:

- It is possible by FIB to select individual cracks (and their orientation in the final TEM foil).
- The samples had a low density of cracks and small gauge length, so that thin foils prepared by IBT had only a small possibility of containing cracks, and the sample attrition rate is unacceptably high
- The artefacts introduced by the FIB were found to be “less bad” than those introduced by the IBT. The FIB implants some gallium in the sample, but the damaged thickness can be contained within 10 nm on each side of the membrane. All the oxidation products were retained, although the FIB preferentially removed the nanocrystalline NiO. The PIPS was also found to preferentially remove the oxides, even when preserving the cracks by impregnating with epoxy, but as the milling process at such a small scale cannot be monitored, the uncertainty about the presence or not of a bigger oxide layer (which might have been lost) in the cracks is very high. Using the FIB, the sample image is updated after every step, so from the first step it is known if the crack is filled or hollow.

The success rate of the FIB sample preparation grew as the project was being developed. Initially, the final thinning and plucking steps could decrease the success rate to below 50%. In the last samples prepared, 8 out of 10 were successfully deposited on the carbon film. Also, it was proven to be a much less time-consuming technique than PIPS as there was no requirement for careful polishing of cross sections to a thickness of a few tens of microns.

FIB samples have approximately parallel sides, if the final stages of thinning and cleaning are performed properly, so thickness and bend effects are eliminated. The use of the modified “lift-out” (or “framed membrane”) technique prevented buckling, whereas PIPS samples are always likely to buckle. Another main advantage is that the total volume of the FIB sample is much smaller than the PIPS sample, so the analytical measurements are less distorted by excitation of the surrounding matrix. The artefacts which do arise, such as Ga, Cu and C peaks from the grid which are readily recognizable.

10.3 Oxides on the surface

The samples analyzed did not show evidence of the expected oxide layers. Only an inner Cr-oxide layer followed by a Ni-rich layer were observed, instead of the Fe-rich spinels described in the literature^{19; 22}. The samples used for this research were cut in 2 identical pieces in Japan, by INSS, one piece only being sent to us. The other half was analyzed in Japan by INSS. It has been reported by them that the expected oxide layers were present in the form of a Cr-rich inner layer and a Fe-rich outer spinel layer. This second layer was actually formed of NiO/NiFe₂O₄ duplex particles⁶.

The reason that the surface oxide was not observed satisfactory in our research is believed to be fracture or separation during handling. This includes cutting in a diamond saw and consequently immersion in the lubricant fluid. However, because INSS characterised the surface oxides for the same oxidising conditions, their results were considered to be valid for this research. This assumption would explain the presence of NiO/NiFe₂O₄ duplex particles embedded in the nanocrystalline NiO (see

Sample 1, particle **i** in Fig. 8.1.18b; Sample 3, particle **a** in Fig. 8.3.5; Sample 4, particles **a** and **b** in Fig. 8.4.1a; Sample 8, particle **b** in Fig. 8.8.17). These particles are likely to have become detached from the surface, and floated in the coolant of the autoclave before being sucked into the crack as it opened.

The near surface structure was found to be formed of small grains (of the order of microns) with long boundaries parallel to the substrate, as revealed by EBSD. The mechanism of formation of these small grains remains uncertain, but they are considered to be relevant to the initial attack of the surface and have been observed by other authors ². One possible explanation of their formation could be dislocation movement and recovery, driven by the high surface temperature generated during mechanical abrasion of the surface, of the highly strained surface layer induced by the abrasion.

10.4 Oxidation of grain boundaries

The superficial oxidation of Alloy 600 in PWR primary water conditions has been detailed in Chapter 2 and the oxidation of the superficial grain boundaries up to depths of 10 μm of unstrained Alloy 600 in primary water conditions has been confirmed ⁹.

It can be assumed that oxygen enters the grain boundaries through the external oxide scales and preferentially oxidises the Cr (thermodynamically, the most likely to be oxidized). Most of the work reported on the diffusion of O in Ni-Cr alloys is on the high temperature region ($\sim 1000\text{ }^{\circ}\text{C}$), and the few papers that mention the diffusion at $\sim 400^{\circ}\text{C}$ have been criticized on the grounds that they did not separate the contributions from grain boundary diffusion and bulk diffusion. Extrapolation of the high temperature results to low temperature predicts much slower O diffusion than observed in the present work. Several reasons can be proposed for this:

- Vacancies created by the removal of chromium could condense and form the observed nanopores. Thus, the oxygen would not only diffuse through the oxide but also through the nanopores network, forming Cr_2O_3 as intergranular oxide. It has also been suggested that the origin of these vacancies which form nanopores could be the

oxide growth stresses or the internal oxidation of carbon ⁴. The internal oxidation of carbon would form bubbles, embrittling the grain boundaries, but this has only been observed at temperatures of around 1000°C, and never at PWR conditions.

- The stress field is modified locally at and ahead of the crack tip (in the plastic region), enhancing the diffusion of oxygen ^{16; 18; 17}.
- The oxygen potential in the grain boundary ahead of the crack tip is assumed to be lower than that in the open boundary, as Ni is only observed in an oxidized form outside the attacked boundary, enhancing the diffusion of the negative ions inwards (O^{2-}).

The growth of this intergranular oxide would develop stress at the grain boundary, as Cr_2O_3 has a Pilling-Bedworth ratio of 2.07. However, the observation of pores along the oxide and the diffusion of alloying atoms (Ni) away from the front of the attack suggest that the oxide is not completely solid. Hence, the value of the Pilling-Bedworth ratio is not necessarily relevant.

The presence of a stress field at the crack tip would affect the diffusion rates and facilitate the diffusion of oxygen along the boundary as predicted by Rauh and Bullough ^{16; 18; 17}. According to Rauh's calculations, Cr and O are expected to diffuse to the crack tip and along the grain boundary ahead of the tip, as their ionic volume is bigger than that of Ni. These calculations also predict the segregation of embrittling solutes such as hydrogen to transgranular cracks, providing evidence consistent with slip band enhanced intergranular segregation. Smaller atoms, conversely, are predicted to plate out on the open crack flanks.

The growth of chromia in the grain boundary has another consequence. Depending on the Cr content of the Ni alloy, the Cr_2O_3 and $NiCr_2O_4$ may or may not act as effective diffusion barriers ¹⁹. If the oxygen partial pressure is high enough, NiO would be formed and short-circuit the Cr-oxide, preventing the "passivation". However, NiO has not been observed in the grain boundaries which suffer intergranular attack (IGA). Instead, many pure Ni-clusters (Sample 1, Figs. 8.1.10 and 11; Sample 4, Fig. 8.4.11; Sample 5, Fig. 8.5.5; Sample 6, Figs. 8.6.8, 9; Sample 7,

Fig. 8.7.6; Sample 8, Fig. 8.8.15; Sample 9, Fig. 8.9.6) were found to be associated with the rejection of the Ni by the formation of Cr_2O_3 . This observation suggests that the oxygen partial pressure was not high enough inside the attacked grain boundaries, being on the Ni stable side of the Ni/NiO stability plot (Fig. 2.9). The bulk temperature and H_2 overpressure will have imposed the opposite. The Ni/NiO stability is a thermodynamic calculation and, therefore, does not necessarily predict the influence of kinetics on the dynamic situation that exists during crack growth and IGA. Some of the boundaries studied showing IGA (e.g. grain boundary C in Sample 2) did not have any Ni-clusters. This might be due to many reasons, but the most likely is the 2-dimensionality of the attack. The sample contains only a ~ 80 nm section of the grain boundary plane, and the Ni clusters have always been found to be evenly distributed, so it is possible that they had been present in the grain boundary but at other positions out the plane of the specimen, i.e. it is just a sampling probability issue.

