

Oxidation and Crystallisation of Amorphous Alloys



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(Abstract)

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Amorphous alloys have a range of desirable ferromagnetic, electrical, mechanical and chemical properties. For instance, the application of Fe-based soft ferromagnetic amorphous alloys as transformer core materials can cut the transformer core losses to about 1/4, with considerable energy saving. However, during manufacture, heat treatment and in service, amorphous alloys may need to be exposed to moderately high temperatures for a period of time, with possible degradation caused by oxidation and crystallisation. There has been almost no previous study of oxidation behaviour and the relationship between oxidation and crystallisation in amorphous alloys.

Eight important amorphous alloys and an industrial crystalline silicon steel have been studied in the present work; amorphous Fe₇₈Si₉B₁₃, Fe₄₀Ni₄₀B₂₀, Fe₄₀Ni₄₀P₁₄B₆, Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Fe₃₂Ni₃₆Cr₁₄P₁₂B₆, Co₆₆Fe₄Ni₁Si₁₅B₁₄, Co₇₆Fe₂Mn₄Si₆B₁₂ and Ni₇₈Si₈B₁₄, and crystalline Fe₉₄Si₆. A combination of thermogravimetry, optical and electron microscopy, electron probe microanalysis, X-ray diffractometry and differential scanning calorimetry has been used to investigate the oxidation and crystallisation kinetics, oxide structure and composition, oxidation and crystallisation mechanisms and the effect of crystallisation on the oxidation behaviour. The results show that the oxidation resistance at 350 C in air increases in the order Fe₄₀Ni₄₀P₁₄B₆ < Fe₉₄Si₆ < Co₆₆Fe₄Ni₁Si₁₅B₁₄ < Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ < Co₇₆MnFe₂Si₆B₁₂ < Fe₄₀Ni₄₀B₂₀ < Si₇₈Si₉B₁₃ < Ni₇₈Si₈B₁₄ < Fe₃₂Ni₃₆Cr₁₄P₁₂B₆. Most of the amorphous alloys obey a parabolic oxidation rate law, but the oxidation kinetics, oxide growth mechanism and resulting oxide structure change sharply when crystallisation takes place in the amorphous alloys. Amorphous Fe₇₈Si₉B₁₃ and Fe₄₀Ni₄₀B₂₀ have better oxidation resistance than the corresponding crystalline alloys, while amorphous Fe₄₀Ni₄₀P₁₄B₆ and Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ have poorer oxidation resistance than the crystalline counterparts. Most of the crystalline alloys also obey a parabolic oxidation rate law, except for the crystalline Co based alloys and Fe₄₀Ni₄₀B₂₀, which obey a logarithmic rate law. In most cases, the amorphous and crystalline alloys oxidise to form a fine-scale multiphase oxide scale, except for amorphous Fe₄₀Ni₄₀P₁₄B₆, which oxidises to form a whisker-like thick layer of Fe₂O₃. In general, ion diffusion through fast transport paths such as grain boundaries and dislocations is the rate controlling process for oxide growth. Different oxidation kinetics and oxide growth mechanisms in amorphous and crystalline alloys of the same composition are caused by micro-chemical segregation of the alloying elements during crystallisation.

To my dear wife and parents

PREFACE

This dissertation describes work carried out in the Department of Metallurgy and Science of Materials, University of Oxford, from October 1985 to June 1988, under the supervision of Dr B Cantor. It is submitted for the degree of Doctor of Philosophy at Oxford University, and no part has been or is being submitted for any other qualification at any University. The dissertation is the result of my own work. Except where references are made to the work of others, the work described here is original. Some of the work described in this dissertation has already been published or will be published very soon (1-10).

I would like to thank my supervisor Dr B Cantor for the very valuable discussions, encouragement and all the help he has given. Without his help, I would not be able to study for the DPhil. degree in Oxford. I am grateful to Professors Sir Peter B Hirsch FRS and J W Christian FRS for provision of laboratory facilities and for supporting the University Fees. This work was conducted during the period October 1985 - May 1988, and was supported by various grants from the UK Science and Engineering Research Council (April 1987 - November 1988), Royal Society Sino-British Fellowship (October 1986 - March 1987), British Council / Chinese Government Award (October 1985 - September 1986) and Department of Metallurgy and Science of Materials, Oxford University (October 1986 - October 1988). I would also like to thank Jesus College, Oxford University for giving me Senior Graduate Status (October 1986-) and financial support to attend international conferences, and Chengdu University of Science and Technology, China for giving me leave of absence from my University Lecturer position.

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Chapter 1 Amorphous Alloys

1.1 Introduction

Amorphous alloys are metallic alloys with no long range atomic order. They are usually produced by rapid solidification of the alloying constituents from the liquid or gas at such a high rate that the atoms are frozen in their liquid configuration and form a metastable glass-like structure. Amorphous alloys are also sometimes called metallic glasses or non-crystalline alloys. Detailed X-ray and neutron diffraction studies indicate that there is short range atomic order in most amorphous alloys but no long range atomic order.

Non-crystalline metallic alloys were first reported quite a long time ago, produced by vapour deposition or electrodeposition (1,2). However, these reports did not draw much attention until in 1960 Duwez and his colleagues discovered a method of preparing amorphous alloys by direct quenching from the melt (3,4). Since Duwez's work, there has been increasingly extensive interest in the study of amorphous alloys, especially in the last 15 years.

Amorphous alloys possess a range of desirable properties. For example, amorphous alloys such as Fe₇₈Si₉B₁₃ have very good soft ferromagnetic properties, i.e. extremely low magnetic losses and high magnetisation, together with electrical resistivities three times higher than conventional ferromagnetic crystalline iron alloys (see section 1.6.3 and Chapter 5). Some amorphous alloys such as Fe₈₀B₂₀ and Fe₄₆Cr₁₆Mo₂₀C₁₈ are exceptionally hard and have very high tensile strength (see section 1.6.1). Other amorphous alloys have thermal expansion coefficients near zero (4), and amorphous alloys such as FeCrMoC and FeCrMoPC have extremely high corrosion resistance (see section 1.6.2). Amorphous alloys have attracted great

theoretical interest, because of their novel atomic structure, and because of the excellent properties which result from their structure. Since 1970, there have been six major international conferences on rapidly quenched metals (5-8), and a number of other conference proceedings and monographs have also been published (9-16). Because of the very extensive background literature on amorphous alloys, the literature survey in this Chapter is limited to aspects which are closely related to the experimental work presented later in this thesis.

1.2 Production of amorphous alloys (17-21)

A number of different methods have been used for producing amorphous alloys (17-21), including sputtering and evaporation, chemical deposition and electrodeposition, ion implantation and ion bombardment of diffused coatings, splat quenching and spray deposition, electron beam or laser surface melting, atomisation and melt chilling techniques. These processes all have different limitations as to quench rate, specimen geometry etc. The resulting structure and properties of amorphous alloys are related to the manufacturing processes.

Among the various techniques, melt-chill methods are the most important ways to produce amorphous alloys (21). Six types of melt-chill technique have been used to produce amorphous alloys: (a) free jet melt-spinning, (b) Taylor wire process, (c) melt-extraction, (d) melt-drag, (e) planar-flow casting, and (f) chill-block melt spinning. These methods can be used to produce amorphous alloys in a wide range of shapes including ribbons, round wire, wide strip and plate, with an initial quenching rate of about 10^6 K/s.

Because the chill-block melt-spinning technique allows continuous fabrication of amorphous alloy strip at a high production rate, it has been widely used as the most important industrial manufacturing method.

Fig.1-1 shows schematically the chill-block melt-spinning process. A stream of melt about 1mm in section is generated by pressurized expulsion through a suitable orifice onto a rapidly rotating metal wheel that acts as the chill substrate, leading to continuous production of a thin amorphous alloy ribbon or strip. The rate of quenching is determined by the liquid-substrate heat transfer coefficient, and the thickness and thermal conductivity of the liquid layer. These factors limit the ribbon thickness for most amorphous alloys to $< 0.1\text{mm}$, with width from approximately 1 to 300mm. Continuous production rates of up to 30m/s can be achieved by this method (21). Most commercially available amorphous alloys, including all the amorphous alloys investigated in the present work, were manufactured by the chill-block melt spinning process.

1.3 Structure of amorphous alloys (22-33)

The atoms of amorphous alloys are "frozen" in their liquid configuration, therefore, the atomic structure in amorphous alloys is degenerate and can not be determined uniquely as is possible for a crystalline structure. This is why the properties of the amorphous alloys depend upon their fabrication process. They may vary from one run of production to the other, and even vary from one portion of the ribbon to another. In early times, researchers attributed this variance to difference in the "amorphousness", implying that some of, or at least portions of, metallic glasses are not truly amorphous, but microcrystalline. This view, however, turned out to be incorrect (22). The reversibility of many of the properties and the structural evidence indicate that the variance of the properties is due to some atomic ordering within the amorphous phase, rather than phase transformation into crystallinity (23,24). Furthermore, statistical information about

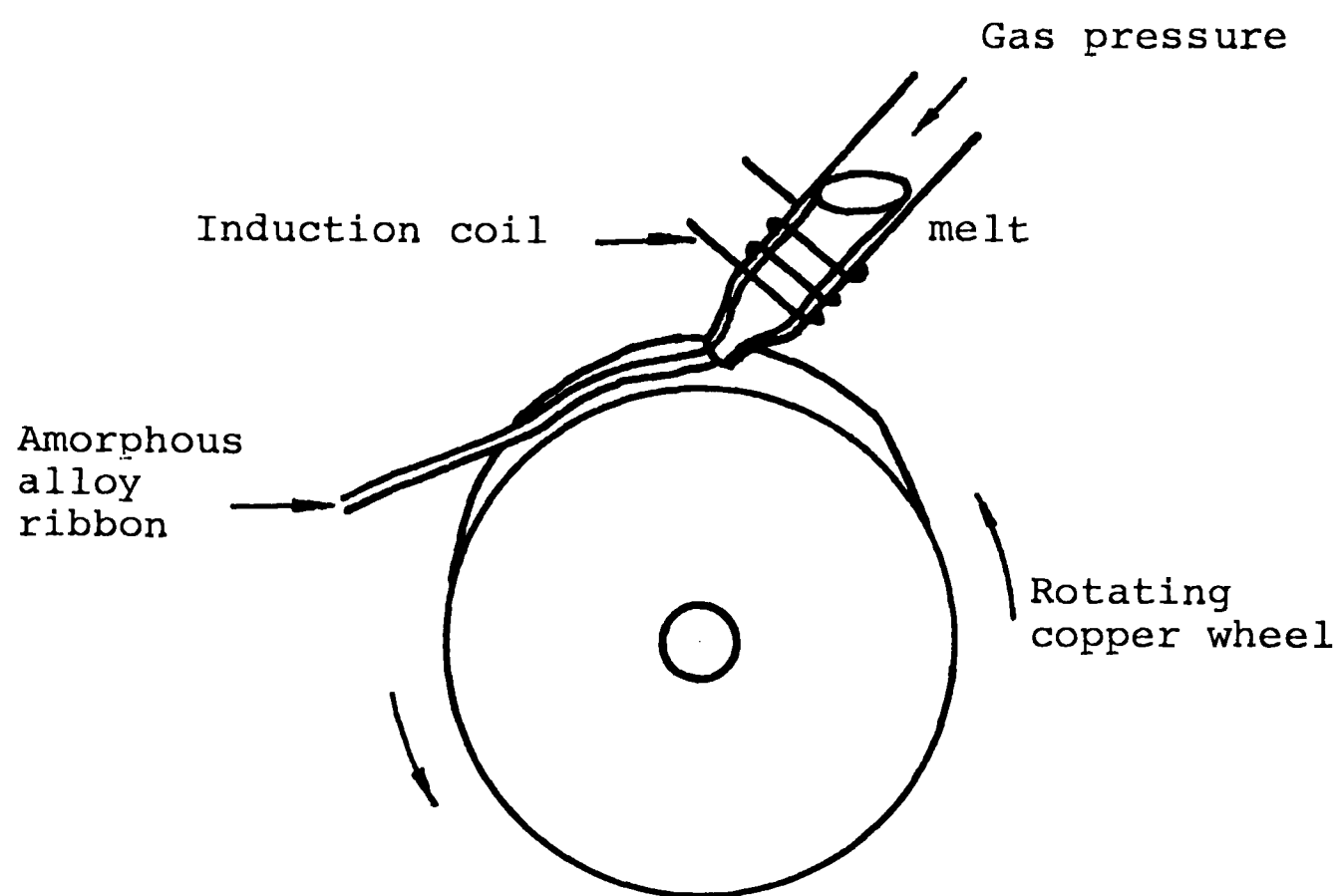


Fig.1-1: Chill-block melt-spinning process.

amorphous structure can be deduced from results of X-ray, neutron and electron diffraction, high resolution transmission electron microscopy and spectroscopical investigations. Reviews of amorphous structural arrangements of atoms have been published by Finney and Egami (25,22).

There are two group of theories to describe amorphous alloy structures. The first group of theories are based on the dense random packing of hard spheres (DRPHS) (22,23). A simple liquid structure is considered to be made up of equal-sized hard sphere atoms packed together at high density without allowing any crystallisation to occur. The first DRPHS model was built experimentally by pouring thousands of steel balls into a flexible container, showing the absence of lattice ordering (25,26). Subsequent DRPHS models have been refined by using computer construction techniques, by introducing several atomic components ie different-sized spheres, and by relaxing the initial structures under the action of realistic interatomic potentials. Calculations on the sphere coordinates demonstrate that DRPHS models possess many of the structural features of simple liquids, and give good qualitative explanation of supercooling, nucleation, melting, fluidity and diffusion (27). The second group of models can be characterised as the re-appearance of order amidst the disorder (28,29). This group of models is based on the results of diffraction experiments, which show that chemical short range order (CSRO) and a certain degree of topological short range order (TSRO) do exist in the atomic structures of many amorphous alloys (30). For example, diffraction and spectroscopy (EXAFS and Mössbauer) show that the local structure (0.3-0.5nm) of metal-metalloid amorphous alloys is non-random. There is a shell of Ni atoms around each B atom in Ni-B amorphous alloys. Because there is no B-B near neighbours and Ni cages are approximately trigonal prisms, it shows both CSRO and TSRO. Thus, the models in this group are established on the basis of the specific

stereochemistry of the local environment of each atom, and the local units made up by several atoms rather than single atoms are packed randomly together (28,31). The major difficulty in modelling real amorphous alloys is to construct a non-crystalline assembly which is consistent with both local chemical ordering and the overall high density packing constraints. Research on understanding the atomic arrangements of amorphous alloys is still very much in progress (32,33).

1.4 Structural relaxation of amorphous alloys (34-46)

The structure of amorphous alloys can be regarded as in a quenched-in liquid state, which usually contains a certain amount of free volume. It is not in an internal equilibrium state, and will relax structurally towards internal equilibrium states of lower energy whenever atoms obtain an appreciable mobility (34,35). Low temperature annealing which does not lead to crystallisation can therefore cause a change in the chemical and topological short range order of atoms in the amorphous state. This phenomenon is called structural relaxation. For instance, amorphous alloys in the Pd-Si, Fe-B and Zr-Cu systems undergo structural relaxation just above room temperature, several hundred degrees below their crystallisation temperatures (34). Associated with structural relaxation during low temperature annealing, many of the physical properties of amorphous alloys change, some slightly, and others drastically. The density, which is closely related to the free volume in the atomic arrangement, changes by rather a small amount, about 0.5% (36). The Young's modulus changes by about 7% (36), enthalpy by 200-300 cal/mole (37), Curie temperature by as much as 40 K (38), and electrical resistivity by 2% (39). Structural relaxation in amorphous alloys reduces the internal friction (40), rates of stress relief (41), and changes a number of magnetic properties (42).

Atomic diffusivity (43) and viscosity also decrease with structural relaxation during annealing, and mechanical ductility falls drastically (34).

Because of inadequate understanding of amorphous atomic structure, the mechanism of structural relaxation is also not clear. As proposed by Egami (44), structural relaxation can be divided into two components: (a) changes in topological short range order (TSRO), which involves changes in the geometrical packing of the atoms, regardless of their chemical nature; and (b) changes in chemical short range order (CSRO), which involves changes in the local surroundings of each atom, taking their chemical nature into account. Changes in CSRO are reversible and relatively fast, while changes in TSRO are irreversible and not usually completed under most experimental conditions before crystallisation occurs. For instance, investigations of structural relaxation in amorphous Fe₄₀Ni₄₀B₂₀ (45,46) showed that the rates of change in CSRO and TSRO can be measured separately, and changes in TSRO are relatively slow and start only when changes in CSRO are nearly completed.

However, Chen (34) described structural relaxation of amorphous alloys in another way. He suggested that the structural relaxation process at low temperatures (more than 150K lower than the glass formation temperature) is different from that at high temperatures (near the glass formation temperature). The structural relaxation processes of amorphous alloys were described as three stages: (a) short-range localised structural relaxation (SLSR), (b) medium-range cooperative structural relaxation (MCSR), and (c) long-range cooperative structural relaxation (LCSR). The SLSR and MCSR processes are both reversible, and SLSR causes the great loss of ductility in many amorphous alloys. The effect of MCSR on the properties of amorphous alloys is not clear. LCSR process only takes place when the

annealing temperature approaches the glass formation temperature and/or when the duration of the anneal is long enough. Detailed explanation of structural relaxation of amorphous alloys can be found in reviews given by Chen (34,35) and Egami (22,44).

1.5 Crystallisation of amorphous alloys (47-65)

Fig.1-2 shows a schematic temperature-time-transformation (TTT) curve for crystallisation either by cooling from the liquid state or by heating from the amorphous solid state. Three zones of liquid, crystal and amorphous states are separated by a C-shape curve, as shown in Fig.1-2. An amorphous alloy is formed by cooling the liquid fast enough to miss the "nose" of the curve, so as to avoid crystallisation. It follows that if the amorphous alloy is heated subsequently, it will first relax structurally, then crystallise. The crystallisation takes place either after a time t_s if held isothermally at a suitable temperature, or at a temperature T_s after having been heated continuously. It should be noted that TTT crystallisation curves can be determined experimentally either by isothermal or continuous cooling, or by isothermal or continuous heating. The C-curves determined in each of these different ways usually show minor differences.

Crystallisation of amorphous alloys takes place in two stages, nucleation and growth. The driving force for crystallisation is the free energy difference between the amorphous state and the corresponding crystalline phase(s). The crystallisation kinetics, crystal structures and mechanisms of nucleation and growth for a number of amorphous alloys can be found in the reviews written by Scott (47,48), Koster (49,50) and Greer (51,52). Three important crystallisation mechanisms for amorphous alloys are briefly described as follows:

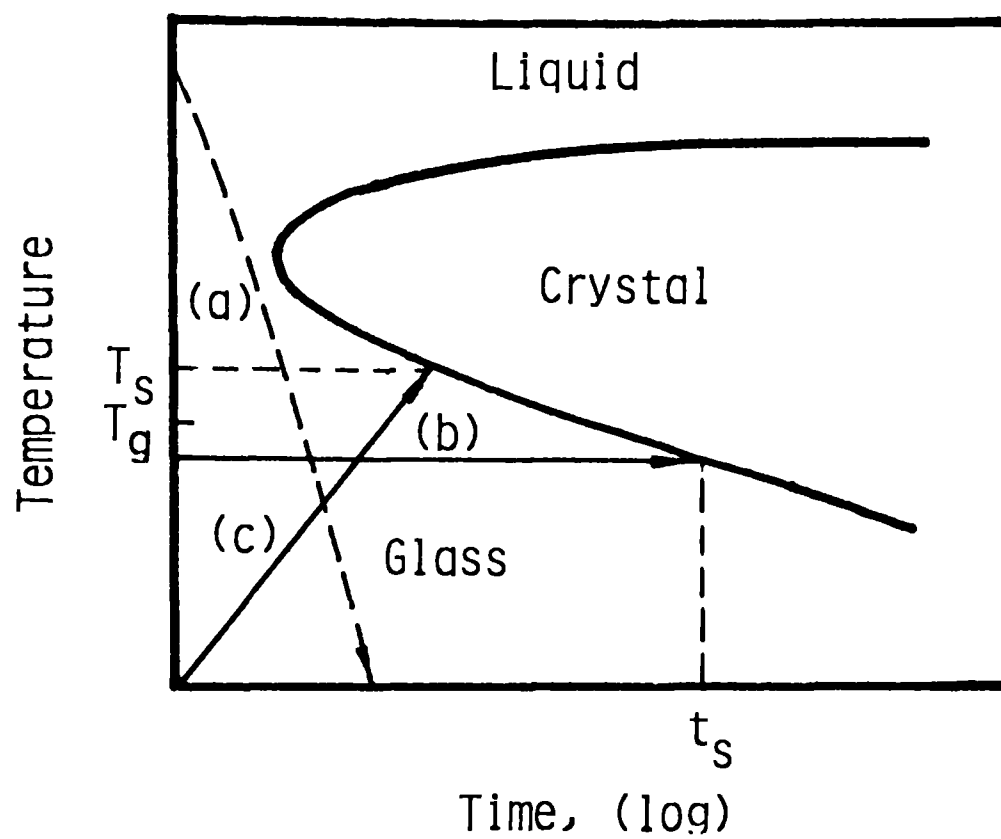


Fig.1-2: Schematic TTT diagram for:
 (a) fast cooling to form an amorphous alloy,
 (b) crystallisation by isothermal heating giving a start time t_s , and
 (c) crystallisation by continuous heating giving a start temperature T_s .
 T_g is the glass transition temperature.

(a) Eutectic crystallisation

Eutectic crystallisation is the simultaneous crystallisation of two crystalline phases in a coupled fashion. The eutectic reaction usually has the largest driving force among the three types of crystallisation and can occur in the whole concentration range between the two stable phases. There is no overall concentration difference across the reaction front, but the two components have to separate into two phases along the reaction front. Eutectic crystallisation is very common in Fe-B based amorphous alloys, and has been seen for instance in amorphous Fe₈₀B₂₀, Fe₄₀Ni₄₀B₂₀ and Fe₄₀N₄₀P₁₁B₆ (49,53-57).

(b) Polymorphous crystallisation

Polymorphous crystallisation is when an amorphous alloy crystallises into a supersaturated alloy or metastable or stable crystalline compound without any change in concentration. This type of crystallisation takes place when the amorphous alloy composition is near to a stable or metastable crystalline compound. For instance, polymorphous tetragonal Fe₃B can form in Fe-B based glasses containing 24-26 at.%B (49). Polymorphous crystals usually nucleate randomly within the alloy and grow until they impinge and consume all the matrix. This is not a very common mechanism for crystallisation of amorphous alloys, but examples have been reported in the Ni-P, Zr-Ni, Fe-B and Fe-Ni-B systems (47,58,59,53,54).

(c) Primary crystallisation

Primary crystallisation is when a crystalline phase, e.g. α -Fe, forms with a different composition from the amorphous alloy matrix. This type of crystallisation mechanism requires diffusion ahead of the growing primary crystals, so that the amorphous alloy becomes enriched in one or more of the constituent elements which did not exist in the primary crystals. Ultimately the remaining untransformed glass crystallises by one of the

other mechanisms mentioned above. The dispersed primary crystalline particles may act as preferred nucleation sites for the subsequent crystallisation. A primary crystallisation mechanism has been found in $\text{Cu}_{56}\text{Zr}_{44}$, $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ and Fe-B systems (47,60,61).

All the three types of crystallisation mechanism have been found to take place in Fe-B amorphous alloys, and the mechanisms are shown schematically in Fig.1-3 (50).

Understanding the crystallisation behaviour of amorphous alloys is important not only from scientific interest, but also for practical application. Many of the special properties of amorphous alloys, such as the excellent mechanical, magnetic and corrosion properties deteriorate sharply when even a small amount of crystals are present (47,62). On the other hand, controlled partial crystallisation can improve some amorphous alloy properties, giving even lower magnetic core losses at high frequency (63), and higher ductility (64). Hard magnets with exceptional high magnetisation energy can be made by crystallising melt-spun Fe-Nd-B alloys (65). Thus, understanding the crystallisation behaviour of amorphous alloys is essential not only for preventing their degradation, but also for controlling and improving their properties.

1.6 Properties of amorphous alloys

1.6.1 Mechanical properties (66-75)

Amorphous alloys have attractive mechanical properties combining ductile behaviour in bending, shear and compression with high flow strength, hardness and fracture strength. Such behaviour contrasts sharply with hard, brittle materials like oxide glasses and ductile, soft materials like crystalline metals. The mechanical behaviour of amorphous alloys has been reviewed by Kimura, Speapen, Li, Taub and Jones (66,67,69-71).

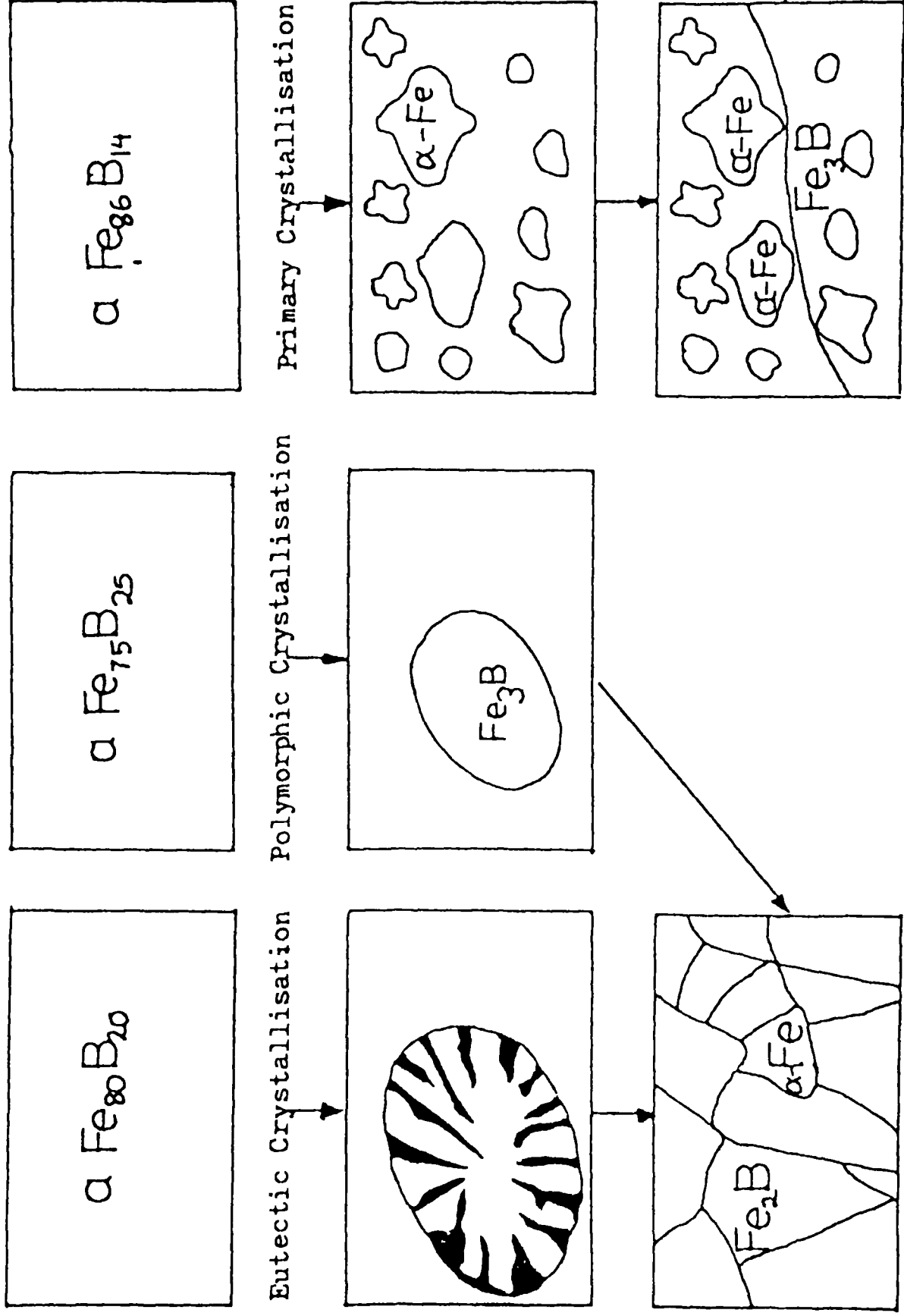


Fig.1-3: Schematic show of three typical crystallisation mechanisms in amorphous Fe-B alloys (50).

(a) Strength and hardness

Some amorphous alloys exhibit very high flow stresses as well as hardness, especially in Fe based systems (66). For example, Fe₈₀B₂₀ has a flow stress of about 3.6GPa and fracture stress of about 7.4GPa, while those of crystalline mild steel are about 0.3 and 0.5 GPa respectively. The hardness of Fe, Ni or Co based amorphous alloys are between 400 and 1400kg/mm², again much harder than mild steel (200kg/mm²) and most alloy steels quoted values (66,67). The high strength and hardness of amorphous alloys are caused by the absence of crystalline slip planes, grain boundaries and other defects. The hardness of transition metal-boron amorphous alloys increases with metalloid content (68), and partial substitution of Fe by Cr, V, or Ti increases the hardness, while substitution with Co, Ni or Cu decreases the hardness (66).

(b) Plasticity and toughness

Most amorphous metallic ribbons can be bent completely back on themselves without fracturing, evidence of high ductility. In tension however, the overall plastic strain is small because specimens do not work harden and they undergo highly localised shear deformation. Thus the bend-back angle of 180 degree indicates that an amorphous alloy is very ductile, while the moderate fracture energy given by the strain-stress curve shows that it is less tough.

The fracture toughness of some Fe based amorphous alloys are also very high, comparable with that of maraging steels (66,67,72,73). Two types of fracture are observed in amorphous alloys, showing either veined (ductile) or featureless (brittle) fracture surfaces (66,67,69).

Annealing at temperatures even well below crystallisation temperature often causes embrittlement for amorphous alloys, especially for those with a high content of metalloid elements. The mechanism of this embrittlement

effect are not well understood, possibly involving local stress concentrations arising from the rearrangement of atoms during structural relaxation (67,74,75). Another shortcoming in the mechanical properties of amorphous alloys is the relatively low resistance to tensile fatigue (66).

1.6.2 Chemical properties (76-88)

Amorphous alloys are new materials not only from their atomic structure, but also from the chemical point of view. Although the potentially high reactivity arising from structural disorder might be expected to reduce general chemical stability, the absence of defects associated with crystalline structures such as grain boundaries, dislocations and stacking faults is ideal for preventing amorphous alloys from localised attack. Furthermore, they can contain in an atomically homogeneous solution high levels of Cr, Mo and metalloid elements such as P or Si, which are particularly favourable for formation of stable passive protective films. The chemical properties of amorphous alloys, including corrosion resistance and catalytic behaviour, have been reviewed by Hashimoto and Reiders et al (75-81).

Fig.1-4 shows a comparison of the corrosion resistance of a crystalline 18Cr-8Ni stainless steel and amorphous Fe₇₀Cr₁₀P₁₃C₇ in 1N HCl solution at 30 C. While the 18Cr-8Ni stainless steel was attacked at a rate of 10mm/year, the amorphous Fe₄₀Cr₁₀P₁₃C₇ suffered no weight loss after 168h immersion (82). As in Fe-based crystalline alloys, the combination of Cr and Mo in Fe-based amorphous alloys leads to an extremely high corrosion resistance against highly aggressive chemical agents. Some of the amorphous alloys can remain in passive state even in hot concentrated HCl solutions. Fig.1-5 shows the critical concentrations of Cr and Mo for spontaneous passivation of Fe-Cr-Mo-metalloid amorphous alloys in HCl solutions with different concentrations (77).

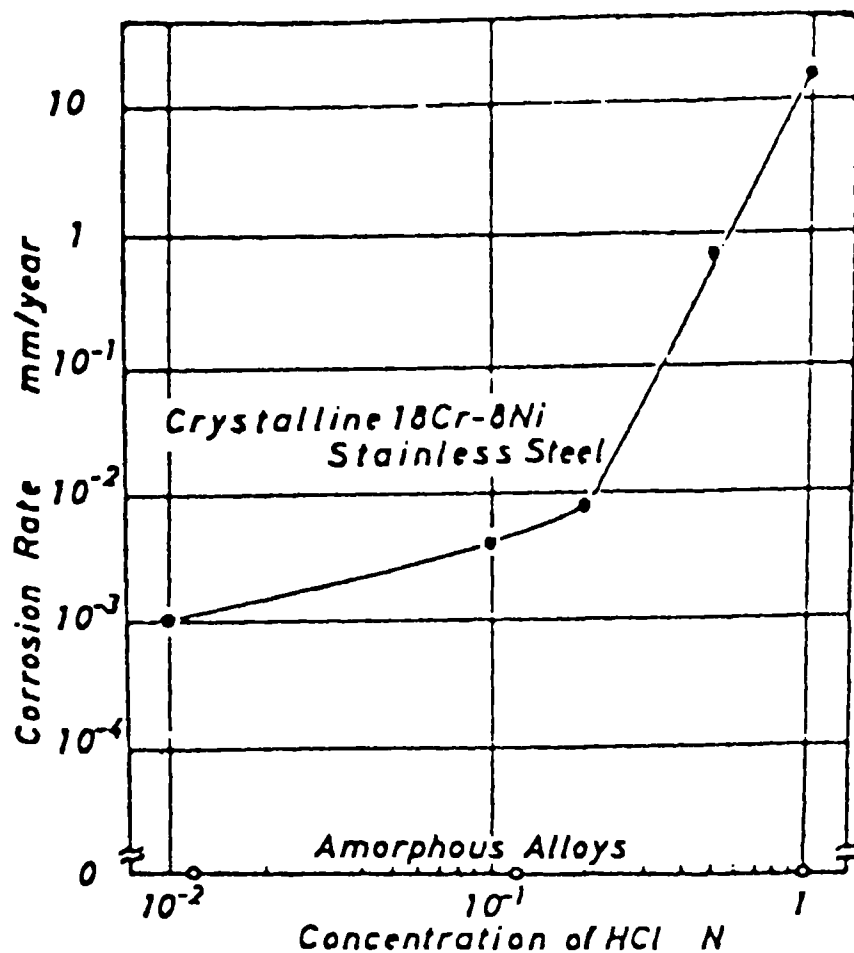


Fig.1-4: Corrosion rate of crystalline 18Cr-8Ni stainless steel and amorphous Fe70Cr10P13C7 (with or without 5 at.%Ni) as a function of HCl concentration at 30°C, showing no detectable weight loss for amorphous Fe70Cr10P13C7 after immersion for 186h (82).

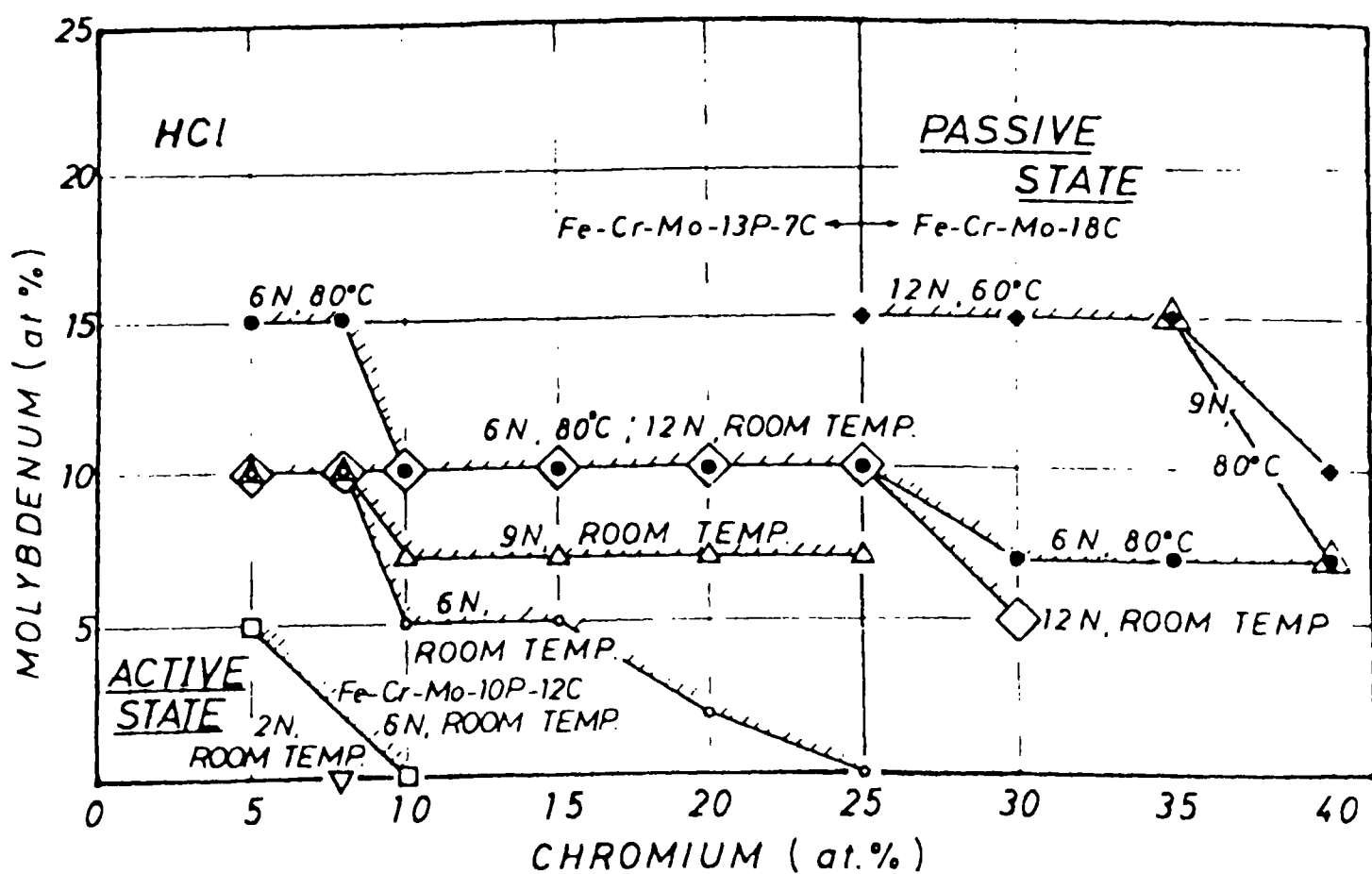


Fig.1-5: Critical concentration of Cr and Mo necessary for spontaneous passivation of amorphous Fe-Cr-Mo-metalloid alloys in HCl with various concentrations and temperatures (77).

Metalloid content in amorphous alloys also has a strong influence on the corrosion behaviour. For instance, a systematic study showed that P accelerates surface active dissolution and enhances the rapid formation of a passive film on amorphous alloys containing Cr, and therefore reduces sharply the corrosion rates of Fe-, Ni- or Co-based amorphous alloys (77). P has also been reported to reduce the corrosion rate of amorphous Cu-Zr alloys due to growth depression of the thick film (83,84). Another metalloid element, Si, has been shown to improve the corrosion resistance of amorphous Fe-Si (85), Fe-Ni-Si-B (86), Fe-Si-B (87), and Fe-Cr-Mo-Si-B (88) systems due to the formation of SiO_2 -rich films. However, the metalloid element B has been reported to have a small or negative effect on amorphous alloy corrosion resistance, because B can be absorbed into the surface film to form chromium borate, reducing the concentration of Cr, and making the passive film less protective (77).

1.6.3 Magnetic properties (89-100)

Because of the lack of atomic ordering, it was believed for long time that amorphous alloys can not possess ferromagnetism. However, Gubanov (89) predicted the existence of amorphous ferromagnets on the basis that ferromagnetism is caused by exchange interaction for the most part between neighbouring atoms, and therefore that rigorous periodicity in the distribution of atoms is not necessary. This implies that the ferromagnetism is only dependent upon short-range ordering, and should not be destroyed in the amorphous structure (90,91).

Typical soft ferromagnetic behaviour was first reported by Duwez and Lin (92,93) for amorphous $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$, which exhibited a characteristic narrow hysteresis loop with a large saturation magnetisation of about 7 kG and a low coercive force of about 3 Oe. Since then, many ferromagnetic amorphous alloys have been developed. Some of these alloys have excellent

soft magnetic properties, with magnetic losses about 5 times smaller than the best quality Fe-3.25 wt.%Si silicon steel. Coupled with very low losses, amorphous alloys have lower exciting power because of the extremely low coercivity and squareness of the hysteresis loop (94). The soft magnetic properties are due to lack of crystalline anisotropy and defects, which interact strongly with domain wall motion in crystalline materials. Domain wall motion is mainly affected by quenched-in or induced local stresses in amorphous alloys. The fundamental magnetic properties of amorphous alloys such as magnetic moment, exchange interaction and magnetic excitation have been reviewed and compared with those of crystalline alloys by O'Handley (95), Durand (91) and Fujimori et al (97-100). Most of the amorphous alloys investigated in the present work are of technological importance because of their soft ferromagnetic properties.

1.7 Application of amorphous alloys (94,100-111)

Although the high strength and ductility of amorphous alloys attracted most initial interest, the favourable soft magnetic properties of ferromagnetic amorphous alloys in combination with good mechanical properties have led to most of the commercial interest and practical applications (94,100). The most important application of amorphous alloys up to date is for the core materials in distribution and other transformers.

Distribution transformers are used by electrical utilities to step-down the voltage in the network that supplies electrical power to residences, shops, offices etc. They are required to be in service for 25-40 years with the transformer coil being continuously energised. Since magnetic core materials incur losses owing to hysteresis and eddy currents, there will be heat generated in the core. A 25kVA commercial distribution

transformer with a grain-oriented silicon steel core has about 85W of core loss, consumes 3×10^7 Wh over a 40-year service life and costs £1,800 at the present price (6p/kWh). Application of amorphous alloys such as Fe₇₈Si₉B₁₃ can reduce this loss to 1/4 - 1/3, with considerable energy saving (94,101,102).

400 Hz transformers are primarily used in airborne and military applications. High frequency airborne transformers of this type can also be improved by using amorphous alloys as the core material, because lower losses means that smaller and therefore lighter cores are required without exceeding a maximum allowable temperature rise.

When amorphous alloys are used in motors, they can reduce core losses by as much as 90%, because their anisotropy can be built-in during a final anneal to develop low reluctance paths in the exact configuration required by the motor (94). Other applications of soft ferromagnetic amorphous alloys include magnetic amplifiers, active power filters, ferroresonant transformers and magnetic modulators, as summarised in Table 1-1 (103-105).

Another important application field for amorphous alloys is for brazing foil used in metal joining operations. Existing filler materials are usually brittle powders either held in an organic binder or noble metal foils, which have contamination problems and are difficult to fit irregular joining surfaces. Amorphous brazing ribbons are strong and flexible, so they conform well to curved surfaces and provide an optimum controlled gap (94). Applications of amorphous filler alloys range from high temperature brazing of superalloys in critical assemblies within gas turbine engines to low temperature soldering of semiconductors and lead frames in microelectronic devices (106,107). Compared to conventional filler alloys, amorphous filler alloys offer superior chemical homogeneity, result in superior joint properties and help to reduce the use of precious metals in

metal joining (107).

The attractive mechanical properties and excellent corrosion resistance of amorphous alloys have not yet been able to find commercial application because of the thin ribbon form and relatively low resistance to cyclic fatigue under tension. The potential uses of high strength amorphous alloys in composites and reinforcement are also included in Table 1-1 (108-111).

Table 1-1 Applications of Amorphous Alloys (103-111)

Field	Application
power electric applications	distribution transformers electric motors high gradient magnetic separators step-up transformers & saturable reactors for high repetition rate pulse compressors 400 Hz airborne transformers
switching mode power supplies	saturable reactors non-saturable inverter transformers
electric circuits	pulse transformers RFI current compensated chocks ground fault interrupters
magnetic heads	audio, video, data recorders
sensors & transducers	magneto-elastic force, displacement and torque transducers magnetic field sensors delay lines temperature transducers, sensors personal identification and anti-pilferage devices bistable pulse generator devices
magnetic shielding	flexible shielding wrap flexible cable shielding cassette shielding spring
linear accelerators	induction core
brazing filler materials	joining of stainless steels and Ni-based superalloys components
composites & reinforcements	epoxy matrix high strength composites high strength cement reinforcements
catalytic materials	hydrogenation of CO to yield hydrocarbons

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Chapter 2: Oxidation of Metals and Alloys

2.1 Introduction

Almost all the metals and alloys which are used in common technological applications tend to form oxides when exposed to the atmosphere at high or low temperatures. In many instances, the rate of oxidation is slow at room temperature because a thin oxide layer forms on the surface preventing the underlying metal from further reaction with oxygen. At higher temperatures, however, the oxidation rates increase like other chemical reactions, and metals and alloys can degrade severely as a result of the accelerated oxidation. The study of oxidation of metals and alloys is an important subject from both the technological and scientific point of view.

A number of text books and monographs have reviewed the chemical and physical principles of metallic oxidation and the most important results in this field (1-9). Because oxidation is such an extensive subject, the review of oxidation behaviour in this thesis has to be limited to those aspects relating closely to the present research.

2.2 Matter transport in oxide scales (10-28)

The transport of matter in oxide scales is a very important issue in high temperature oxidation and corrosion. This is not only because the matter transport process determines the rate of scale growth and hence the rate of oxidation, but also because it is related to many important aspects of scale structure, composition and stability, such as oxide grain growth mechanism, stress generation by lateral and internal oxide growth, penetration by aggressive elements, etc. The mechanism of matter transport in an oxide scale depends upon the structure of the oxide.

2.2.1 Oxide structure and matter transport mechanism (10,11)

All metal oxides are ionic semiconductor compounds. Matter transport takes place by transport of cations, anions and electrons through the defects in the oxide structure. A number of transport mechanisms have been suggested according to the nature of the oxide, which can be divided into two groups: stoichiometric and non-stoichiometric ionic compounds. Although all the possible defects are present to some extent in all oxides, certain types of defects predominate in most cases.

a) Stoichiometric compounds

The predominant defects in stoichiometric ionic compounds are either Schottky and Frenkel defects. In Schottky defect structures, ionic mobility is explained by the existence of ionic vacancies, ie there is an equivalent number of vacancies on both cation and anion sub-lattices. Both cations and anions are mobile since vacancies exist in both sub-lattices. In Frenkel defect structures, the anion lattice is perfect and the cation lattice contains cation vacancies and interstitials. Therefore, only the cations are mobile. NaCl and AgBr are samples of Schottky and Frenkel defect structures respectively, as shown schematically in Figs.2-1 and 2-2.

b) Non-stoichiometric compounds

Non-stoichiometry means that the metal to non-metal atom ratio is not exactly as given by the chemical formula, even though the compound is electrically neutral. There are two types of non-stoichiometric compounds: N-type and P-type semiconductors.

Fig.2-3 shows schematically the structure of a N-type metal excess semiconductor, ZnO. The chemical formula of this type of oxide can be written as $M_{1+a}O$. Interstitial cations, Zn^{2+} , exist with an equivalent number of electrons. Cations and electrons are expected to be mobile in this structure.

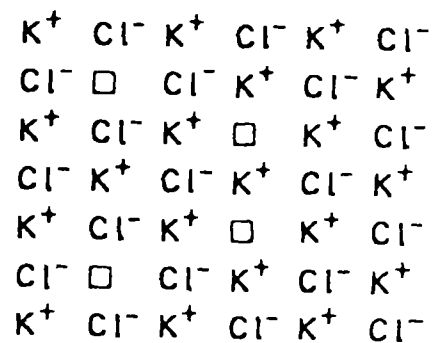


Fig.2-1: Schottky defect in KCl.

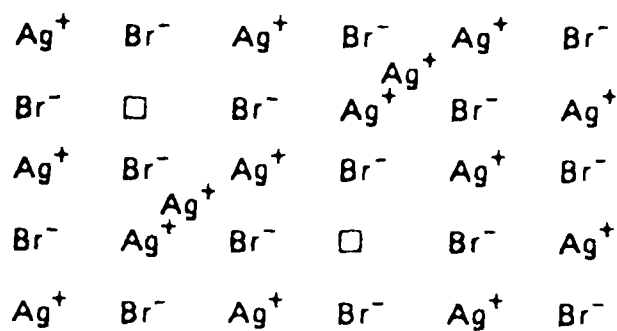


Fig.2-2: Frenkel defect in AgBr.

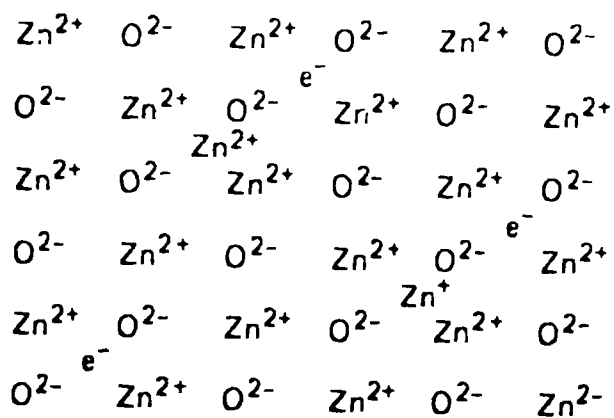


Fig.2-3: N-type metal

excess semiconductor ZnO.

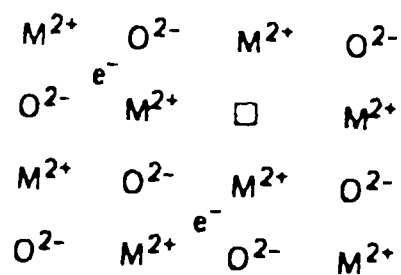


Fig.2-4: N-type

non-metal deficit oxide MO_{1-a}.

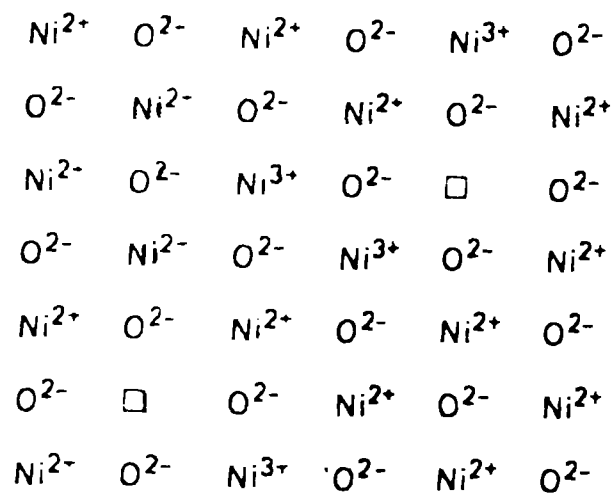


Fig.2-5: P-type metal deficit semiconductor NiO.

Fig.2-4 shows the structure of a N-type non-metal deficit semiconductor schematically. This structure can be regarded as the result of discharge and evaporation of an oxygen ion. Electrons enter the conduction band and vacancies exist on the anion lattice. Anions and electrons are both expected to be mobile in this structure.

Fig.2-5 shows a P-type metal deficit semiconductor NiO. The formula of this type of oxide can be written as $M_{1-a}O$. Cation vacancies and electron holes are in existence for the transport of cations and electrons. Since many metal ions exist in several valence states, it is relatively easy for an electron to transfer, e.g. in NiO, from a Ni^{2+} to Ni^{3+} . The site of Ni^{3+} , therefore, offers a low energy position for an electron, and is called an "electron hole".

2.2.2 Fast matter transport paths in oxide scales (12-21)

In the last section, only the transport through the lattice has been considered. However, during the past 20 years, evidence has been accumulated to suggest that transport along fast diffusion paths in oxide scales, such as grain boundaries and dislocations, often plays an important role in oxide scale growth, and perhaps control the oxidation rate of many metals and alloys. The early oxidation data (pre-1970) based on the bulk lattice diffusion are greatly in error (12-15). For instance, research on Cr^{3+} lattice diffusion, electrical conductivity and non-stoichiometry in Cr_2O_3 indicates that the majority of the point defects in Cr_2O_3 are Cr vacancies and electron holes under high oxygen partial pressure. The diffusion rates calculated with this model are consistent with the experimental results obtained from diffusion of Cr^{3+} in single-crystal Cr_2O_3 , but 4-7 orders of magnitude lower than the values calculated from Cr_2O_3 growth during Cr oxidation. This implies that Cr_2O_3 grows by so-called short-circuit diffusion through grain boundaries and/or

dislocations rather than by diffusion through the bulk lattice. Fig.2-6 shows the parabolic rate constants calculated from Cr_2O_3 growth data and from Cr diffusion data for polycrystal and single-crystal Cr_2O_3 , showing two widely differing values (13,14). Similar results have been reported for the growth of Fe_2O_3 , Fe_3O_4 , NiO, ZrO_2 and Al_2O_3 (12-18).

Some basic features of diffusion along dislocations and grain boundaries have been studied. In Cr_2O_3 and NiO, the effective width of a grain boundary or dislocation is approximately 1nm , i.e. of the same order as the dislocation core size (14,19). According to theoretical simulations in Fe and MgO, the major contribution to more rapid diffusion through grain boundaries than in the lattice comes from an increased concentration of defects rather than a higher mobility of the defects (13,20,21).

The study of fast diffusion in oxide scales is very important for both understanding and controlling the oxidation and corrosion reactions at high temperatures. Research on this topic is very much in progress and there are still many gaps in our knowledge. Detailed microstructural investigations in oxide scales should be able to help understanding of these mechanisms.

2.2.3 Growth mechanism of fast-growing oxide whiskers (22-28)

When certain types of fast diffusion path exist in an oxide scale, the oxide grows very fast sometimes in the form of whiskers or lamellae. This is a type of non-protective oxide scale, and leads to a breakdown oxidation process. Research on the whiskers and lamellae oxide growth mechanisms are necessary to interpret some important oxidation phenomena such as oxide lattice extension, lateral-scale growth and fast matter transport in oxide scales, and to prevent this type of breakdown oxidation. Attention has not yet been paid to this subject and the current understanding in the growth mechanism of fast growing oxide is rather inadequate (22).

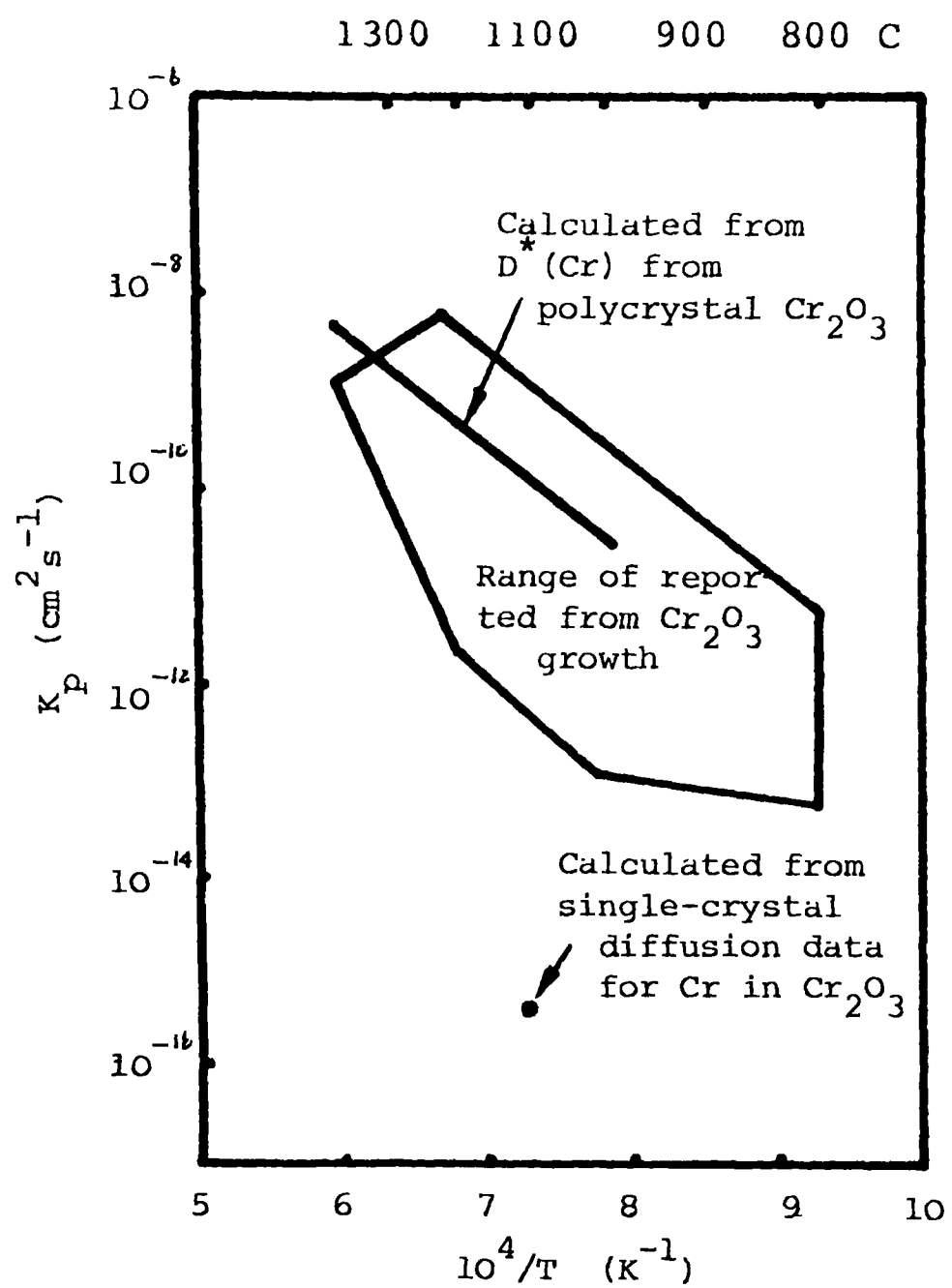


Fig.2-6: Parabolic rate constants calculated from Cr_2O_3 growth during oxidation, and the Cr diffusion data in polycrystal and single-crystal Cr_2O_3 . (14)

Whisker- or lamella-like oxides have been observed in the oxidation of Cu, Fe, Ni, Cr, Mo, Ta, Ni-Cr and Fe-Ni-Cr alloys, sometimes in the presence of water vapour (22-27). Investigations show that the oxide whisker is a single crystal with certain crystal growth orientation. For instance, the oxide whiskers were found to be $\alpha\text{-Fe}_2\text{O}_3$ in Fe based alloys and NiCr_2O_4 in Ni-Cr alloys (25-27). TEM observation of Fe_2O_3 whiskers show that there are open and closed hollow cores associated with bundles of dislocations, which have been suggested as the fast ion transport paths (22,28). In the whole, however, the growth mechanism of the fast-growing oxide whiskers are not clear (see Chapter 4).

2.3 Oxidation mechanisms and kinetics (29-37,3-5)

The reaction rate of a metal in the gaseous media at all temperatures determines the possible uses of that metal, and the reaction rate is determined by the reaction mechanism. Different mechanisms may take place with only a very small change in material composition or oxidation conditions, leading to a sharp increase or decrease in the reaction rate.

2.3.1 Oxidation rate and reaction rate controlling process

The oxidation rate of a metal under given conditions of atmosphere and temperature can be monitored experimentally by thermogravimetric or scale thickness measurements. The thermogravimetric measurements are traditional methods to assess oxidation resistance for metals and alloys, and probably are still the most convenient and essential way to study oxidation kinetics, and therefore oxidation mechanisms.

When a metal is exposed to an oxidising atmosphere, the reaction rate of the bare metal surface with oxygen is extremely high, because of the large decrease in free energy as the metal becomes oxide. After this initial stage of oxidation, the oxide growth rate in most cases decreases

rapidly, and further growth of oxide depends upon the supply of the reaction species. The transport of ions and electrons through the growing oxide layer is the oxidation rate controlling process in most cases, because this is usually slower than the chemical reactions at the gas/scale or scale/metal interface. However, if the matter transport through the oxide is fast enough, then matter transport in the metal or gas atmosphere, or chemical reactions at the gas/scale or scale/metal interface can become the rate controlling process for the overall reaction. Thus the oxidation rate is often decided by the nature of the oxide scale formed on the metal surface and the diffusion mechanism through the oxide scale, as discussed in the last section. Because the oxide scales formed on metals and alloys usually have complex structures and compositions, microscopy and microanalysis are often used to help understand the oxidation mechanisms.

Three most important oxidation rate laws which express the relationship of the thickness of oxide scale and reaction time are briefly described here: 1) the linear rate law, 2) the parabolic rate law, and 3) the logarithmic rate law.

2.3.2 Linear oxidation rate law (29-31)

Linear oxidation is the simplest type of oxidation kinetics:

$$dY/dt = K \quad (2.1)$$

$$Y = Kt + \text{Constant} \quad (2.2)$$

with a constant reaction rate K , and a scale thickness Y which is proportional to oxidation time t , as shown in Fig.2-7. Linear oxidation kinetics are found whenever the reaction rate is not affected by the thickness of the oxide scale. For instance, if the oxide scale is non-protective, the actual thickness of the scale has no influence on the oxidation rate. Linear oxidation kinetics are also found when the oxide scale continually fractures, because of growth and/or heat stresses. In

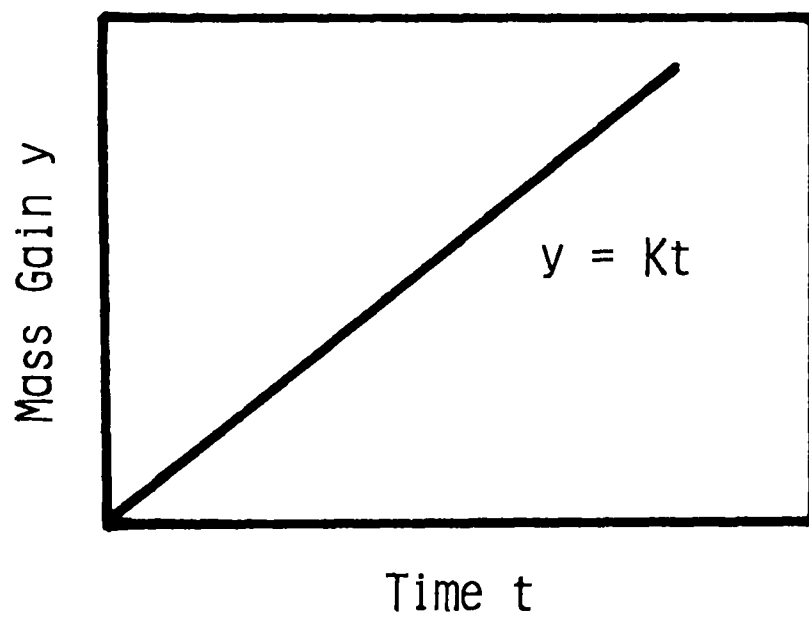


Fig.2-7: Linear oxidation rate law.

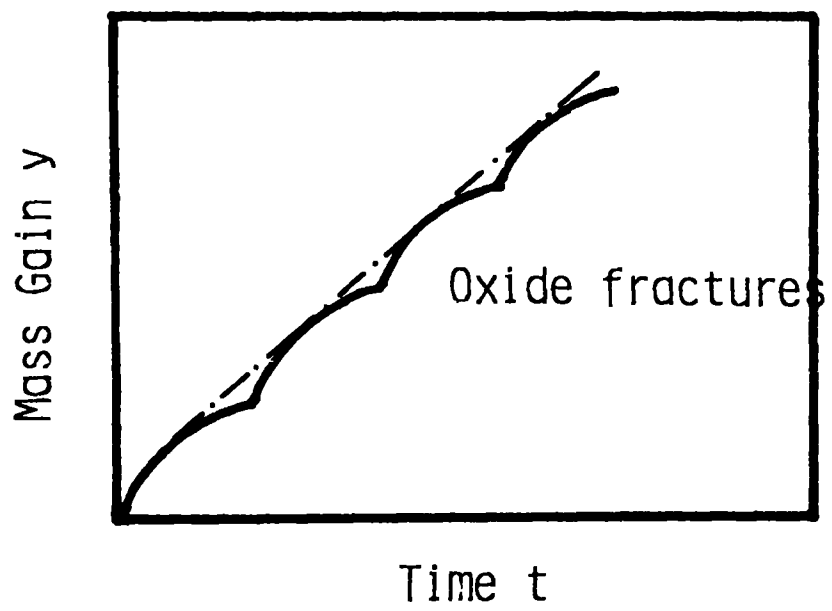


Fig.2-8: A linear oxidation rate law obtained from a metal on which the oxide scale keeps fracturing.(73)

this case, the oxide scale thickens parabolically for short periods of time, but the overall oxidation kinetics are still linear, as shown in Fig.2-8.

2.3.3 Parabolic oxidation rate law (31-34)

Parabolic oxidation is the most common oxidation law found in high temperature oxidation of metals and alloys, and is known as Wagner's oxidation law (32,33). In parabolic oxidation, the diffusion of ions or migration of electrons through the oxide scale is the rate controlling process, and the oxidation rate is inversely proportional to scale thickness:

$$dY/dt = 2K/Y \quad (2.3)$$

$$Y^2 = Kt + \text{Constant} \quad (2.4)$$

A linear relation is obtained by plotting Y^2 with t , as shown in Fig.2-9.

The parabolic rate constant K is related to the driving forces of the reaction. The driving forces come from the concentration gradient and the electric potential gradient across the oxide scale, which are responsible for ion diffusion and electron migration respectively. Considering the ion diffusion process only, and assuming that grain boundary reactions can be ignored, the concentration gradient across the scale produces a difference in chemical potential, and results in diffusion according to Fick's law:

$$dm/dt = -DA dC/dx \quad (2.5)$$

Where dm/dt = rate of mass of diffusion, D = diffusion coefficient, A = cross sectional area and dC/dx = concentration gradient. Integrating equation (2.5):

$$m = -DA dCt/dx + \text{constant} \quad (2.6)$$

As m is the mass of the diffusing species in an oxide, if d' = oxide density, W = molecular weight of the oxide, M = atomic weight of the diffusing species and n = number of atoms of the diffusing species in a

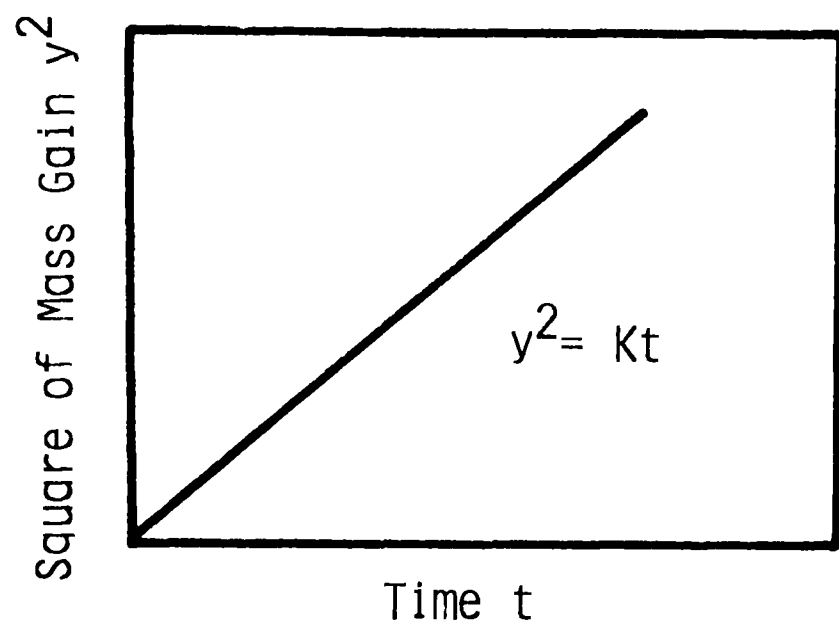


Fig.2-9: Parabolic oxidation rate law.

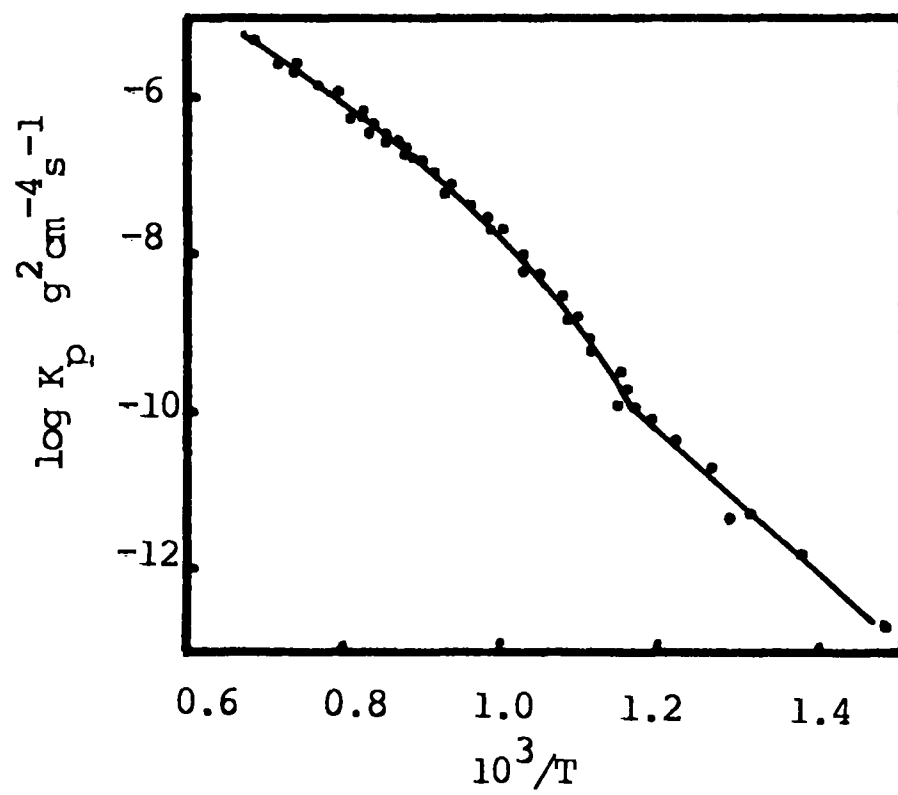


Fig.2-10: Relation between parabolic rate constant and temperature for the oxidation of high purity Fe (34).

molecule of oxide, then

$$m = YAd'nM/W \quad (2.7)$$

Substituting m in equation (2.7) from equation (2.6), assuming m = 0 when t = 0, and dx = Y:

$$YAd'nM/W = -DAdCt/Y \quad (2.8)$$

$$Y^2 = -WDdCt/d'nM = Kt \quad (2.9)$$

Thus, the parabolic rate constant K is proportional to the diffusion coefficient D. Since diffusion is a thermally activated process, the parabolic rate constant obeys the Arrhenius equation:

$$K = K_o \exp(-Q/RT) \quad (2.10)$$

where Q is activation energy for the diffusion process, R is gas constant, T is absolute temperature and K_o is a constant. The Arrhenius variation for the oxidation of high-purity iron in the temperature range 400-1180 has been given by Davies et al and Schmahl et al (34), as shown in Fig.2-10.

2.3.4 Logarithmic oxidation rate law (3-5,35-37)

Logarithmic oxidation kinetics are usually found in oxidation at relatively low temperatures (<400 C). A number of metals, including Cu, Fe, Zn, Ni, Pb, Cd, Sn, Mn, Al, Ce, Zr, Mg and Ta have been reported to obey a logarithmic oxidation rate law in a certain temperature range (35). Under the logarithmic rate law, the oxidation rate is initially fast, then falls down quickly to a low level. Logarithmic oxidation kinetics can be expressed as

$$Y = K \log(t + t_o) + \text{constant} \quad \text{for a direct log law} \quad (2.11)$$

$$1/Y = B - K' \log t \quad \text{for a inverse log law} \quad (2.12)$$

where K, K' and B are constants. Fig.2-11 shows schematically the logarithmic oxidation rate law. Due to the difficulties of obtaining accurate measurements of oxidation rate at low temperatures and assessing the nature of very thin oxide films, the interpretations of logarithmic

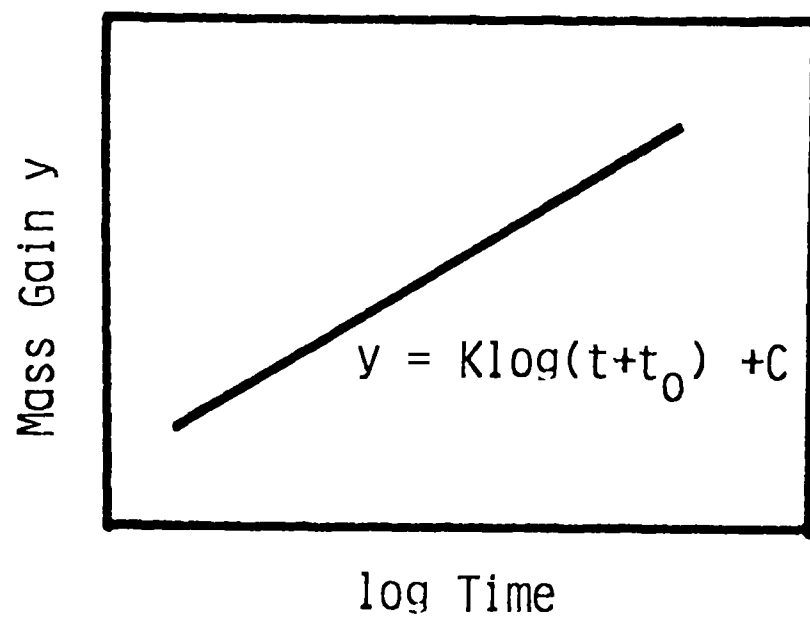


Fig.2-11: Logarithmic oxidation rate law.

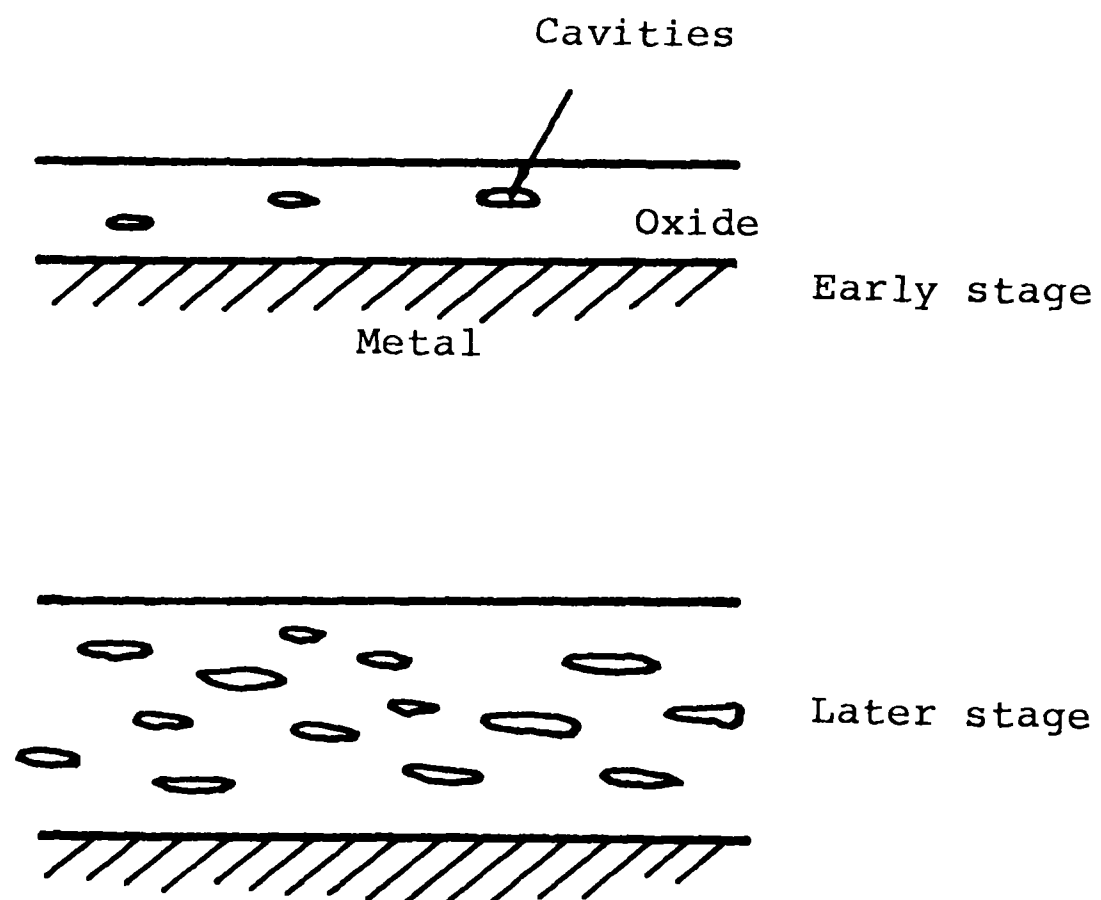


Fig.2-12: Elongated cavities found in some oxide scales over period of oxidation time, which may cause logarithmic oxidation kinetics.

oxidation kinetics is still among the least understood areas of metal oxidation. However, several interpretation of logarithmic oxidation kinetics have been suggested (3-5,36,37), which are based on the following mechanisms:

- a) progressive blocking of low resistance diffusion paths in the oxide scale;
- b) absorption of reactive species;
- c) effects of electric fields developed across oxide layers;
- d) quantum-mechanical tunnelling of electrons through the thin scales;
- e) non-isothermal conditions in the oxide layer.

The blocking effect was suggested by Evans et al (37), related to fast matter transport mechanism, i.e. the ions of reaction species diffuse through rapid transport paths such as grain boundaries, dislocation pipes or surface of pores. As oxide growth proceeds, the fast transport paths are blocked progressively, either by recrystallisation and grain growth in the oxide scale, or by blocking of pores due to growth stresses in the oxide. Pores in the scale can also act as vacancy sinks and grow into cavities large enough to reduce the cross section area of compact oxide scales, through which ion transport occurs (see Fig.2-12). Formation of a second oxide phase with low ionic conductivity may also give the same progressive resistance to the ion transport, and result in logarithmic oxidation kinetics. It is unlikely that any one theory will explain logarithmic oxidation kinetics for all metals, since the nature of oxide scales varies tremendously. It is possible that each of the different factors may be important in different cases.

2.4 Oxidation of pure metals

2.4.1 Oxidation of Fe (38-47)

The oxidation behaviour of iron has been extensively studied in different atmospheres over a wide range of temperature (40-47).

When Fe is oxidised in air at high temperatures, it grows a scale consisting of three layers of oxide, in the following sequence: FeO, Fe₃O₄ and Fe₂O₃, with FeO next to the metal. Fig.2-13 shows the Fe-O phase diagram.

The wustite phase FeO is a P-type metal deficit semiconductor which exists over a wide range of stoichiometry at high temperatures, narrowing to a single composition of Fe₄₈O₅₂ at 570 C, below which does not exist at equilibrium. The mobility of cations and electrons via vacancies and electron holes is rather high, so that FeO has a relatively high growth rate.

The magnetite phase Fe₃O₄ is also a P-type semiconductor oxide with an inverse spinel structure. It can be written as FeO Fe₂O₃. Fe²⁺ ions occupy octahedral sites and Fe³⁺ ions occupy tetrahedral sites. Defects occur on both sites and iron ions may diffuse over both octahedral and tetrahedral sites.

The haematite phase Fe₂O₃ is a N-type oxide with anion defects. Haematite has two structures: α-Fe₂O₃, which has a rhombohedral structure, and γ-Fe₂O₃, which has a spinel structure similar to Fe₃O₄, with which it forms a continuous solid solution. Since Fe₃O₄ oxidises to form α-Fe₂O₃ above 400 C, α-Fe₂O₃ is more important than γ-Fe₂O₃ in the study of iron oxidation. In the rhombohedral α-Fe₂O₃ crystal, O²⁻ ions exist on the close packed hexagonal positions with Fe³⁺ ions in the interstices. With such a structure, it may be expected that Fe ions would be mobile. However, there are still uncertainties about the diffusion mechanism in

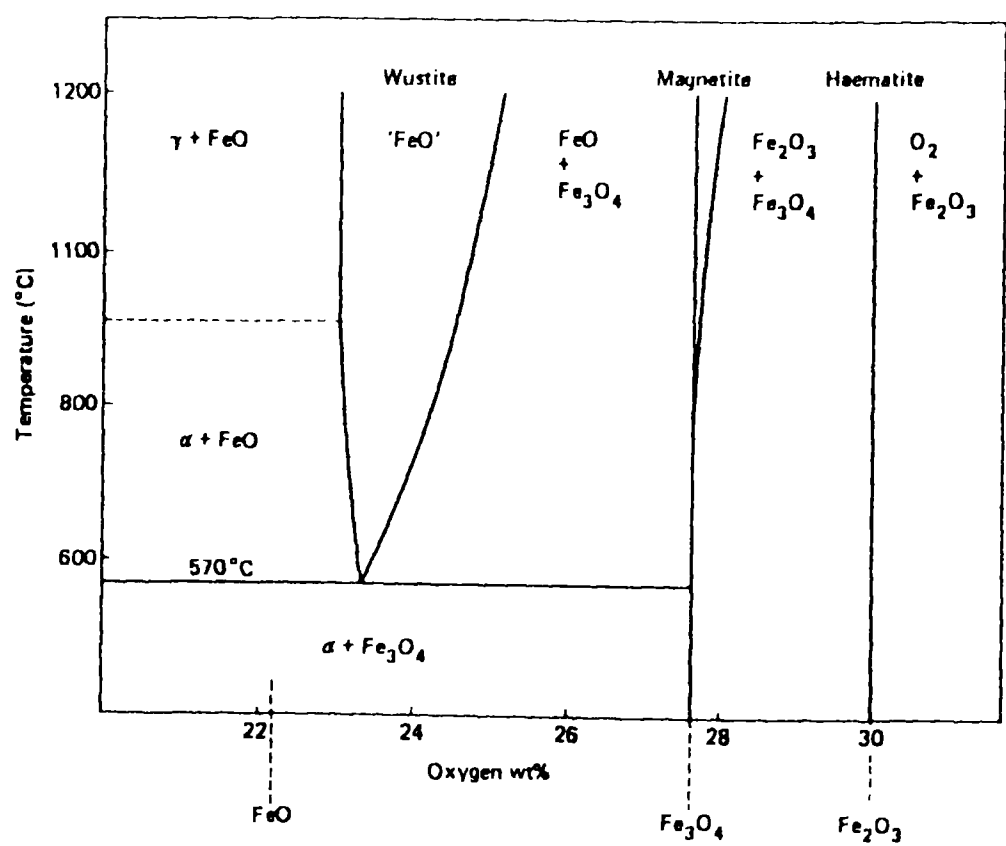
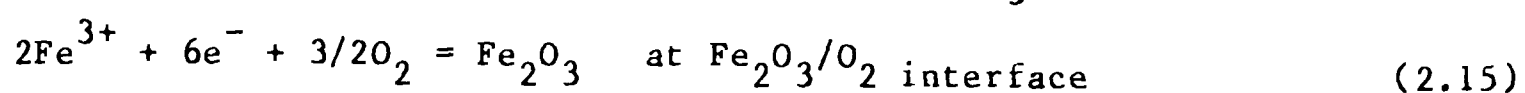
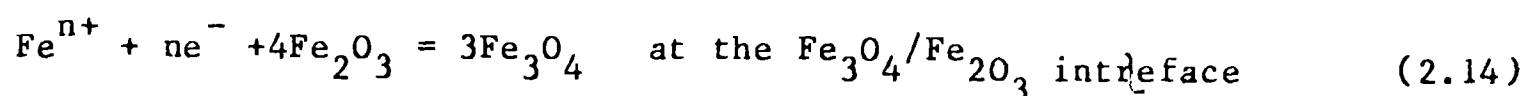
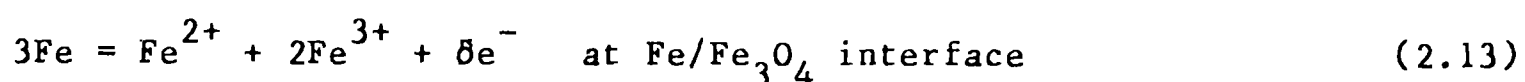


Fig.2-13: Fe-O phase diagram.⁽¹⁾

$\alpha\text{-Fe}_2\text{O}_3$ as $\alpha\text{-Fe}_2\text{O}_3$ has been reported to show disorder on the anion sub-lattice only (41), from which only the O^{2-} ions can move, while oxidation experiments showed that Fe_2O_3 growth occurs by outward cation migration (42).

At temperatures above 570 C, the FeO layer is much thicker than Fe_3O_4 and Fe_2O_3 because of the much great mobility of defects in FeO, for instance the relative thicknesses of $\text{FeO} : \text{Fe}_3\text{O}_4 : \text{Fe}_2\text{O}_3 = 95 : 4 : 1$ at 1000 C (43). At temperatures below 570 C, however, the oxidation rate is correspondingly lower in the absence of FeO. Based on the structures and properties of Fe_3O_4 and Fe_2O_3 , the mechanism of Fe oxidation below 570 C is expected to be as shown in Fig.2-14, with the following reactions scheme:



where n is 2 or 3 for Fe^{2+} or Fe^{3+} ions respectively.

2.4.2 Oxidation of Ni (48-55)

Ni has better oxidation resistance than Fe and most other commercial metals, and Ni based alloys are widely used as oxidation resistant alloys at high temperatures. Pure Ni oxidises according to a parabolic rate law in the temperature range 700-1327 C, and it forms only one oxide NiO, which is a P-type metal deficit semiconductor (48-52). Platinum markers placed on the Ni surface before oxidation are found at the metal-scale interface afterwards, indicating that the scale forms by outward migration of cations and electrons. Therefore, the mechanism of Ni oxidation is a relatively simple one, as shown in Fig.2-15. A review of Ni oxidation in comparison with the oxidation behaviour of other transition metals has been published by Smeltzer et al (53).

However, the oxidation rate of Ni is very sensitive to its purity. Ni

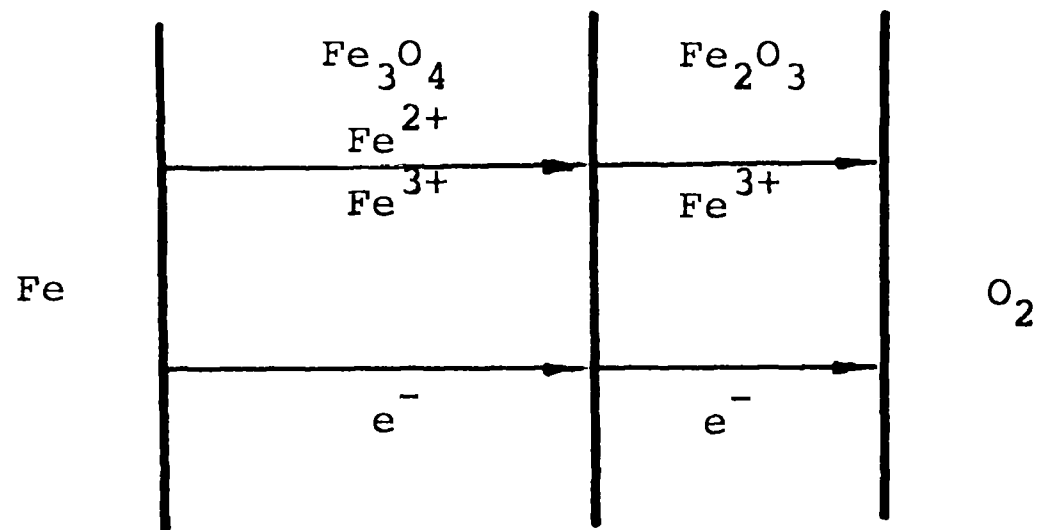


Fig.2-14: Mechanism of Fe oxidation below 570°C to form a two-layer oxide scale of Fe_3O_4 and Fe_2O_3 .

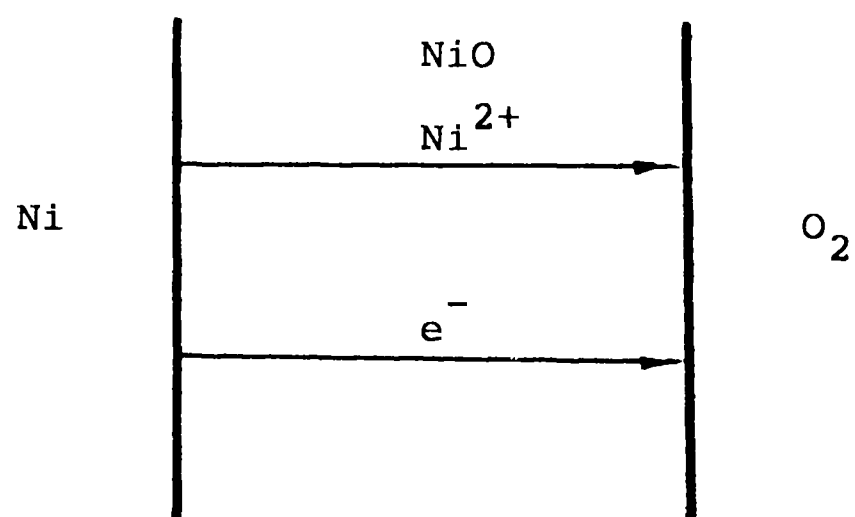
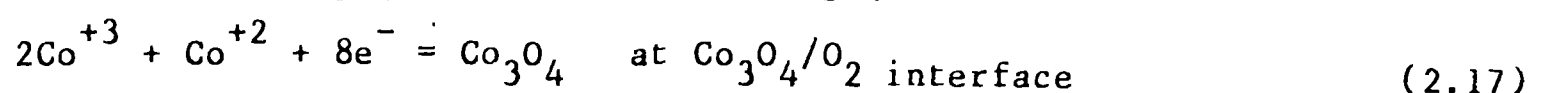
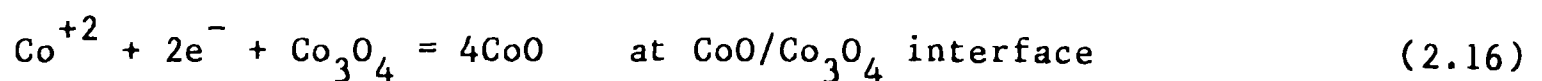


Fig.2-15: Mechanism of pure Ni oxidation to form a single oxide layer NiO .

containing as little as 0.1% impurities shows different oxidation behaviour (54,55). The oxide scale formed on impure Ni consists of two NiO layers, the outer layer compact and the inner layer porous. The outer layer grows by outward cation migration and the inner porous layer grows by inward migration of oxygen. The proposed mechanism for this oxidation behaviour assumes that the oxide is separated from the metal in the early stage due to insufficient oxide plasticity, which is caused by the impure Ni (48). Once the scale loses contact with the metal, the oxygen activity at the inner oxide surface rises. Oxygen then migrates across the pores and begins to form new oxide on the metal surface. A schematic representation of this process is shown in Fig.2-16.

2.4.3 Oxidation of Co (56-62)

When pure Co oxidises in air in the temperature range 225-900 C, a two-layer oxide consisting of CoO and Co_3O_4 is formed with CoO adjacent to the metal surface. At lower or higher temperatures (<225 C or >900 C), only CoO is formed (56,57). CoO is a P-type cation deficient semiconductor with a fcc structure like NaCl. Cations and electrons can migrate easily through CoO over the cation vacancies and electron holes, so CoO growth is relatively fast. Co_3O_4 has a spinel structure, and decomposes at 900 C (57,58). Pt markers applied to the Co sample surface before oxidation are found at the metal-scale interface afterwards, indicating that the oxide forms by outward diffusion of the metal ions. The reaction mechanism by which the two layer oxide scale formed is shown in Fig.2-17, with the following reaction scheme:



The oxidation kinetics of Co are reported to obey a parabolic rate law in the temperature ranging from 400-1200 C. The parabolic rate constants,

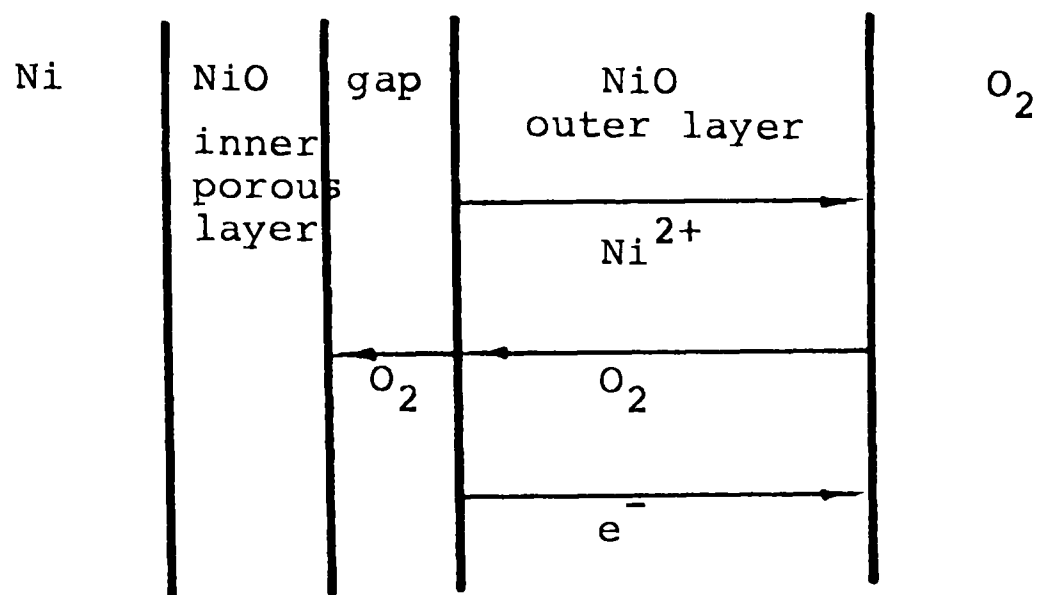


Fig.2-16: Mechanism of impure Ni oxidation to form two-layer oxide scale.