Many of the qualitative line profiles acquired across the attacked boundaries show a very evident decrease in the Ni counts but almost no significant enrichment in Cr or Fe (e.g., Sample 2, Fig. 8.2.9; Sample 6, Fig. 8.6.10). Assuming that the thickness of the attacked region remained approximately the same as that of the displaced matrix, this suggests that the Ni is more mobile in the Cr_2O_3 and/or the matrix than Cr is in the Cr_2O_3 . When a grain boundary is attacked, the Ni is rejected by the formation of chromia and ends up free. As has been shown, the Ni oxidizes and forms NiO outside the boundary but remains as pure Ni inside, suggesting a gradient of the oxygen potential (higher outside than inside the attacked grain boundary) .

No Ni-clusters were observed in direct contact with the environment or with the nanocrystalline NiO that filled the cracks, except at the crack tip of crack α in Sample 1, where the attack of grain boundary B begins. In this area (Fig. 8.1.10d), it is possible to observe NiO (particle a, in green) and Ni-clusters (in red) in close contact, suggesting a rapid local change of potential where it is possible to observe Ni and NiO in close proximity.

For the Constant Load Test samples, an estimated depth of the attack was measured. On average, the diffusion of oxygen along the grain boundaries ahead of the open cracks had a depth of $\sim 10 \mu\text{m}$, for an exposure time of 4840 hours. Thus, assuming that one-dimensional diffusion is an acceptable approximation, equation 10.1 is used:

$$x = a\sqrt{Dt} \quad \text{Eq. 10.1}$$

where x is the diffusion distance, a is a constant, D the diffusion coefficient and t the exposure time. Substituting the data (x and t), the following value for x^2/t is obtained:

$$x^2/t = 3.4 \cdot 10^{-16} \text{ m}^2/\text{s} \quad \text{Eq. 10.2}$$

Woodford and co-workers¹⁰ measured the diffusion of oxygen in grain boundaries of Ni at higher temperatures (800°C to 1300°C) by measuring the depth of CO_2 cavities formed at grain boundaries in unstressed specimens exposed to air. Their results for x^2/t are shown in Fig. 10.1 and a line was fitted in order to extrapolate a result for lower temperatures. The depth of the grain boundary penetration measured for the present study is 6 orders of magnitude larger than that estimated from the data at high temperatures. This result suggests that other mechanisms must operate for the diffusion of oxygen along grain boundaries, such as presence of nanopores, applied stress or potential gradient, and not diffusion through a bulk matrix or even through a disordered zone along grain boundaries.

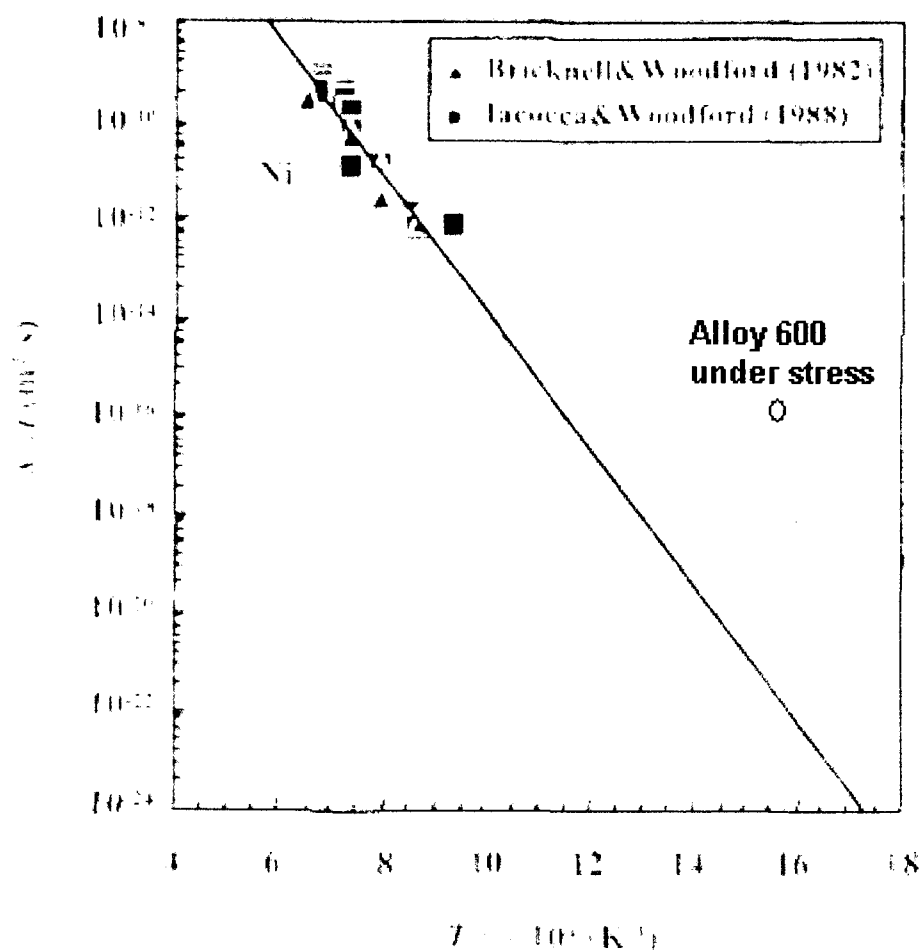


Fig. 10.1. Depth of oxygen penetration along grain boundaries versus $1/T$

10.5 Evidence for cracks forming by abrupt grain boundary opening

Using EBSD analysis, it was observed that only high-angle boundaries (HAB) were cracked. No twin-boundaries and almost no special boundaries, according to the Coincident Site Lattice (CSL) model, were found attacked. The CSL model^{24; 27; 28} classifies grain boundaries depending on their degree of order. CSL boundaries or “special boundaries” are those which have greater order and higher density of shared sites on average than HABs. Twin boundaries are the grain boundaries with the most special coincidence orientation or, in another words, with the largest number of coinciding lattice points. It is well known that an enhancement of the fraction of low-energy, fracture-resistant boundaries is beneficial to toughening²⁸. Simulations of crack propagation also show that the crack arrest distance decreases dramatically when the number of low-energy grain boundaries is increased¹².