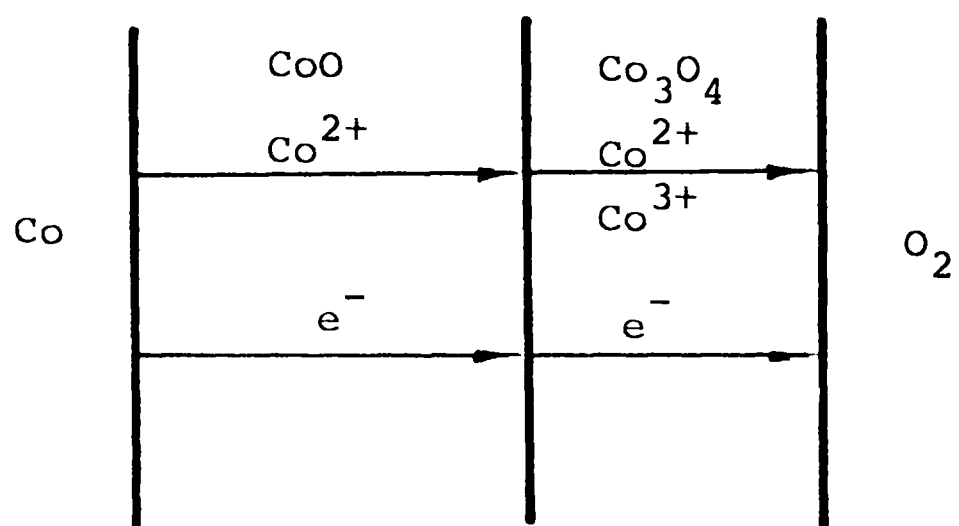


Fig.2-17: Mechanism of Co oxidation over temperature range 300 - 850°C.

however, have been found to follow Arrhenius equations with different K_0 and Q above and below 700 C:

$$400-700 \text{ C: } K_p = 4.1 \times 10^{-6} \exp(-20,000/RT) \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \quad (2.18)$$

$$700-1200 \text{ C: } K_p = 6.4 \times 10^4 \exp(-65,500/RT) \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \quad (2.19)$$

It has been suggested that the break in the $\log K_p - 1/T$ plot around 700 C is caused by diffusion through the oxide occurring predominantly along grain boundaries at lower temperatures, and through the grains at higher temperatures (59,60). The oxidation kinetics of Co at temperatures lower than 400 C are found to be more complicated, and different kinetics such as logarithmic rate law and fourth root rate law have been reported (61,62).

2.5 Oxidation of alloys

2.5.1 Oxidation of Fe-Ni alloys (63-65)

Small additions of Ni (2-6wt.%) have little effect on the oxidation resistance of Fe (63). With a high concentration of Ni (30-42wt.%) however, oxidation is 30-40 times slower than Fe, ie about the same level as Ni (64). When Fe-Ni alloys oxidise, the oxide scale consists mainly of Fe oxides, similar to oxidation of Fe. Ni is therefore enriched in the metal surface and causes the oxidation rate to slow down. The scale formed on an Fe-42%Ni alloy was found to have a two phase-structure consisting of Ni ferrite NiFe_2O_4 and Fe_2O_3 , with NiFe_2O_4 next to the metal. The rate controlling process in this case is probably the diffusion of cations across the spinel NiFe_2O_4 , which is slower than the diffusion of Fe and Ni ions in Fe oxides (65).

2.5.2 Oxidation of Fe-Cr and Fe-Ni-Cr alloys (66-77)

Fe-Cr and Fe-Ni-Cr alloys are among the most important oxidation resistant alloys, and are widely used in industry. Both Cr_2O_3 and Fe_2O_3 have rhombohedral structure and show a continuous series of solid

solutions. The Fe- and Cr-oxides also react to form spinel oxide FeCr_2O_4 which forms solid solutions with Fe_3O_4 (66,67). Low concentration Cr steels show only slightly better oxidation resistance than Fe. However, Fe-12%Cr alloys below 900 C and Fe-17%Cr alloys below 1100 C show oxide growth rates almost 100 times slower than Fe (66,67). In the initial oxidation stage, when the oxide thickness is $< 100\text{nm}$, the oxidation rate of Fe-Cr or Fe-Ni-Cr alloys is not slower than plain steels, but as soon as a layer consisting of $(\text{Cr,Fe})_2\text{O}_3$ and/or FeCr_2O_4 is formed, the oxidation rate slows down and the oxidation kinetics obey the parabolic rate law.

Fe-Cr alloys with moderate Cr content (about 10wt%Cr) have a good combination of mechanical properties, oxidation and corrosion resistance, and relatively low price. They can withstand oxidation without any problem over the temperature range 600-800 C as long as a protective scale of Cr_2O_3 or mixed spinel FeCr_2O_4 is formed. However, non-protective Fe-rich oxide can develop under certain circumstances, leading to an accelerated breakdown oxidation (68,69). A number of mechanisms have been suggested for this type of oxidation breakdown (70-72).

When the Cr contents is $> 20\%$, a permanent protective scale of Cr_2O_3 is formed on the surface of Fe-Cr and Fe-Ni-Cr alloys, with a corresponding reduction in the parabolic rate constant. This protective oxide has a self-healing ability, which means that the proportion of Cr atoms presents in the alloy and their diffusion rate can together ensure that there is an adequate supply of Cr^{3+} cations to rebuild the Cr_2O_3 protective film if it is broken by growth or heat stresses (73,74). However, a high concentration of Cr leads to a deterioration in the mechanical properties of Fe-Cr alloys. This is why Ni is often added to improve the mechanical properties.

2.5.3 Oxidation of Fe-Si alloys (78-80)

As with Cr in Fe, a relatively high concentration of Si (3-10wt.%) in the Fe-Si is beneficial for oxidation resistance. The oxides involved in Fe-Si system include SiO_2 , FeO , Fe_2O_3 , Fe_3O_4 and Fe_2SiO_4 .

At low Si content, SiO_2 is formed at the alloy surface, distributed in very fine scales, and reacts with FeO to form Fe_2SiO_4 . When the Fe_2SiO_4 particles become large, they are engulfed by the scale, as shown in Fig.2-18. With higher Si concentration, more Fe_2SiO_4 is formed. The Si content can be increased to provide a continuous protective SiO_2 layer, but formation of intermetallic compounds in the alloy makes the alloy very brittle.

The effects of some alloying elements on the oxidation resistance of Fe alloys are summarised in Fig.2-19 (81).

2.5.4 Oxidation of Co-alloys (81-85)

Fig.2-20 shows the effects of some alloying elements on the oxidation resistance of Co alloys at 1000 C in air. A brief introduction to the oxidation of Co-Cr and Co-Ni is given as follows:

Cr content up to 10% slightly increases the oxidation rate of Co since the scale still consists mainly of CoO with small amount of CoCr_2O_4 . CoO is a P-type cation deficient semiconductor, and Cr^{3+} increases the cation vacancy concentration in CoO . With further increase in Cr content, up to 25%, the oxidation rate falls down sharply as shown in Fig.2-20, because a protective Cr_2O_3 scale is formed on the surface. Further increase of Cr content causes oxidation resistance to decrease slightly because the scale has poor resistance to spalling (81-83).

Co-Ni alloys have similar oxidation behaviour to pure Co, because NiO and CoO have similar stabilities and can form a single phase solution in the oxide scale (81,84). Addition of up to 40% Ni causes a small, linear

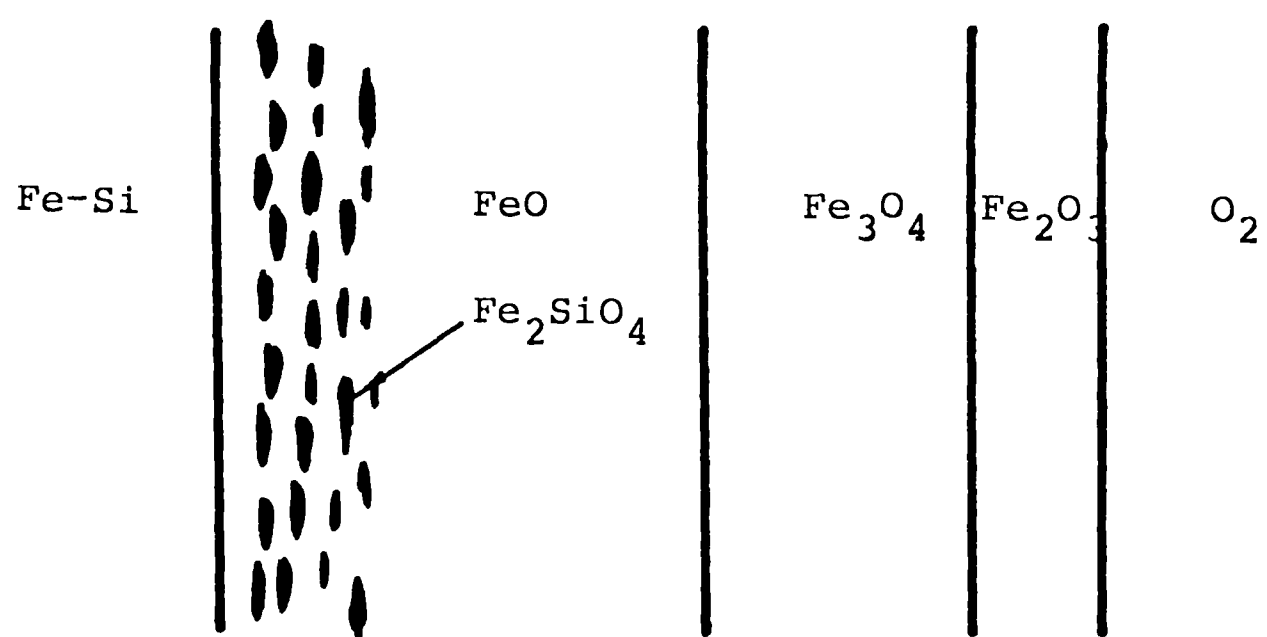


Fig.2-18: The oxide scale formed on dilute Fe-Si alloys (70).

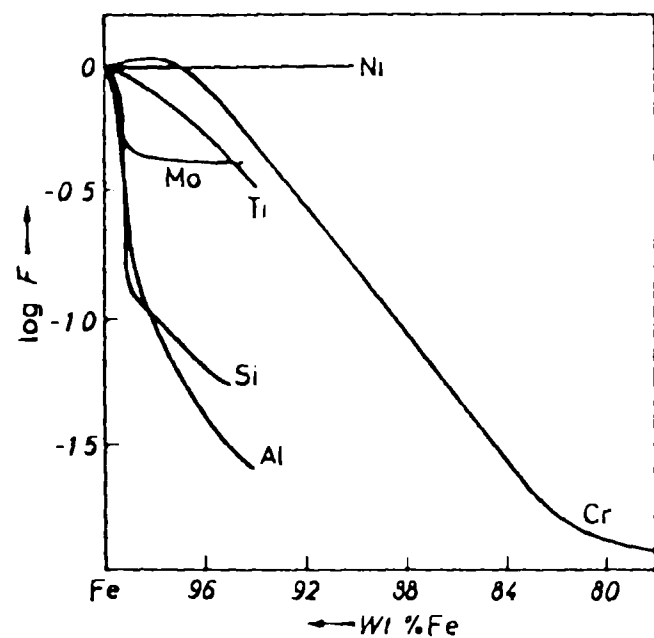


Fig.2-19: The effect of some alloying elements on the oxidation resistance of Fe. F is the factor representing relative mass gains after 4h at 890°C in air (81).

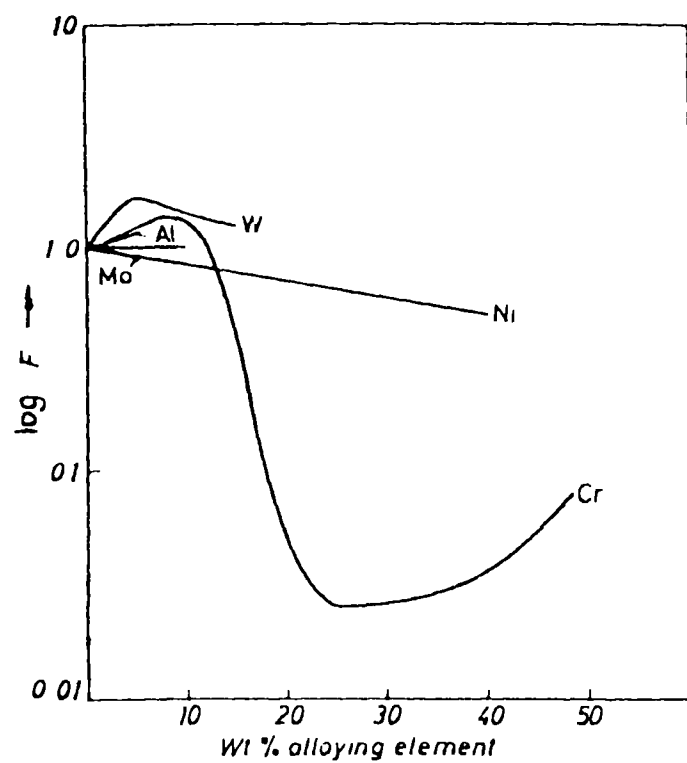


Fig.2-20: The effect of some alloying elements on the oxidation resistance of Co at 1000°C in air (81).

decrease in oxidation rate, as shown in Fig.2-20.

2.6 Oxidation of amorphous alloys (86-98)

A search of the literature revealed only 13 papers that dealt with the oxidation behaviour of amorphous alloys.

2.6.1 Oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ (86-88)

Fusy and Pareja (86) investigated oxygen uptake on the surfaces of amorphous and crystallised Fe₄₀Ni₄₀P₁₄B by using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). They found it difficult to detect differences in oxidation of amorphous and crystallised Fe₄₀Ni₄₀P₁₄B₆, because initial absorption of surface phosphorus inhibited the oxygen uptake. However, Fusy and Pareja reported that Ni was present only in the oxide formed on crystallised Fe₄₀Ni₄₀P₁₄B₆, while the oxide layer on amorphous Fe₄₀Ni₄₀P₁₄B₆ consisted mainly of Fe₃O₄ and a small amount of B.

Thube et al (87) studied the initial oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ at room temperature, also by using AES. They suggested that the interreaction of oxygen with amorphous Fe₄₀Ni₄₀P₁₄B₆ involved a combination of reconstructive chemisorption and diffusion. The oxygen uptake could be classified into two stages, fast below 15 Langmuirs (a unit of oxygen uptake) and slow above 15 up to 500 Langmuirs. The defects in the surface region were thought to cause this two-stage oxygen uptake process. They reported that B and Fe segregated on the surface of the annealed Fe₄₀Ni₄₀P₁₄B₆ samples, and also suggested that the mechanism of initial oxide formation is diffusion of Fe through the rapidly oxidising P-segregated surface and its subsequent oxidation at the surface.

Hunderi and Bergersen (88) studied the oxidation behaviour of amorphous Fe₄₀Ni₄₀P₁₄B₆ by AES, as well as ellipsometry to monitor the oxidation

kinetics. They found that the alloy obeys a piecemeal parabolic oxidation rate law in the temperature range 150–250 C, with no effect of moisture on the oxidation kinetics. AES results showed that Fe was enriched with oxygen at the surface region and the Ni and P concentrations were very low there after 48h oxidation at 150 C in dry air, indicating the formation of Fe oxides.

These three previous studies of oxidation on amorphous Fe₄₀Ni₄₀P₁₄B₆ were all carried out near to room temperature. The very thin oxide films formed on the surface of amorphous and crystallised Fe₄₀Ni₄₀B₂₀ were analysed by AES, but the results were rather confusing, and no attempts were made to identify the oxide structure. It is still not clear whether or not amorphous and crystallised Fe₄₀Ni₄₀P₁₄B₆ exhibit different oxidation behaviour.

2.6.2 Oxidation of amorphous Fe₇₈Si₉B₁₃ (89)

Karve et al (89) investigated the oxidation behaviour of amorphous and annealed Fe₇₈Si₉B₁₃ at room temperature by AES. They found the native oxide layers on the amorphous and annealed alloys were quite similar, but the oxide layer on the amorphous alloy was thinner than that on the annealed alloy. In-situ oxidation tests were carried out in the AES chamber using pure oxygen at room temperature, and no significant differences were found between the amorphous and annealed samples. Unfortunately, the annealing treatment which Karve et al used to crystallise amorphous Fe₇₈Si₉B₁₃ was 1h at 200 C, far too low to crystallise amorphous Fe₇₈Si₉B₁₃ (89). Detailed differential scanning calorimetry (DSC) in the present thesis shows that using continuous heating at 10K/min amorphous Fe₇₈Si₉B₁₃ starts to crystallise at about 530 C (see Table 3-4 and Fig.3-7).

2.6.3 Oxidation of amorphous Cu₆₀Zr₄₀ (90)

The oxidation behaviour of a binary amorphous metal-metal alloy Cu₆₀Zr₄₀ was investigated by a combination of thermogravimetric measurements, X-ray diffraction and differential thermal analysis (90). Oxidation tests were carried out at 167 C for up to 250h in different atmospheres. The results showed that samples oxidised in Ar, ie with an oxygen partial pressure of 6.6×10^{-5} atm had the highest mass gains, followed by those in air, and then those in oxygen. This was explained by suggesting that a protective oxide film forms at high oxygen partial pressures, thereby preventing significant further absorption of oxygen by the amorphous alloy. Heat treatment and surface polishing were also found to influence the oxidation kinetics as shown in Fig.2-21. Mechanically polished and as-quenched amorphous Cu₆₀Zr₄₀ had much higher oxidation mass gains than crystallised or heat treated Cu₆₀Zr₄₀. Following explanations were suggested: (a) amorphous Cu₆₀Zr₄₀ has a higher surface activity than crystallised Cu₆₀Zr₄₀; (b) a passive oxide film was formed during the heat treatments and resulted in a better oxidation resistance for heat treated and crystallised Cu₆₀Zr₄₀; and (c) surface polishing removed the passive oxide film and caused a higher oxidation rate (90).

2.6.4 Oxidation of amorphous Ta₅₅Ir₄₅ (91)

Amorphous Ta₅₅Ir₄₅ has a high crystallisation temperature of ~950 C, so that the oxidation studies can be conducted at relatively high temperatures without causing crystallisation. The oxidation products and oxide growth mechanism of amorphous Ta₅₅Ir₄₅ at 500 and 700 C in an Ar-0.1%O₂ gas mixture were studied by Cotell and Yurek (91) using AES, electron microscopy etc. A layer of Ta₂O₅ grew rapidly on the amorphous alloy surface, with diffusion of oxygen anions from the Ta₂O₅/gas interface to the alloy/Ta₂O₅ interface, where Ta was selectively oxidised. Because the

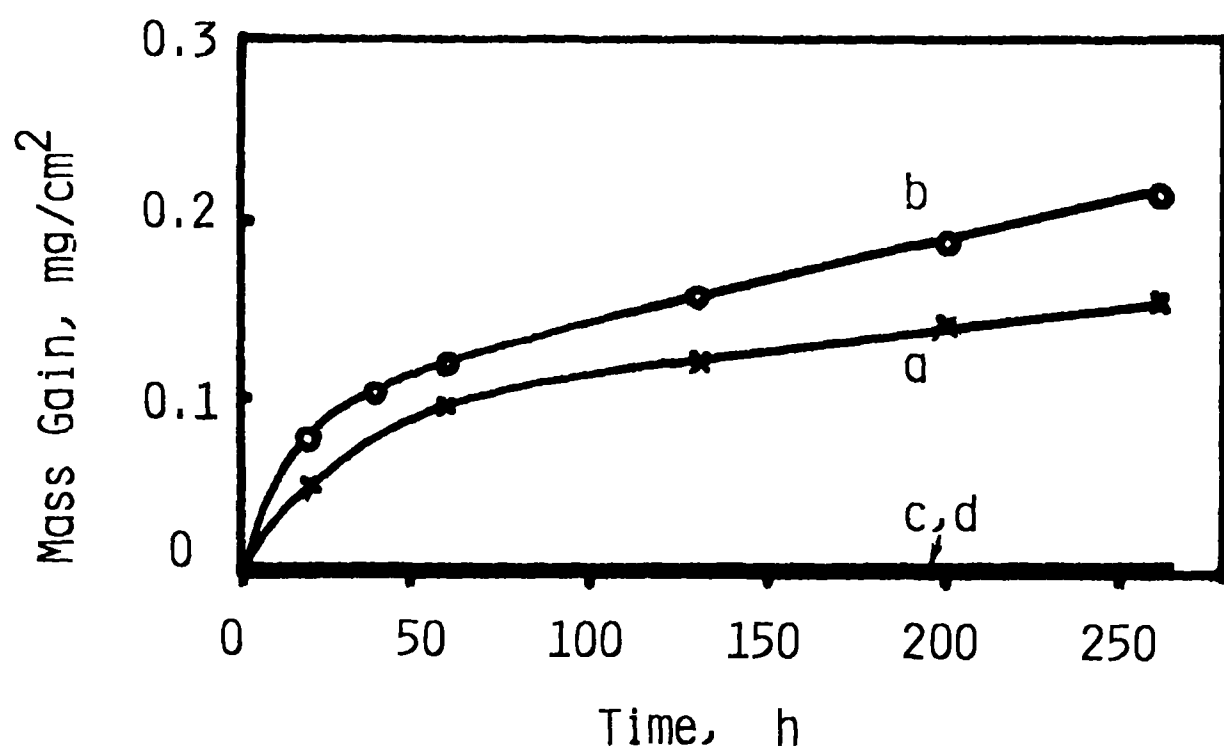


Fig.2-21: Oxidation mass gain of amorphous and crystallised Cu60Zn40 at 167°C in 99.995%Ar;
 (a) as-quenched amorphous Cu60Zn40,
 (b) as-quenched and mechanically polished amorphous Cu60Zn40,
 (c) mechanically polished, then heated under UHV for 2h at 387°C, and
 (d) fully crystallised Cu50Zn60.

oxide grew more quickly than Ir could diffuse back into the amorphous alloy, Ir coalesced into crystalline platelets which became embedded in a matrix of the growing Ta_2O_5 oxide scale. Dissolution of oxygen into the unoxidised alloy caused the amorphous alloy to become embrittled.

2.6.5 Oxidation of other amorphous alloys (92-99)

Surface oxidation investigations on some other amorphous alloys include amorphous Fe₄₀Ni₄₀B₂₀ (92), Fe₄₀Ni₃₈Mo₄B₁₈ (93), Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ (94), Fe₆₇Co₁₈Si₁B₁₄ (95), Fe₈₃P₅Cl₁₂ (96), Fe₈₀P₁₃C₇ (97) and P₈₁Si₁₉ (98). The main experiments which have been performed and their results are summarised in Table 2-1.

2.6.6 Summary

Amorphous alloys are intrinsically unstable materials and can decompose when exposed to moderate temperatures. The two main potential causes of degradation are crystallisation and oxidation. Thus, investigating the oxidation behaviour of amorphous alloys is important for both understanding and preventing of this type of degradation. Furthermore, amorphous alloys are presently available in the form of ribbons, strips and wires, which have very high surface-to-bulk ratio. Thus, surface reactions such as oxidation are expected to influence magnetic, electrical, mechanical, corrosion and other properties to a greater extent than in a bulk form, so that surface studies are particularly important in amorphous alloys. From the review above it is obvious that present knowledge on the oxidation behaviour of amorphous alloys is inadequate. There have been very few previous investigations. In addition, the previous work has concentrated mainly on native oxide layer composition analysis and in-situ low temperature oxidation observations. The results were confusing and no attempt was made to study the structure of oxide formed on the amorphous alloys. A range of fundamental and technological questions still remain to

Table 2-1 Oxidation Studies of Some Other Amorphous Alloys (92-98)

Alloys	Main experiments	Main results & conclusions	ref.
Amorphous & crystallised Fe40Ni40B20	AES analysis of native oxide & in-situ oxidation products, at room temperature	The surface oxide produced by in-situ oxidation of amorphous alloy contains 20-28%Ni, much higher than Fe-70%Ni crystalline alloy; O uptakes are similar for both amorphous & crystalline alloys	(92)
Amorphous & crystallised Fe40Ni38-Mo4B18	in-situ oxidation at room temperature XPS surface composition analysis	Amorphous alloy shows a more reactive surface in initial oxidation stage and less O uptake at longer oxidation exposure than crystalline alloy	(93)
Amorphous & crystallised Fe32Ni36Cr14P12B6	AES surface analysis of native oxide & in-situ oxidation products, at room temperature	Native and in-situ oxidation products have different compositions, O uptake on crystalline alloy is 10 times as on amorphous alloy, Cr:P ratio is constant in both amorphous & crystalline alloys	(94)
Amorphous & crystallised Fe67Co18Si1B14	AES surface analysis of native oxide & in-situ oxidation products, at room temperature	Native and in-situ oxidation products are similar in composition; B segregates on the surface, Co and Fe are depleted; the B segregation may prevent further oxidation	(95)

to be continued

Table 2-1 Oxidation Studies of Some Other Amorphous Alloys (cont.)

Alloys	Main experiments	Main results & conclusions	ref.
Amorphous Fe ₈₃ P ₅ C ₁₂	oxidation at room temperature for 1 year, at 630 K for 15 min Mossbauer surface analysis	crystalline oxides α -Fe ₂ O ₃ at room temperature & Fe ₃ O ₄ at 630 K, and crystalline Fe, Fe ₃ P and Fe ₃ C formed on the alloy surface; surface oxidation changed the domain structure	(96)
Amorphous Fe ₈₀ P ₁₃ C ₇	oxidation in air, Ar and vacuum of 3×10^{-2} torr, AES surface analysis, at temperatures up to 600 C	Fe-rich oxide film formed in all cases, P segregated to the oxide/metal interface	(97)
Amorphous & crystallised Pd ₈₁ Si ₁₉	oxidation in air at 160 C and in a vacuum of 10^{-5} torr at room temperature, XPS surface analysis	in the both cases, a SiO ₂ film formed on the alloy surface, Pd was not oxidised; oxides formed on amorphous and crystallised Pd ₈₁ Si ₁₉ had similar composition	(98)

be answered:

- (a) What are the oxidation kinetics of amorphous alloys?
- (b) Is the oxide formed on amorphous alloys amorphous?
- (c) Are there differences in the oxidation behaviour between amorphous and crystalline alloys with identical chemical composition?
- (d) Amorphous soft ferromagnetic alloys are being used as core materials in transformers and other electrical and electronic devices, which must work at moderate temperatures (e.g. 200 C) for long times (20-45 years). Can they withstand degradation by oxidation?
- (e) Does the surface oxidation accelerate surface crystallisation?
- (f) Does the surface oxidation influence amorphous alloy magnetic and other properties?

Answering these questions is the aim of the research work described in this thesis.

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Chapter 3 Experimental Techniques

3.1 Oxidation thermogravimetric measurements (1,2)

3.1.1 Introduction

Thermogravimetric methods are commonly applied to determine oxidation reaction rate and kinetics because of their directness and convenience (1,2). Three ways are usually used to assess the mass change in oxidation experiments:

(a) Metal specimens are weighed, placed in the hot zone of a furnace for a certain time, then removed, cooled and weighed again to assess the mass gain, which represents the mass of oxygen taken by the specimen during oxidation. This procedure can be repeated a number of times for suitable heating periods.

(b) Metal specimens are weighed, placed in the furnace in the same way as in method (a), but after removing from the furnace and cooling down, the scale formed during the oxidation is mechanically or chemically removed from the metal surface. Then the weight loss of the specimens is measured and the oxide scale is analysed to determine the composition and structure.

Both methods (a) and (b) are discontinuous method of assessment.

(c) Metal specimens are suspended in a hot vertical tube on a wire which is connected to a balance, and the mass change of the specimen is recorded without taking the specimen out of the hot zone in the furnace. This is a continuous method of measuring oxidation kinetics, and equipment to do this is called a thermobalance.

Method (a) is the simplest way to measure oxidation kinetics. It requires only a furnace and a balance, and does not involve many difficulties which are associated with methods (b) and (c). Thus the

results of method (a) are usually reliable. Also it allows the use of the most sensitive balance to measure very small mass changes accurately. However, this method has some shortcomings, and certain precautions have to be observed in order to reduce the errors. These shortcomings include:

- (1) The heating has to be intermittent to allow cooling and measuring. Cooling can introduce thermal stresses in the oxide scale, which may cause the scale to be broken and affect the subsequent oxidation kinetics.
- (2) The progress of the reaction between measurements is not monitored, so that the detailed oxidation kinetics may still be difficult to decide.
- (3) The experiment is difficult to perform under a controlled atmosphere. When the specimens are removed from the furnace, they should be placed in a desiccator in order to avoid contamination with moisture. Relative errors can be reduced to a minimum level if all specimens are handled with care in the same manner, ie with the same cooling time, weighing order etc.

Method (b) has similar problems to method (a), as well as the extra difficulty of removing the scale from the specimen surface completely without affecting the underlying metal. This is not always easy, and some metal matrix can be lost during the mechanical or chemical removal process.

Method (c) allows a continuous assessment of the oxidation kinetics, and is most suitable for oxidation tests in a controlled atmosphere. However, the sensitivity and accuracy of this method are not particularly high, and it is difficult to test a relatively large number of specimens. Because the balance has to be connected with the furnace and a gas flow passes the hot tube, gravimetric errors can be introduced due to the changes of temperature, gas pressure and gas composition. Thus relatively large specimens have to be used in order to reduce the relative error. Typical sensitivity of the mass change in a thermobalance used for metallic oxidation is about 0.1mg, with a load carrying ability of about 25g (2).

This sensitivity is much poorer than that in the present work using method (a) with a microbalance (see section 3.1.3).

3.1.2 Sample preparation

Eight amorphous alloys and one industrial crystalline Si steel were investigated in the present work. The amorphous alloys had nominal compositions of Fe₇₈Si₉B₁₃, Fe₄₀Ni₄₀B₂₀, Fe₄₀Ni₄₀P₁₄B₆, Fe₃₂Ni₃₆Cr₁₄P₁₂B₆, Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Co₆₆Fe₄Ni₁Si₁₅B₁₄, Co₇₆Fe₂Mn₄B₁₂Si₆ and Ni₉₂Si₅B₃. Alloy samples were supplied by General Electrical, Allied Chemical and Vacuumshmelze Companies, and manufactured by Allied Chemical and Vacuumshmelze, as listed in Table 3-1.

All the amorphous alloys were supplied in the form of ribbon, with thickness from 20-55μm and width from 2-50mm, as shown in Table 3-1. The amorphous alloy ribbons arrived with nominal compositions supplied by the manufacturing companies, and then were all checked by X-ray microanalysis using a Cameca Camebax wavelength dispersive electron probe microanalyser. The results were in reasonable agreement with the nominal compositions and listed in table 3-2.

The as-supplied amorphous alloys were examined by using differential scanning calorimetry (DSC), X-ray diffractometry and transmission electron microscopy (TEM). X-ray diffraction of the as-supplied amorphous alloys always shows two broad peaks. TEM observation also shows a featureless bright field image and an electron diffraction pattern consisting of two broad haloes, clear evidence of an amorphous atomic structure. Very little crystallinity was observed in the as-supplied amorphous alloys.

Amorphous alloy specimens used for oxidation and crystallisation studies were either directly cut, or first polished with 1200 SiC then cut, into pieces with measured surface area of about 5cm². The specimens were

Table 3-1 The amorphous alloys tested in the present work

Alloy No.	Manufacturing name	Nominal composition at. %	Thickness um	Width mm
1	VITROAC 0040 **	Fe40Ni40B20	30	15.0
2	METGLAS 2826 *	Fe40Ni40P14B6	45	12.8
3	METGLAS 2605 S2	Fe78Si9B13	20	25.0
4	VITROVAC 6010	Co58Ni10Fe5Si11B16	40	10.0
5	METGLAS 2826A	Fe32Ni36Cr14P12B6	55	2.0
6	Silicon Steel ***	Fe94Si6	240	
7	METGLAS 2714A	Co66Ni1Fe4Si15B14	25	25.0
8	METGLAS 2705MN	Co76Fe2Mn4Si6B12	25	25.0
9	METGLAS MBF-30	Ni78Si8B14	35	25.0

* METGLAS is a trade name for Allied Chemical

** VITROVAC is a trade name for Vacuumschmelze GmbH

*** Fe94Si6 is a crystalline silicon steel received from British Steel

Table 3-2 Nominal and measured compositions of the tested alloys

Alloy	Nominal composition	Measured composition, at.%							
No	at%	Fe	Ni	Co	Cr	Mn	Si	P	B*
1	Fe40Ni40B20	39.5	40.4	-	-	-	-	-	20.1
2	Fe40Ni40P14B6	42.2	39.0	-	-	-	-	12.9	5.9
3	Fe78Si9B13	77.2	-	-	-	-	9.4	-	13.4
4	Co58Ni10Fe5Si11B16	5.1	9.8	60.5	-	-	12.2	-	12.4
5	Fe32Ni36Cr14P12B6	31.6	35.2	-	14.7	-	-	12.5	6.0
6	Fe94Si6	93.7	-	-	-	-	6.2	-	-
7	Co66Ni1Fe4Si15B14	4.2	1.4	66.7	-	-	14.0	-	13.7
8	Co76Fe2Mn4Si6B12	2.2	-	75.2	-	3.9	4.6	-	3.4
9	Ni78Si8B14	-	79.0	-	-	-	7.4	-	13.6

* B contents measured by subtraction from 100%

thoroughly cleaned in an ultrasonic cleaner, first with acetone and then with methanol, and finally dried in warm air. There was no evidence of any oxide with the naked eye on any of the samples. In general, polished and unpolished amorphous alloy samples did not show significant differences in oxidation behaviour, and are therefore not described separately below.

Crystallised samples were prepared by annealing amorphous alloy ribbons in sealed evacuated silica glass tubes under $<10^{-7}$ torr pressure. One end of each^{of} the silica glass tubes was first sealed, then the silica tubes were heated in a furnace at 500 C for at least 24h to remove any adsorbed moisture before evacuation. After evacuating and sealing the other end, the tubes were then annealed in the furnace to crystallise the amorphous alloys. The crystallisation temperatures and times for the various amorphous alloys were chosen on the basis of differential scanning calorimeter crystallisation experiments (see section 3.7.4), and are listed in Table 3-3. After crystallisation annealing in the evacuated silica tubes, most of the sample surfaces remained as bright as before annealing. Light mechanical polishing was applied to those which showed a slight tarnish after annealing. Polishing in this way was found to have no significant effect on the subsequent oxidation tests. Similar anneals were performed in sealed silica tubes containing 99.995% pure Ar at 200torr with or without a Ti getter, but the results were not significantly different to annealing in vacuum (see Chapter 4 and 8).

3.1.3 Oxidation tests

Oxidation experiments were carried out in ambient atmosphere in a Severn TF38 tube furnace with a 3-term Eurotherm 810 controller. The furnace had an ~ 8cm hot zone over which the temperature profile was constant to within ± 0.5 K, as shown in Fig.3-1. The comparison on oxidation tests on amorphous and pre-crystallised alloys were always

Table 3-3 The annealing temperatures and times for pre-crystallisation treatment

No	Alloy	Temperature (C)	Time (min)
1	Fe40Ni40B20	500	30
2	Fe40Ni40P14B6	500	30
3	Fe78Si9B13	600	20
4	Co58Ni10Fe5Si11B16	600	20
7	Co66Ni1Fe4Si15B14	600	20
8	Co76Fe2Mn4Si6B12	600	20

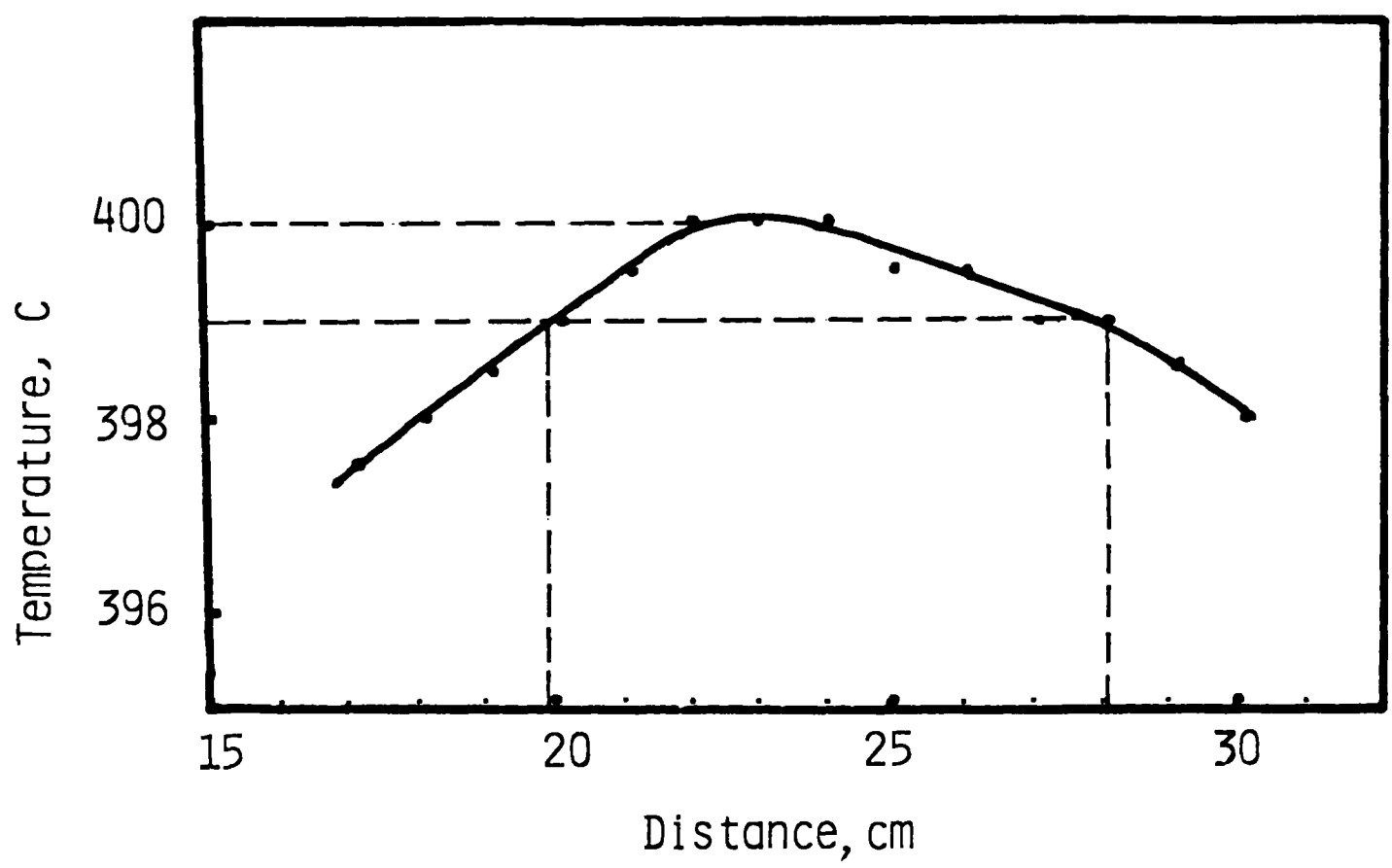


Fig.3-1: The furnace temperature profile.

carried out in the same run, with the two compared samples side by side in order to ensure the same oxidation conditions. Oxidation annealing temperatures ranged from 150 to 500 C and oxidation annealing times were up to 750h. The details of all oxidation temperatures and times for all the different amorphous and crystallised alloys are listed in Table 3-5.

A Perkin-Elmer AD-2 microbalance was used for the thermogravimetric mass gain measurements. The microbalance gave readings accurate to 0.1ug for < 2mg loads, 1ug for 2 - 20mg loads, and 10ug for > 20mg loads. In order to have the best sensitivity and accuracy, which were about 0.5ug and 1.0ug respectively, special care was taken during the weighing operations: (a) The zero point was adjusted before using the balance, then left for some time to stabilise. If the zero point drifted during subsequent weighing, the actual zero point was subtracted or added to the measured weight. In this way, the error caused by zero point drift was reduced to +/- 0.5ug.

(b) An inert sample with similar mass to the measured sample was used in the reference balance pan to make the weight measurement less than 2mg. This technique gave the best sensitivity and accuracy with relatively large specimens (~ 5cm² area and 100mg mass).

3.1.4 Errors in the oxidation thermogravimetric experiments

The mass changes measured by the microbalance were used to calculate the oxidation kinetics for amorphous and crystallised alloys. Errors may have come from:

- (a) Microbalance zero drifting; up to +/- 0.5ug.
- (b) Absorption of moisture during the experiments; usually < 2ug.
- (c) Furnace temperature and atmosphere variations; since comparison specimens were oxidised under identical conditions for each run, these variation of temperature and atmosphere should have had very little effect.

(d) Oxide cracking and spalling; very little oxide cracking or spalling was found during most experiments as the oxidation temperatures were not high.

(e) The main variations in the present thermogravimetric experiments came from the amorphous and crystallised alloys themselves. The measured results from different specimens of the same alloy in the same run showed up to $\pm 7\%$ variation in mass gain. For instance, amorphous Fe₄₀Ni₄₀Pl₄B₆ alloy had an average mass gain of $70\text{ug}/\text{cm}^2$ after 500h oxidation at 300 C, with the measured results from 6 specimens ranging from $65\text{--}75\text{ug}/\text{cm}^2$. This variation ($\pm 5\text{ug}/\text{cm}^2$) was equivalent to $\pm 25\text{ug}$ in the measured mass gain for a specimen with 5cm^2 surface area, an order of magnitude greater than all the other errors together. In order to reduce the variations caused by different specimens, at least three specimens were tested for each alloy under each set of oxidation conditions and the average was taken as the result.

3.2 Optical metallography (3-6)

Optical microscopy has long been used to examine both top surface and cross section oxide morphology (7,8). However, since the development of scanning electron microscopes (SEM), the top surface morphology of oxide scales has widely been observed by SEM because of the much larger depth of focus compared with optical microscopes (see section 3.3). Optical microscopes have still been applied extensively to the examination of oxide cross sections, and occasionally to the examination of oxide top surface morphology. In the present work, optical microscopy was used to examine oxide cross sections and colour micrographs were taken for the oxide top surface features.

The top surfaces of oxide scales on the freshly oxidised amorphous and crystallised alloys were examined directly in an optical microscope. When

the cross section samples were prepared, the oxidised alloy samples were first Ni plated to prevent the oxide scale from disintegrating during sample mounting and polishing. Ni plating was carried out in an electrolytic cell with a circular sheet of pure Ni as the anode and the oxidised specimen as the cathode, as shown in Fig.3-2. The electrolyte consisted of 90g NiSO_4 , 12.5g NH_4Cl and 15g H_3BO_3 dissolved in 500ml distilled water (9). The cell was operated at 35-40 C with a current density of $\sim 500\text{A/m}^2$. A coherent Ni layer approximate 5 μm thick was deposited after 1000s, which was found to give good protection to the oxide scale during subsequent mounting and polishing.

Ni plated samples were mounted in epoxy resin. The samples were carefully positioned in the mould with an angle of 3-5 degrees between the specimen surface and the bottom of the mould, as shown in Fig.3-3, and then the liquid resin was poured in. The sample moulds were put in an ultrasonic cleaner for 10 min to remove air bubbles, and then were left for hardening.

Sample polishing was carried out in the same way as normal metallographic polishing, by using successive grades of abrasive paper and diamond paste, but the time spent on each grade paper or diamond was considerably longer than metallographic polishing. The reason for this was that the oxide scales were usually scratched to a greater depth than the metal surface, so that longer polishing times were needed to obtain a smooth oxide scale surface. Polishing was carried out parallel to the bottom surface of the mould, so that the specimen surface/polishing surface angles was again 3-5 degrees. With this technique, the thin cross section of oxide layer had a visual thickness in the microscope which was 10-20 times greater than the true thickness (see Fig.3-3).

Optical microscope examination was carried out on an Olympus BHM

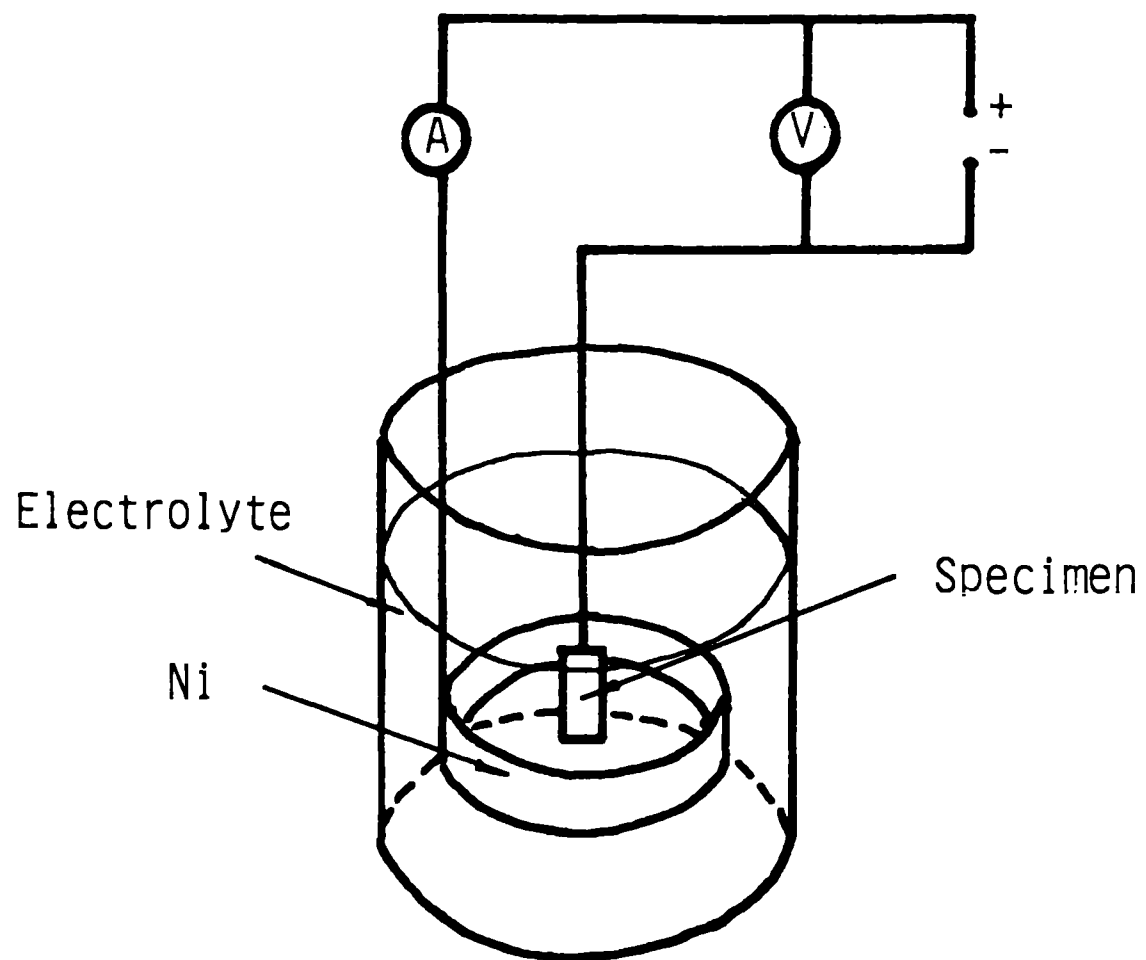


Fig.3-2: Electrolytic cell for Ni plating.

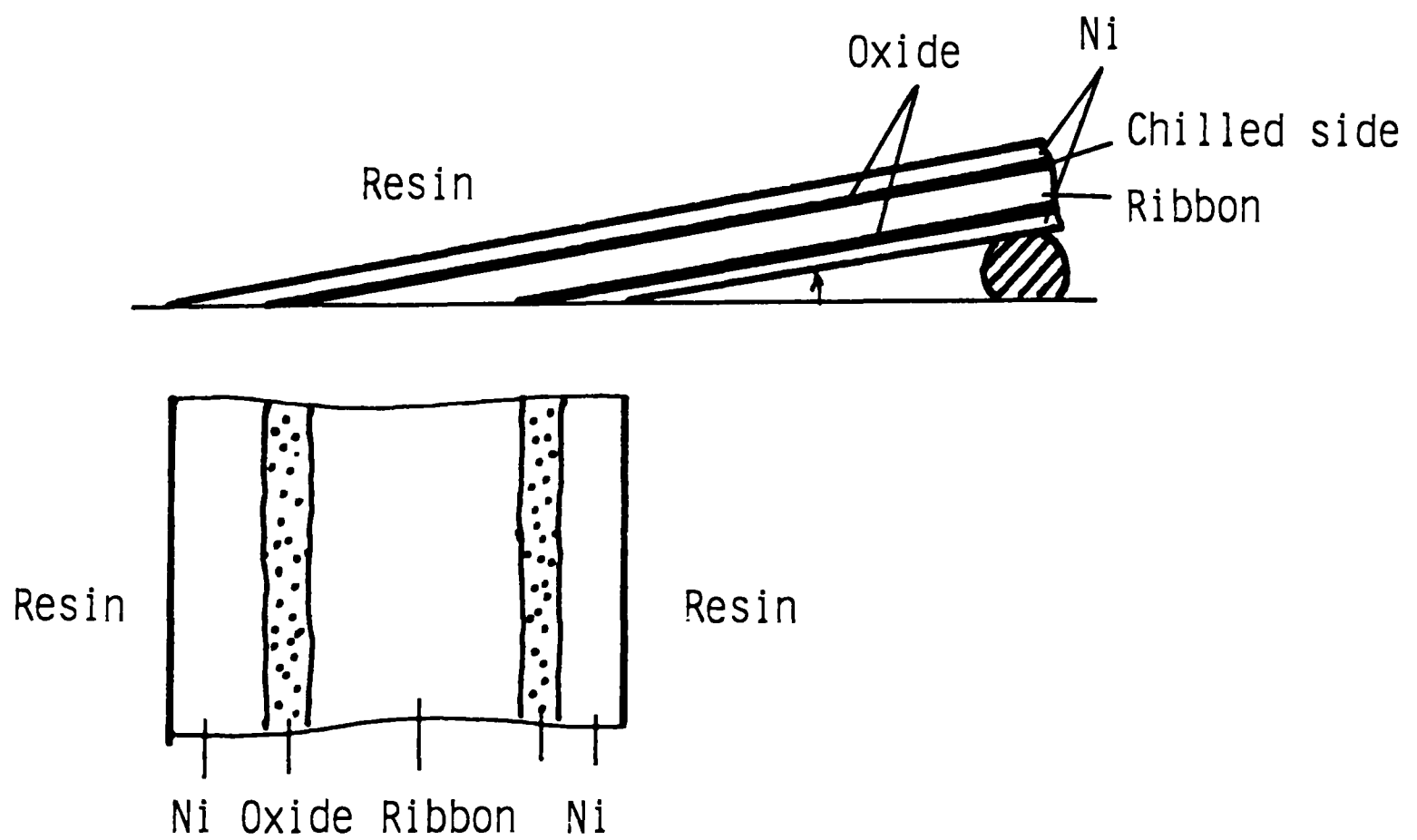


Fig.3-3: Taper cross section sample preparation.

optical microscope with an auto exposure Olympus OM20 camera. Quantitative metallographic measurements were used to determine oxide grain sizes in the oxide layer, and crystal grain sizes in the crystallised alloys. For equiaxed, uniformly distributed oxide or crystal grains, point-counting measurements from the optical or electron micrographs were used. In the oxide grain size measurements, for instance, 3-6 representative optical micrographs or electron micrographs were used to count the total number of grains, then the total area was divided by the number of grains to obtain the average grain size.

3.3 Scanning electron microscopy (SEM) (10-12)

Scanning electron microscopy (SEM) has been used extensively in oxidation research, mainly for observation of the oxide scale morphology. Compared to optical microscopy, SEM improves the resolution by more than one order of magnitude to approximately 10nm in routine instruments, with ultimate values below 3nm. Useful magnifications thus extend to 15 - 50K, closing the gap between the optical and transmission electron microscopes. The depth of focus in the SEM ranges from 1um at 10K to 2mm at 15 times, and is two orders of magnitude larger than in optical microscopes. This is because SEM has a very small beam aperture. The great depth of focus is particularly useful for observation of rough oxide surfaces (10-12).

The surface oxide scales of all the oxidised samples and some cross section samples were examined with JEOL JSM35 and Hitachi S530 scanning electron microscopes, and a JEOL 100C transmission electron microscope with a SEM attachment, mainly using secondary electron imaging and in some cases using backscattered electron imaging.

For SEM oxide top surface examination, the oxidised metal ribbons were cut into small pieces and mounted directly into the SEM sample holder with

silver-loaded glue. Both sides of the ribbon, the chilled (wheel) and unchilled (free) surfaces, were observed for comparison. The results showed that although the chilled and unchilled surfaces of the ribbons usually had a different appearance before oxidation, the morphology of the oxide on both surfaces was usually quite similar. For comparison of oxide scales on amorphous and crystallised alloys, equivalent surfaces (usually the chilled surfaces) were observed. Microanalysis on the cross section samples was carried out in SEM mode with a Cameca Camebax electron probe microanalyser.

3.4 Transmission electron microscopy (TEM) (13-19)

Transmission electron microscopes (TEM) became commercially available in the 1950s, and are now widely used in applied and fundamental research in materials science and physical metallurgy. Modern TEM instruments have very high resolution, for instance the JEOL 4000EX THG-Z (with an acceleration voltages of 400kV) at Oxford possess a point-to-point resolution of 0.165nm. The high magnification in TEM (1K-1000K) allows detailed microstructural observation.

3.4.1 Conventional transmission electron microscopy (13-15)

Conventional TEM can be operated in different modes, including bright-field imaging (BF), dark-field imaging (DF), lattice imaging, selected area electron diffraction (SAED), convergent-beam electron diffraction (CBED) and scanning transmission electron microscopy (STEM). A bright-field image is formed when only the direct beam is used to form the image, and a dark-field image is formed when only one diffracted beam is used, with the objective aperture preventing the passage of all other beams to the TEM screen or camera. The objective lens also produces a diffraction pattern of the specimen in its backfocal plane, and the

selected area aperture allows the electron beam to go only through the area of interest to produce a selected area electron diffraction pattern (SAED).

With convergent-beam electron diffraction (CBED), the size of the area producing the diffraction pattern is reduced to 20-40nm, by focusing the electron beam onto the specimen. Because the electron beam is no longer parallel and some convergence is introduced, the diffraction spots become expanded into discs. Information on crystal symmetry, orientation and lattice parameters etc can be obtained from SAED diffraction patterns or CBED diffraction discs (16). In scanning transmission electron microscopy (STEM), the electron beam is also focused into a fine probe on the specimen, and then scanned over the specimen as in a scanning electron microscope, and the transmitted intensity is recorded to give an image. STEM mode is extensively used for microanalysis of thin foil specimens by recording the intensity of characteristic X-rays generated.

3.4.2 Analytical transmission electron microscopy (ATEM) and electron probe microanalysis (EPMA) (17-19)

Analytical transmission electron microscopy (ATEM) is a unique technique for materials characterisation because it combines the micromorphology, microstructure and microchemical analysis together with very high resolution and magnification. The instrument usually includes a modern TEM with SEM and STEM modes, and one or more of the microchemical composition analysis attachments such as X-ray energy dispersive spectrometer (EDS), electron energy loss spectrometer (EELS) etc. In ATEM, microanalysis can be operated either in TEM, SEM or STEM mode. Because it uses thin foil specimens to do microanalysis, electron beam spreading effects can be eliminated and the analysis area resolution can be improved to about the beam size, ie the diameter of the measurement region is reduced from about $\sim 1\mu\text{m}$ in EPMA for bulk specimens to $\sim 20\text{nm}$ in ATEM (JEOL 2000FX)

for thin foils. Because ATEM allows microstructural imaging, crystal structure determination, and microchemical analysis to be done in the same instrument with same specimen under very high resolution and magnification, it is particularly useful for the present oxidation study where the oxide scales formed on the amorphous and crystallised alloys consisted of very fine oxide grains with complicated structure. Information on oxide morphology, crystal structure and chemical compositions have to be collected together for identification of these complicated oxide scales. Most of the transmission electron microscopes used in the present work, including JEOL 100C, JEOL 2000FX and Philips CM12 are analytical electron microscopes.

Electron probe microanalysis (EPMA) is an analytical instrument for qualitative and quantitative elemental analysis. The Cameca Camebax microanalyser which was used in the present work has two X-ray wavelength dispersive spectrometers and an energy dispersive spectrometer, together with digital beam control and image processing systems. The microanalyser detects elements with atom number ≥ 5 (B), and quantitative analysis is successful for those with atomic number ≥ 11 (Na). However, accurate quantitative analysis is limited to well polished specimens. It is usually easy to prepare a well polished specimen in a cross section sample, but not for the rough oxide surfaces, from which only semi-quantitative results were achieved.

In traditional oxidation research, scale morphology is studied by using optical and/or SEM microscopes. The structure of oxide scales is usually examined by X-ray diffractometry or chemical analysis. TEM is more or less a new method for oxidation study, although it has sometimes been used for studies of the early stages of oxidation (20-22). In the present work, TEM was used extensively for examination of oxide films and oxidised metal

foils. Very detailed information about the oxide microstructures and microchemical compositions was obtained from ATEM, either by using stripped oxide films or oxidised metal foils.

3.4.3 ATEM examination of oxide films

Oxide films were stripped from the oxidised alloy samples for subsequent examination by ATEM. Oxidised specimens were cut into small pieces about 1mm in size, the oxide scale on one side was ground away, and the oxide on the other side (usually the chilled side) was left for subsequent examination. A saturated iodine-methanol solution was then used to dissolve the underlying metal (23). When the oxide films were free from the metal, they were lifted, rinsed twice in clean methanol, and put carefully on Cu grids. Sometimes two Cu grids were used to keep the film stretched and prevent film buckling. The thickness of the stripped oxide films ranged from 20 to 300nm, in reasonable agreement with the thickness expected from the thermogravimetric measurements, and in the observable thickness range by ATEM at the acceleration voltage of 100 - 200kV. ATEM examination of stripped oxide films allowed: (a) direct examination of the oxide morphology over a large area, (b) detailed observation at very high magnifications, and (c) microanalysis and microdiffraction of the oxide films in the same area without any influence from the metallic matrix.

3.4.4 ATEM observation of oxidised thin metal foils

Specimens of amorphous and crystallised alloys with or without mechanical pre-polishing were cut into small discs of ~ 3mm diameter, then put in an Ion Tech 1020 ion beam thinner. Two Ar ion beams each with a current of 0.1mA and voltage of 5keV were used to thin the discs, with one beam incident on each side of the specimen. The ion beam incidence angles were about 15 degrees for the first 2/3 of the thinning time (~ 10h), then 10 degrees for the rest of the thinning time (~ 5h) to make the hole edge

flatter. The resulting thin foils were thoroughly cleaned and dried, and put into a furnace for a suitable oxidation anneal before examination in the ATEM. ATEM observation of oxidised metal foils allowed examination of the early stages of oxide nucleation and growth with the oxide layer still attached to the metal. This was particularly suitable for observation of the oxide grains on amorphous alloys, because the amorphous matrix contributed very little contrast to the TEM images. However, the geometry of the thin metal foil may have influenced the matter transport mechanism during subsequent oxidation, and therefore, the oxide growth mechanism. A discussion of this effect is given in Chapter 4.

3.5 X-ray diffractometry (24-26)

X-ray diffraction is an important technique in characterisation of crystalline materials. It has widely been used to identify the phases, determine crystal symmetry and orientation, and provide other structural information such as grain size, texture and crystal perfection. For phase identification by X-ray diffractometry, powder or polycrystalline samples are usually used, and standard structural data such as the JCPDS powder diffraction file of inorganic phases are required for comparison. The advantages of this method are: (a) it can be applied for identification of phases contained in unknown samples, and (b) it allows qualitative as well as quantitative phase analysis. Compared with electron diffraction, the disadvantages of X-ray diffractometry are: (a) relatively large samples are needed, so that spatial resolution is rather poor, about 1mm^2 in area; (b) the analysis time is long, for instance several hours are typically needed to achieve good angular resolution, especially for identification of trace phases or quantitative analysis.

In the present work, X-ray diffractometry was performed in a Philips

PW1130 X-ray diffractometer, using Cu K α X-rays at 40kV and 20mA, and a scanning speed of 0.25-0.5 degree/min, mainly for identification of crystalline phases in the fully or partially crystallised alloys. Crystalline silicon was used as a standard for calibration of the diffraction angles.

3.6 Differential scanning calorimetry (DSC) and thermal analysis (27-30)

3.6.1 Introduction

A DuPont 910 Differential Scanning Calorimeter and DuPont 1090 Thermal Analysis System were used in the present work to monitor the rate of crystallisation and to determine oxidation conditions under which the alloy structure changed from amorphous to crystalline. DSC is a technique in which the difference in heat input into a tested specimen and a reference material is measured as a function of temperature while the specimen and reference material are subjected to a controlled temperature programme. A schematic diagram of the DuPont DSC cell is shown in Fig.3-4. The sample pan and reference pan are placed on raised platforms on a constantan disc. Heat is transferred through the disc and up into the specimen and reference via the pans. A feedback control system measures the specimen and reference temperatures, and ensures that they remain the same, and the differential heat flow to the specimen and reference is monitored by the chromel-constantan area thermocouples. The principles and main techniques of DSC have been reviewed by Greer (27) and Baxter (28).

The Dupont thermal analyzer (TA) is a microcomputer-based thermal analysis system that is able to perform a programmed experiment, collect, record and analyse data, and display or transmit results automatically. The whole system (910 DSC and 1090 TA) had the following specifications (29):

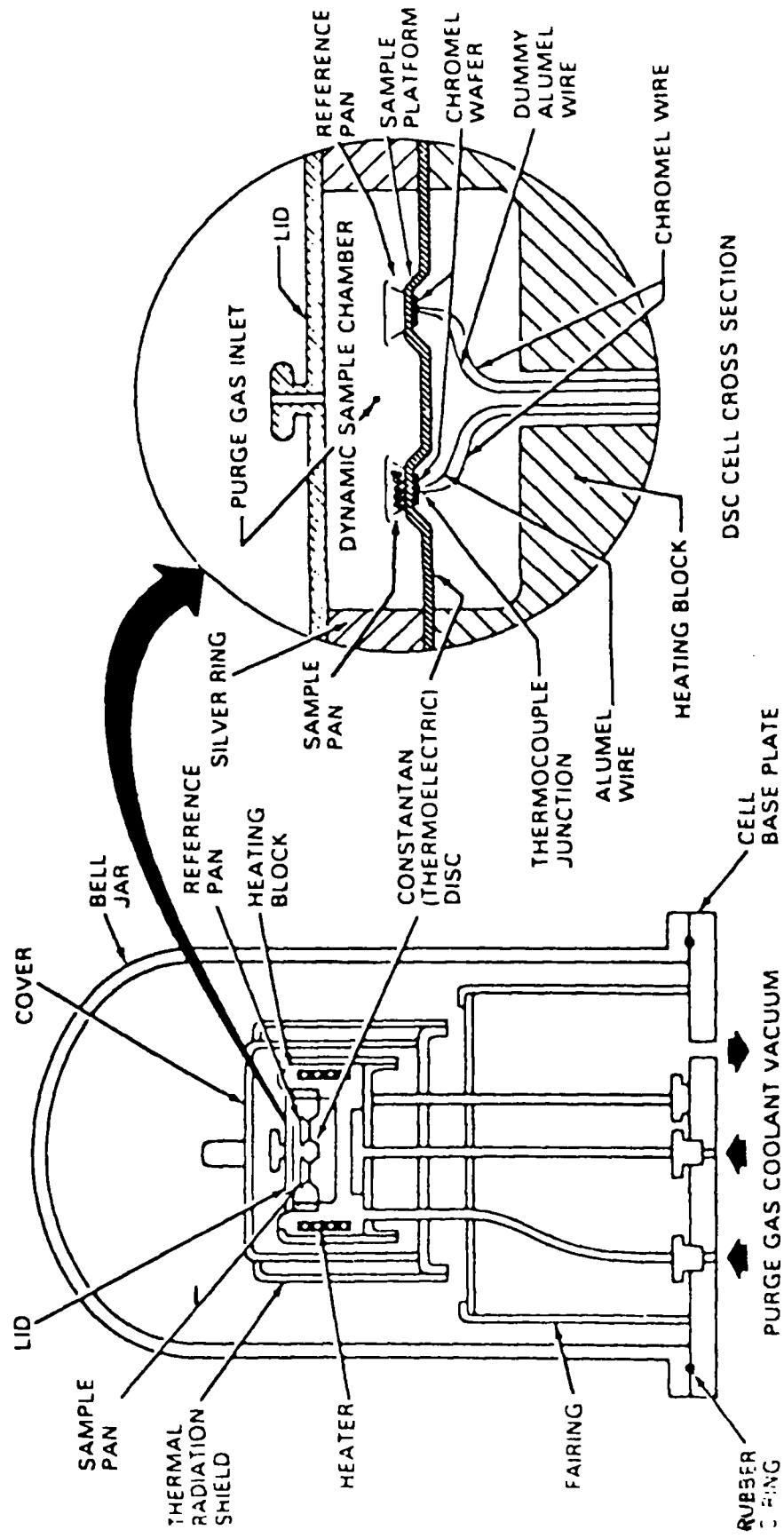


Fig.3-4: Dupont DSC cell.

Temperature range: -180 to 725 C (up to 1600 C when use a high temperature Differential Thermal Analyzer (DTA) cell)

Heating rate: 0.1 - 100K/min

Calorimetric sensitivity: 0.003mcal/sec

Calorimetric accuracy; +/- 0.2%

Baseline stability: 0.005mcal/sec for short term at 200 C

0.1mcal/sec for long term to 600 C

Derivative sensitivity: 0.05mcal/sec/min

Derivative accuracy: +/- 0.2%

3.6.2 Isothermal DSC experiments

In principle, DSC curves give a plot of the rate of enthalpy change with time as a function of temperature or time. In isothermal mode, the deflection from the baseline of an inert sample is directly proportional to the mass rate of reaction dx/dt at that instant, as shown in Fig.3-5.

$$dx/dt = K(y - y_o) \quad (3-1)$$

where y is the heat flow, y_o is the baseline level and K is a constant.

Integrating equation (3-1) from the reaction start time t_o to finish time t :

$$\int_{t_o}^t dx = K \int_{t_o}^t (y - y_o) dt$$

$$M = KQ \quad (3-2)$$

where M is the mass of the material formed during the reaction, and Q is the whole reaction enthalpy, which can be obtained directly from the DSC result. Thus $K = M/Q$ and equation (3-1) can be rewritten as:

$$dx/dt = M(y - y_o)/Q \quad (3-3)$$

The Dupont 1090 system has software available for direct integration of exothermic and endothermic heat peaks, and determination of the transformation start time, peak time and finish time etc from the recorded results. An integrated DSC curve is also included in Fig.3-5, which

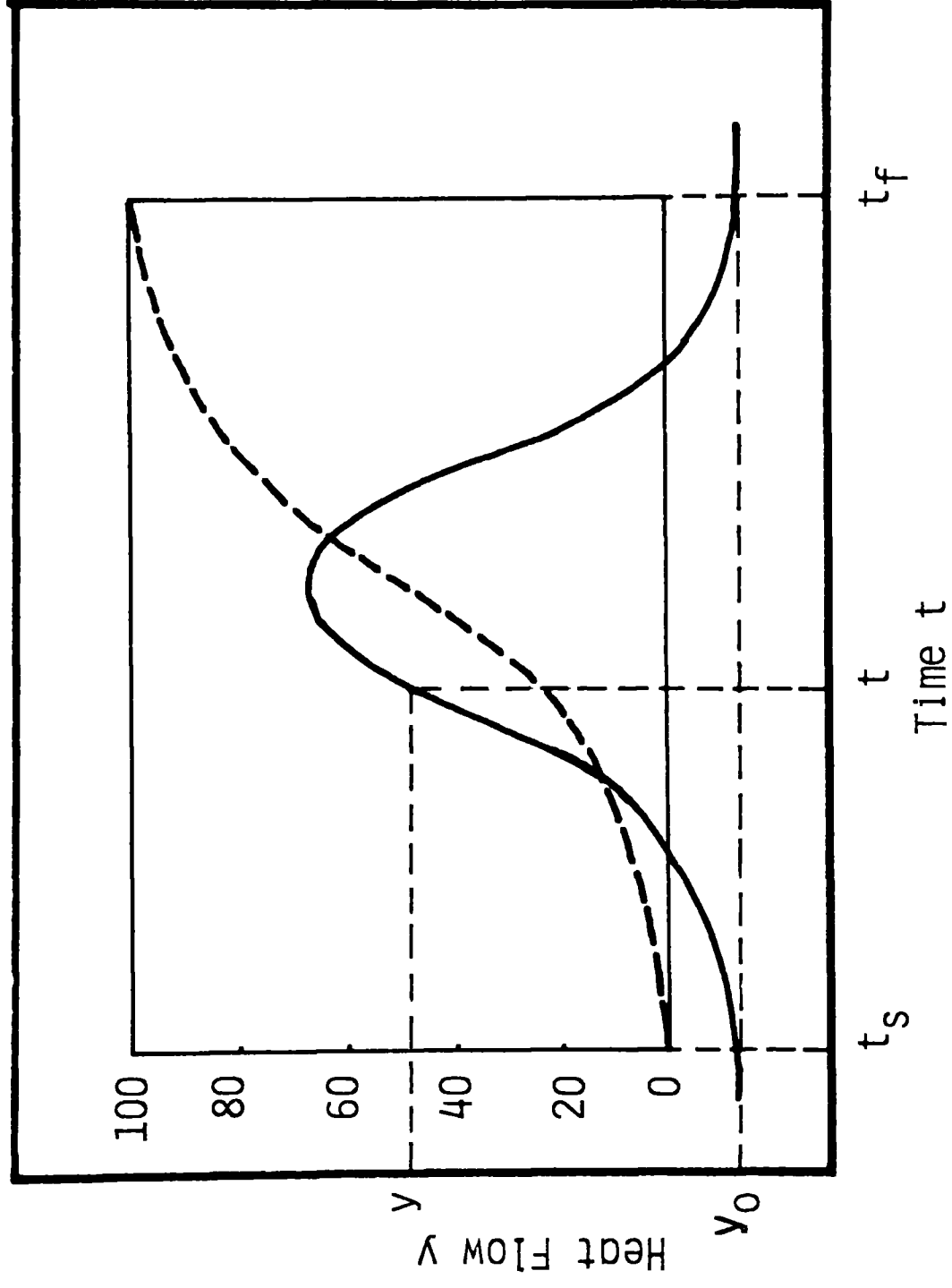


Fig.3-5: Typical isothermal heating DSC curve and its integrated curve.

represents the variation of the mass of the reacted material versus reaction time ($x-t$).

Although isothermal DSC results are direct and convenient for interpretation, there are some practical limitations in using this technique. Firstly, the baseline is often not easy to determine with the required accuracy. Secondly, the temperature range in which isothermal experiments can be conducted is limited: if the temperature is too high, the reaction starts before the isothermal hold is reached, and overlaps the instrumental transients; if the temperature is too low, the rate of reaction is too small to be determined accurately.

Two methods were used in isothermal DSC experiments to reduce baseline problems in the present work. (a) Dry Al_2O_3 powder with a similar heat capacity to the specimen was used as reference material. (b) For crystallisation experiments on amorphous alloys, the isothermal heating programme was run twice. The first isothermal run was with the amorphous alloy specimen, and the DSC data were recorded in a file. The specimen was then heated to about 100 K above the crystallisation temperature for 10min, to make sure that the specimen was fully crystallised, then it was cooled down and subject to a second isothermal run to obtain a DSC trace as baseline for the first run. The second run baseline was subtracted from the data recorded in the first run, using the 1090 computer. This 2-run procedure substantially reduced baseline variations, as shown in Fig.3-6.

3.6.3 Continuous heating DSC experiments (27,30)

Another important way to perform DSC experiments is to use a continuous heating programme with the temperature increased linearly with time. For continuous heating DSC experiments, the DSC curves are plotted with temperature on the abscissa. This method can avoid the disadvantages of isothermal DSC mentioned in section 3.6.2, and the operation time is usually

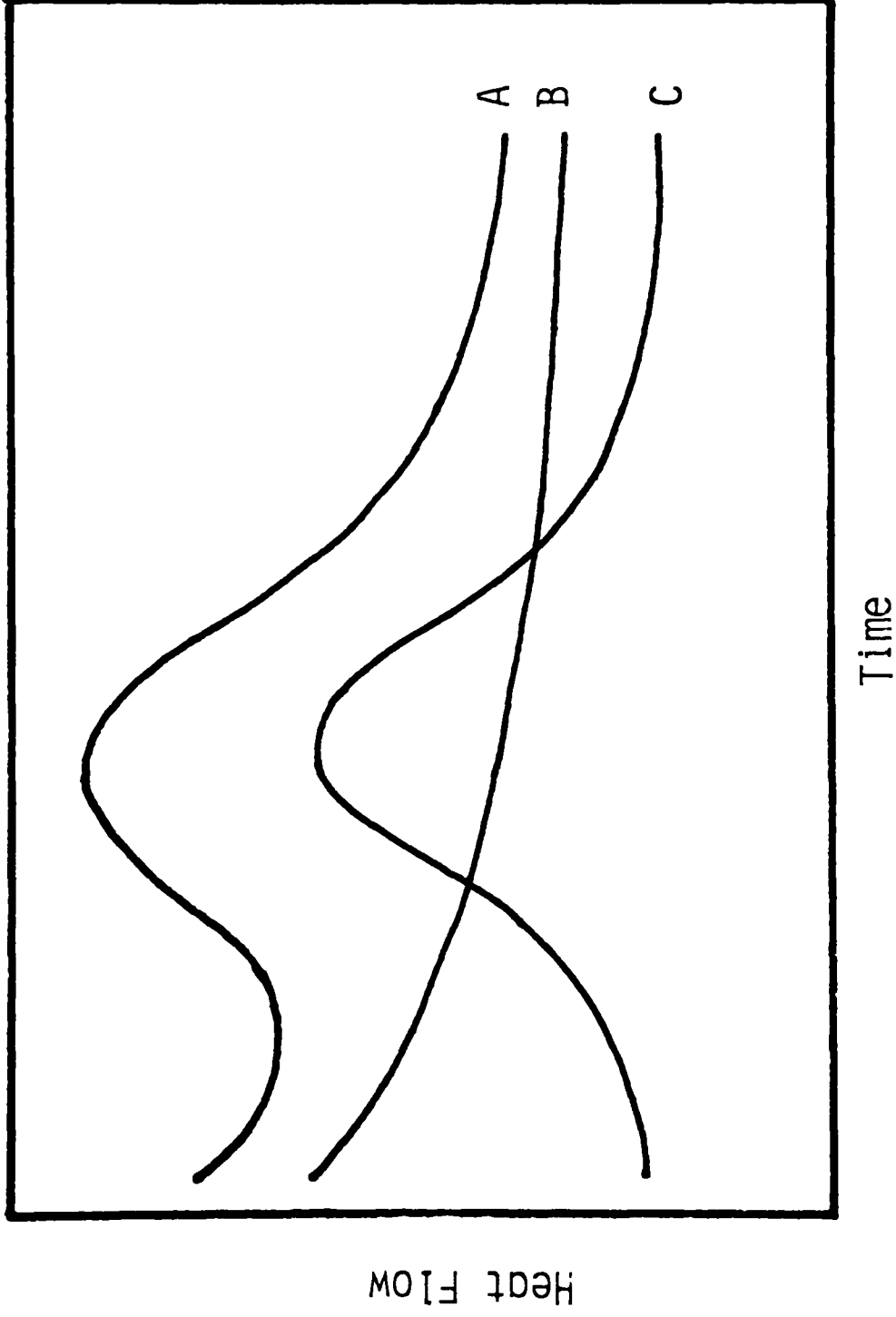


Fig.3-6: Baseline effect in isothermal heating DSC curve:
A - first run DSC curve showing the crystallisation exothermic heat peak with baseline effect,
B - second run DSC curve with the same fully crystallised specimen, showing the effect of baseline, and
C - obtained from A - B, showing a modified isothermal crystallisation DSC curve.

much shorter than with isothermal DSC. However, non-isothermal DSC curves cannot be interpreted as simply as isothermal DSC, and some corrections have to be made to obtain accurate reaction rate data (27).

In the present work, continuous heating DSC experiments were mainly used for assessing the crystallisation temperatures of the amorphous alloys and checking the oxidation conditions under which the alloy structure changed from amorphous to crystalline. A relatively low heating speed of 10K/min was used in all experiments to reduce any errors.

3.6.4 Assessment of crystallisation temperatures of the amorphous alloys

Continuous heating DSC experiments were performed at a heating rate of 10K/min with a dynamic Ar flow to assess the crystallisation temperatures for all of the eight amorphous alloys investigated in the present work, and the results are shown in Fig.3-7. The crystallisation exothermic heat peaks for these amorphous alloys were found to extend over quite a large temperature range from 407 to 595 C, indicating that their amorphous structures have different stabilities. The crystallisation start, peak(s) and finish temperatures, and the heat of crystallisation for each of the amorphous alloys are listed in Table 3-4. Pre-crystallisation and oxidation temperatures were decided on the basis of these results.

3.7 Summary of the experiments performed in the present work

As a summary, the main experiments conducted in the present work are listed in Table 3-5.

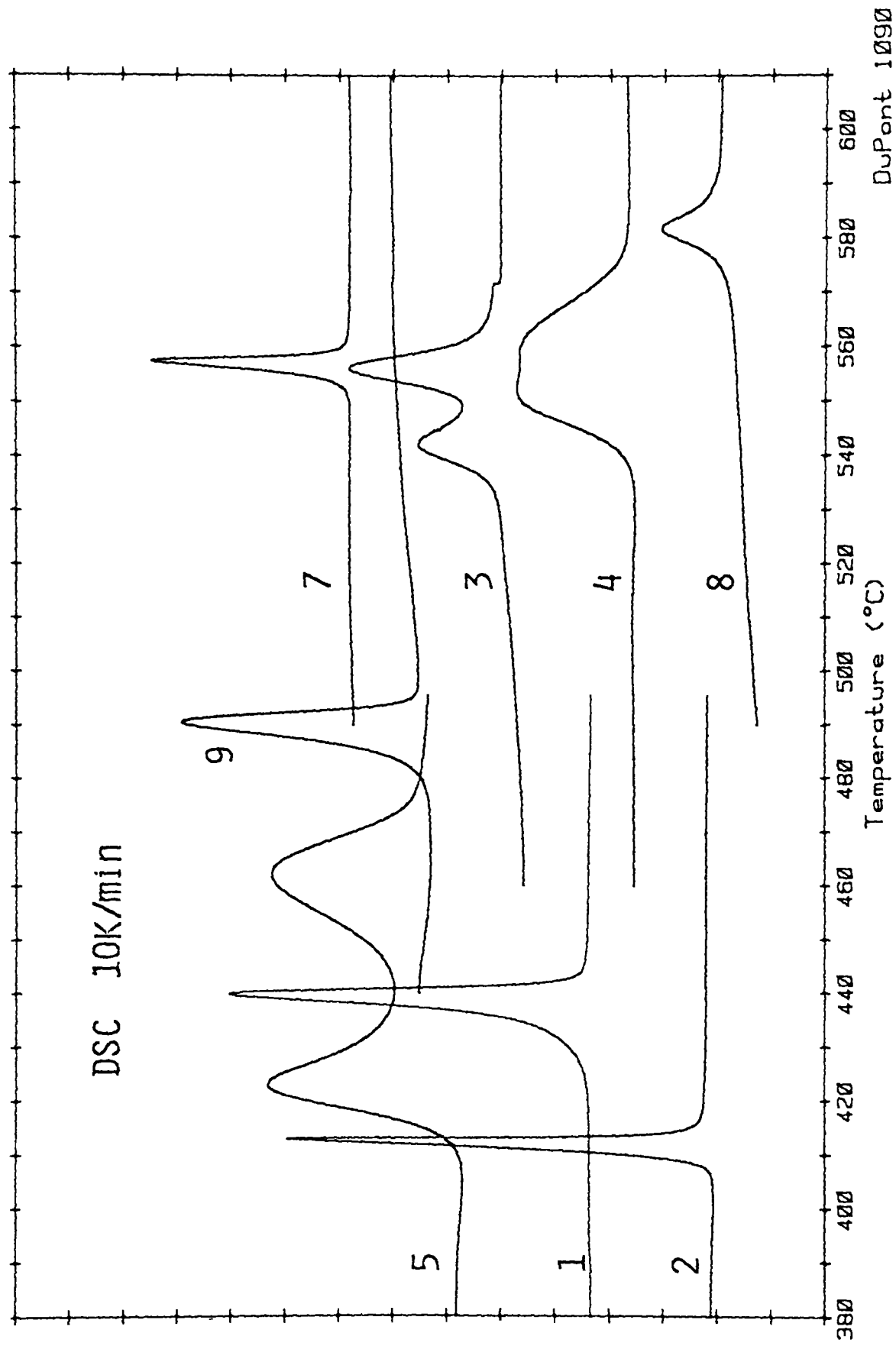


Fig.3-7: Continuous heating crystallisation DSC traces of the all amorphous alloys tested in the present work: 1 - Fe40Ni40B20, 2 - Fe40Ni40P14B6, 3 - Fe78Si9B13, 4 - Co58Ni10Fe5Si11B16, 5 - Fe32Ni36Cr14P12B6, 7 - Co66Ni1Fe4Si15B14, 8 - Co76Fe2Mn4Si6B12 and 9 - Ni78Si8B14.

Table 3-4 Crystallisation start, peak(s) and finish temperatures (Ts, Tp and Tf) and crystallisation heat (H) for all tested amorphous alloys

No	Alloy	Crystallisation temperature				Heat
		Ts	Tp1	Tp2	Tf	H
		(C)				(J/g)
1	Fe40Ni40B20	422	439		455	85
2	Fe40Ni40P14B6	407	412		418	82
3	Fe78Si9B13	530	542	557	570	130
4	Co58Ni10Fe5Si11B16	535	552	560	581	75
5	Fe32Ni36Cr14P12B6	407	422	462	480	82
7	Co66Ni1Fe4Si15B14	551	558		561	73
8	Co76Fe2Mn4Si6B12	571	582		595	42
9	Ni78Si8B14	477	491		498	52

Table 3-5 Experiments performed in the present work

Nominal alloy composition (at.%)	Alloy structure	Thermogravimetric measurements, in air, up to 750 h				Oxide morphology & structure study				
						Optical micros- copy top cross mor- sec- pho- tion logy	SEM		TEM	
		150 200 250 C	300 350 400 C	450 500 500 C	> 500 C		top cross mor- sec- pho- tion logy	top cross mor- sec- pho- tion logy	remo- ved oxide scales	oxi- dised thin foils
Fe40Ni40B20	amor.	y*	y	y		y	y	y	y	y
	cryst.	y	y					y	y	y
Fe40Ni40P14B6	amor.	y	y	y		y	y	y	y	y
	cryst.	y	y	y		y	y	y	y	y
Fe78Si9B13	amor.	y	y	y		y	y	y	y	y
	cryst.	y	y	y		y	y	y	y	y
Co58Ni10Fe5 Si11B16	amor.	y	y	y		y	y	y	y	y
	cryst.	y	y	y		y	y	y	y	y
Co66Fe4Ni1 Si15B14	amor.		y					y	y	
	cryst.		y					y	y	
Co76Fe2Mn4 Si6B12	amor.		y					y	y	
	cryst.		y					y	y	
Fe32Ni36Cr14 P12B6	amor.	y	y					y	y	
	cryst.			y	y			y		y
Ni92Si5B3	cryst.			y	y					
Fe88Si12 Si steel	cryst.		y	y		y		y		

continued on next page.

* 'y' means the experiment has been performed.

Table 3-5 Experiments performed in the present work (cont.)

Nominal alloy composition (at.%)	Alloy structure	Microanalysis with		Crystallisation behaviour		Effect of oxidation	Effect of oxid. &
		EDS &/or WDS oxide scales	alloy	DSC cryst. kinetics	OP+TEM cryst. structure	on crys- tallisation behaviour	cryst. on magnetic proper- ties
Fe40Ni40B20	amor.	y	y	y	y	y	y
	cryst.	y		-	y	-	-
Fe40Ni40P14B6	amor.	y	y	y	y	y	
	cryst.	y	y	-	y	-	
Fe78Si9B13	amor.	y	y	y	y	y	y
	cryst.	y		-	y	-	-
Co58Ni10Fe5 Si11B16	amor.	y	y	y	y	y	y
	cryst.	y		-	y	-	-
Co66Fe4Ni1 Si15B14	amor.	y	y	y			
	cryst.	y		-			
Co76Fe2Mn4 Si6B12	amor.	y	y	y			
	cryst.	y		-			
Fe32Ni36Cr14 P12B6	amor.	y	y	y			
	cryst.	y		-			
Ni92Si5B3	cryst.		y	y			
Fe88Si12 Si steel	cryst.		y	-			

* 'y' means the experiment has been performed.

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4.1 Introduction

Fe₄₀Ni₄₀P₁₄B₆ (METGLAS 2826) was one of the first soft ferromagnetic amorphous alloys which was developed, and its structure and properties have been studied in considerable detail (1-43). As-quenched amorphous Fe₄₀Ni₄₀P₁₄B₆ exhibits a low coercivity of 100 mOe(8A/m), which can be further lowered to less than 10 mOe(0.8A/m) by suitable annealing treatments (1). Previous research into the structure and properties of amorphous Fe₄₀Ni₄₀P₁₄B₆, include studies of the amorphous structure (2), structural relaxation (3-6), viscosity flow (7-10) and atomic diffusion (11-14), crystallisation (15-21), mechanical behaviour (22-25), corrosion and catalytic properties (26-28), magnetic properties (1,29-34), thermal properties (35), electrical resistivity (36), manufacturing processes (37,38), and various soft ferromagnetic applications (39,40).

However, there has been very little study of the oxidation behaviour of amorphous Fe₄₀Ni₄₀P₁₄B₆, and the results which have been obtained are confusing, as reviewed in section 2.6.1 (41-43). This chapter describes a systematic investigation of the oxidation behaviour of amorphous and crystallised Fe₄₀Ni₄₀P₁₄B₆, which was carried out in the present work. The main research topics are as follows:

(a) the oxidation kinetics and oxide growth mechanisms on amorphous and crystalline Fe₄₀Ni₄₀P₁₄B₆;

(b) the oxide morphology, structure and composition on amorphous and crystalline Fe₄₀Ni₄₀P₁₄B₆; and

(c) the effect of alloy structure on the oxidation behaviour of amorphous Fe₄₀Ni₄₀P₁₄B₆; in other words, whether amorphous and crystalline

Fe₄₀Ni₄₀Pl₄B₆ have different oxidation behaviour.

4.2 Experimental results

4.2.1 Oxidation kinetics

Fig.4-1(a) shows the results of thermogravimetric measurements of the oxidation mass gain of amorphous Fe₄₀Ni₄₀Pl₄B₆ as a function of oxidation annealing time over an oxidation temperature range of 200 to 500 C.

Fig.4-1(b) and (c) shows the same results plotted as mass gain versus square root of oxidation time and as ln(mass gain) versus ln(time) respectively. Best fit linear slopes and intercepts from the data in Fig.4-1(b) are given with correlation coefficients in Table 4-1. As shown in Fig.4-1(b), the mass gain was proportional to the square root of oxidation time at the lower oxidation temperatures of 200, 250 and 300 C, indicating that the oxidation reaction obeyed a parabolic rate law:

$$Y^2 = K t$$

$$Y = K' t^{1/2} \quad (4-1)$$

where Y is mass gain, t is oxidation time, and K and K' are the parabolic rate constants, as described in section 2.3.3. As shown in Table 4-1, the parabolic rate constant K' increased from 1.8×10^{-3} to $2.9 \times 10^{-2} \text{ g/m}^2 \text{ h}^{1/2}$ with increasing oxidation temperature from 200 to 300 C. At the higher oxidation temperatures of 450 and 500 C, the oxidation reaction also obeyed the parabolic rate law in eqn.(4-1), with higher values of 6.7×10^{-2} and $2.0 \times 10^{-1} \text{ g/m}^2 \text{ h}^{1/2}$ for the parabolic rate constants as shown in Table 4-1.

However, the amorphous alloy oxidation behaviour was considerably more complicated at the intermediate oxidation temperatures of 350 and 400 C, where the oxidation rate law clearly changed with the oxidation time. At 350 C, the oxidation reaction obeyed the parabolic rate law of eqn. (4-1) for the first 20h of oxidation with a high parabolic rate constant of

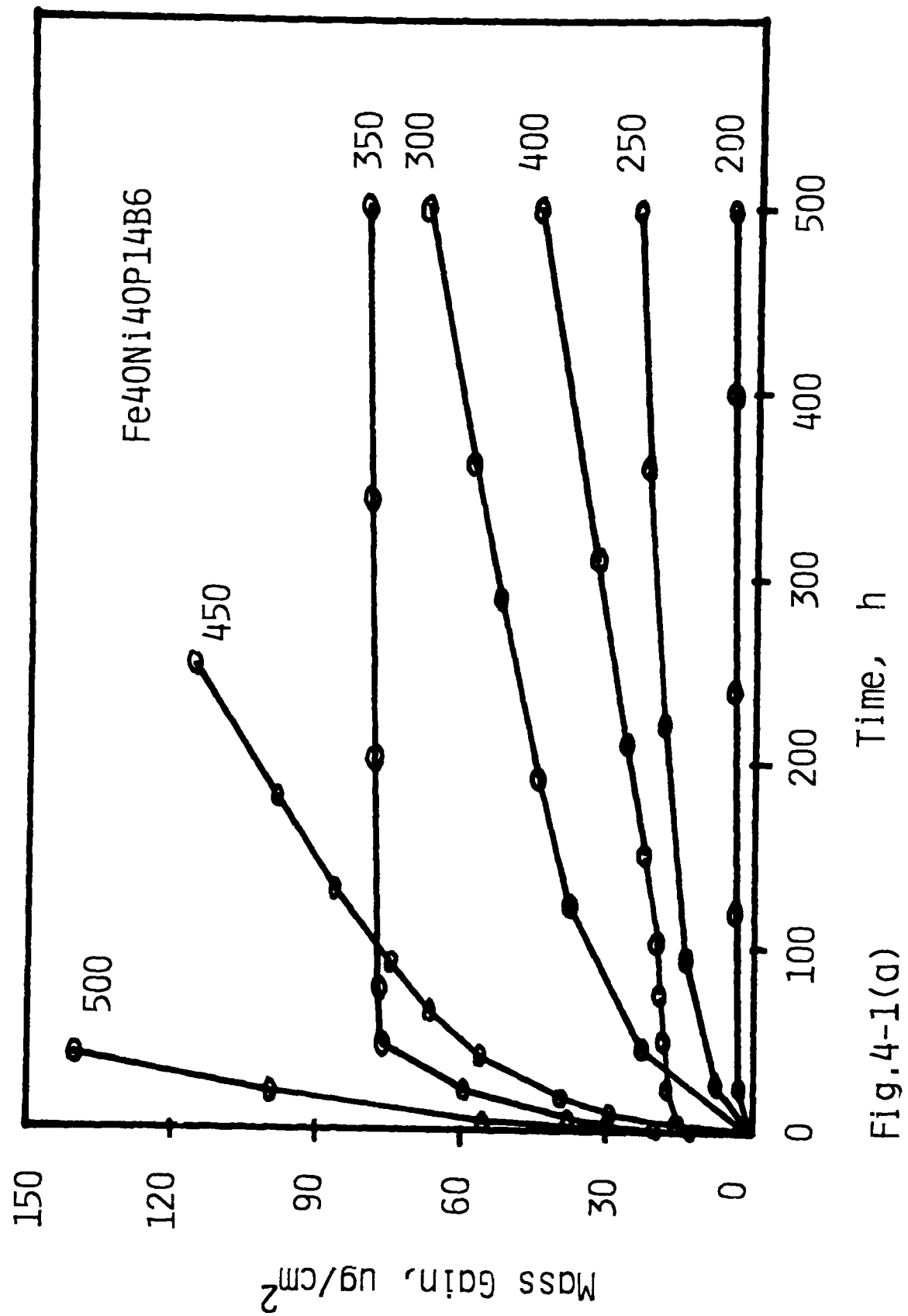


Fig.4-1(a)

Fig.4-1: Oxidation kinetics of Fe40Ni40P14B6 over the temperature range 200-500°C in air; (a) Mass gain Y versus oxidation time t, (b) Mass gain Y versus square root of oxidation time t, (c) ln mass gain Y versus ln oxidation time t.