The grain boundary energy is known to be dependent on the type and the structure of the grain boundary (i.e., grain boundary misorientation, inclination, etc). It is expected that low-energy grain boundaries need more energy to break than high-energy grain boundaries. After EBSD analysis it can be said that low-energy boundaries are more resistant to fracture. Calculating grain boundary energies is not an easy task, although some experimental data can give an estimation of the grain boundary energy depending on the misorientation angle (See Fig. 10.2)¹⁵. These results confirmed that “special boundaries” tend to have lower energies than average.

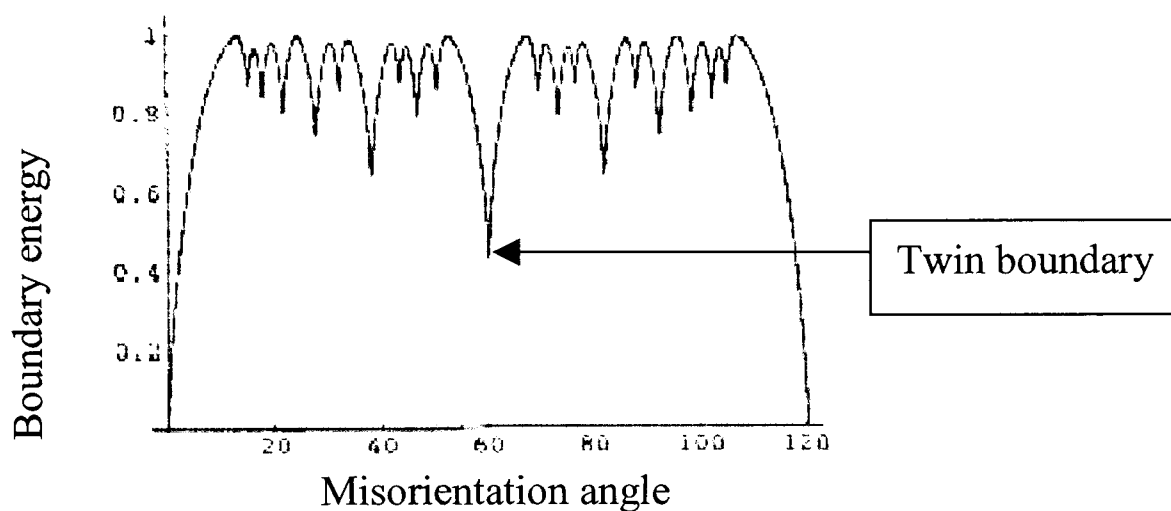


Fig. 10.2. Calculated grain boundary energy for symmetric tilt boundaries in Al produced by rotating around a $\langle 111 \rangle$ axis. The y-axis has been normalized dividing by 600 erg/cm^2 ¹⁵.

Two main observations support the hypothesis that these high-energy (or high-angle) grain boundaries open abruptly to form an intergranular crack, rather than such cracks being produced by internal oxidation:

- Presence of “large” particles inside the cracks. These particles were found embedded in the nanocrystalline NiO and were often completely isolated from the flanks. Two kind of particles were found: Oxides which were expected on the external surface oxide layer (as mentioned in the previous section) and “foreign” particles which could be present in the autoclave during the testing. The latter particles include: a Ti-oxide (particle **k** in sample 1 ,Fig. 8.1.19b), CaCO_3 particles (particle **a** in sample 8, Fig. 8.8.1a) and a Fe-Si particle (particle **b** in sample 7, Fig. 8.7.16). Some of these particles might also be inclusions, as they have been observed frequently during this research, within the matrix.

- Complementary features on each flank of the crack. Multiple observations of the flanks of the opened cracks suggested that those were not heavily attacked, maintaining the same morphology as before separation. In other words, if the nanocrystalline NiO was removed and the crack “closed up” again, then the details of opposing flanks would correspond exactly. If the volume filled by nanocrystalline NiO was due to internal oxidation, the morphology of both flanks would not necessarily be correlated. This can be easily observed in sample 1 (Fig. 8.1.2a), sample 2 (features **2** and **2'** in Fig. 8.2.1a), sample 4 (almost parallel flanks, although the orientation of the boundary changed, Fig. 8.4.1a), sample 7 (features **1** and **1'** and **2** and **2'** in Fig. 8.7.1a). A specific example of this is shown by the Cr₂O₃ layer present on both flanks. This layer did not have a constant thickness, showing “thicker” regions on a flank that corresponded with “thinner” regions on the other flank (sketched in Fig. 8.1.6). This is very obvious in sample 7 (crack α , Figs. 8.7.1a, 2, 3 and 4), sample 5 (Fig. 8.5.5) and sample 9 (Fig. 8.9.4), although it was also found in samples 1, 2, 3, 5, 6 and 11.

10.6 Nanocrystalline NiO

All the open boundaries (cracks) studied in this project were found to be filled by nanocrystalline NiO. It is suggested that the high concentration of Ni ions in the water provided a source of Ni for the deposition of the “amorphous” NiO by the same growth mechanism that occurs on the sample surfaces. Although it could seem that the NiO had an amorphous character, it was confirmed by HR imaging that it was actually formed of many nanocrystals (Fig. 3.16). NiO monocrystals have been also found embedded in the nanocrystalline NiO, but the mechanisms of growth appear to be completely different. While the NiO monocrystals with sizes of 200 nm grew on the external surface of the sample and were deposited later inside the opened crack, the nanocrystalline NiO formed gradually from the Ni ions dissolved in the solution and from the dissolution of any pure-Ni clusters that reached the environment.

In order to check if the nanocrystalline NiO contained more oxygen due to its porosity than a NiO monocrystal, their EELS spectra were compared. The spectra can

be found in Fig. 8.3.10 for the NiO monocrystal and in Fig. 8.8.13 for the nanocrystalline NiO. The procedure followed to quantify the Ni/O ratio was:

- The background before the O-K edge was subtracted
- The intensity from the O edge onset was measured, using a 40 eV integration window in order to avoid contributions from the Cr-edge.
- The background before the Ni L-edge was subtracted
- The intensity from the Ni L-edge was integrated using a 40 eV integration window.
- The measured integrated intensities were scaled using Hydrogenic cross-sections plus white line correction subroutines in the Gatan EL/P software (Beam Energy = 300keV, Collection angle = 10 mrad).

For the NiO monocrystal, the following value for the Ni/O ratio was obtained: 1.02 ± 0.14 . This is the expected value, and confirms the validity of the method.

For the nanocrystalline NiO, a value of 0.17 ± 0.08 for the Ni/O ratio was obtained, indicating that the oxygen content was ~ 5 times higher than that of the monocrystalline NiO. This is suggesting that the nanocrystalline NiO contained a high amount of oxygen in ionic form due to its porous nature, suggesting possible hydration.

At this point is interesting to note that the autoclave had an inner layer of Alloy 690, in contact with the water used in the test simulating the primary water. At the test conditions, Alloy 690 is reported to have a Cr-rich inner layer (NiCr_2O_4) and an outer layer mainly formed of NiO¹⁹. This outer layer is believed to act as a source of NiO nanocrystals for the observed nanocrystalline NiO which grew inside the cracks. A similar environment is expected in a PWR, where the coolant is in contact with thousands of Alloy 600 tubes which will have an external oxide layer of NiO. As the coolant will be recirculating, this external layer is likely to be removed/dissolved acting as a constant source of NiO .