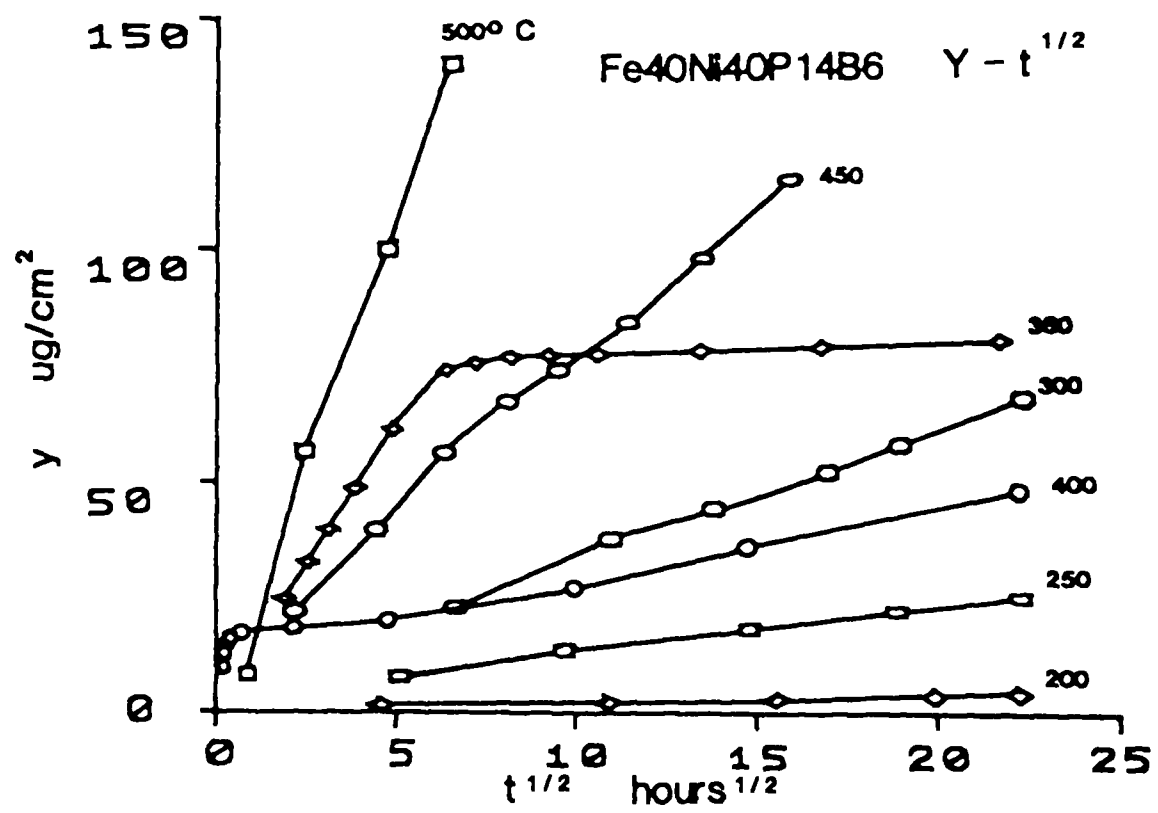


Fig.4-1(b)

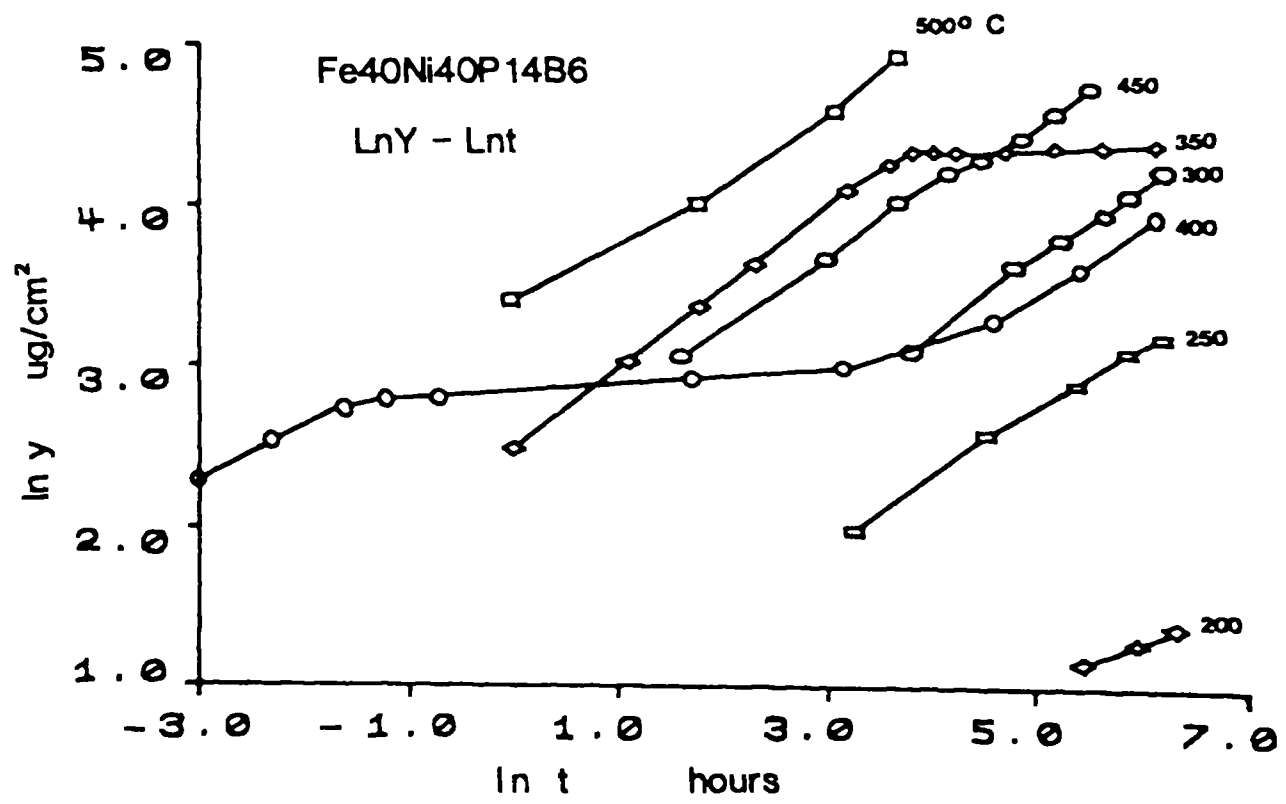


Fig.4-1(c)

Table 4-1

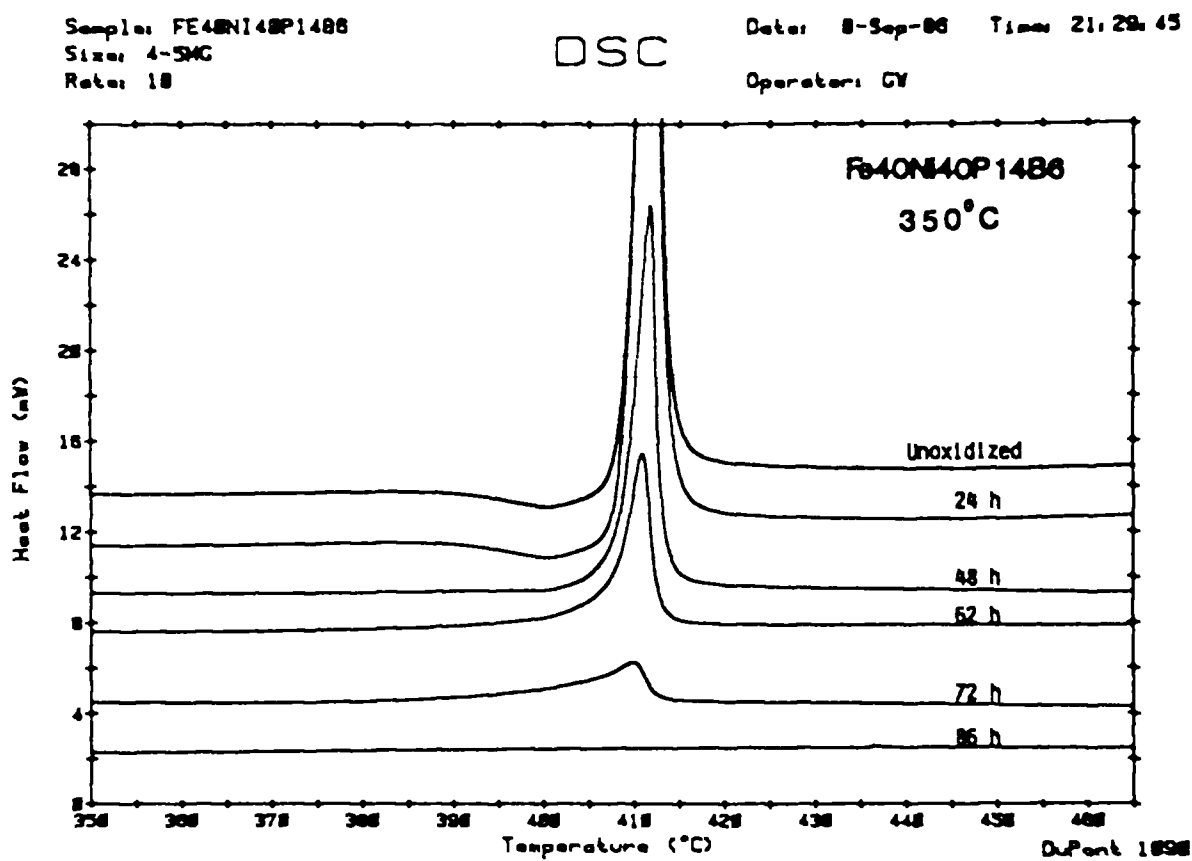
The best fit linear slopes and intercepts from the mass gain measurements as a function of square root of oxidation annealing time in Fig.1(b). The linear slopes are equal to the parabolic rate constant for the oxidation reaction.

Temperature °C	Oxidation period (h)	Slope (g/m ² h ^{1/2})	Intercept (g/m ²)	Correlation coefficient
200	0-500	1.8×10^{-3}	2.6×10^{-3}	0.999
250	0-500	9.8×10^{-3}	3.1×10^{-2}	0.994
300	0-500	2.9×10^{-2}	3.7×10^{-2}	0.999
350	0-20	1.2×10^{-1}	-5.8×10^{-3}	0.999
350	75-620	1.5×10^{-3}	7.7×10^{-1}	0.985
400	0-0.1	4.0×10^{-1}	1.8×10^{-3}	0.996
400	100-500	1.8×10^{-2}	1.2×10^{-1}	0.997
450	0-250	6.7×10^{-2}	1.0×10^{-1}	0.996
500	0-41	2.0×10^{-1}	7.5×10^{-2}	0.998

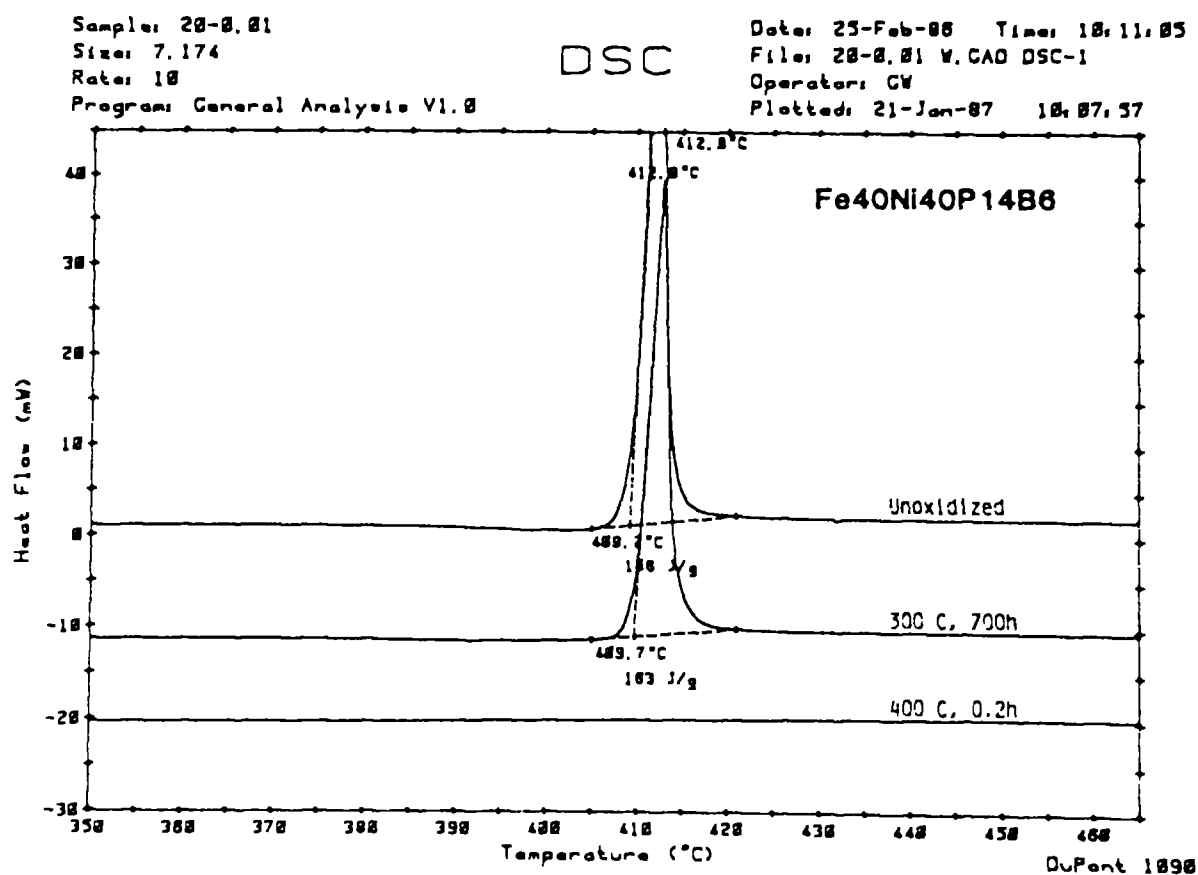
$1.2 \times 10^{-1} \text{ g/m}^2 \text{ h}^{1/2}$, and then the reaction rate dropped to almost zero, with little further mass gain up to 625h of oxidation. At 400 C, the oxidation reaction obeyed eqn. (4-1) for the first 0.1 h of oxidation, with a high parabolic rate constant of $4.0 \times 10^{-1} \text{ g/m}^2 \text{ h}^{1/2}$; then the reaction rate dropped suddenly to almost zero, with no mass gain from 0.1 to 50h; and finally the reaction rate increased slowly after 50h to follow again the parabolic rate law in eqn. (4-1), with a rate constant of $1.8 \times 10^{-2} \text{ g/m}^2 \text{ h}^{1/2}$, much smaller than in the first stage of oxidation. Because of this deceleration in oxidation rate, Fig.4-1 shows unusual shaped curves for the oxidation behaviour at 350 and 400 C, and the total oxidation mass gain after 500h at 400 C was much less than that at 350 C or even 300 C.

The change in oxidation behaviour at 350 and 400 C was found to correspond to a change in the Fe₄₀Ni₄₀P₁₄B₆ alloy structure from amorphous to crystalline. Fig.4-2 shows DSC traces for the exothermic heat of crystallisation as a function of prior oxidation time. Crystallisation of amorphous Fe₄₀Ni₄₀P₁₄B₆ was complete within 10min during oxidation at 400 C; crystallisation began after about 24h and was complete after about 70h during oxidation at 350 C; and no crystallisation was detected even after 750h of oxidation at 300 C. These results indicate that the onset of crystallisation caused the sharp drop in oxidation rate after 0.1h at 400 C and 20h at 350 C, as shown in Fig.4-1.

In order to investigate further the effect of crystallisation on the oxidation behaviour of amorphous Fe₄₀Ni₄₀P₁₄B₆, comparison oxidation tests were performed on amorphous and pre-crystallised samples. Figs.4-3(a) and (b) show the measured mass gain for both amorphous and crystallised Fe₄₀Ni₄₀P₁₄B₆ alloys as a function of oxidation time in air at 300 and 350 C respectively. The results show very clearly that amorphous Fe₄₀Ni₄₀P₁₄B₆ oxidised very much more rapidly than pre-crystallised Fe₄₀Ni₄₀P₁₄B₆. As

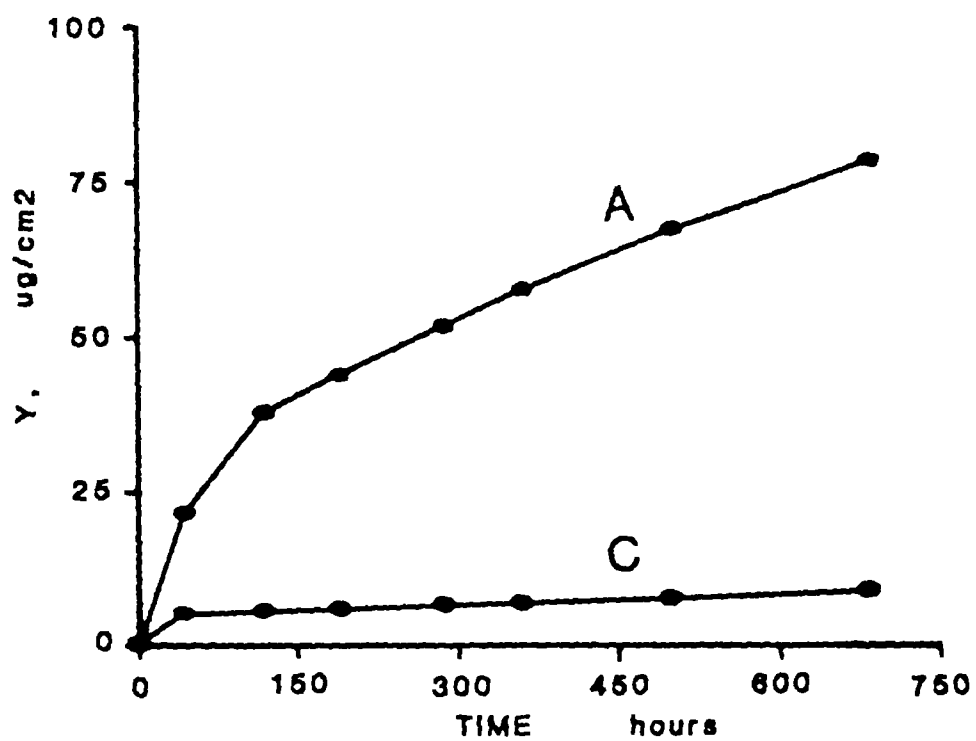


a)

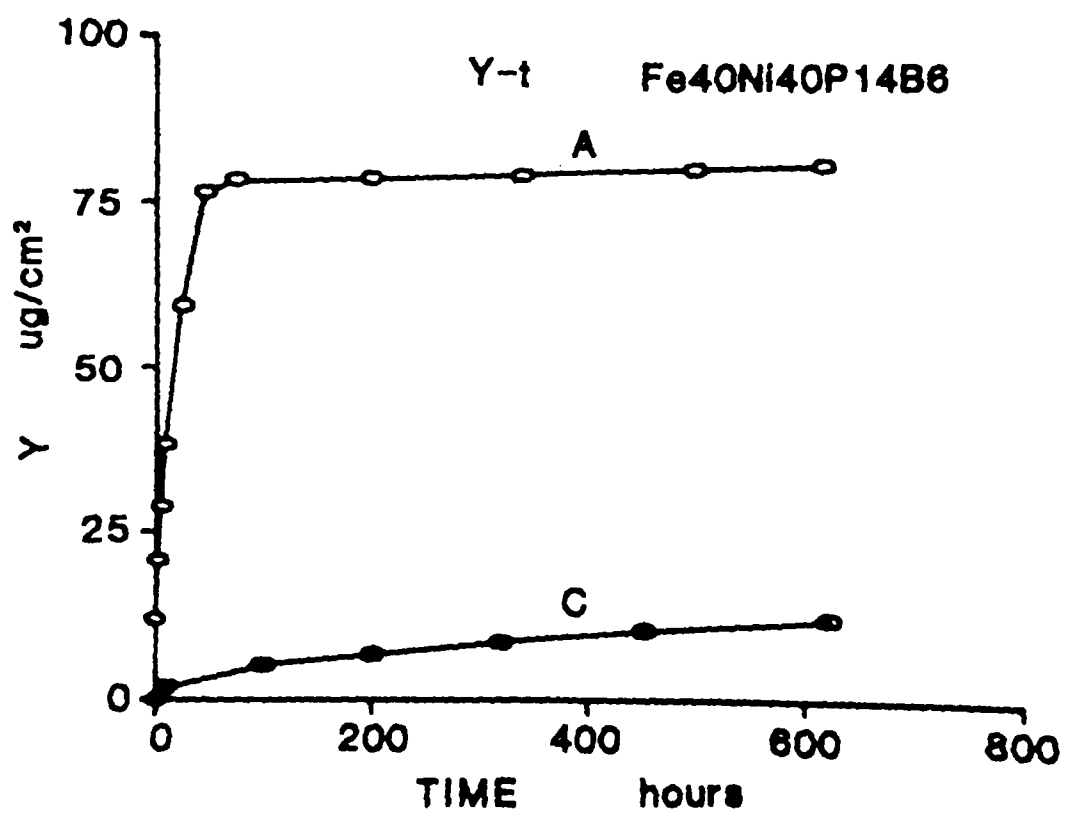


b)

Fig.4-2: DSC results showing exothermic heat of crystallisation for amorphous Fe₄₀Ni₄₀P₁₄B₆ as a function of oxidation time at (a) 350°C, (b) 300 and 400°C.



a)



b)

Fig.4-3: Mass gain Y versus oxidation time t showing comparison of amorphous (A) and pre-crystallised (C) Fe₄₀Ni₄₀P₁₄B₆; (a) at 300°C in air, (b) at 350°C in air.

shown in Fig.4-3, the amorphous alloy has a mass gain about eight times greater than the pre-crystallised alloy after 700h oxidation at 300C, and about six times greater after 625h oxidation at 350 C.

4.2.2 Optical and scanning electron microscopy of oxide morphology

Fig.4-4 shows typical taper cross section optical micrographs of both amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ after 700h oxidation at 300 C in air. Fig.4-5 shows a set of typical SEM pictures for amorphous Fe₄₀Ni₄₀P₁₄B₆ oxidised over the temperature range 200 to 500 C, while Fig.4-6 shows SEM pictures for pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ oxidised at temperatures of 300 and 350 C. After oxidation for 500h at 300 C, the top surface of oxidised amorphous Fe₄₀Ni₄₀P₁₄B₆ had a dark grey colour, while the top surface of oxidised pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ had a bright blue and purple colour. As shown in Fig.4-4, amorphous Fe₄₀Ni₄₀P₁₄B₆ had a layer thickness of approx. 1µm, much greater than the oxide layer thickness of approx. 0.1µm on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆, in agreement with the mass gain measurements shown in Figs.4-1 and 4-3. In addition, Figs.4-4, 4-5 and 4-6 show a sharp difference in oxide morphology between the amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ specimens. The oxide formed on amorphous Fe₄₀Ni₄₀P₁₄B₆ was not compact and had a whisker structure towards the top surface over the temperature range 250 to 400 C, as can be seen clearly in the SEM pictures in Figs.4-4(a) and 4-5(b)-(e). At the lower temperature of 200 C, there was network of oxide on the surface after 500h oxidation, as shown in Fig.4-5(a), delineating the initial fast oxide growth regions, although oxide whiskers were not yet fully developed. At the higher temperatures of 450 and 500 C, the oxide scale on amorphous Fe₄₀Ni₄₀P₁₄B₆ was found to exhibit different features. A double-layer scale was formed at these temperatures, and when the top layer broke away after a period of oxidation time, the underlying oxide layer exhibited

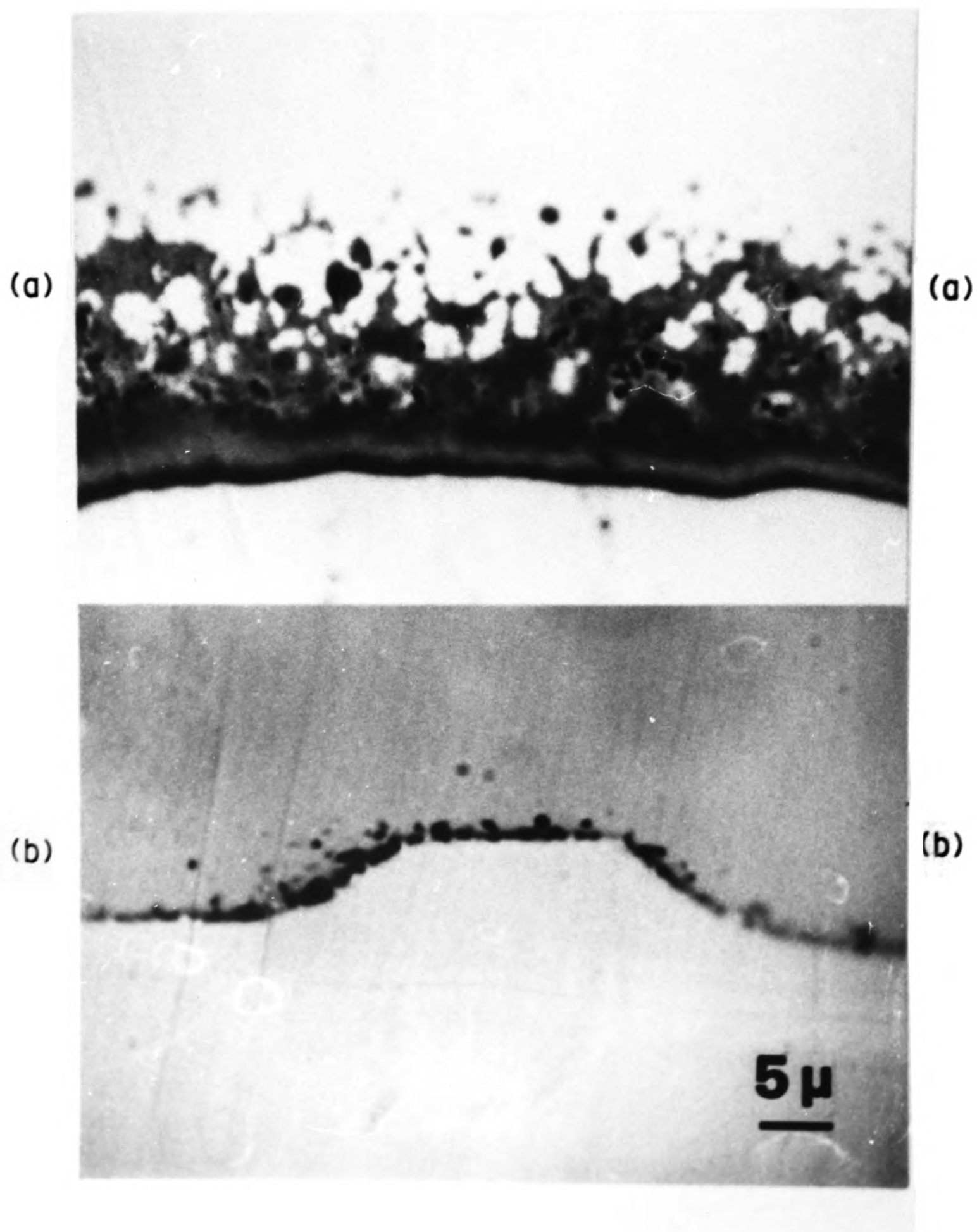
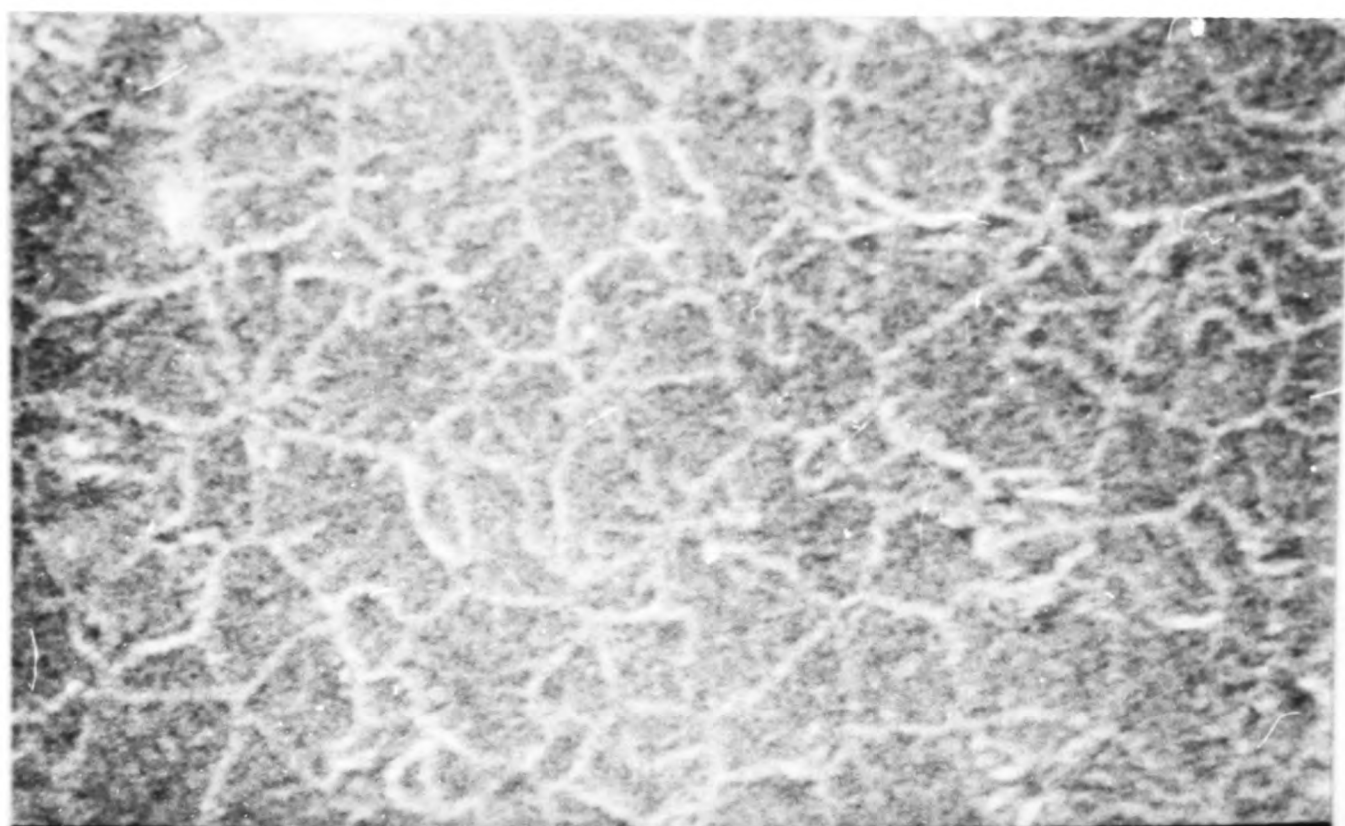


Fig.4-4: Taper cross section optical micrographs of the through thickness structures of oxide layer on (a) amorphous, (b) pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ oxidised at 300°C in air for 700h.

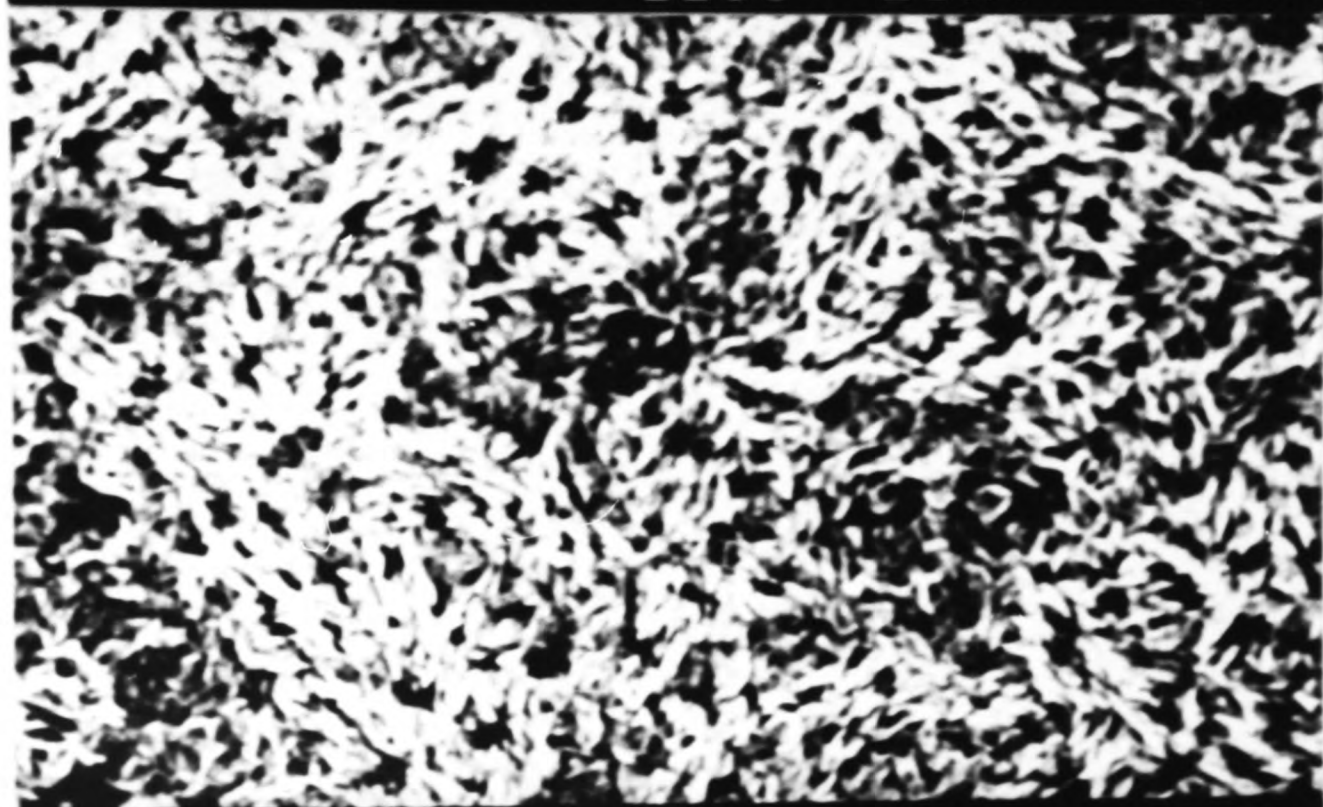
Fig.4-5

(a)

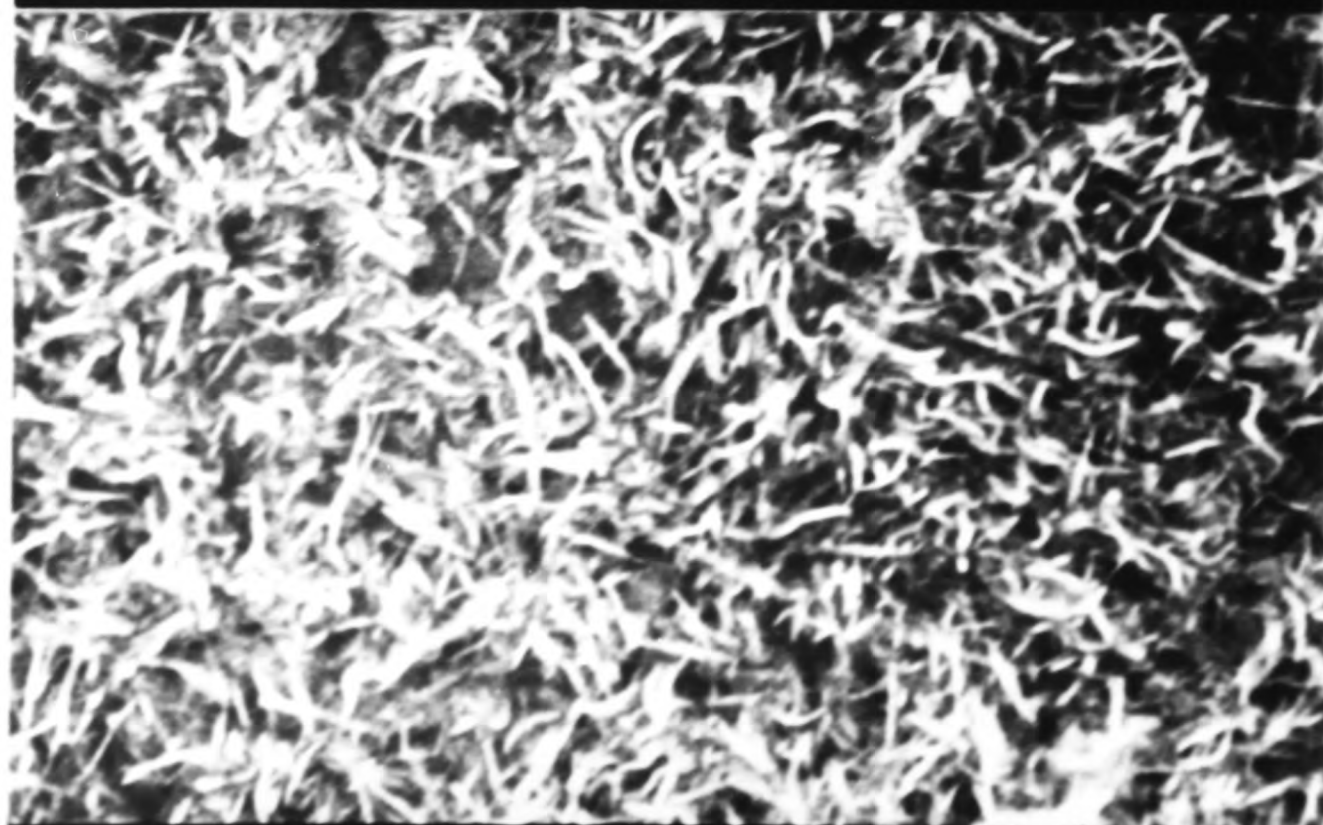


2205 25KV 10um

(b)

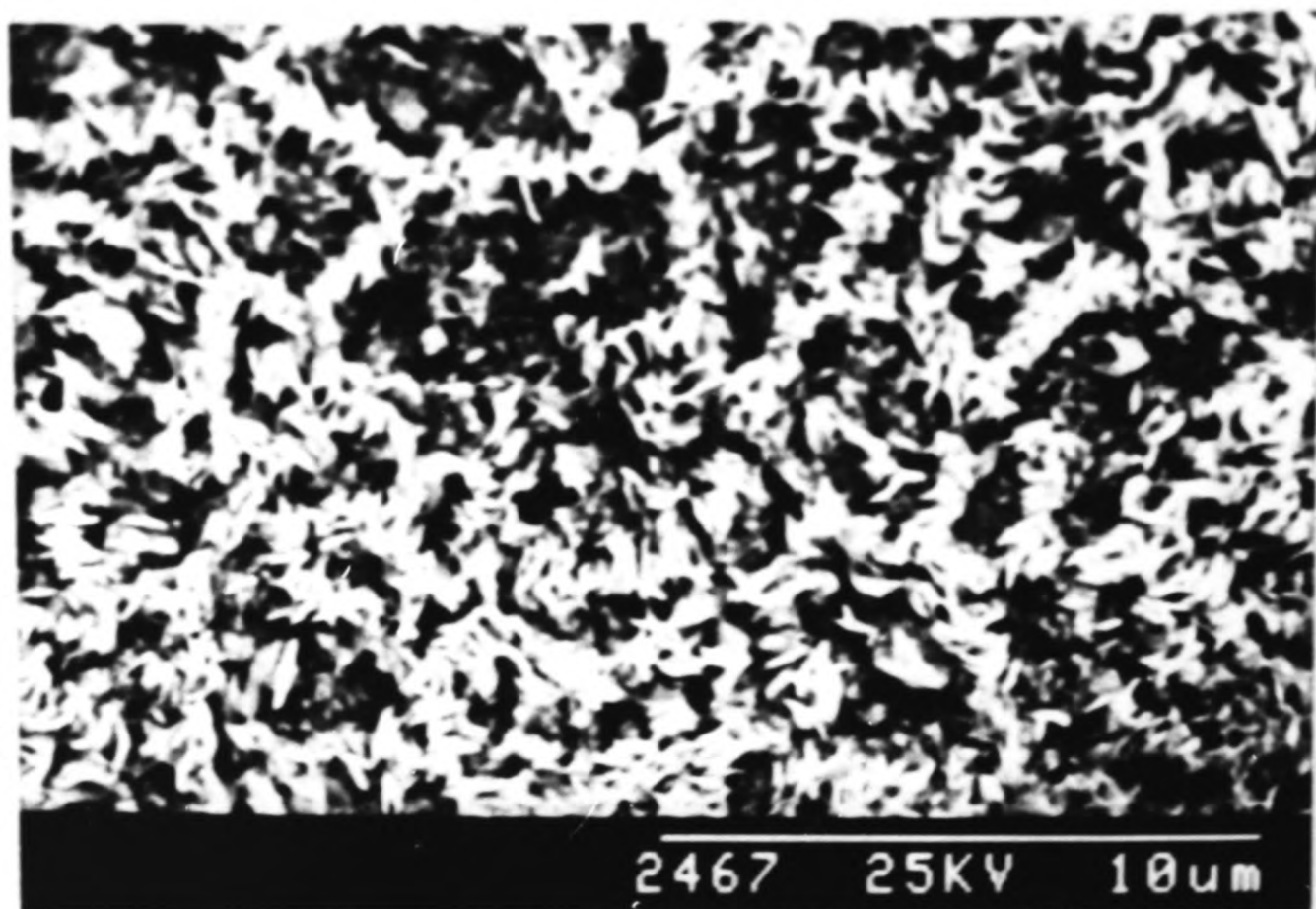


2680 25KV 10um



2310 25KV 10um

(d)



(e)

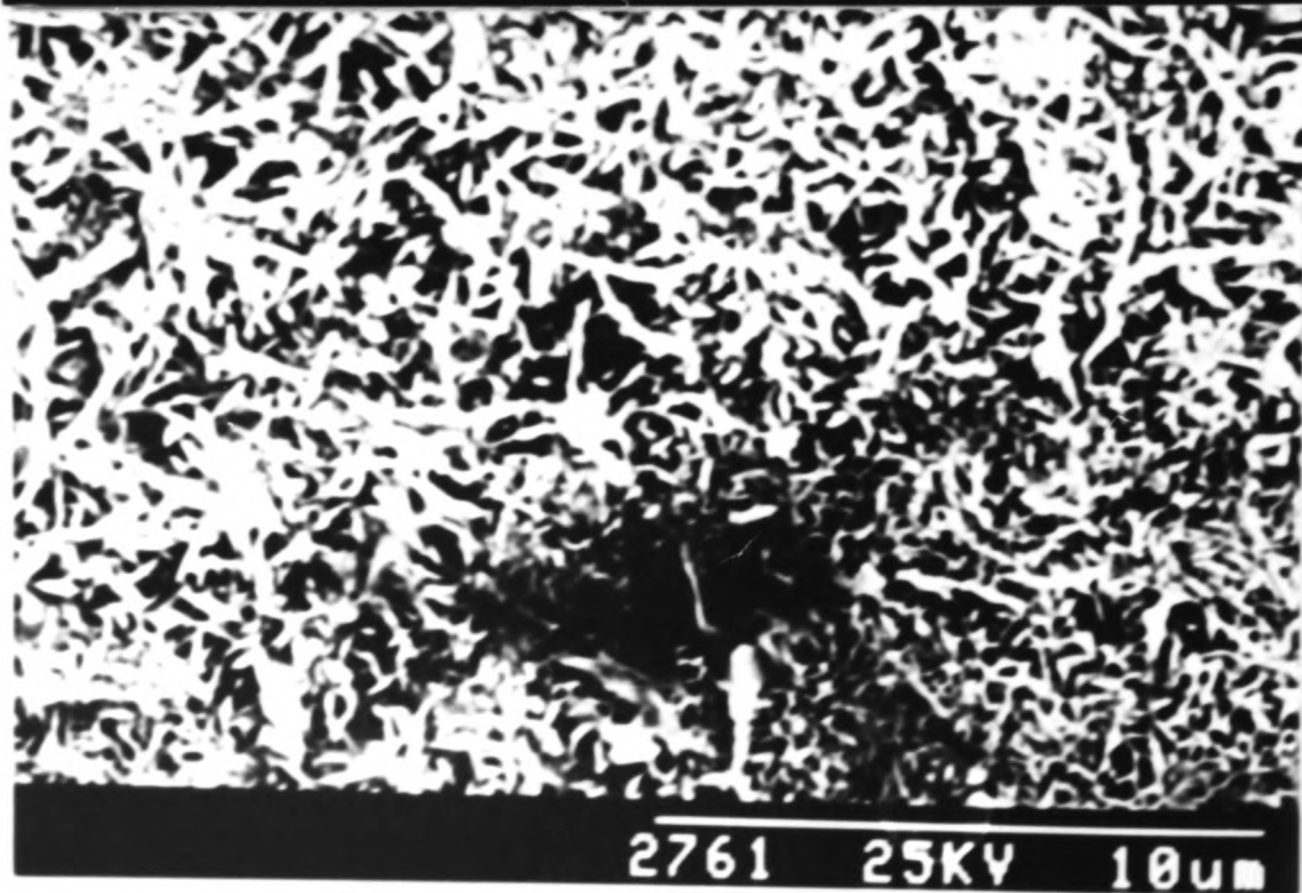


Fig.4-5: SEM micrographs of the oxide top surface formed on amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ oxidised in air at the temperature range $200\text{--}500^\circ\text{C}$; (a) at 200°C for 500h, (b) at 250°C for 500h, (c) at 300°C for 500h, (d) at 350°C for 500h, (e) at 400°C for 500h, (f) at 450°C for 310h, (g) at 500°C for 250h.

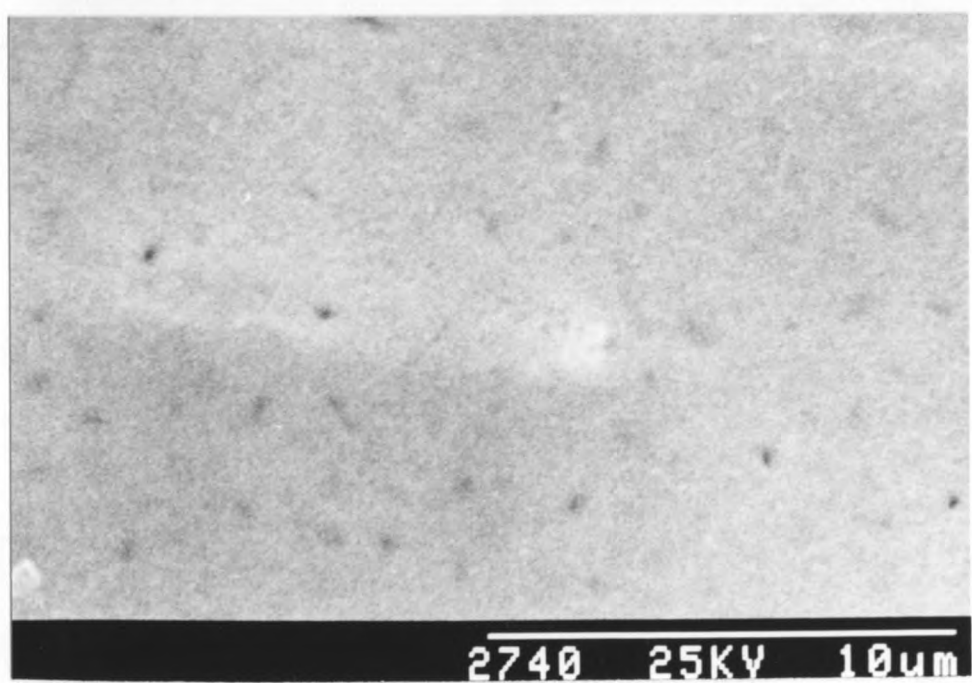
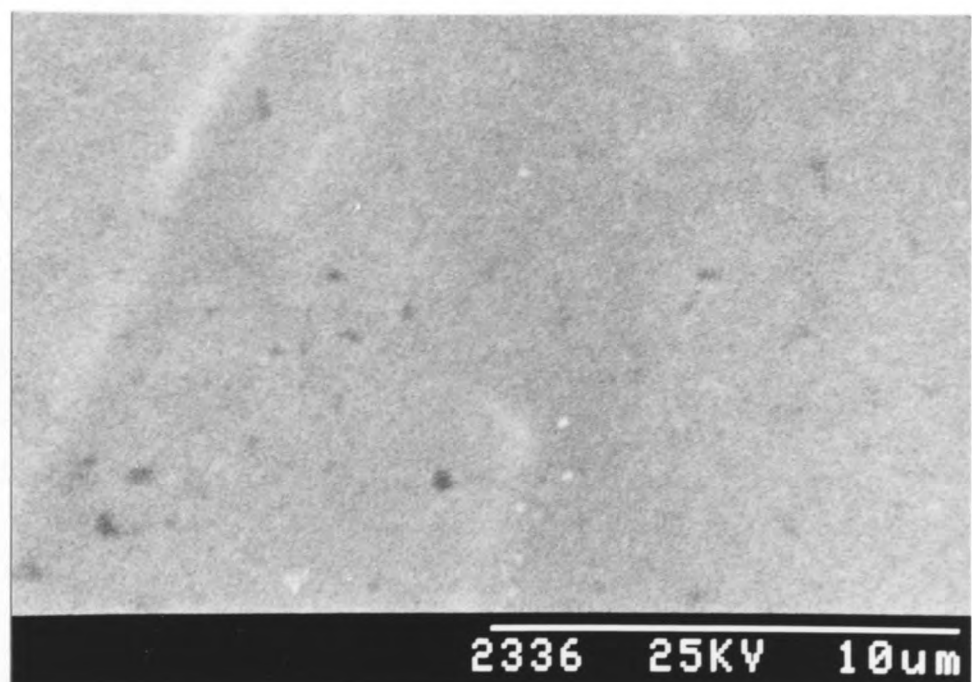
Fig.4-5

(f)



(g)





(a)

(b)

Fig.4-6: SEM micrographs of the oxide top surface formed on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ oxidised in air (a) for 500h at 300 C, (b) for 500h at 350 C.

again a fast-growing, non-protective feature, as shown in Fig.4-5(f) and (g). The whisker-like oxide on amorphous Fe₄₀Ni₄₀P₁₄B₆ grew very fast and had poor protective ability due to its brittleness. From TEM observation, the oxide whiskers grew typically to a length of 1-2μm, a width of 0.1-0.2μm and a thickness of 5-10nm after 100h oxidation at 300 C, as shown in Fig.4-7. In complete contrast, the oxide layer formed on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ had a compact structure of microcrystalline grains, as shown in Fig.4-6.

4.2.3 Transmission electron microscopy of oxide scales

Figs.4-8 and 4-9 show bright field TEM micrographs and selected area electron diffraction patterns of the oxide films stripped from amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ respectively after 240h oxidation at 300 C. The oxide grain size formed on the pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ was much smaller than on the amorphous alloy. This can be seen directly on the bright field images of Figs.4-8(a)(b) and 4-9(a)(b), and is also shown by the spot diffraction pattern of Fig.4-8(c) compared with the ring pattern of Fig.4-9(d). Even using the smallest available selected area aperture of 0.2μm diameter, the oxide diffraction patterns from pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ still contained many rings as shown in Fig.4-9(d). Indexing selected area diffraction patterns showed that the oxide layer formed on amorphous Fe₄₀Ni₄₀P₁₄B₆ consisted mainly of α-Fe₂O₃, while the oxide layer formed on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ consisted of a mixture of NiO, Fe₃O₄, Fe₂O₃, NiFe₂O₄ and some other compounds. The detailed results obtained from indexing selected area electron diffraction patterns are given in Tables 4-2 and 4-3 for amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ respectively. Crystal structures found in the two types of oxide are given in table 4-4, together with composition measurements obtained from electron probe microanalysis.

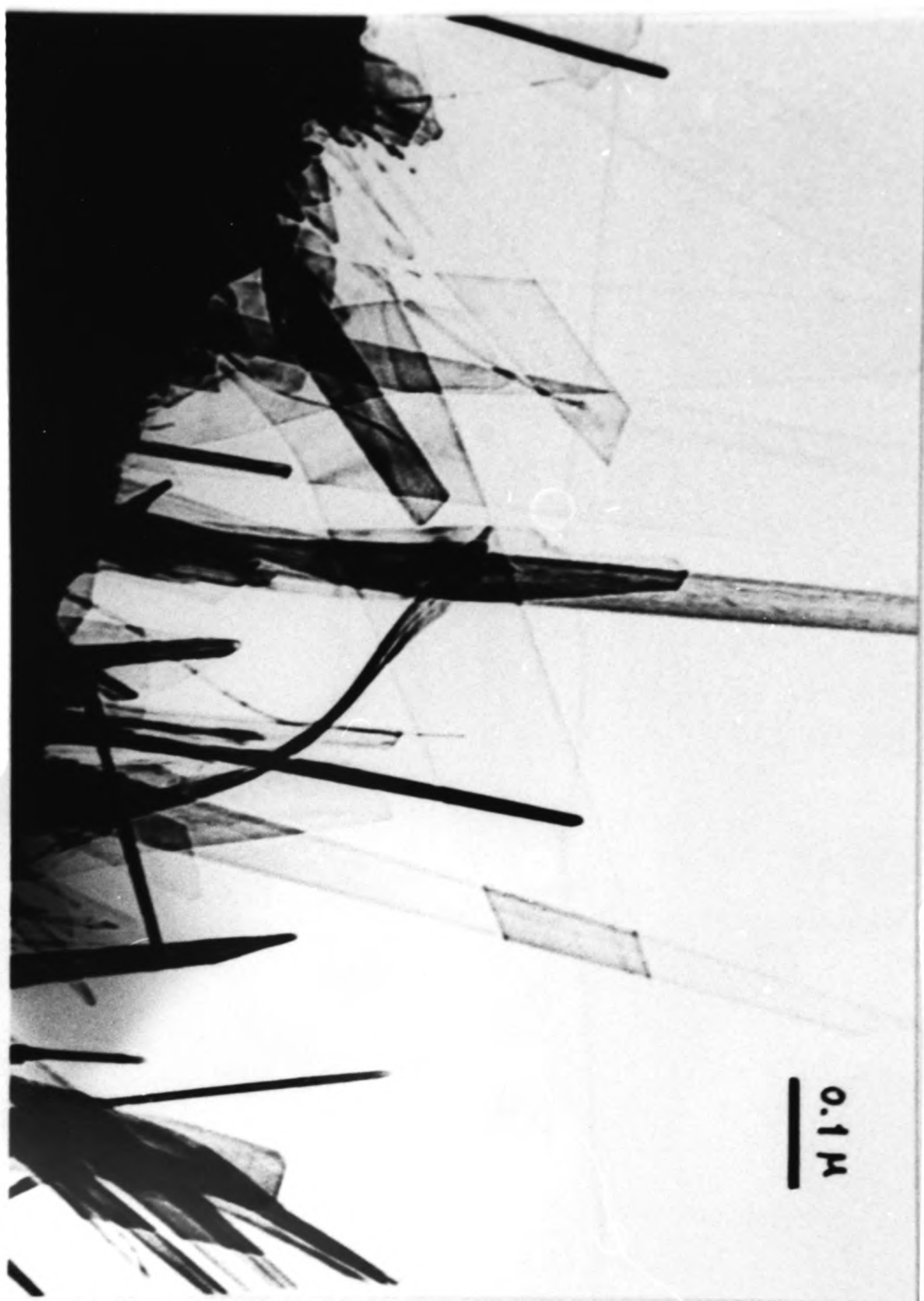
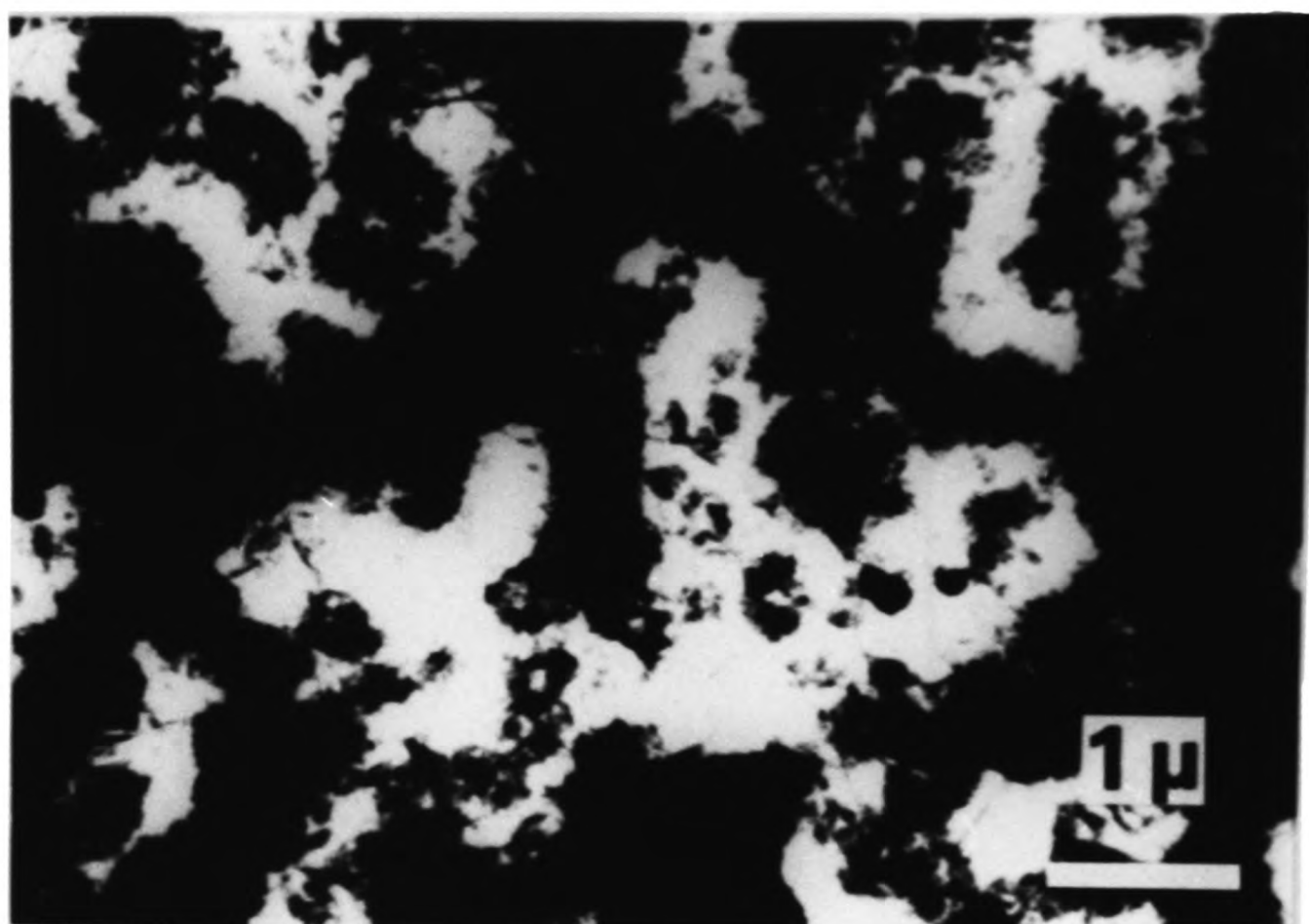


Fig.4-7: Bright field TEM image of the whisker-like oxide structure on amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ oxidised in air at 300°C for 100h.

(a)



(b)

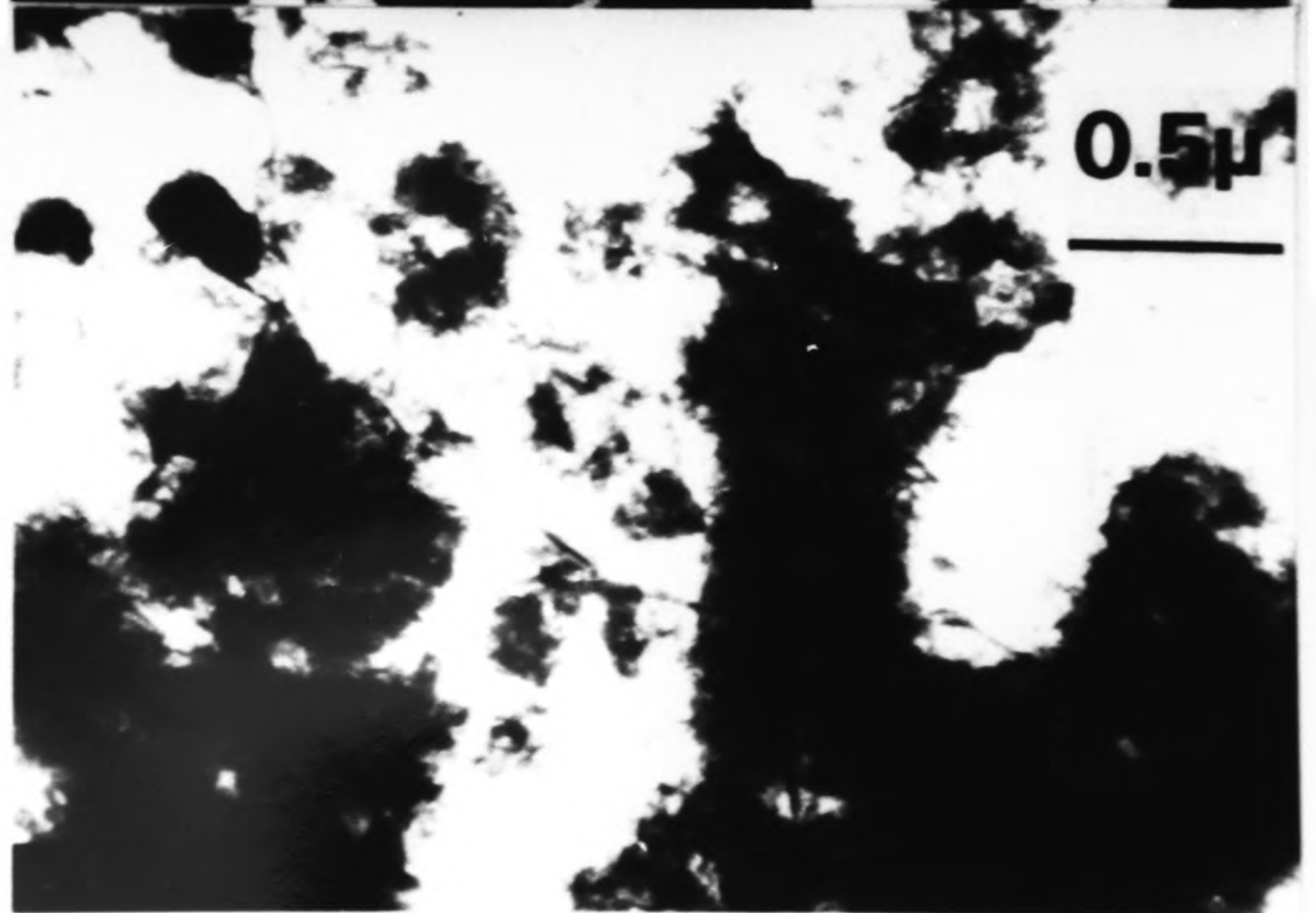
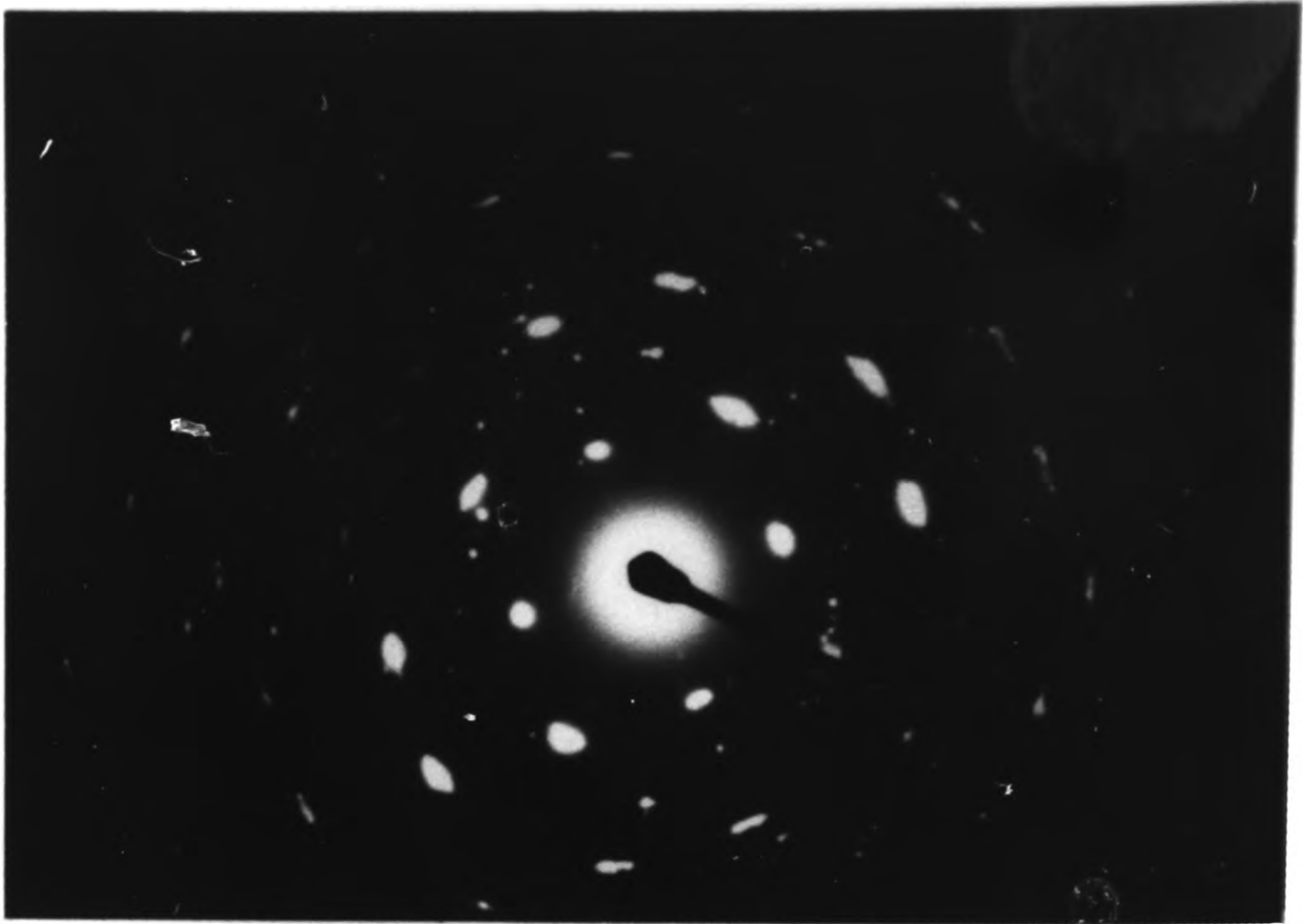


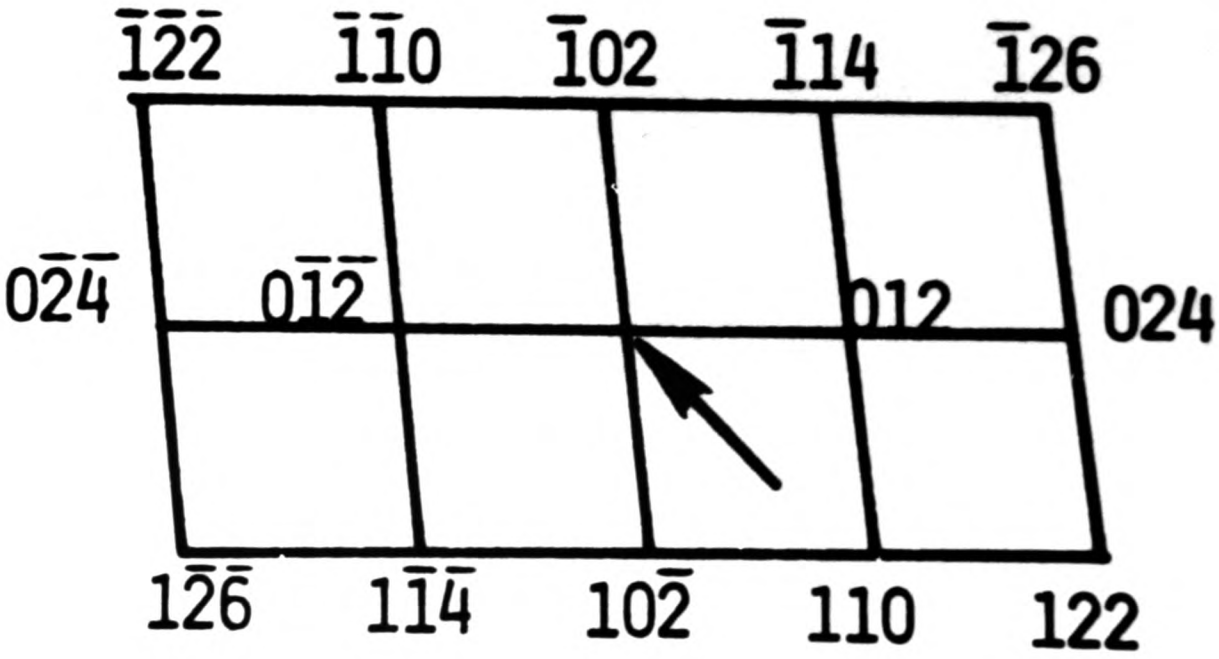
Fig.4-8: TEM micrographs of the oxide films removed from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{Pl}_4\text{B}_6$ oxidised in air for 240h at 300°C ; (a) and (b) bright field images, (c) SAED pattern from (a), (d) indexing of the SAED pattern in (c).

Fig.4-8

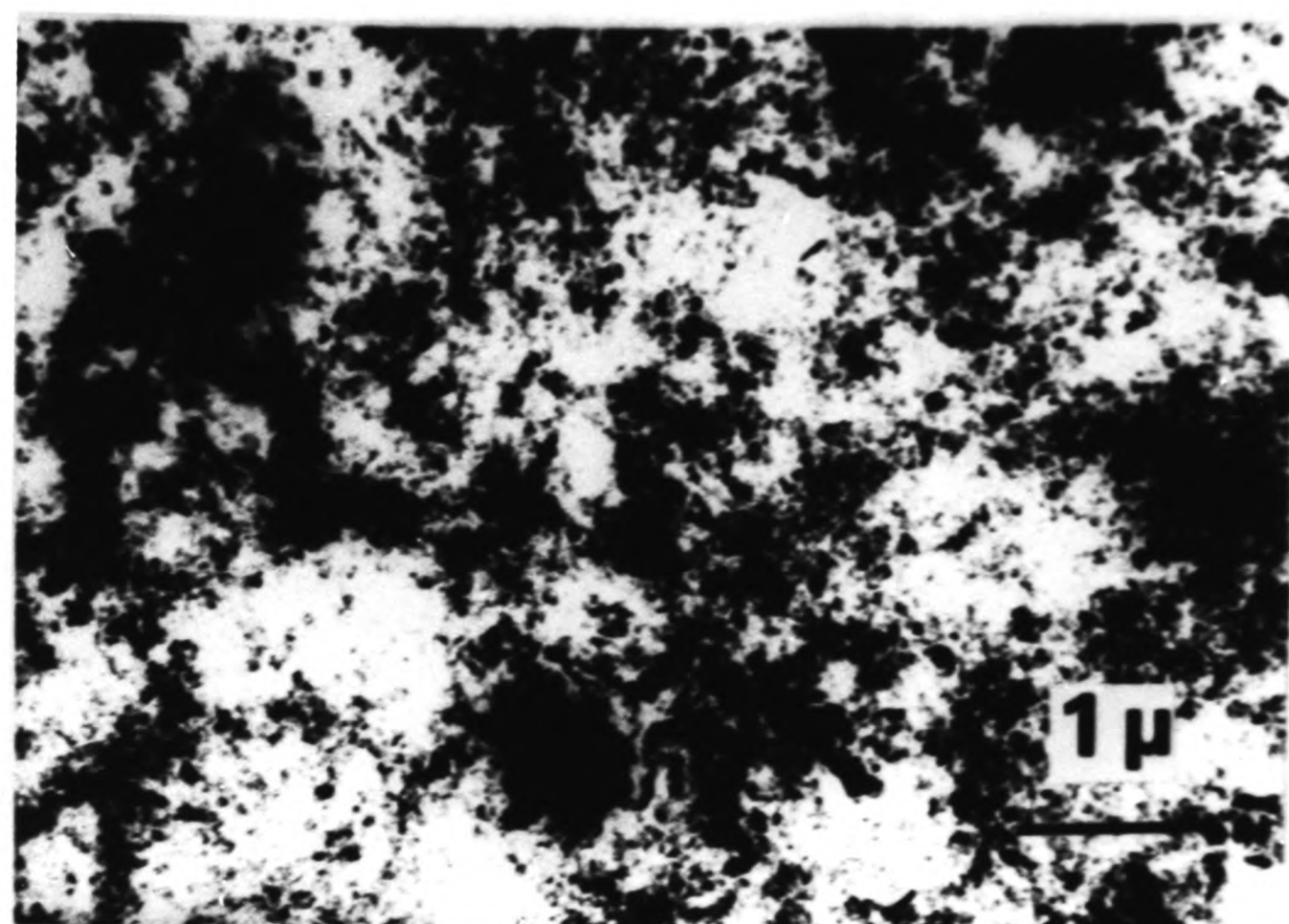
(c)



(d)



(a)



(b)

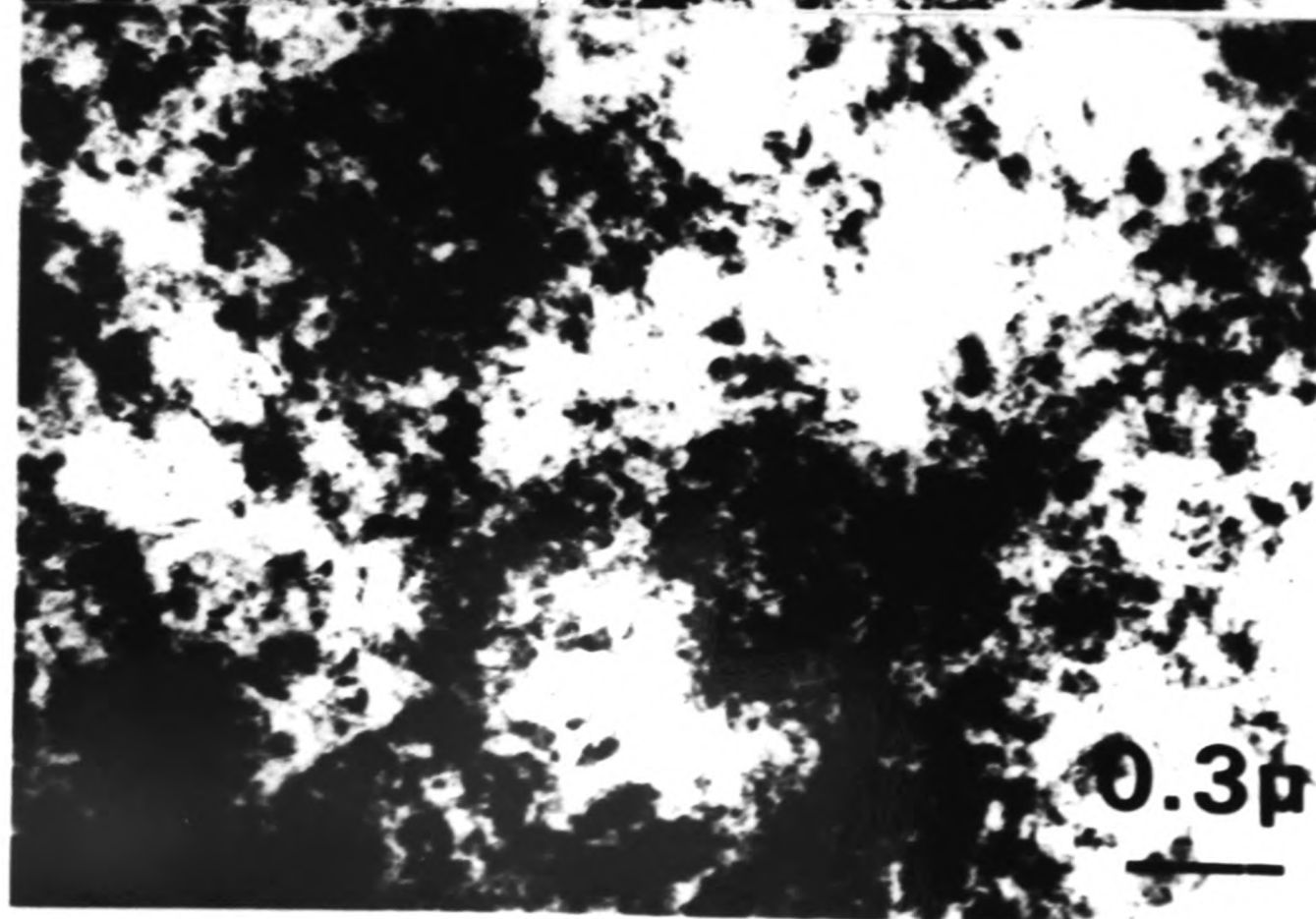
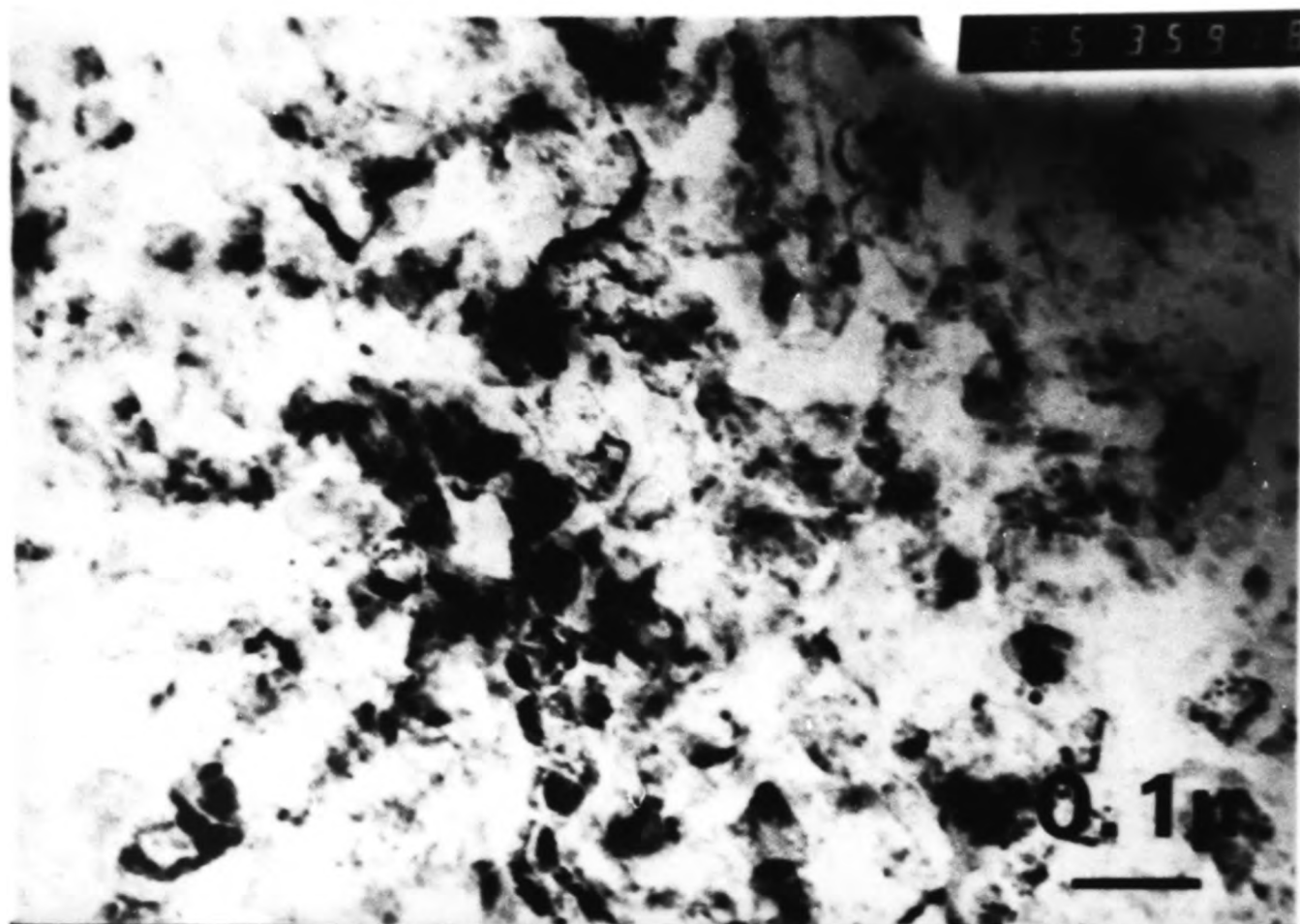


Fig.4-9: TEM micrographs of the oxide films removed from pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ oxidised in air for 240h at 300°C; (a), (b) and (c) bright field images, (d) SAED pattern from (a).

Fig.4-9

(c)



(d)

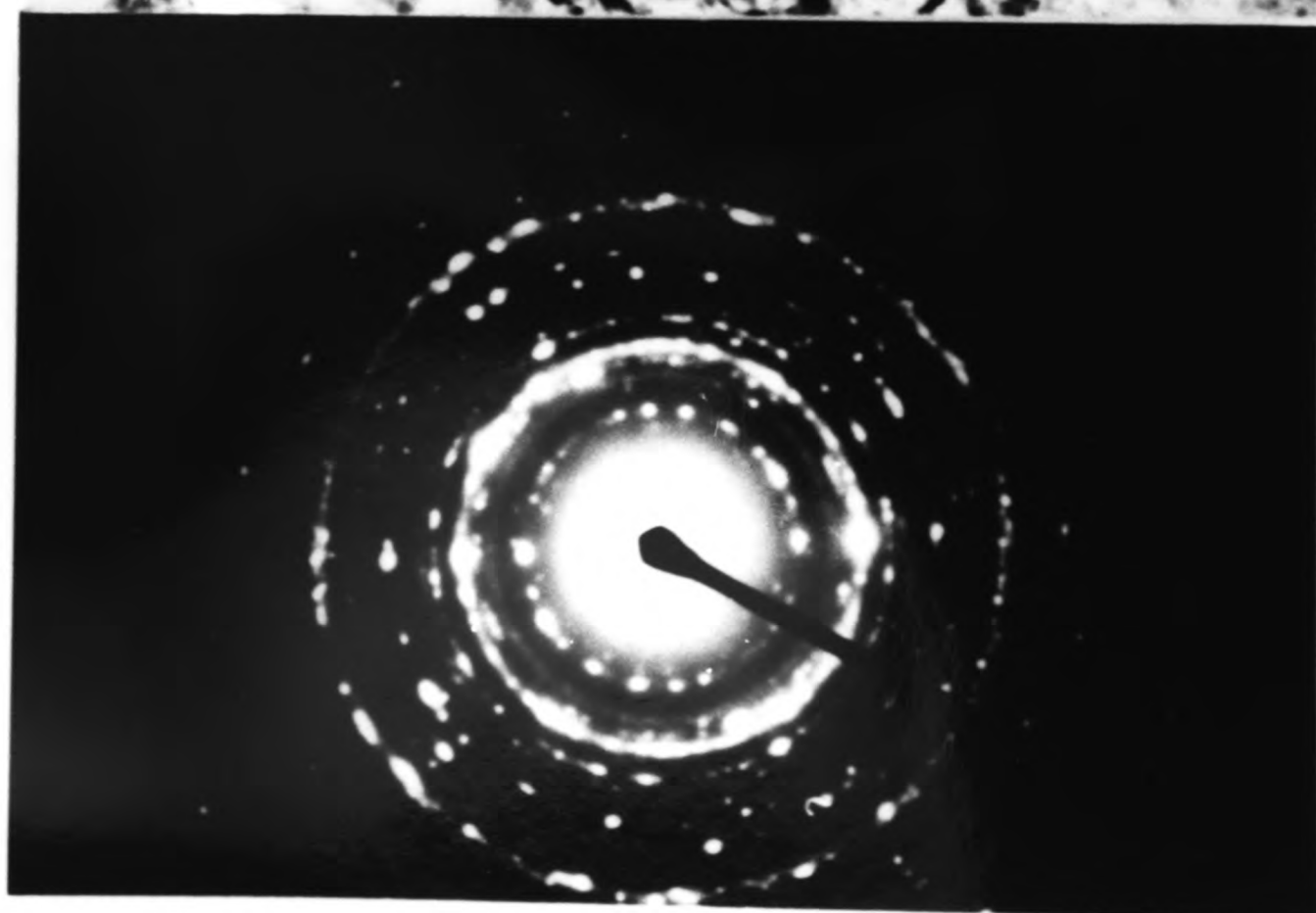


Table 4-2

Calculated d spacings for typical diffraction patterns obtained from
 an oxide film stripped from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ after
 240h oxidation at 300°C (d_1), and an oxidized amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$
 thin foil specimen after 50h at 300°C (d_2)

d_1 (Å)	d_2 (Å)	$d_{\alpha\text{-Fe}_2\text{O}_3}$ (13-534)	(hkl)
3.66	3.66	3.66	012
2.69	2.67	2.69	104
2.52	2.51	2.51	110
2.29		2.285	006
2.21	2.20	2.201	113
2.08	2.07	2.070	202
1.83	1.85	1.838	024
1.69	1.68	1.690	116
	1.60	1.596	018
1.49	1.48	1.484	214
	1.45	1.452	300
1.32		1.310	10 <u>10</u> , 119
	1.26	1.258	220
1.23		1.226	036
1.18		1.189	128
1.15		1.162	02 <u>10</u>
1.13	1.13	1.141	134
1.10		1.102	226
1.04	1.06	1.055	21 <u>10</u>
0.99	0.99	0.989	232, 318
	0.95	0.951	140, 02 <u>13</u>
0.903	0.91	0.908	13 <u>10</u>

Table 4-3

Calculated d spacings for typical diffraction patterns obtained from an oxide film stripped from pre-crystallized $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{10}\text{B}_6$ after 240h oxidation at 300°C, together with ASTM powder card index α spacings of several Fe and Ni oxides.

d (Å)	Fe_3O_4 (11-614)	Fe_2O_3 (13-534)	NiO (22-1189)	NiFe_2O_4 (10-325)
4.19				
3.70		3.66		
2.97	2.966			
2.94				2.948
2.69		2.69		
2.52	2.530	2.51		2.513
2.42	2.419		2.412	
2.32				
2.21		2.20		
2.10	2.096		2.088	2.085
1.98				
1.85		1.84		
1.72	1.712			
1.70		1.690		1.702
1.61		1.596		1.605
1.55				
1.48	1.483	1.484	1.477	1.476
1.41		1.452		
1.32	1.327	1.310		
1.27	1.279, 1.264	1.258	1.260, 1.259	1.271
1.21	1.211		1.2064	
1.145		1.141		
1.109				
1.096	1.092	1.102		
1.085				1.0857
1.048	1.049	1.055	1.0458	
0.969	0.9692	0.9601	0.9592	0.9630
0.938	0.9386		0.9345, 0.9337	0.9324
0.908		0.9080		
0.882	0.8794			
0.856	0.8565		0.8529, 0.8519	
0.812	0.8113			

Table 4-4

Results of selected area electron diffraction patterns and electron probe microanalysis from oxide layers removed from amorphous and pre-crystallized $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$

ALLOYS	Oxidation conditions	Oxide Structure	Oxide Composition* (at%)
amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	300°C 240h in air	$\alpha\text{-Fe}_2\text{O}_3$	Fe > 99%
pre-crystallized $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	300°C 240h in air	$\text{Fe}_3\text{O}_4, \text{NiO},$ $\text{Fe}_2\text{O}_3, \text{NiFe}_2\text{O}_4$ + ...	Fe: 52-83% Ni: 11-43% P: 4-15%

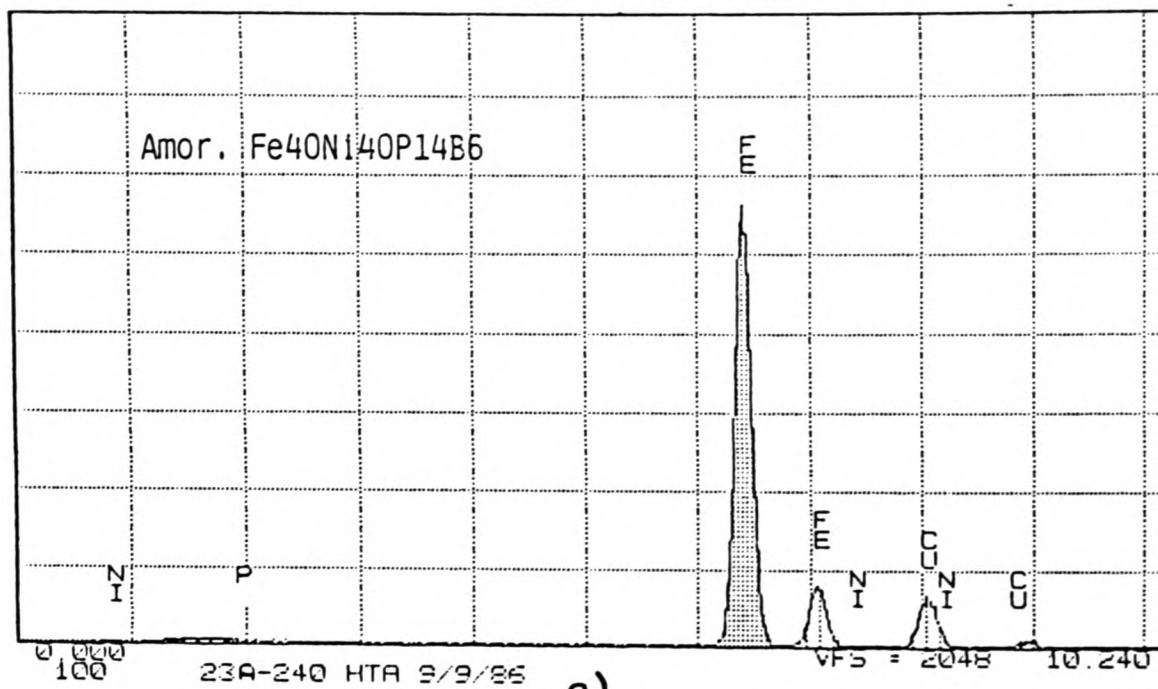
*Elements with atomic number < 11 cannot be measured by electron probe microanalysis.

Fig.4-10 shows typical X-ray energy dispersive spectra (EDS) from the oxide layers removed from both amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆, and the resulting oxide compositions are included in Table 4-4. The measured compositions were found to be quite different for the oxide films removed from amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆, as shown in Table 4-4 and Fig.4-10. The oxide formed on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ had a variable composition in the range 52-83at.%Fe, 11-43%Ni and 4-15%P, similar to the composition of the matrix alloy (boron cannot be measured by EDS). In contrast, the oxide film formed on amorphous Fe₄₀Ni₄₀P₁₄B₆ contained only Fe, with no Ni or P detected in the X-ray spectra. As shown in Table 4-4, the EDS results were in agreement with the oxide crystal structures obtained by analysis of the selected area diffraction patterns. The oxide layer formed on pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ clearly had a much more complicated structure and composition than the oxide layer formed on amorphous Fe₄₀Ni₄₀P₁₄B₆.