10.7 Intragranular attack

In 1994, Magnin^{13, 14} reported for the first time pseudointergranular microcracking. He performed Constant Extension Rate Tests (CERTs) in simulated primary water conditions (360°C), observing that SCC of Alloy 600 can be achieved either by a purely intergranular microcracking or by a zigzag microcracking on microfacets at the vicinity of the grain boundary. A new SCC model was presented emphasizing the role of localized corrosion-deformation interactions during SCC. The role of corrosion (anodic dissolution and hydrogen effects) is then essential but indirect. It would modify the dislocation behaviour and the fracture mode very locally. So, trans and intergranular SCC mechanisms can be similar in some respects and differ mainly in the localization of the corrosion-deformation interactions.

Many of the samples examined during this project exhibited intragranular cracking. They were normally located close to the areas at which a crack blunted (triple points or intergranular precipitates) and the Cr concentration showed in EDX maps was found to be constant across the crack again (See cracks β and χ in Sample 1; χ in Sample 4; β in Sample 6; β , χ and δ in Sample 7; χ in Sample 8). These cracks were generally very difficult to see in the TEM, except by EDX mapping. This suggests that :

- The cracks were very tight or possibly they were not true cracks in the sense that the matrix had fractured.
- The diffusion of O occurs down the slip band and into matrix.
- Ni diffuses outwards through the oxide.

The intragranular cracks were found to be filled by Cr_2O_3 and had a high O-content. E.g., in Sample 7 the diffusion of O was found to be considerable on the right flank of crack β and ahead of the crack tip of crack β as can be seen in the O map in Fig. 8.7.4a. This observation suggests enhanced diffusion of O and Cr either by stress intensity or dislocations. An EDX qualitative line profile was acquired ahead of the crack tip, across a low-angle boundary located at a slip band that followed crack β , as can be seen in Fig. 8.7.5. Again, as shown in Fig. 8.7.5b, the number of counts from

the Cr (Fig. 8.7.5b) was constant across the attacked zone, while the number of counts from the Ni (Fig. 8.7.5d) decreased considerably. At the slip band line, the O counts (Fig. 8.7.5e) are increased suggesting diffusion of O along the slip plane and rejection of Ni.

No transgranular cracks were observed in the SS304 sample.

Short intragranular attacks might contribute to the total intergranular cracking behaviour. It has been proved that IG cracking was dominant in small grain size samples²³, but slip bands are more likely to completely cross a small grain than a large grain, providing an alternative route for attack and a range of possible loading orientations. Many reports have shown that surface roughness plays a crucial role in anion enrichment on the surface. Much faster attack has been observed on abraded surfaces compared with polished^{3; 21}. Thus, transgranular attack might be very important for SCC crack nucleation plus a reduction of initiation time. There is no direct evidence that it plays a role in crack growth.

It has also been observed that the presence of impurities or precipitates in grain boundaries can promote intragranular attack. This will be discussed in the next section.

10.8 Influence of intergranular precipitates or impurities

Although no grain boundary segregation (of elements with $Z > 6$) has been detected in the samples, several intergranular precipitates have been observed, e.g. Cr-carbides or Ti nitrides. These precipitates have been found to reduce intergranular attack by either promoting intragranular attack or by locally reducing O diffusion. Specifically:

- In Sample 1, cracks β and χ could have been originated after the free Ni ions in the grain boundary precipitated in a Ni cluster, slowing down the O-diffusion along the grain boundary oxides.

- In Sample 4, crack χ seemed to be a consequence of the blunting of crack β . This might have happened because the stress was relieved when grain boundaries **A** and **C** opened or more likely because grain boundary **B** changes its orientation beyond the tip of crack β . This last hypothesis would have increased the stress locally, promoting intragranular attack.
- In Sample 5, the Cr-carbide labeled as **a** in Fig. 8.5.1a appeared to divert the attack around it. The matrix surrounding the carbides (positions labeled as **1** and **2** in Fig. 8.5.2) seemed to be attacked more than that in areas without carbides. As these areas do not appear as “transparent” as the rest of the boundary in the TEM BF micrographs (Figs. 8.5.1a and 8.5.2), it is suggested that the attack is slowed down locally around the carbides.
- Crack β in Sample 6 seems to be a consequence of the blunting of crack α . Crack α might have blunted because grain boundary **A** changed its orientation at position **1** (in Fig. 8.6.2a) or because the multiple Ni-clusters found around this area prevented the crack from advancing.
- The best example of this behaviour was found in Sample 9 in which particle **a** clearly blunted and stopped the advance of crack α (Fig. 8.9.1a). This particle might have changed the diffusion rate of oxygen along the boundary and represented an obstacle strong enough to locally retard the advance of the crack. As can be observed in Figs. 8.9.6 and 8.9.7, the intensity of the attack seems to have decreased after the particle until the position labelled as “**2**” in Fig. 8.9.7f. The particle appeared to have promoted intragranular attack, with the crack following different slip bands (labelled as **1**, **1'** and **2** in Fig. 8.9.6g). Another interesting observation in this sample is the presence of a large Ni-cluster immediately after the crack tip. As can be seen in the Ti elemental map (Fig. 8.9.6c), the Ti particle is exactly at the position where the crack blunted. The Ni-cluster developed ahead of the crack; probably because the Ti particle acted as an obstacle for Ni diffusion towards the open crack. It is known that without stress the oxygen would not diffuse that deep intragranularly. The fact that the oxygen diffusion continued despite the Ti obstacle shows the important role of the stress.

- Thomas and Bruemmer⁵ showed the oxidation of a Cr-carbide and suggested that the oxide formed had a denser crystal structure and would impede or slow down the oxygen diffusion. Similar observations were found in Sample 5. This mechanism would explain how the formation of grain boundary carbides by heat treatment is known to reduce IGSCC in Alloy 600. Indeed, it might be that many different particles at grain boundaries might be beneficial if they oxidise to form a denser oxide, rather than a nanocrystalline/porous structure.

10.9 Comparison of CLT and SSRT results

Although it was not possible to analyze the SSRT samples in the same detail as the CLT samples due to time constraints, the following similarities/differences were found:

- Both test methods induced stress corrosion cracks in the Alloy 600 sample under PWR primary water conditions.
- After optical and SEM observations and EBSD results, it can be said that in both samples the boundaries with a high-angle misorientation and a plane orientation perpendicular to the load direction cracked preferentially. No twin boundary cracked in any of the samples.
- In both types of samples Cr-oxide formed along grain boundaries prior to cracking.
- The CLT cracks were found to blunt with a higher frequency than the SSRT cracks. The SSRT cracks were longer and sharper in general, although the testing times cannot be directly compared.

The SSRT tests eventually force the material to yield and fracture but the fact that this occurs along grain boundaries indicates some SCC mechanism. Otherwise, more widespread ductility would occur. The faster imposed deformation would lead to a prediction of smaller IGA zones ahead of the crack tip and, possibly, more intragranular attack/cracks.