4.2.4 Transmission electron microscopy of oxidised thin foils

Figs.4-11 to 4-14 show TEM bright field micrographs and selected area electron diffraction patterns from as-thinned and oxidised metal foils of amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ respectively. With no oxidation annealing, the amorphous Fe₄₀Ni₄₀P₁₄B₆ exhibited a featureless bright field image and a diffraction pattern consisting of two broad haloes, characteristic of an amorphous atomic structure, as shown in Fig.4-11. After only 0.5h oxidation at 300 C, the oxide microstructure which formed on the amorphous alloy thin foil could easily be detected, as shown in Fig.4-12(a). Bright field images showed many dark stripes, which corresponded to the initial stages of whisker-like oxide growth on the amorphous thin foil. Near the edges of the thin foils as shown in Fig.4-12(a), a different oxide structure was found, with no stripes but

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 Cursor: 0.000keV = 0 ROI (2) 7.250: 7.730



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 Cursor: 0.000keV = 0 ROI (2) 7.250: 7.730

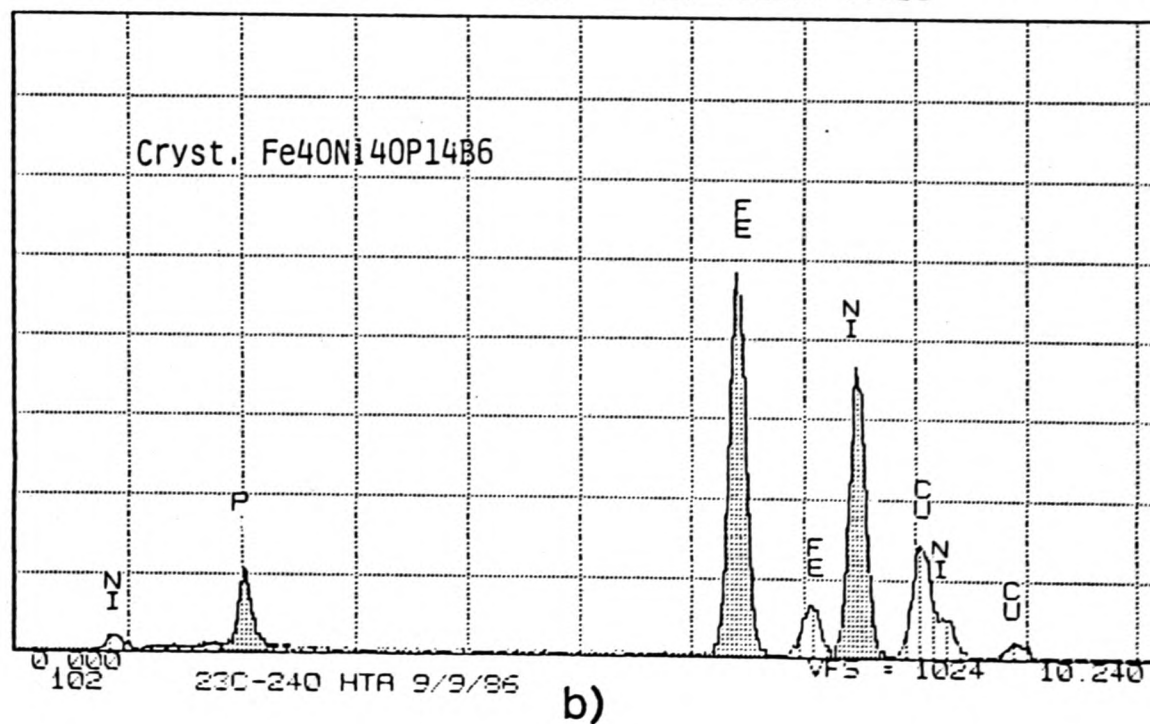
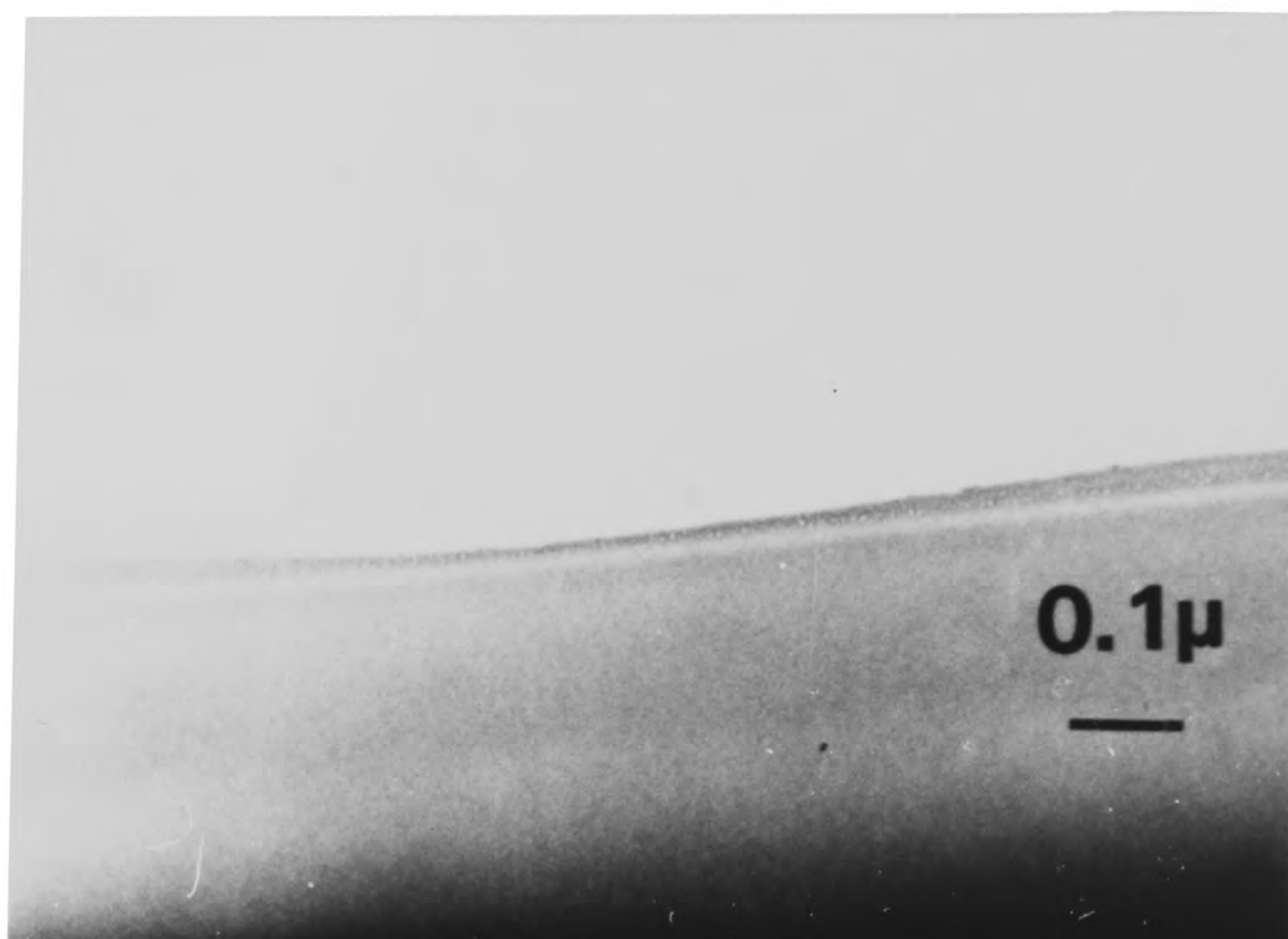


Fig.4-10: Typical EDS spectra from the oxide films removed from (a) amorphous Fe₄₀Ni₄₀P₁₄B₆, (b) pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ oxidised at 300°C for 240h.

(a)



(b)



Fig.4-11: TEM micrographs of unoxidised amorphous Fe₄₀Ni₄₀P₁₄B₆ foils; (a) bright field image, (b) SAED pattern.

(a)

0.1 μ

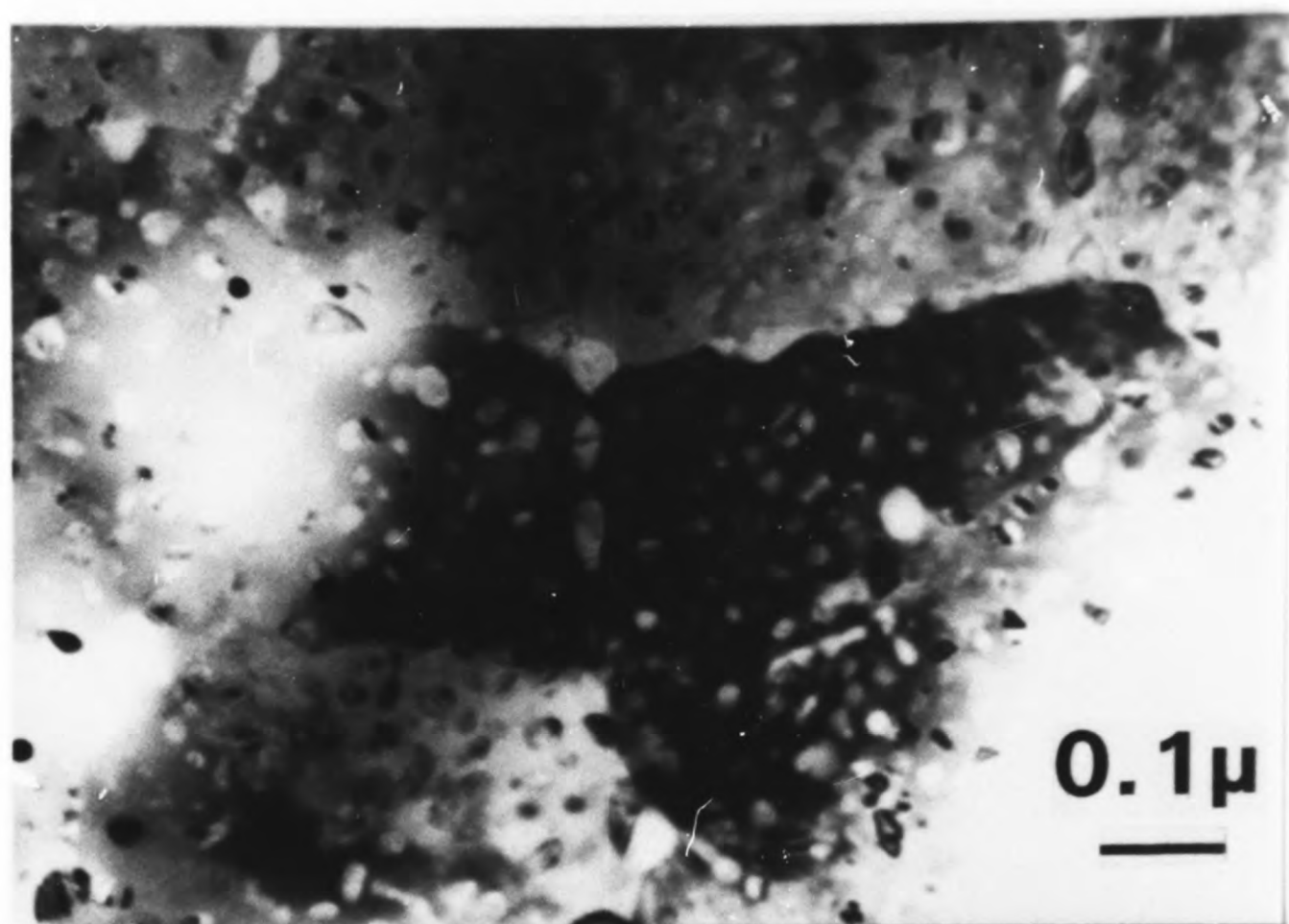
(b)

50 nm

(c)

Fig.4-12: TEM micrographs of amorphous Fe₄₀Ni₄₀P₁₄B₆ foils oxidised at 300°C for (a) 0.5h, (b) 50h, (c) SAED pattern for (b).

(a)



(b)

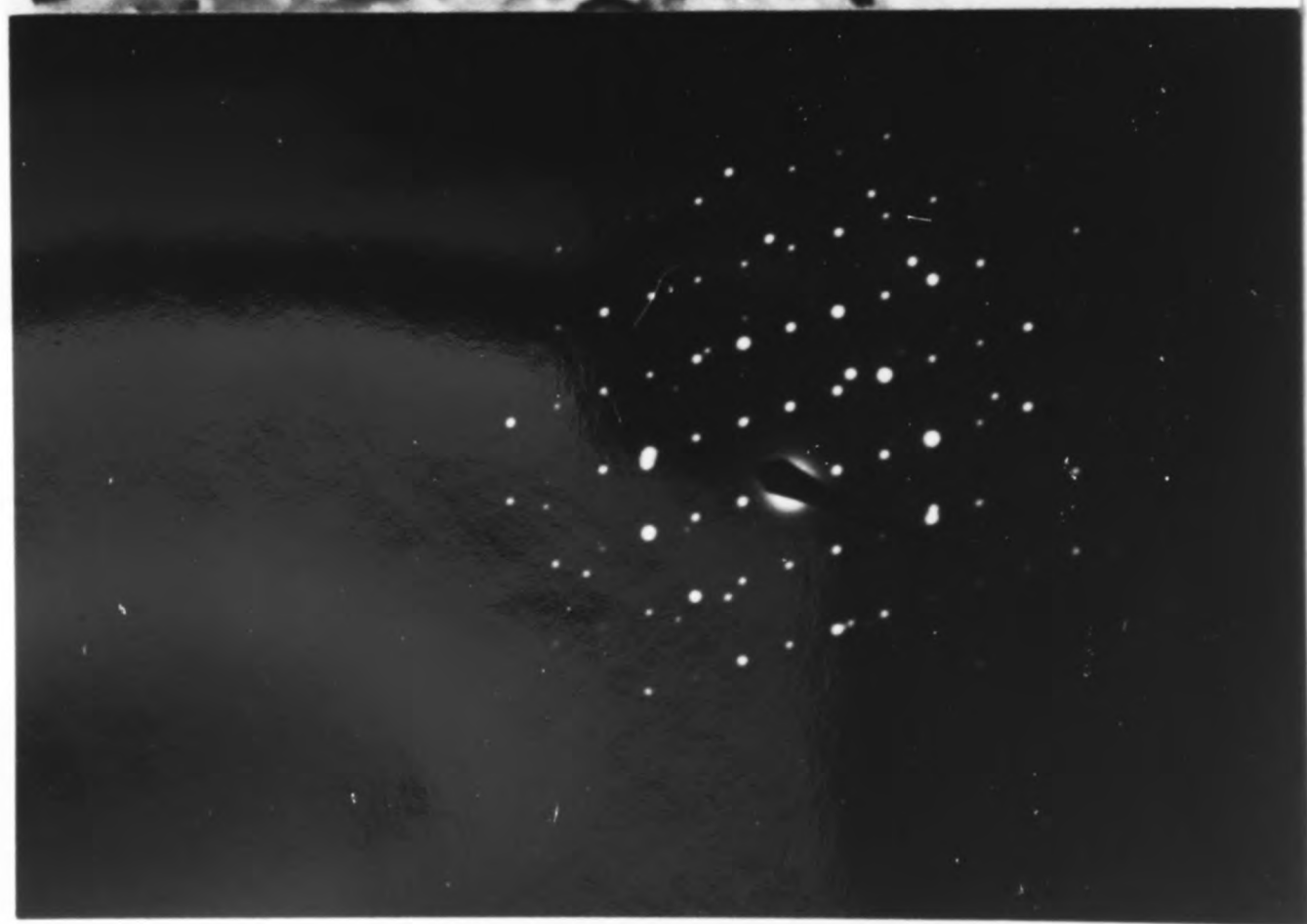
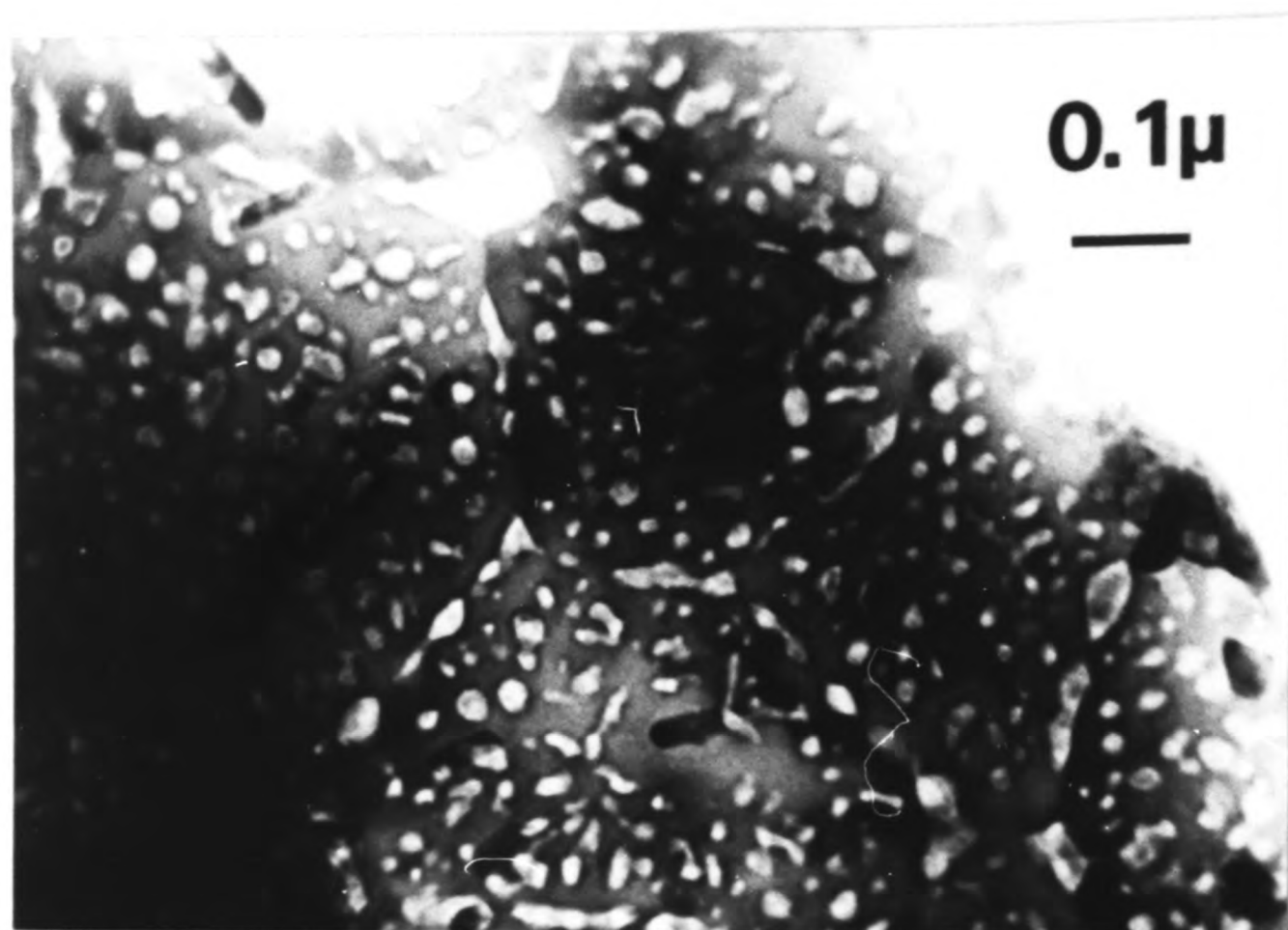


Fig.4-13: TEM micrographs of unoxidised pre-crystallised $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ foils; (a) bright field image, (b) SAED pattern.

(a)



(b)

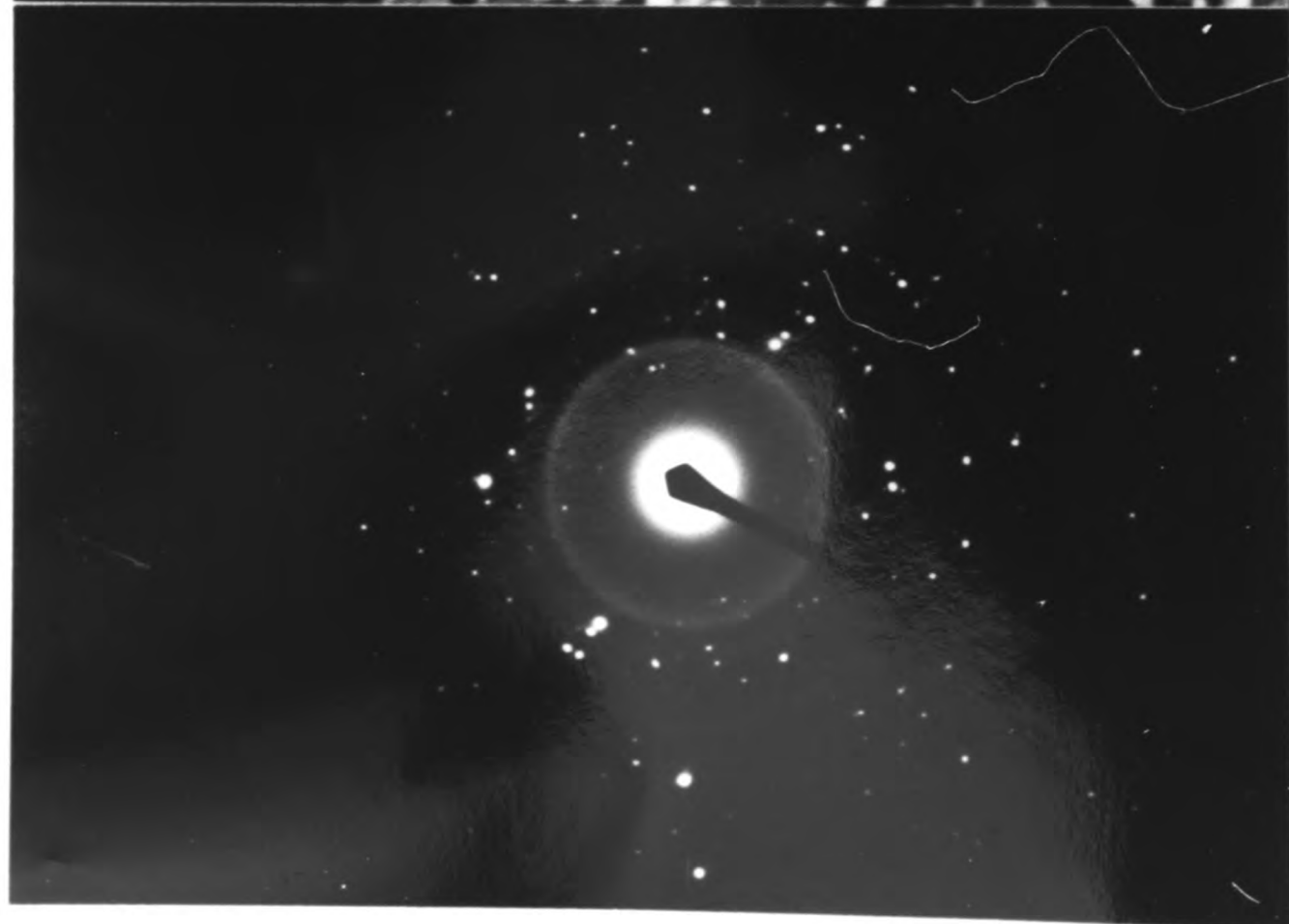


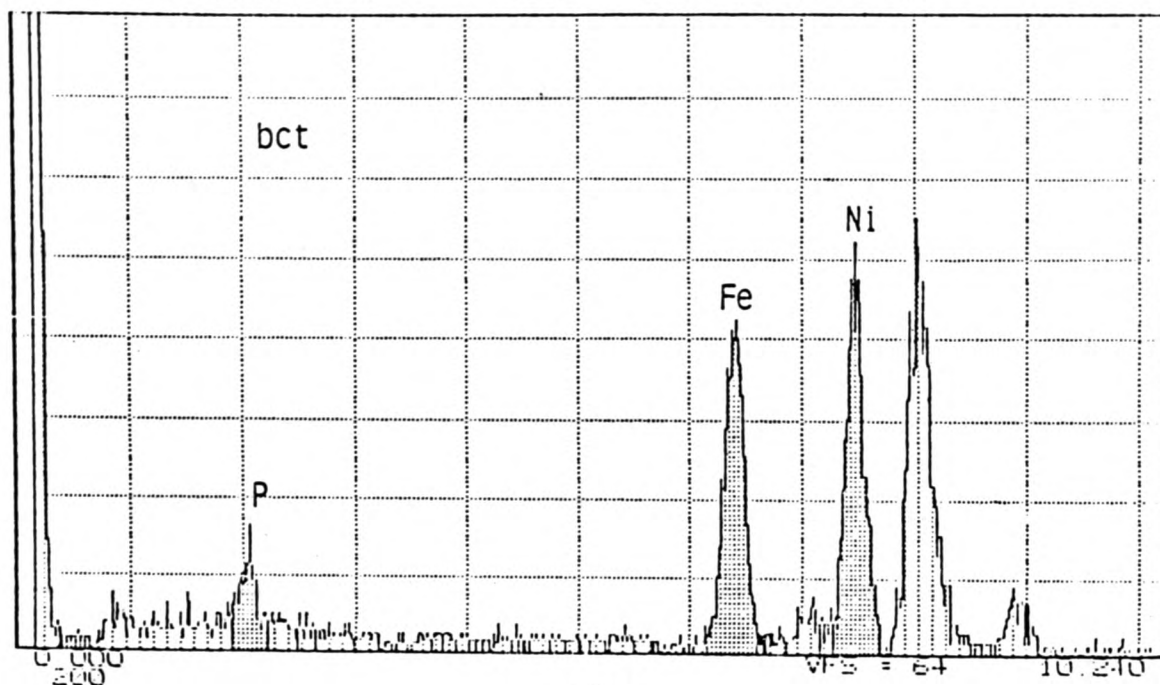
Fig.4-14: TEM micrographs of pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ foils oxidised at 300°C for 240h; (a) bright field image, (b) SAED pattern.

small oxide grains instead. The d spacings calculated from the diffraction patterns of the dark stripes areas were confirmed to be those of $\alpha\text{-Fe}_2\text{O}_3$, as given in Table 4-2, in agreement with the results obtained from diffraction patterns from oxide layers removed from the amorphous alloy.

The pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ thin foils produced very different results from the amorphous thin foils, as can be seen by comparing Figs.4-11 and 4-12 with Figs.4-13 and 4-14. According to Watanabe and Scott (15), amorphous Fe₄₀Ni₄₀P₁₄B₆ crystallises by a eutectic mechanism to form an alternating two-phase lamellar structure of fcc (Fe,Ni) austenite and bct (Fe,Ni)₃(PB). In the present experiments, the lamellar structure coarsened because of the higher annealing temperature and longer annealing time which were used during pre-crystallisation (500 C, 30min). Fig.4-13(a) shows the typical resulting two-phase structure of pre-crystallised Fe₄₀Ni₄₀P₁₄B₆, which consisted of small particles of the fcc (Fe,Ni) phase, about 10-30nm in size, embedded in a matrix of bct (Fe,Ni)₃(PB). Typical EDS of the two phases are shown in Fig.4-15, and the resulting composition analyses are given in Table 4-5. The discrete fcc (Fe,Ni) phase particles contained a high concentration of Fe, while the matrix phase was depleted in Fe and contained a high concentration of Ni and P.

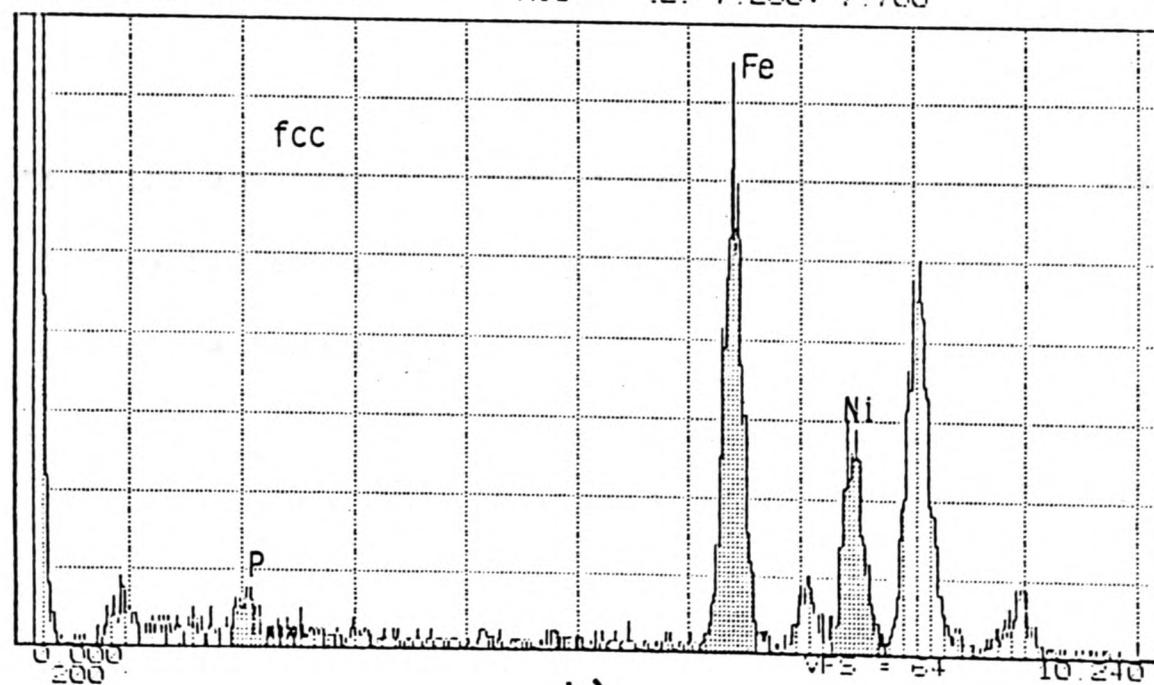
As shown in Figs.4-13(a) and 4-14(a), very little change was detected in the TEM micrographs from pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ thin foils, even after 240h oxidation at 300 C, when compared with the same sample before oxidation. However, the electron diffraction patterns from pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ after 240h oxidation at 300 C contained three continuous rings which did not exist before oxidation(Fig.4-14(b)). These extra three rings corresponded very well to the three strongest lines of NiO as can be seen in Table 4-6, which indicated that a layer of very

III-5500 CHEMICAL CRYSTALLOGRAPHY OXFORD TUE 28-OCT-86 11:20
 Cursor: 0.000keV = 0 ROI (2) 7.280: 7.700



a)

III-5500 CHEMICAL CRYSTALLOGRAPHY OXFORD TUE 28-OCT-86 11:35
 Cursor: 0.000keV = 0 ROI (2) 7.280: 7.700



b)

Fig.4-15: Typical EDS spectra from the two phases in pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ foils; (a) from bct phase, (b) from fcc phase.

Table 4-5

Microanalysis of the two phases in crystallized $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ * (at%)

phase	Fe	Ni	P
bcc phase	37 - 40	45 - 48	15 - 18
fcc phase	55 - 62	29 - 36	9 - 10

*8 point analyses for each phase; the results for the small fcc particles may have been affected by the matrix; boron cannot be measured.

Table 4-6

The calculated d spacings from the three rings in Fig.4-14(b)

d (Å)	d_{NiO} (22-1189)	relative intensity	(hkl)
2.42	2.412	60%	101
2.08	2.088	100%	012
1.47	1.477	70%	110, 104

thin Ni oxide (grain size < 10nm) had formed on the surface of pre-crystallised Fe₄₀Ni₄₀P₁₄B₆.

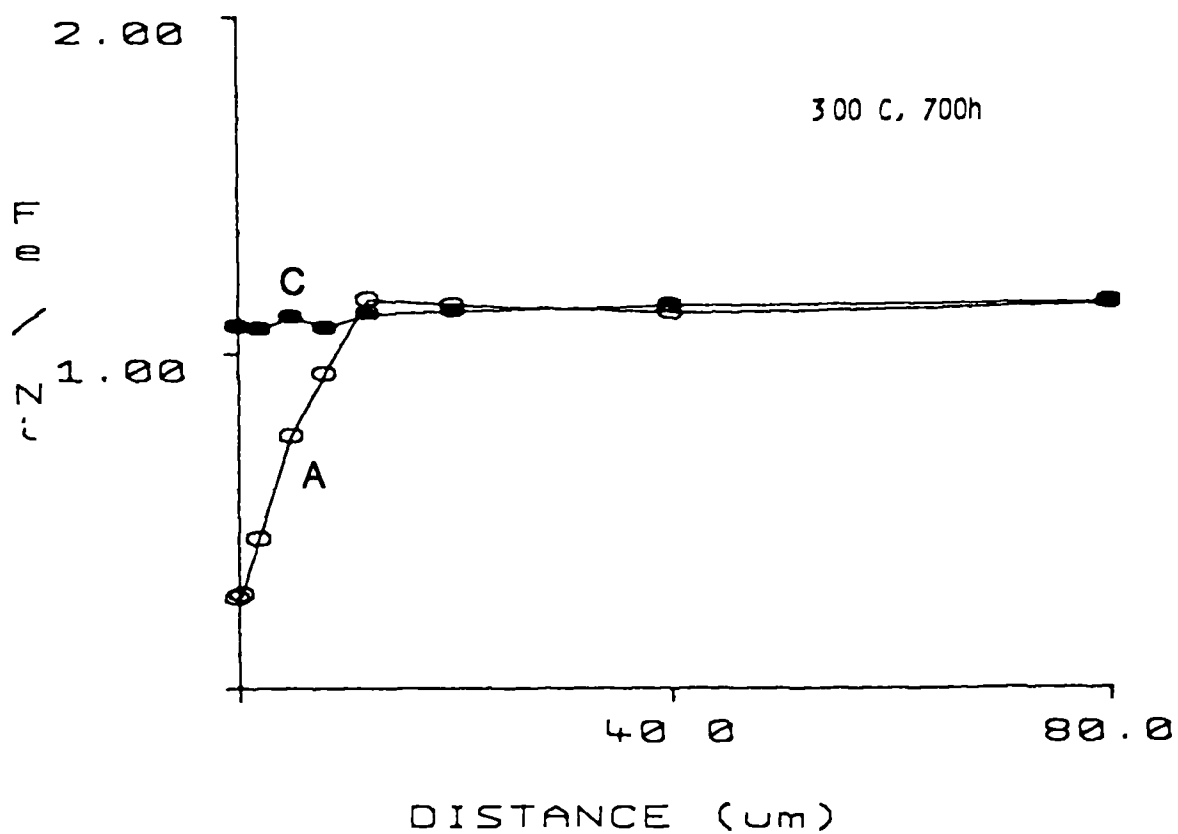
4.2.5 Electron probe microanalysis of taper cross section samples

Wavelength dispersive probe microanalysis (WDS) was used to measure Fe concentration profiles through the alloy/oxide interface. Typical results are shown in Figs.4-16 (a) and (b) for taper cross section samples of amorphous and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ after 700h oxidation at 300 C and for amorphous Fe₄₀Ni₄₀P₁₄B₆ after 80h oxidation at 350 C respectively. As shown in Fig.4-16(a), the amorphous alloy was depleted in Fe over a region of approx. 15µm from the alloy/oxide interface. However, there was no equivalent depletion of Fe in the case of pre-crystallised Fe₄₀Ni₄₀P₁₄B₆, which implied that different diffusion mechanisms were operating. A greater thickness of Fe depletion was detected near the interface of amorphous Fe₄₀Ni₄₀P₁₄B₆ after 80h oxidation at 350 C, as shown in Fig.4-16(b).

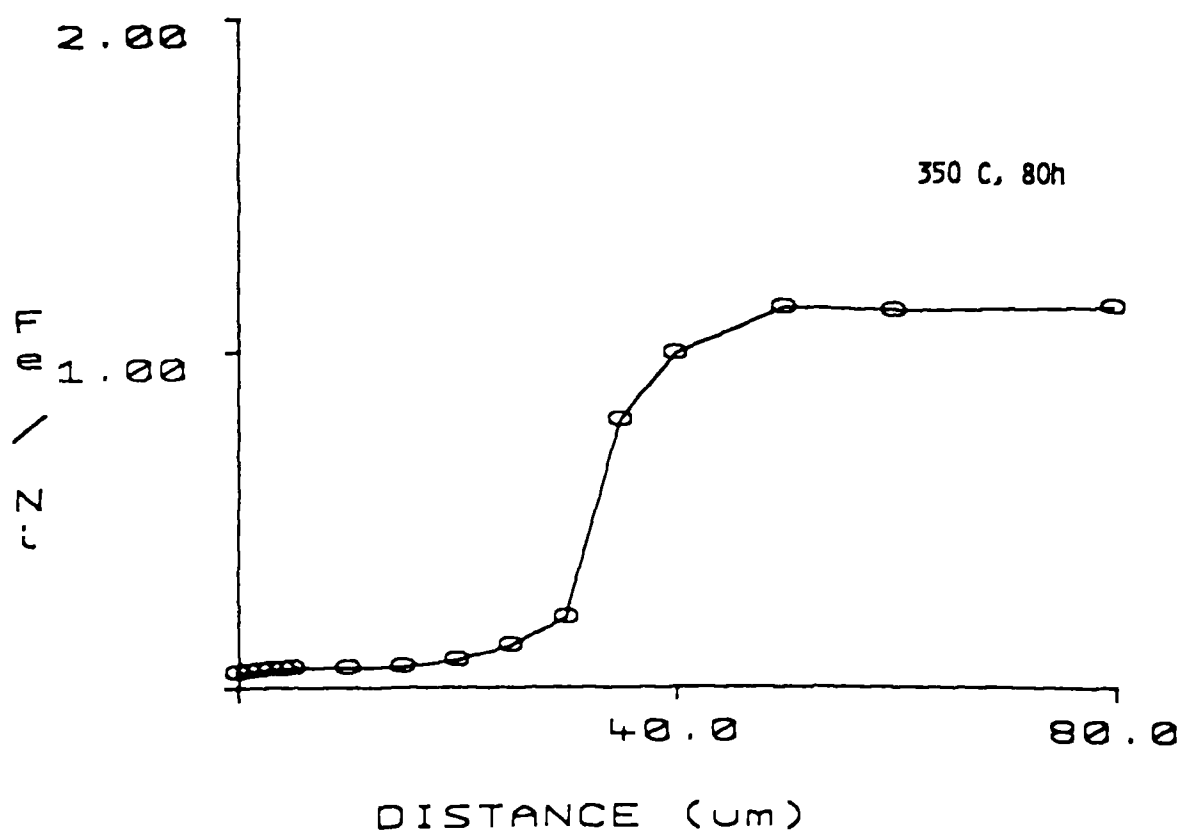
4.3 Discussion

4.3.1. Oxidation kinetics

Figs.4-1 and 4-2 shows that the oxidation behaviour of Fe₄₀Ni₄₀P₁₄B₆ is strongly affected by structural changes in the alloy. At relatively low temperatures in the range 200-300 C, the oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ obeys a parabolic rate law, since during oxidation annealing at these temperatures the alloy remains amorphous. At relatively high temperatures such as 450 and 500 C, crystallisation takes place almost immediately at the beginning of the oxidation anneal, and the oxidation reaction again obeys a parabolic rate law. However, there are significant variations in oxidation kinetics during annealing at intermediate temperatures such as 350 and 400 C. At these intermediate temperatures,



a)



b)

Fig.4-16: Typical profiles of the ratio of Fe to Ni measured by WDS in the taper cross section samples; (a) amorphous Fe₄₀Ni₄₀P₁₄B₆ (A) and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ (C) after 700h oxidation at 300°C, (b) amorphous Fe₄₀Ni₄₀P₁₄B₆ after 80h oxidation at 350°C. The thickness z shown here is about 1/20 of the true thickness.

crystallisation takes place relatively slowly, after the amorphous alloy has already oxidised to a certain extent, and the crystallisation process clearly interferes with the otherwise steady growth of the oxide scale. The three stages of oxidation at 400 C can be explained as follows, as a consequence of simultaneous crystallisation. The first stage of oxidation up to 0.1h of annealing represents the oxidation behaviour of amorphous Fe₄₀Ni₄₀P₁₄B₆, similar to that found at the lower temperatures of 200-300 C. The third stage represents oxidation of crystallised Fe₄₀Ni₄₀P₁₄B₆, similar to that found at the higher temperatures of 450 and 500 C. The second intermediate stage is a period of transition. The alloy has already crystallised but the oxide is characteristic of that formed on the amorphous alloy. For reasons discussed further below, this causes the oxidation rate to decrease sharply and remain at a very low level for a period of oxidation time. The oxidation kinetics of amorphous Fe₄₀Ni₄₀P₁₄B₆ over the whole temperature range of 200-500 C can be explained on the same basis as that just outlined for oxidation at 400 C. This is shown schematically in Fig.4-17. At all temperatures, there are the same three stages in oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆, but there is only a limited region of accessible experimental results, as shown by the rectangular box in Fig.4-17. The three oxidation stages are only seen clearly at 400 C.

The parabolic rate law found in fully amorphous and fully crystalline Fe₄₀Ni₄₀P₁₄B₆ suggests that the oxidation reaction is controlled by the diffusion of ions brought about by a concentration gradient (44,45). As discussed in Chapter 2, for a thermally activated process like diffusion, the parabolic rate constant K is given by an Arrhenius equation:

$$K = K_0 \exp(-Q/RT) \quad (4-2)$$

Fig.4-18 shows $\ln K$ versus inverse T for the oxidation of Fe₄₀Ni₄₀P₁₄B₆.

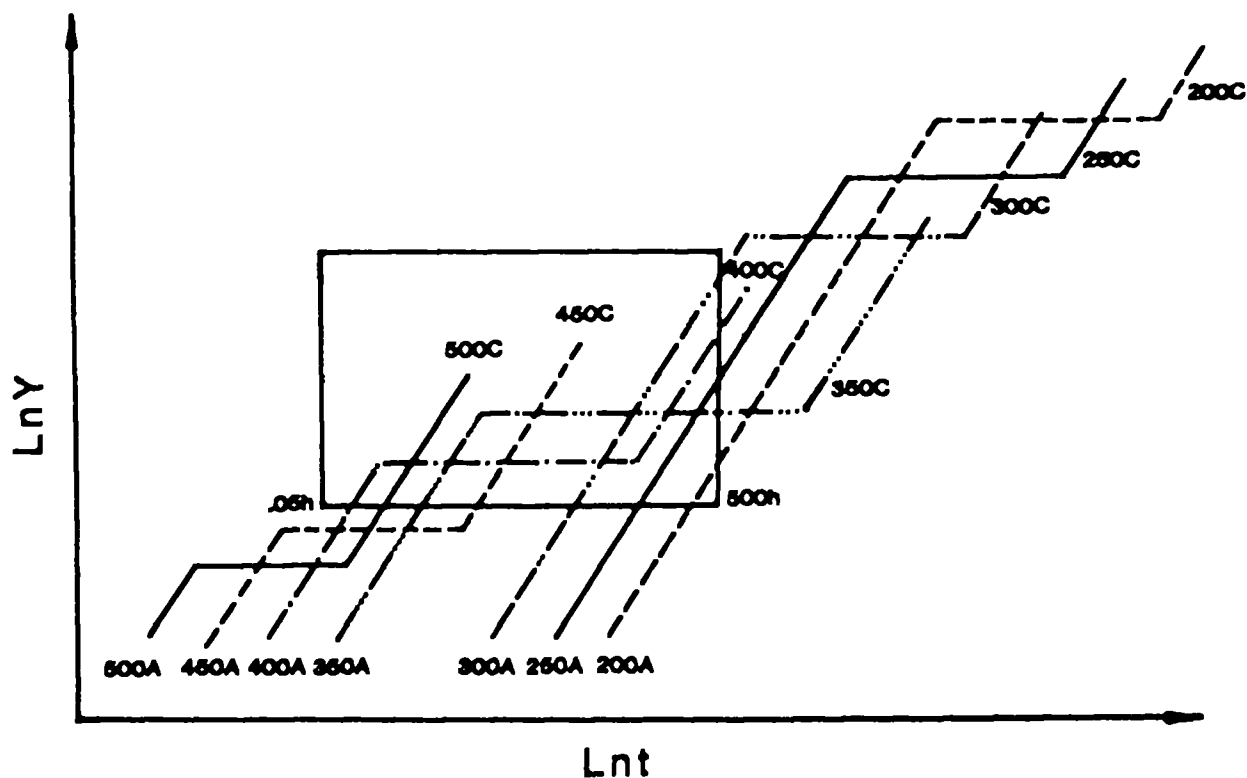


Fig.4-17: Schematic $\ln Y - \ln t$ diagram for the general oxidation kinetics of Fe40Ni40P14B6 over the temperature range of 200-500°C. The rectangular box shows the accessible area for obtaining experimental results.

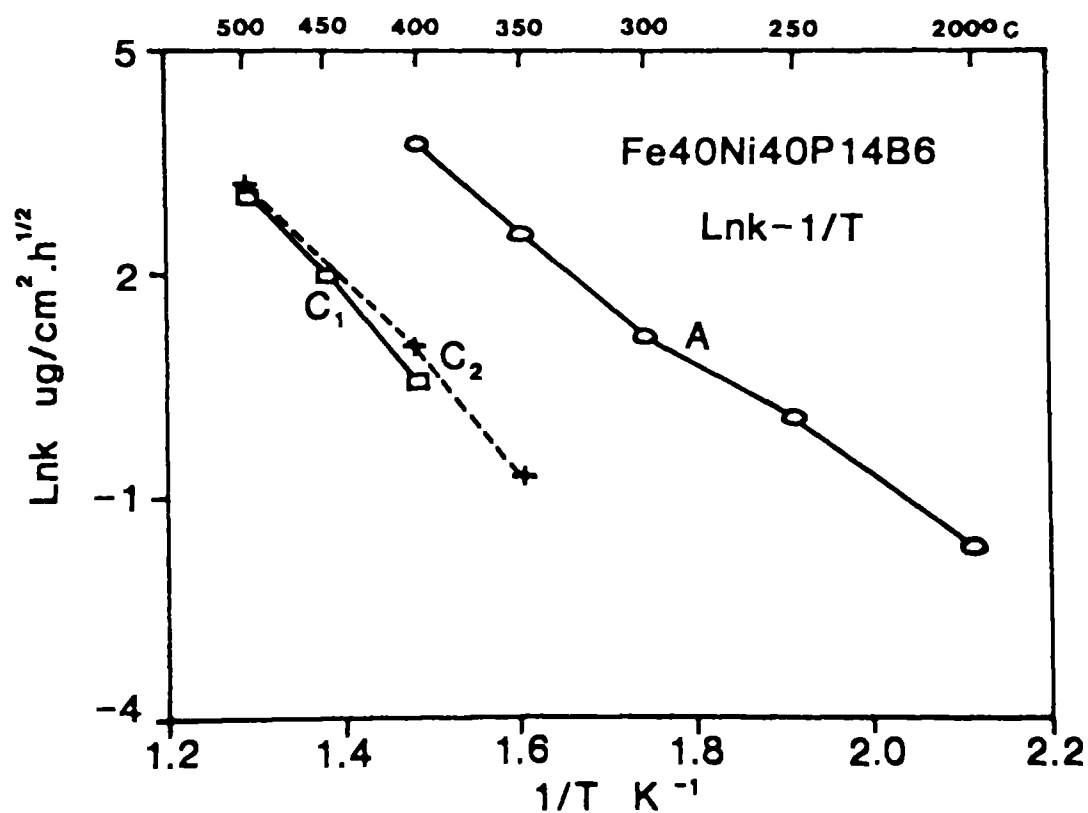


Fig.4-18: The Arrhenius variation of $\ln$ parabolic rate constant versus inverse absolute temperature ($\ln K - 1/T$) for amorphous Fe40Ni40P14B6 (A), oxidation-crystallised Fe40Ni40P14B6 (C1), and pre-crystallised Fe40Ni40P14B6 (C2).