10.10 Comparison of Alloy 600 and SS304 results

It is not easy to compare directly the results on the Alloy 600 samples with those of the SS304 samples, mainly because the lengths of the cracks were very different. While the Alloy 600 cracks were all in an initiation stage, the cracks in SS304 were fully developed and almost traversed the sample. However, some basic differences and similarities are noted:

- Both materials crack preferentially along high-angle boundaries.
- No twin boundary was found attacked in either of the materials.
- Cr-carbides were found to be beneficial in Alloy 600.
- A duplex oxide layer developed on the flanks of the open cracks in the SS304. In Alloy 600 only a single, thin (a few nm) Cr-oxide layer was found. Furthermore, cracks in SS304 did not fill with the nanocrystalline NiO found in Alloy 600 nor any other oxide.

10.11 Cracking: Sequence of events in Alloy 600

The previous discussion of the observations has led to the conclusion that the sequence of events that occur during SCC crack nucleation in PWR primary water is as described below and summarized schematically in Figs. 10.5-10.9.

- Initially the Alloy 600 sample with an average grain size of $\sim 15\ \mu\text{m}$ is strained in an environment which simulates the primary coolant in a PWR system (Fig. 10.3).
- Oxide grows on the surface of the sample (Fig. 10.4).
- IGA: Some of this oxide penetrates the grain boundaries, as grain boundaries are easy paths for the diffusion of oxygen. Cr_2O_3 and Ni clusters are formed, embrittling the grain boundaries before these open (Figs. 10.5 and 10.6).

- Cracks formed easily along those grain boundaries which had an orientation closer to mode I or mixed mode I+II loading (see EBSD results in Chapter 6). Cracks propagated intergranularly and covering complete grain boundary facets unless impeded by intergranular obstacles. Cracks appeared to open quickly. This is supported by the observed shapes of the flanks and the ingress of large oxide particles. Fig. 10.7 illustrates a common observation, where the crack propagating along grain boundary **A** has subsequently diverted along a second boundary **B** after encountering a triple point. In other cases single boundary opening occurs, where the crack is arrested by a change in orientation of the boundary or a grain boundary obstacle. A plastically deformed region is commonly observed near the crack tip, while the rest of the sample does not show signs of plastic deformation.

- Once the boundary has opened, the Ni quickly dissolves into NiO, evidenced by the fact that no Ni-clusters are observed on the flanks of an opened boundary (crack). The Cr₂O₃ which formed in the attacked boundary remained on both flanks of the crack but with non-uniform width. Some parts of the flanks are found to have wider oxide layers than others, always coinciding with narrower layers on the opposite flank. This indicates that as the boundary opens, the Cr-oxide is not broken symmetrically.

- The grain boundary ahead of the crack tip is always found to be attacked by Cr-oxide, and Ni-clusters were common observations. No unattacked grain boundaries are observed ahead of crack tips. This observation is extremely important, as it gives evidence against fracture through metal and, hence, against hydrogen-bond weakening or slip-dissolution mechanism.

- NiO nanocrystals from the environment, from dissolved Ni-clusters on the flanks of the open boundary and from the outward diffusion of Ni ions from the oxide in the attacked boundary ahead of the crack tip which oxidize start depositing in the opened crack (Fig. 10.8). Sometimes an oxide particle from the external scale falls into the open crack and it is embedded by the nanocrystalline NiO.

- The position of the crack tip will be determined by:

a) the presence of intergranular precipitates which would slow down the diffusion of oxygen through the grain boundary plane and also represent mechanical obstacles

b) triple points that locally change the propagation direction and thus the loading mode and the stress intensity factor ¹¹.

- Fig. 10.9 shows a typical SC crack as found when cross-sectioning the sample, with the open crack completely filled by nanocrystalline NiO.

As none of the existing models was found to be adequate, a new model taking these observations into account must be proposed. The results obtained during this project support a solid state diffusion mechanism strongly affected by dislocations, loading state/mode and precipitation:

- Dislocations have been shown to provide easy diffusion paths for oxygen, as low angle grain boundaries induced by slip at blunt crack tips are frequently observed to be attacked. In addition, high-angle boundaries are attacked preferentially.
- Loading mode is another key factor, as the grain boundaries that have opened always tend to have a considerable mode I component and there is a reduced tendency to open as mode I decreases.
- Precipitates have been shown to slow down the diffusion of oxygen along grain boundaries and, hence, the attack. Precipitates can be capable of arresting a crack, as shown in Sample 9.

10.12 Consequences for SCC models

As a general observation, it should be mentioned that most of the mechanisms which have been proposed in the literature seem to concern themselves with the chemical side of SCC and ignore the specific role of stress (See Chapter 2). The results presented in this project take stress into consideration both through the oxide rupture and the effect of the crack tip stress. Next, the implication of the present observations to the proposed models is described:

Slip dissolution/film rupture model: The idea of film rupture and crack advance could fit with the observed behaviour, but not in the terms presented in this model. No bare metal in contact with the environment was observed, as the grain boundary ahead of the crack tips was always found oxidized and hence embrittled. For intragranular cracks, it is more difficult to discard this model, although the observations suggest that even in this case oxygen diffusion and selective oxidation of Cr occurred before cracking. This model does not take into account the role of the grain boundary microstructure, orientation and misorientation, which were proven to be key issues in the samples analysed.

Galvele's enhanced surface mobility model: This model does not predict or take into account the diffusion of oxygen along grain boundaries and the formation of Cr-oxides ahead of the crack tips. The facts that only high-angle boundaries opened and mode I loading was favoured were not explained by this model. The observed cracks seemed to have opened abruptly and not in the gradual way described by Galvele.

Internal oxidation mechanism: This mechanism reproduces well what has been observed during this research, that the diffusion of oxygen along grain boundaries produces embrittlement. However, no bubbles have yet been observed. This mechanism may be relevant in the initiation stage as it infers that the presence of the PWR primary water is capable of inducing embrittlement without requiring stress^{8; 7}. The presence of stress, together with the creation of an electropotential cell at the crack tip might explain the differences in observed and calculated diffusion rates of oxygen. This model does not however explain the preferential opening of high-angle boundaries in mode I loading that has been observed nor the presence of intragranular cracks, i.e. the relevance of stress in SCC is not addressed.

Hydrogen-induced cracking model: As the same hydrogen concentration in the coolant has been used for all the test samples used in this project, not much can be said apart from the fact that all the features observed can always be explained using another model. Recent studies of the H₂ fugacities and hydrogen permeation rates^{1; 20} are inconsistent with a hydrogen-controlled mechanism of cracking, indicating that the role of hydrogen is not essential in the SCC of Alloy 600 in PWR primary water

conditions, although it is evident that it plays a secondary role because its reduction in concentration in the primary water leads to enhanced SCC growth probably due to increased oxygen ion content in the water.

Cavity formation model: No cavities were observed during this project apart from some nanopores in the Cr_2O_3 in the attacked boundaries. These nanopores might have been formed for any of the reasons described by Bricknell ⁴, although it seems that the oxide formation induced stresses or the vacancy mobility in the electrochemical potential gradient are the more plausible ones. Apart from this, no other evidence supports this model as it does not explain the main features observed during SCC.

Corrosion Enhanced Plasticity model: Although this model explains the observation of intragranular cracks/attack, it does not account for the observed abrupt opening of the boundaries without any apparent plastic deformation.

Comparison of results with Thomas & Bruemmer papers: Due to the similar nature of the studies performed by Thomas and Bruemmer ^{26; 25; 5} and this project, a summary of similarities and differences between these studies will now be shown. It has to be noted that most of their work was published during the course of this project and was compared “*a posteriori*”.

- Thomas and Bruemmer used PIPS while FIB was used for this project. The advantages of using FIB for shallow cracks have already been discussed, together with the benefits of choosing the orientation of the sample plane. They only looked at deep cracks i.e. during the crack propagation stage, not nucleation.

- Both studies found that only high-angle boundaries tend to crack and that cracking did not occur along twin boundaries.

- No NiO artefacts were observed in this project when observing the sample surface. NiO was found to be present only in a nanocrystalline form filling the open cracks and never in the IGA region whereas Thomas and Bruemmer found it in the attacked region.

- Both studies revealed the presence of a porous Cr-oxide in the attacked zones plus Ni-rich metal particles.

- Intragranular attack along sub-grain (or low-angle) boundaries was observed in this project and not in Thomas and Bruemmer's work.

- EDX mapping has been proven to be an excellent tool for studying SC cracks in this project. Thomas and Bruemmer have not used elemental mapping.

10.13 References

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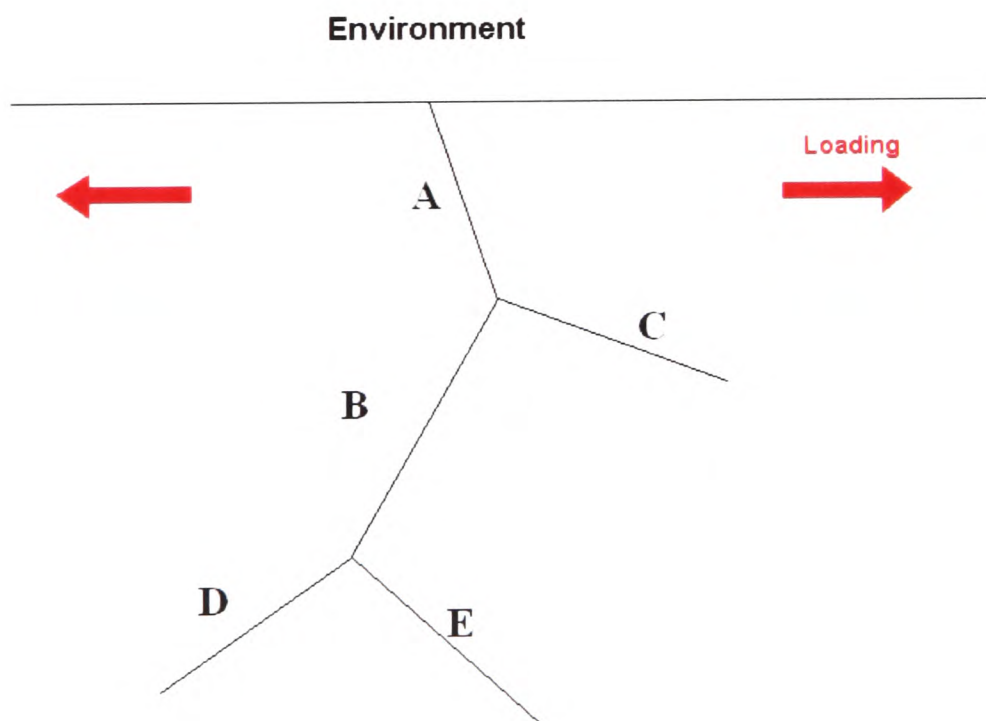


Fig. 10.3. Bulk sample is placed in contact with the environment. Grain boundaries are labelled as capital letters.

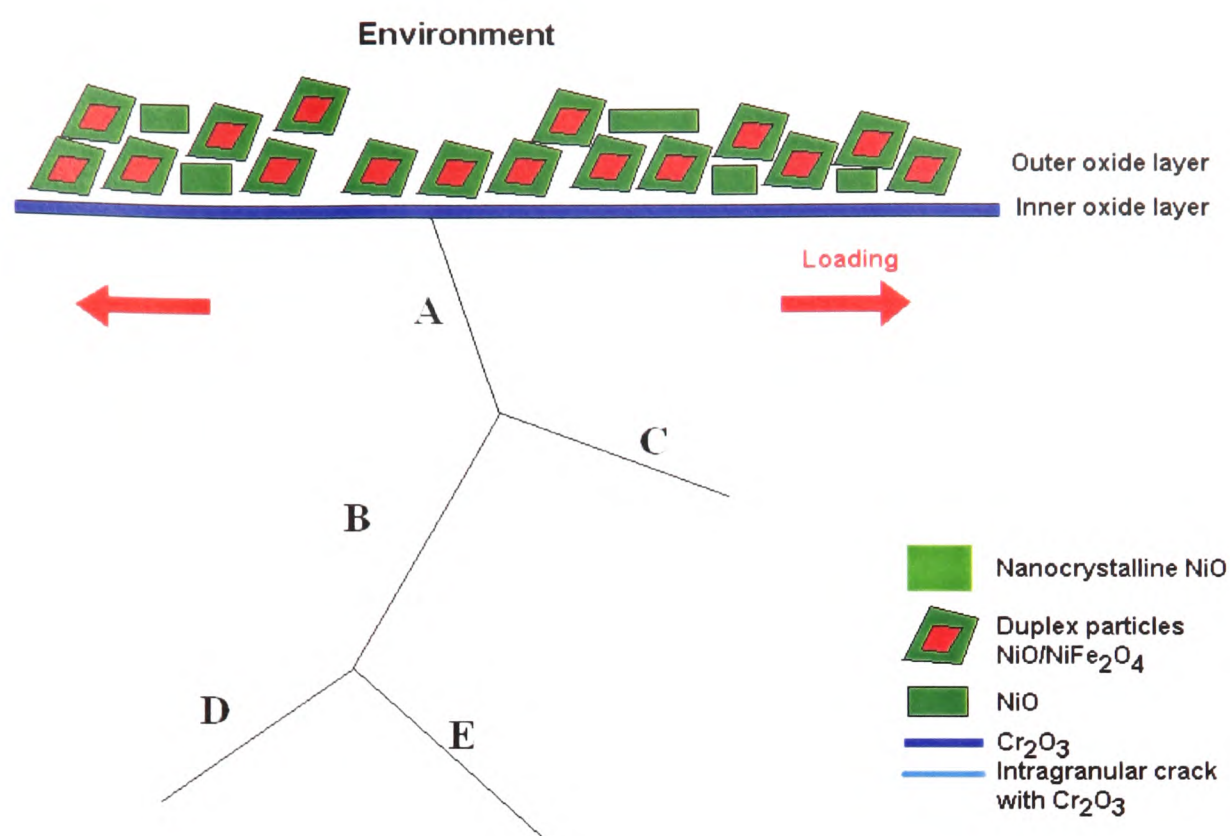


Fig. 10.4. Oxide layers start growing on the external surface of the sample.

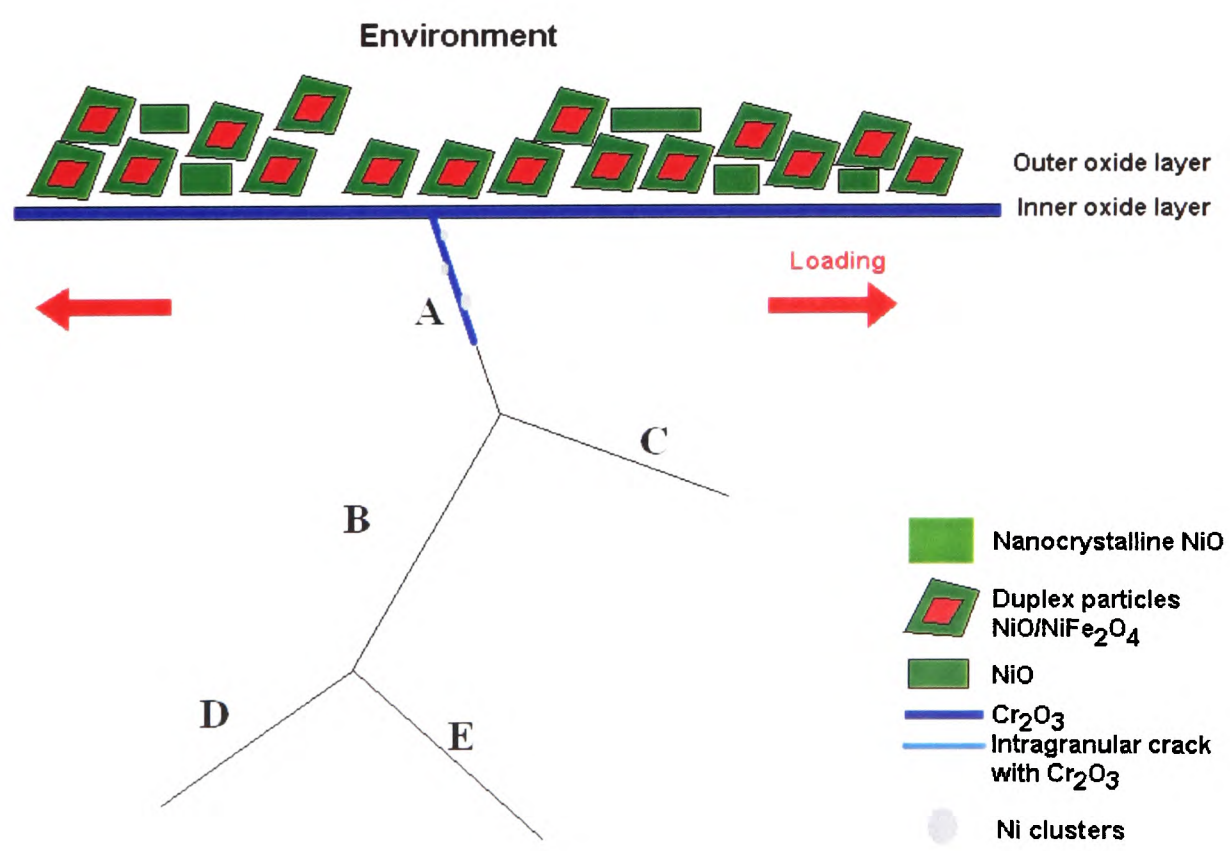


Fig. 10.5. Intergranular attack starts.

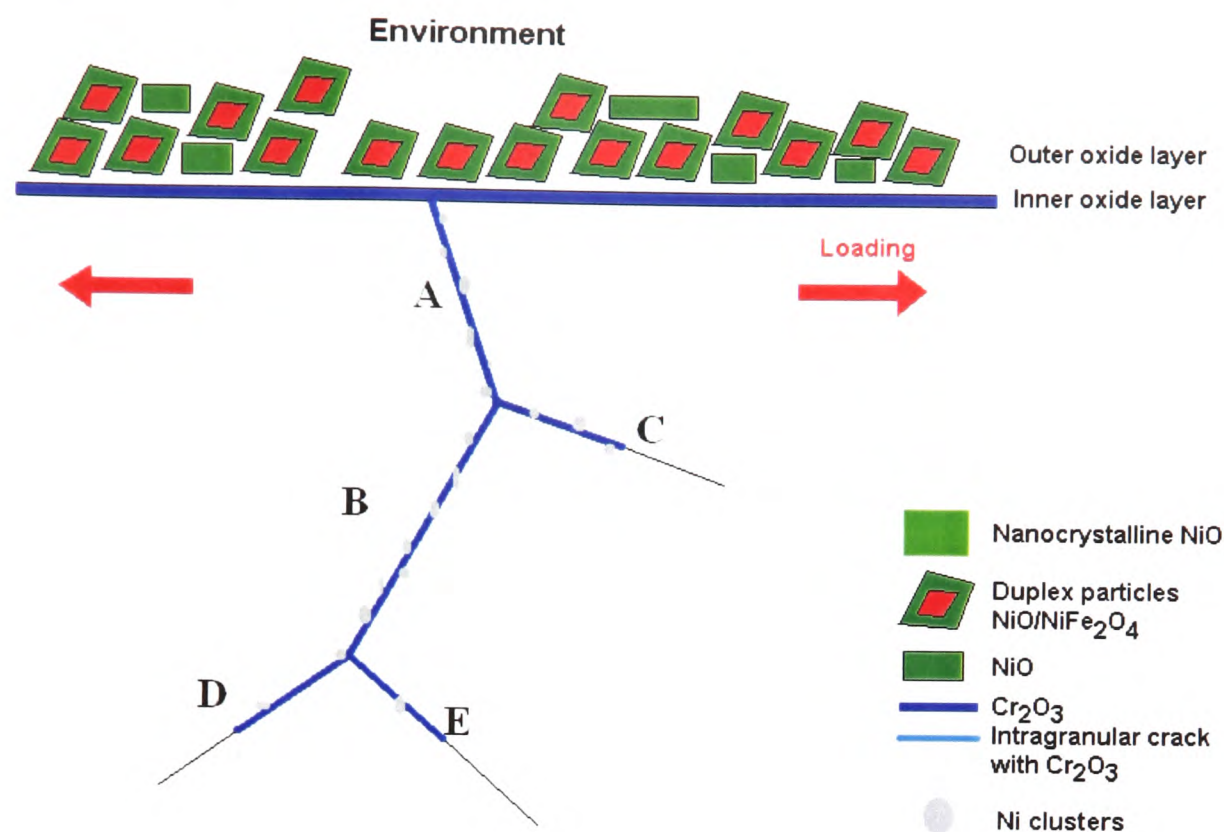


Fig. 10.6. Intergranular attack extends along grain boundary A to other grain boundaries.

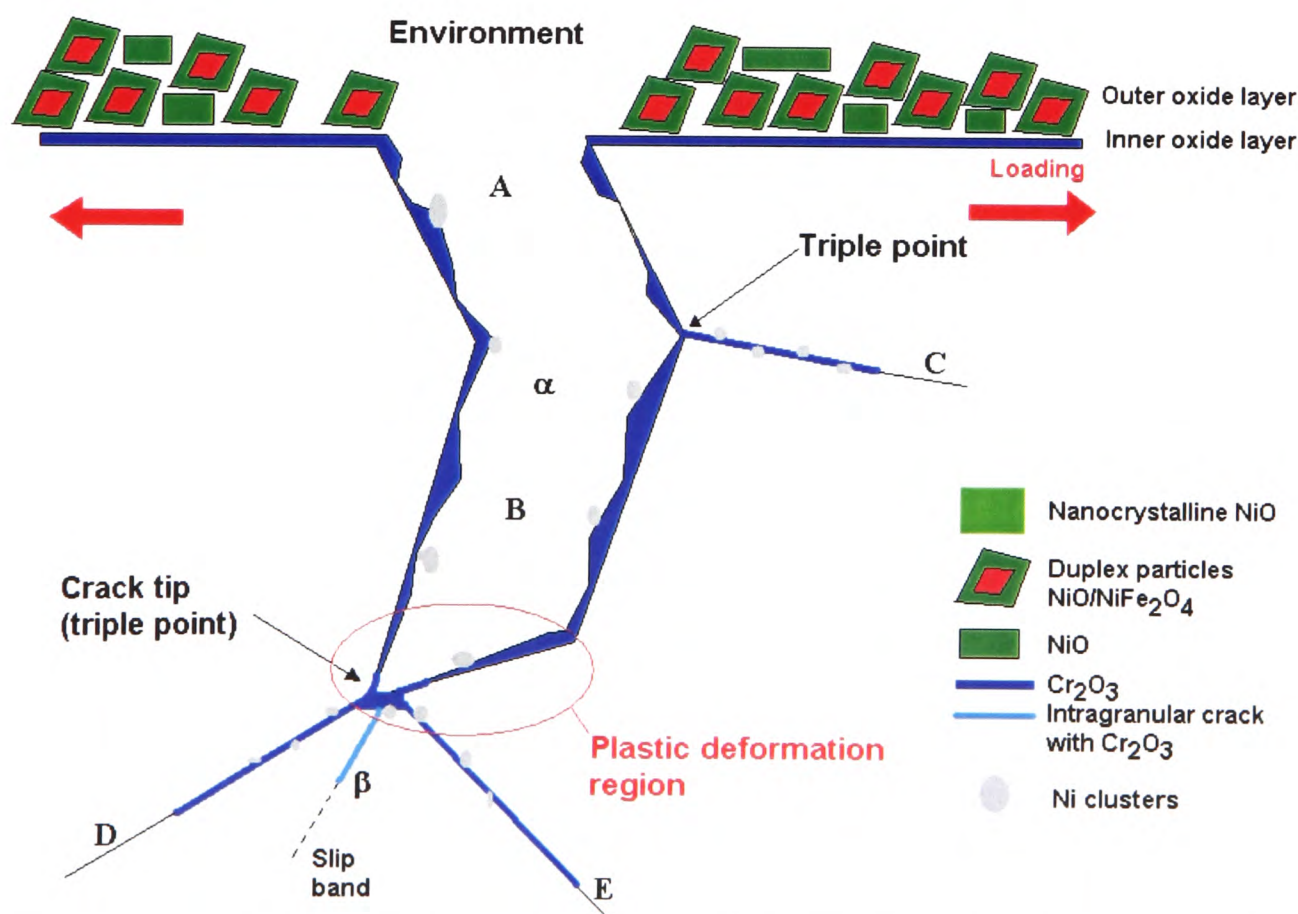


Fig. 10.7. The accumulated stress breaks the embrittled boundary A in an elastic way, with some plastic deformation close to the crack tip. A transgranular crack has grown in the plastic region through a slip band.

Chapter 11:

Suggestions for future work

This project has tried to contribute to clarify some aspects of IGSCC of Alloy 600 in PWRs under primary circuit conditions. However in order to achieve a further understanding, some extra research is suggested for future projects.

There are some concerns that lab testing with autoclaves often uses SSRT to ensure cracking with realistic time scales. However, cracking in plant mostly occurs over many years and incubation times are uncertain. The validity of SSRT needs to be established and the similarity of microscopic results observed from such tests with those of the present constant load test needs to be demonstrated.

This project has focussed on the initiation stage. It would be useful to know what happens when a crack propagates along a few boundaries and progresses beyond the initiation stage. As suggested in Chapter 5, the distribution of boundary orientations determines which become the dominant crack. Hence, more CL tests with larger times are suggested, so that only 1 dominant crack is generated in the sample. The other cracks would be expected to suffer more IGA as the stress field would be concentrated in the dominant crack. This way, the role of plasticity around a deeper crack tip would be better understood.

The role of intergranular precipitates needs further investigation. This would require heat treatment to generate suitable precipitates and selection of appropriate testing environments. Grain boundary precipitates in Alloy 600 are often associated with high SCC resistance and present indications suggest that when particles are oxidised, a dense, crystal oxide structure may occur that reduce oxygen and Ni ion diffusion. The nature of the oxides around grain boundaries exposed to IGA and deep crack propagation needs to be clarified.

The role of hydrogen should be clarified by testing the alloy at different H and/or O concentrations. Although a bond weakening mechanism cannot be rationalized with present observations, further investigation of the Ni/NiO stable region should be undertaken.

Tracer/isotope experiments would provide information on the distribution of light elements that are not easy to obtain using standard techniques. E.g. $^{16}\text{O}/^{18}\text{O}$

experiments could be used to check the enhanced O diffusion due to stress ahead of the crack tips. The use of SIMS or the new nanoSIMS (with an expected resolution of 50nm) would allow the identification of dopants in very small quantities in the grain boundaries, such as B, Li, C and isotopes e.g. H^1 and H^2 .

The improved resistance of Alloy 690 compared to Alloy 600 has to be better understood. Due to the nature of IGA, the Cr concentration in the alloy might affect the oxide structure/type in the grain boundary, i.e. density, grain size, etc. It is difficult to generate IGA in Alloy 690 under PWR primary water conditions in a short time. There is a need to generate such attack, possible under more extreme conditions to determine potential IGA mechanisms in Alloy 690 that might affect the reactor after operation for long times.

It is also suggested that low temperature O diffusion in Ni data is needed. The lack of reliable data might be due to the long times needed in autoclaves, although it would be worthy of further study.

Once the TEM sample preparation technique is available, it can be used in all the different aspects/problems of SCC. A whole new way forward to generate information about the dynamics of crack nucleation or propagation is available. Some suggestions for further examination are:

- Comparison of abraded/polished surfaces to determined the nature of the attack in heavily deformed regions,
- Study different stainless steels and Ni-base alloys.
- Study the secondary side effects and the different water chemistries.
- Obtain more HREM data right at the crack tip.