Three sets of data are included in Fig.4-18. Curve A represents the variation of $\ln K - 1/T$ for amorphous Fe₄₀Ni₄₀P₁₄B₆ using the full range of data in Fig.4-1 at 200-300 C but taking only the first stage of oxidation mass gain at 350 and 400 C. Curve C1 represents the $\ln K - 1/T$ variation for amorphous Fe₄₀Ni₄₀P₁₄B₆ specimens which crystallised during oxidation annealing, using the full range of data in Fig.4-1 at 450 and 500 C, but taking only the last stage of oxidation at 350 and 400 C. Curve C2 represents the $\ln K - 1/T$ variation for the specimens of pre-crystallised Fe₄₀Ni₄₀P₁₄B₆. As shown in Fig.4-18, C1 and C2 give very similar results, confirming the interpretation given above of the amorphous Fe₄₀Ni₄₀P₁₄B₆ oxidation behaviour at 450 and 500 C and in the third stage at 400 C.

Activation energies for the three curves in Fig.4-18 were calculated by using linear regression analysis. The results are given in Table 4-7, together with other relevant diffusion data from the literature. As shown in Table 4-7, the measured activation energy for oxidation of crystallised Fe₄₀Ni₄₀P₁₄B₆ is close to the activation energies for diffusion of ions in Fe₃O₄ and Ni ions in NiO. This is in good agreement with the parabolic kinetics of oxidation of crystallised Fe₄₀Ni₄₀P₁₄B₆ shown in Figs.4-1 and 4-3, and suggests that the oxidation reaction rate controlled by diffusion of metal ions (Fe and Ni) through the oxide layer (Fe₃O₄ and NiO).

The results are quite different for oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆, which has an oxide layer consisting mainly of α -Fe₂O₃. As shown in Table 4-7, the measured activation energy for oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ is much smaller than activation energy for diffusion of Fe ions in Fe₂O₃. This can be explained as follows. Whisker-like oxide growth takes place when a fast diffusion mechanism can operate in some of the oxide grains to supply the rapid advance of the whisker tip (46-48). Although the exact mechanism of this type of fast

Table 4-7

Activation energies for oxidation of amorphous and crystallized $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ together with other relevant diffusion data obtained from the literature (49,50,52,53)

Diffusion ions	Diffusion matrix	Temperature range °C	Frequency Factor ($\text{m}^2 \text{s}^{-1}$)	Activation energy (kJ/mol)	Correlation Coefficient	Source
Fe	$\alpha\text{-Fe}_2\text{O}_3$	200-400		142	0.997	Curve A
Fe+Ni	$\text{Fe}_3\text{O}_4, \text{NiO},$ $\text{Fe}_2\text{O}_3, \text{NiFe}_2\text{O}_4,$	400-500		226	0.999	Curve C ₁
Fe+Ni	...	350-500		209	0.997	Curve C ₂
Fe	$\text{FeO}_{1.087}$	690-1010	1.4×10^{-6}	126.4		
	Fe_3O_4	750-1000	5.2×10^{-4}	230		ref.(52)
	Fe_2O_3	930-1270	4.0	469		
	NiFe_2O_4	850-1190	5.2×10^{-3}	298		
Fe	Fe_3O_4			190		ref.(53)
	Fe_2O_3			430±40		
Ni	NiO	740-1400	1.7×10^{-6}	234		ref.(52)
Fe	$\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	268-344	1.0×10^{-3}	192		ref.(49, 50)

diffusion is not yet clear (see section 2.2.3), the existence of fast diffusion paths means that the diffusion of Fe ions through the oxide scale is no longer the oxidation reaction rate controlling process. In the present case, the reaction is limited by the rate of supply of Fe ions into the oxide at the oxide/metal interface. An Fe depletion layer is built up in the underlying amorphous alloy, as shown in Fig.4-16, and the parabolic reaction rate constant has an activation energy as shown in Table 4-7 near to that measured previously for diffusion of Fe in amorphous Fe₄₀Ni₄₀P₁₄B₆ (49,50). The diffusion coefficient D can be calculated approximately from the depletion layer thickness z using

$$z = 2(Dt)^{1/2} \quad (4-3)$$

From Fig.16(a), $z = 0.5\mu\text{m}$ for $t = 2.5 \times 10^6\text{s}$ at 300 C, and eqn.(4-3) gives $D = 2.5 \times 10^{-20}\text{m}^2/\text{s}$. This agrees moderately with the value of $3 \times 10^{-21}\text{m}^2/\text{s}$ calculated from previous radiotracer measurements of activation energy and frequency factor for diffusion of Fe in amorphous Fe₄₀Ni₄₀P₁₄B₆ (49,50), as also listed in Table 4-7.

4.3.2 Oxide growth mechanism

Oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ take place by rapid growth of $\alpha\text{-Fe}_2\text{O}_3$ whiskers. However, the crystalline Fe₄₀Ni₄₀P₁₄B₆ oxidises much more slowly by forming a compact microcrystalline multiphase oxide layer of Fe₃O₄, NiO, Fe₂O₃ and NiFe₂O₄. It seems difficult to explain this strong effect of alloy structure, when oxidation is a chemical reaction and the amorphous and crystalline alloys have identical chemical composition. However, an explanation for the strong effect of microstructure on oxide growth can be given as follows.

At the very early stages of oxidation, a thin oxide layer forms on the surface of most metals and alloys even at room temperature because of the free energy decrease when metal becomes oxide (51). After a short period

of oxidation, a continuous layer of oxide is built up and the oxidation reaction reaches a stage in which the oxide growth depends upon mass transport through the oxide layer. If some sort of fast transport paths exist in the oxide film, the rate controlling process of oxide growth will be diffusion in the underlying metal (or rate of gas supply), as in the case of amorphous Fe₄₀Ni₄₀P₁₄B₆. Amorphous Fe₄₀Ni₄₀P₁₄B₆ has a very uniform chemical composition which can supply a reasonable concentration of Fe continuously to feed the rapid growth of the Fe₂O₃ whiskers. Thus, the whisker-like oxide grows on the surface, and builds up to form a thick scale of α-Fe₂O₃. Therefore, amorphous Fe₄₀Ni₄₀P₁₄B₆ has poor oxidation resistance and a unusual high oxidation mass gain.

On the other hand, crystalline Fe₄₀Ni₄₀P₁₄B₆ consists of a two-phase structure with discrete particles of fcc(Fe,Ni) austenite embedded in a matrix of bct (Fe,Ni)₃(PB) phase. The fcc phase contains a high concentration of Fe, while the matrix is rich in Ni and dilute in Fe, as shown in Table 4-5. Although a layer of small grains of mixed oxides NiO, Fe₂O₃ and Fe₃O₄ was formed on the surface at the early stage, the fast growing mechanism of whisker-like oxide cannot apply because it requires a continuous supply of Fe from the matrix. As indicated above, the matrix bct phase is dilute in Fe. The fcc phase does contain high concentration of Fe, but it is in the form of discrete particles with a size from 10 to 30nm. Small grains of Fe oxides (Fe₂O₃ and Fe₃O₄) grow on the fcc phase, but once again, no fast growing Fe oxide can continuously develop because the discrete fcc phase particles become rapidly depleted in Fe. Eventually, the small NiO and other oxide grains make a compact oxide layer which grows relatively slowly and can protect the metal effectively from further oxidation. Thus, crystalline Fe₄₀Ni₄₀P₁₄B₆ has a much lower oxidation reaction rate than the amorphous alloy. A similar effect also is

observed near the edges of amorphous Fe₄₀Ni₄₀P₁₄B₆ thin foils, where the thin metal cannot supply Fe continuously. As a result, no whisker-like oxide structure is found at the edges of TEM foils even after 240h oxidation at 300 C, while whisker-like oxide is fully developed on the thick foil areas, as shown in Fig.4-12(a).

During oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ at 350 and 400 C, there is a transition period of exceptionally slow oxidation. The mechanism of oxide growth in this transition period must be quite complicated. A thick layer of Fe₂O₃ has already developed on the amorphous samples during the first stage of oxidation, and the amorphous alloy surface region adjacent to the oxide layer is depleted in Fe, as shown in Fig.4-16(b). When crystallisation takes place in this depleted region, the crystallisation reaction as well as the resulting structure is likely to be different from the unoxidised alloy, with little or no formation of fcc (Fe,Ni) phase. This not only inhibits the fast growing Fe oxide but also reduces further the total growth rate of oxide. Because the matrix has a very high Ni/Fe ratio, the oxidation reaction must be dominated by the formation of NiO, thus the oxidation rate becomes exceptionally low. Fig.4-19 summarises schematically the mechanisms of different types of oxide growth discussed above.

4.4 Conclusions

From the present investigation into the oxidation behaviour of amorphous and crystalline Fe₄₀Ni₄₀P₁₄B₆, the following conclusions can be drawn:

1. Oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ in air obeys a parabolic rate law over the temperature range 200-400 C as long as no crystallisation takes place. The parabolic rate constant for amorphous Fe₄₀Ni₄₀P₁₄B₆ increases with the oxidation temperature according to an Arrhenius law,

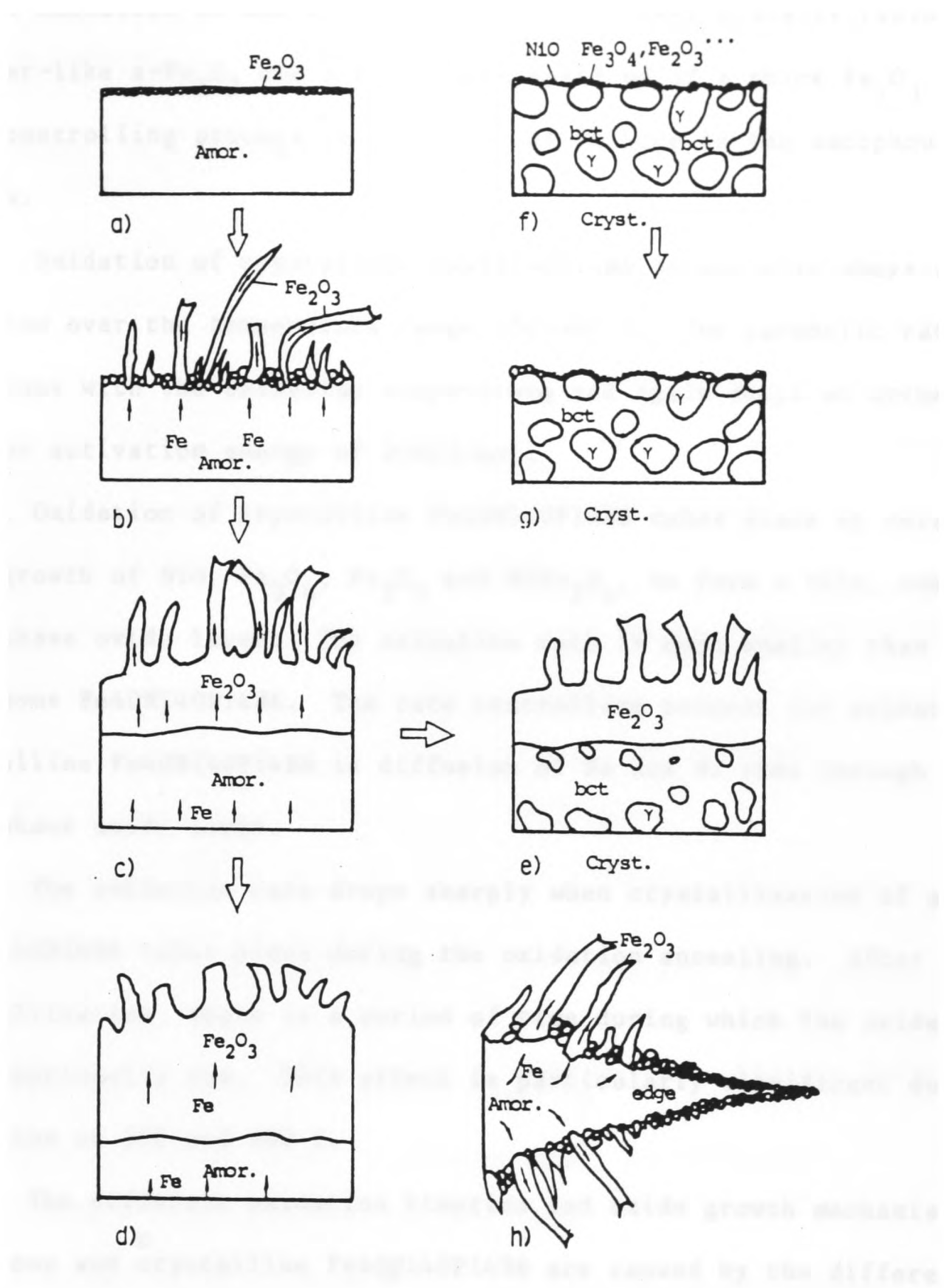


Fig.4-19: Schematic oxide growth on amorphous Fe₄₀Ni₄₀P₁₄B₆ (a → b → c → d), oxidation-crystallised Fe₄₀Ni₄₀P₁₄B₆ (a → b → c → e) and pre-crystallised Fe₄₀Ni₄₀P₁₄B₆ (f → g); (h) shows the oxide growth near the edges of amorphous Fe₄₀Ni₄₀P₁₄B₆ thin foil specimens.

with an activation energy of 142kJ/mol.

2. Oxidation of amorphous Fe₄₀Ni₄₀P₁₄B₆ takes place by rapid growth of whisker-like α -Fe₂O₃ and a subsequent build up of a thick Fe₂O₃ layer. The rate controlling process is diffusion of Fe ions in the amorphous alloy matrix.

3. Oxidation of crystalline Fe₄₀Ni₄₀P₁₄B₆ in air also obeys a parabolic rate law over the temperature range 350-500 C. The parabolic rate constant increases with the oxidation temperature and again obeys an Arrhenius law, with an activation energy of 209kJ/mol.

4. Oxidation of crystalline Fe₄₀Ni₄₀P₁₄B₆ takes place by relatively slow growth of NiO, Fe₃O₄, Fe₂O₃ and NiFe₂O₄, to form a thin, compact multiphase oxide layer. The oxidation rate is much smaller than that of amorphous Fe₄₀Ni₄₀P₁₄B₆. The rate controlling process for oxidation of crystalline Fe₄₀Ni₄₀P₁₄B₆ is diffusion of Fe and Ni ions through the multiphase oxide layer.

5. The oxidation rate drops sharply when crystallisation of amorphous Fe₄₀Ni₄₀P₁₄B₆ takes place during the oxidation annealing. After crystallisation, there is a period of time during which the oxidation rate is exceptionally low. This effect is particularly significant during oxidation at 350 and 400 C.

6. The different oxidation kinetics and oxide growth mechanisms for amorphous and crystalline Fe₄₀Ni₄₀P₁₄B₆ are caused by the different alloy microstructures. The two-phase microstructure of crystalline Fe₄₀Ni₄₀P₁₄B₆ consists of discrete particles of Fe-enriched fcc (Fe,Ni) austenite embedded in a matrix of Ni-enriched bct (Fe,Ni)₃(PB). This microstructure prevents the rapid formation of whisker-like α -Fe₂O₃ and the subsequent build up of a thick oxide layer of Fe₂O₃ which is formed on amorphous Fe₄₀Ni₄₀P₁₄B₆.

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Chapter 5 The Oxidation Behaviour of Amorphous and Crystalline Fe₇₈Si₉B₁₃

5.1 Introduction

Fe₇₈Si₉B₁₃ (METGLAS 2605 S) is one of the most important soft ferromagnetic amorphous alloys which have been with improved magnetic properties and thermal stability (1,2). Compared with a standard transformer core material, oriented Fe-3.25wt.%Si silicon steel, amorphous Fe₇₈Si₉B₁₃ has lower exciting volt amperes by a factor of five (3), lower coercivity H_c by a factor of four, higher electrical resistivity by a factor of three, and lower core loss by a factor of five (4,5). It also possesses reasonably good mechanical properties, hardness $H_v = 910$, fracture strength $= 340 \text{ kg/mm}^2$ and Young's modulus $E = 1.2 \times 10^4 \text{ kg/mm}^2$ (6). Because of the excellent soft magnetic properties, and because it does not contain expensive elements like Co or Ni, amorphous Fe₇₈Si₉B₁₃ has already been used commercially as a core material in distribution and other transformers in the US, Japan and some other countries, resulting in considerable energy savings (1,4,5,7).

Because of its great technological importance, amorphous Fe₇₈Si₉B₁₃ has also been investigated in considerable detail. Fundamental research studies of amorphous Fe₇₈Si₉B₁₃ have covered glass formation ability (8), amorphous structure and structural relaxation (9), viscosity (10), ion diffusion (11,12), and the crystallisation kinetics and crystal structure (13-20). Technological research studies of amorphous Fe₇₈Si₉B₁₃ have concentrated mainly on magnetic properties (1,3,21-25) and applications as a soft ferromagnetic material in transformers and various other electrical and electronic devices (1,2,4,5,7,26). Other research on amorphous Fe₇₈Si₉B₁₃ includes thermal expansion behaviour (27) and mechanical properties (28-30).

In applications such as distribution and other transformers, amorphous Fe₇₈Si₉B₁₃ ferromagnetic cores have to work at moderate temperatures for very long time. The two potential causes of degradation of amorphous alloys under thermal exposure during manufacture and in service are crystallisation and oxidation. There have been relatively extensive investigations of the crystallisation behaviour of amorphous Fe₇₈Si₉B₁₃ (13-20), however surprisingly little attention has been given to the oxidation behaviour of amorphous Fe₇₈Si₉B₁₃ ((31), also see section 2.6.2), which must be understood to prevent this type of degradation. Therefore the aims of the investigation of the oxidation behaviour of amorphous Fe₇₈Si₉B₁₃ are:

- (a) oxidation rate and oxidation kinetics: Can amorphous Fe₇₈Si₉B₁₃ withstand oxidation at moderate temperatures for very long time?
- (b) oxide morphology, structure and composition: Does Si have beneficial effect on the oxidation resistance like in some conventional Si alloys?
- (c) the effect of alloy structure on the oxidation behaviour: Do the amorphous and crystalline Fe₇₈Si₉B₁₃ alloys have different oxidation behaviour?
- (d) the effect of surface oxidation on the magnetic properties of amorphous Fe₇₈Si₉B₁₃.

5.2 Experimental results

5.2.1 Oxidation kinetics

Fig.5-1 shows the measured mass gains of amorphous Fe₇₈Si₉B₁₃ specimens as a function of (a) the oxidation time and (b) the square root of oxidation time over a range of oxidation temperatures. The mass gains were found to agree reasonably well with a linear variation with the square root of oxidation time at temperatures of 300, 350 and 400 C over the whole 500h

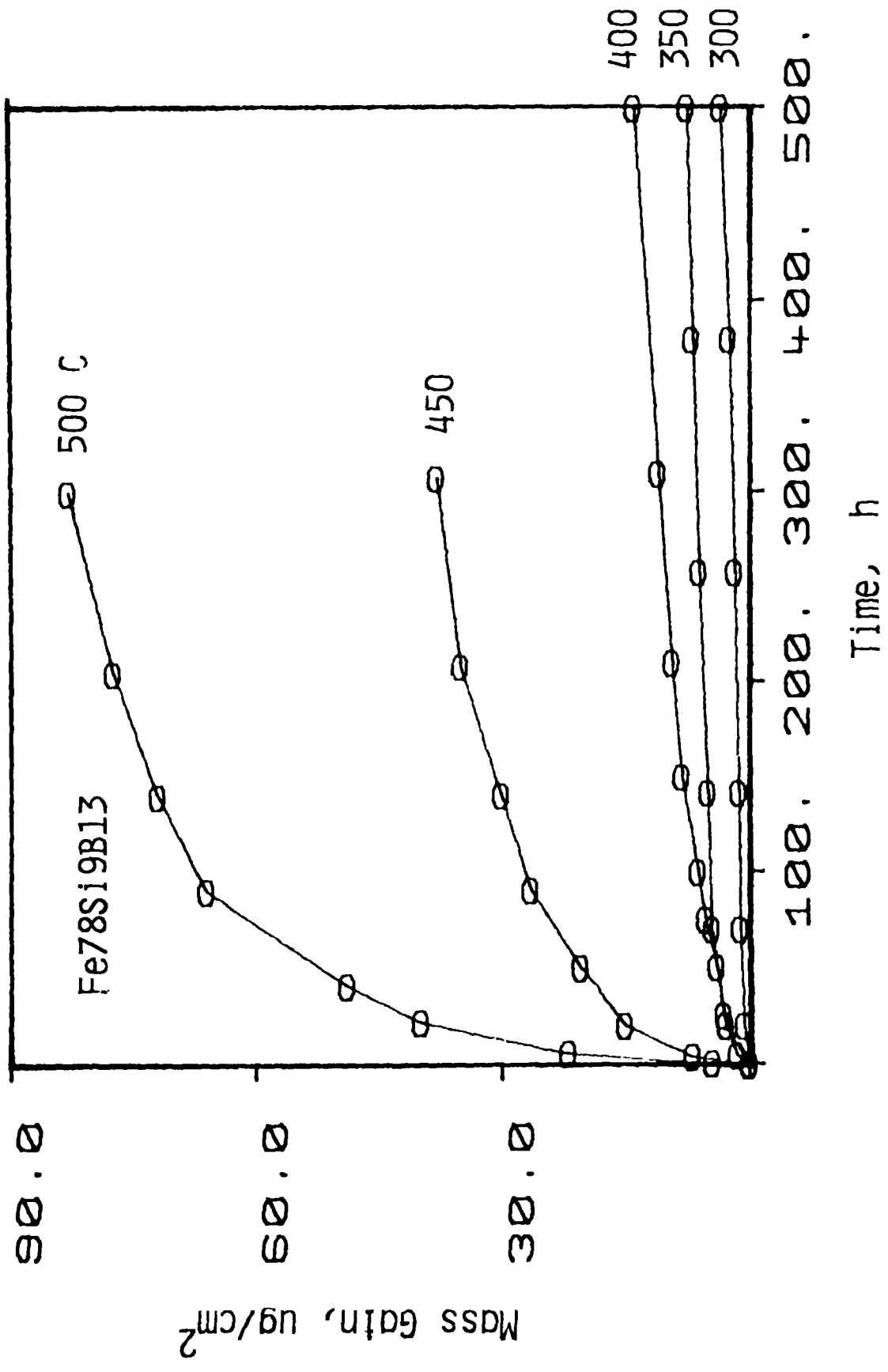


Fig.5-1(a)

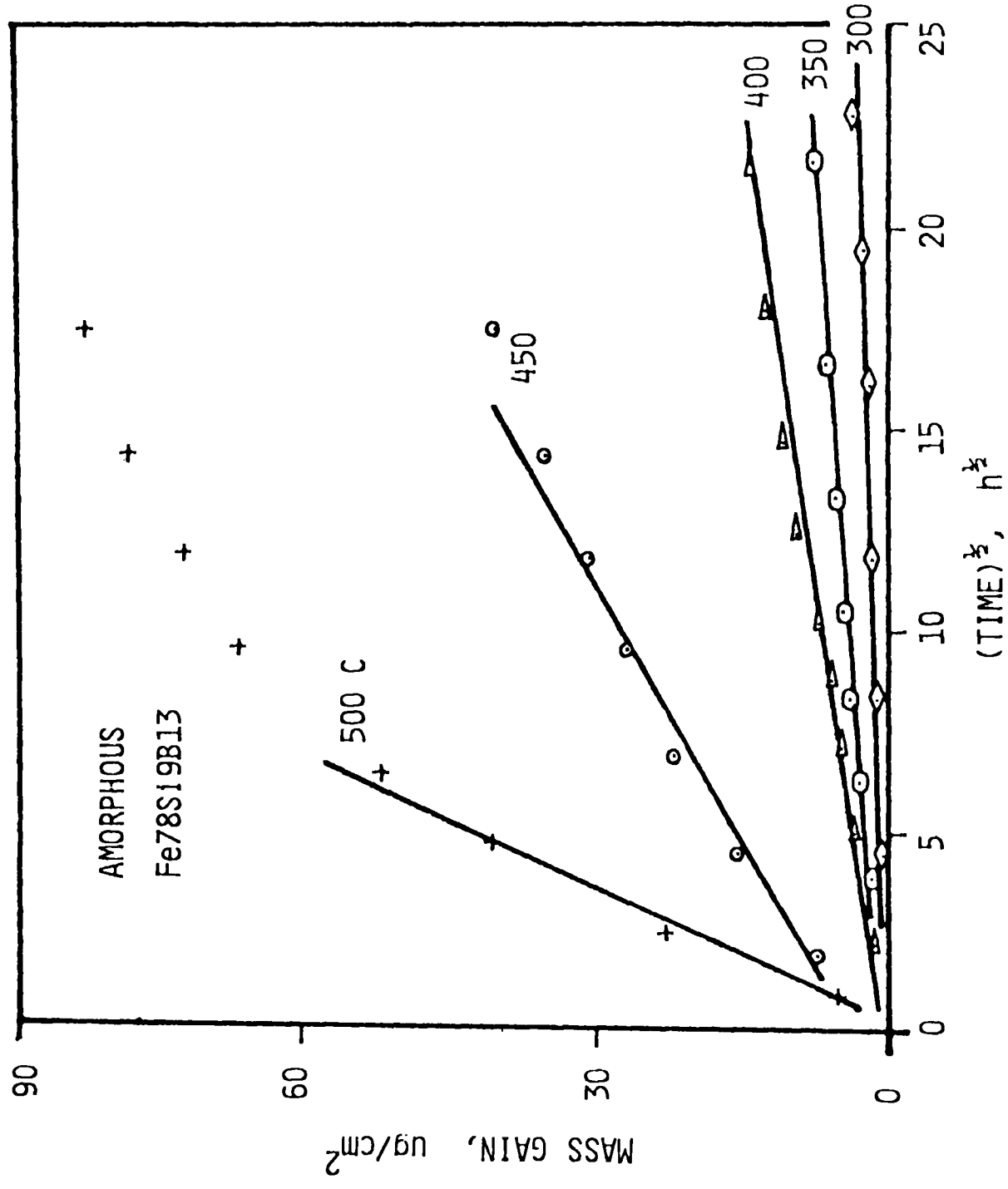


Fig.5-1 Mass gain Y versus (a) oxidation time t, and (b) square root of oxidation time t for amorphous Fe78Si9B13 over the temperature range 300-500°C in air.

period of oxidation testing, at 450 C for the initial 300h period of oxidation testing, and at 500 C for the initial 50h period of oxidation testing. This showed that for these time and temperatures the oxidation reaction obeyed a parabolic rate law:

$$y^2 = Kt$$

$$y = K't^{1/2} \quad (5-1)$$

At 450 and 500 C, the oxidation rate decreased from parabolic at longer times. As shown in Table 5-1, the parabolic rate constant K' for amorphous Fe₇₈Si₉B₁₃ increased slowly from 0.10 to $0.64 \times 10^{-2} \text{ gm}^{-2} \text{ h}^{-1/2}$ as the temperature increased from 300 to 400 C, and then increased more sharply to 1.99 and then $8.10 \times 10^{-2} \text{ gm}^{-2} \text{ h}^{-1/2}$ at temperatures of 450 and 500 C respectively. This suggested^t that the oxidation reaction of amorphous Fe₇₈Si₉B₁₃ underwent a change in mechanism as the temperature range increased from 400 to 450 C.

Like amorphous Fe₄₀Ni₄₀Pl₄B₆ described in Chapter 4, the observed change in oxidation behaviour for amorphous Fe₇₈Si₉B₁₃ was again found to correspond to the onset of crystallisation during oxidation annealing. Table 5-2 and Fig.5-2 show DSC results for isothermal annealing of as-supplied amorphous Fe₇₈Si₉B₁₃ samples over the temperature range 480-530 C, with additional data for 450 C obtained by isothermal annealing in a tube furnace. Figs.5-3(a) and 5-3(b) show DSC results for continuous heating of amorphous Fe₇₈Si₉B₁₃ samples after being oxidised at 450 and 400 C for a various periods of time. As shown in Table 5-2, and Figs.5-2 and 5-3, crystallisation of amorphous Fe₇₈Si₉B₁₃ took place between 0.3-2.0h at 500 C, 20-90h at 450 C, and had not begun after 500h oxidation at 400 C. Thus, the amorphous Fe₇₈Si₉B₁₃ crystallised during oxidation annealing at 450 and 500 C, leading to an increase in parabolic reaction rate constant.

Comparison oxidation tests were performed on amorphous and

Table 5-1

Best fit linear slopes, intercepts and correlation coefficients
for the oxidation kinetic curves of amorphous
and pre-crystallised Fe₇₈Si₉B₁₃, and
industrial crystalline Fe₉₄Si₆

Oxidation Temperature	Sample & Structure	Oxidation Time	Slope K $10^{-2} \text{ g/m}^2 \text{ h}^{1/2}$	Intercept 10^{-2} g/m^2	Correlation Coefficient
300 C	amorFeSiB pre-cryst	0-540h	0.10	0.7	0.962
		0-540h	0.36	-0.3	0.984
350 C	amorFeSiB pre-cryst	0-500h	0.26	2.0	0.988
		0-500h	0.77	-1.1	0.995
350 C	Fe ₉₄ Si ₆	0-500h	1.38	-0.8	0.997
400 C	amorFeSiB pre-cryst	0-500h	0.64	0.5	0.991
		0-500h	1.35	1.0	0.979
400 C	Fe ₉₄ Si ₆	0-44h	2.02	0.0	0.999
		44-500h	8.70	-39.0	0.999
450 C	amorFeSiB* pre-cryst	0-300h	1.99	2.1	0.990
		0-300h	2.35	3.4	0.992
500 C	amorFeSiB*	0-50h	8.10	-3.0	0.987

* Crystallisation has taken place during oxidation annealing

Table 5-2

Start and finish times for crystallisation of amorphous $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ measured by isothermal heating in a differential scanning calorimeter

Heating Temperature (°C)	Start time (h)	Finish time (h)
530	0.020	0.243
520	0.052	0.477
510	0.160	0.933
500	0.367	1.967
490	0.883	4.200
480	2.050	8.567
450	20	90

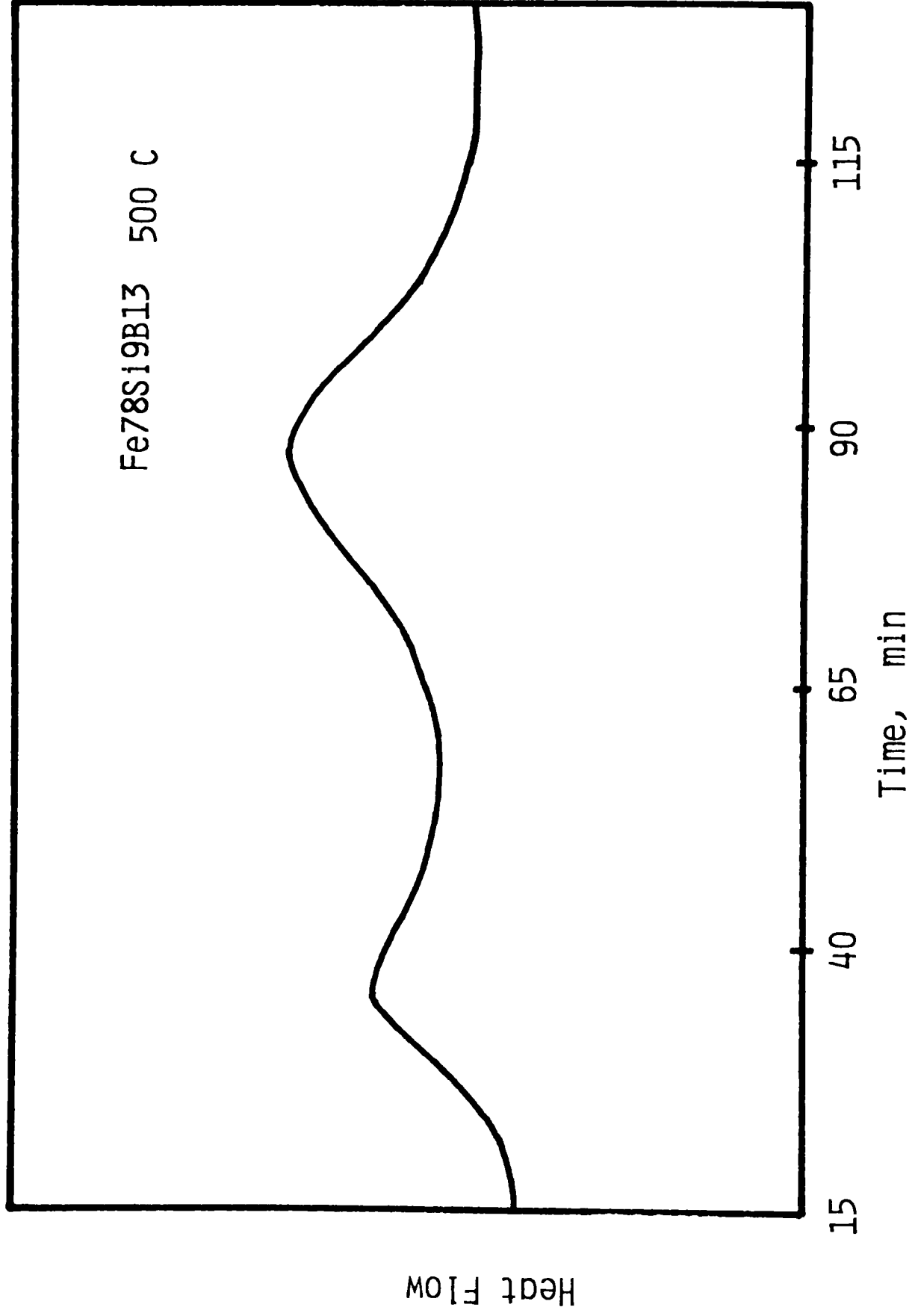


Fig.5-2 (a) Isothermal heating DSC crystallisation curve at 500°C for amorphous Fe₇₈Si₉B₁₃. (b) Isothermal heating crystallisation TTT curve for amorphous Fe₇₈Si₉B₁₃ over the temperature range 450 - 530°C.

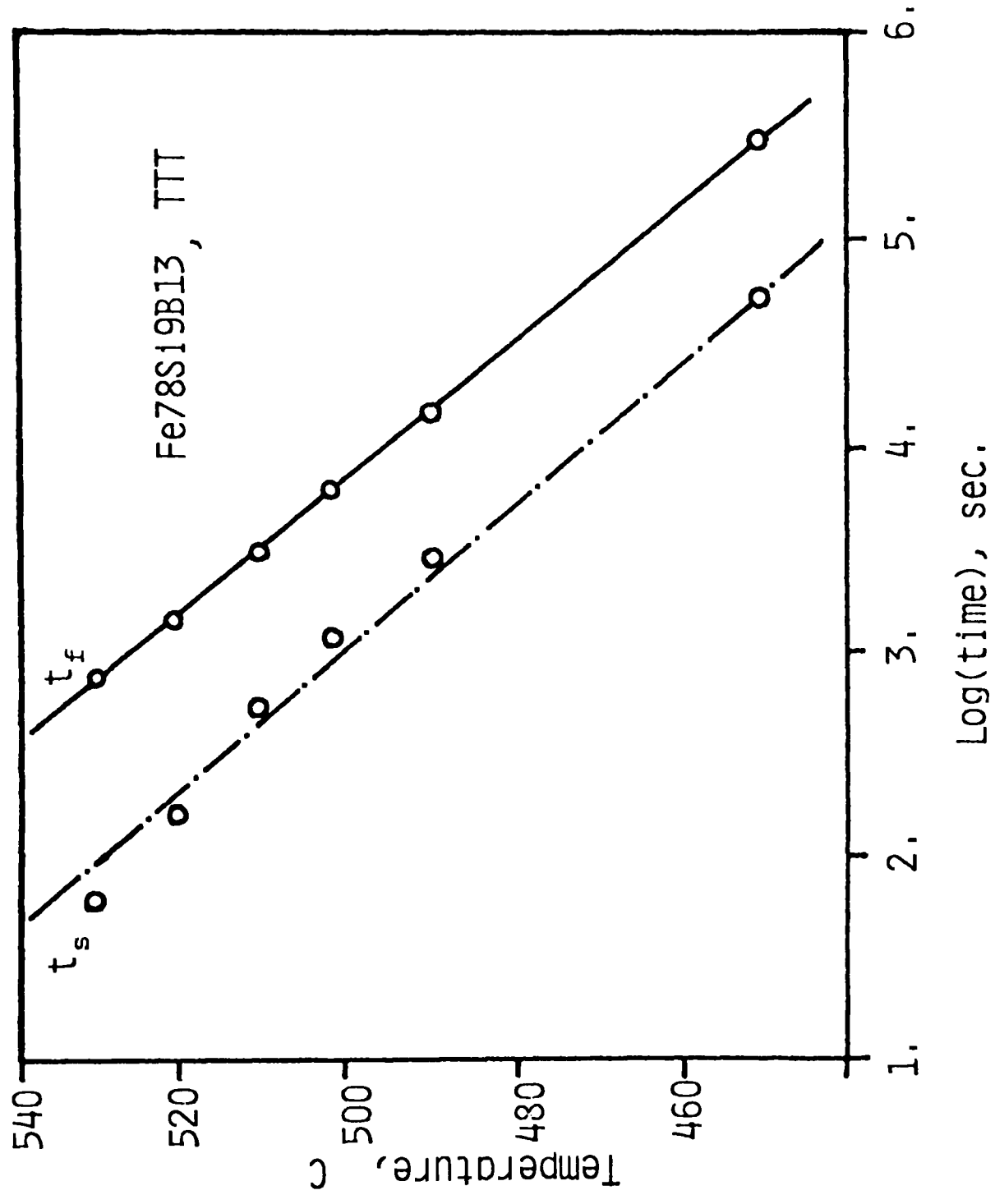


Fig.5-2(b)

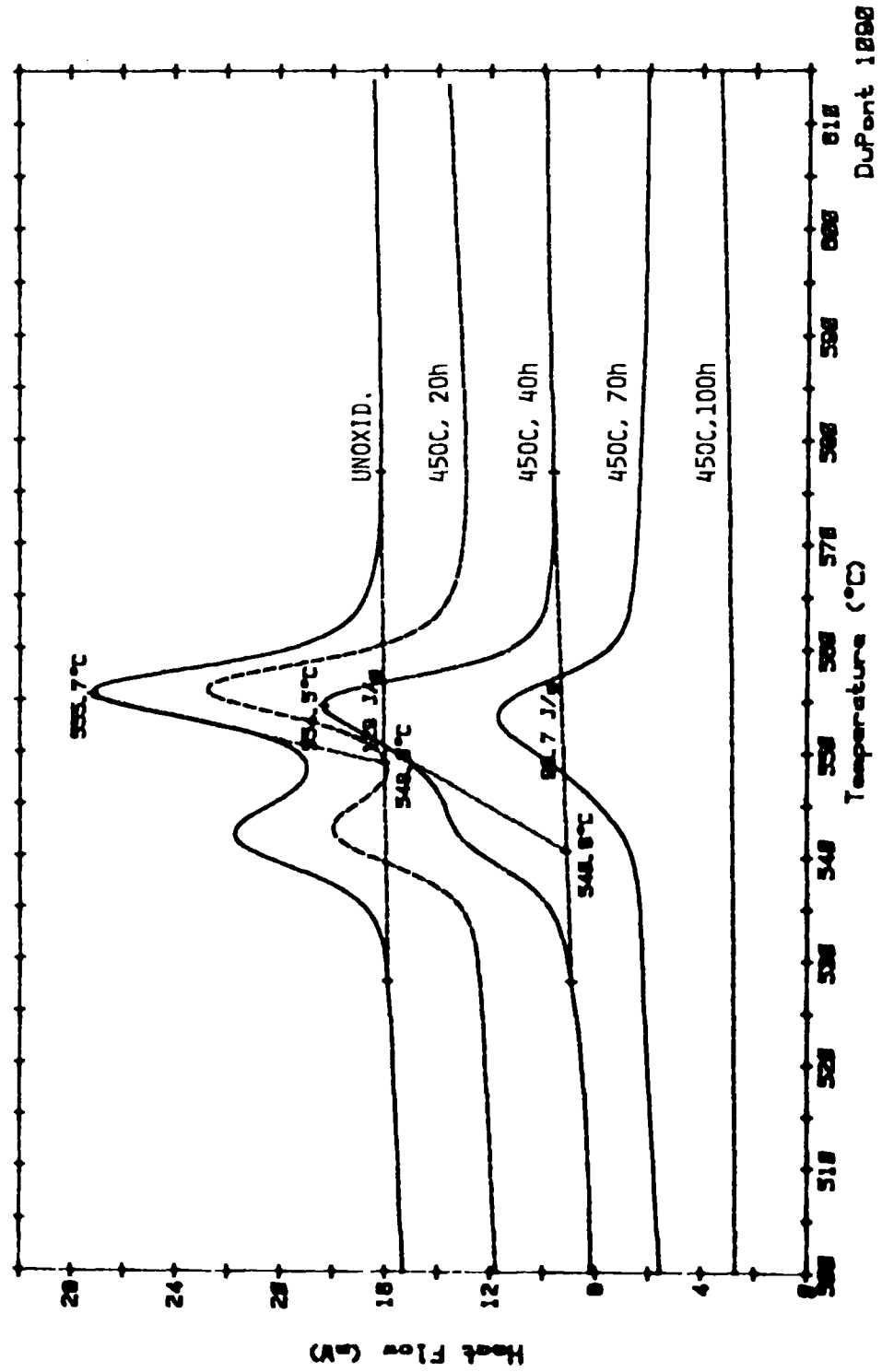


Fig.5-3 Continuous heating DSC curves showing exothermic heat of crystallisation for amorphous Fe78Si9B13 as a function of prior oxidation time (a) at 450°C, and (b) at 400°C.

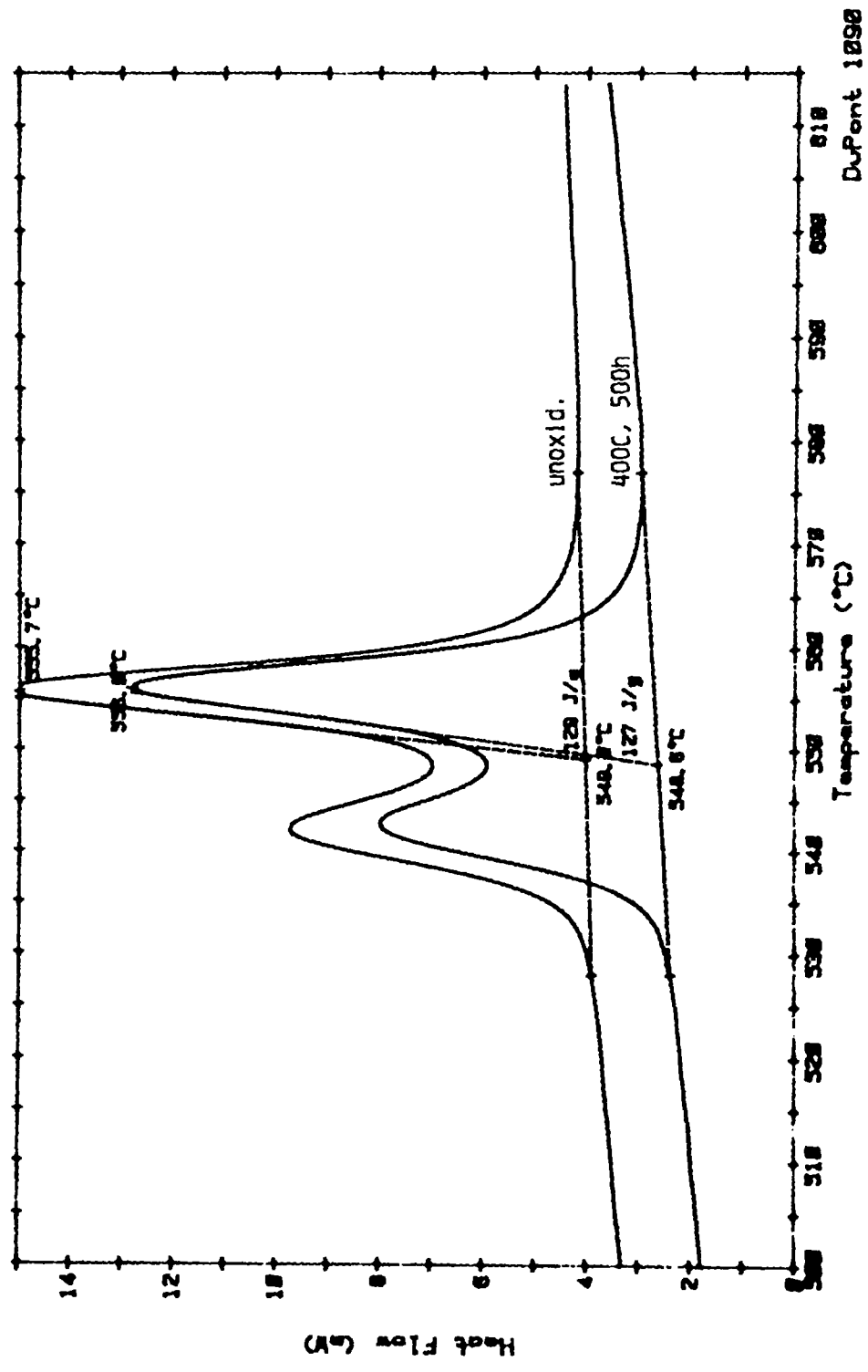


Fig.5-3 (b)

pre-crystallised Fe₇₈Si₉B₁₃ in order to investigate further the effect of crystallisation on the oxidation behaviour. Fig.5-4 shows the measured mass gains for pre-crystallised Fe₇₈Si₉B₁₃ as a function of square root of oxidation time at temperatures of 300, 350, 400, 450 and 500 C, with the equivalent data for amorphous Fe₇₈Si₉B₁₃ (dashed lines) included for comparison. The parabolic rate constants for pre-crystallised Fe₇₈Si₉B₁₃ are also given in Table 5-1. As shown in Fig.5-4, oxidation of pre-crystallised Fe₇₈Si₉B₁₃ again obeyed a parabolic rate law over the temperature range from 300 to 400 C over the whole 500h period of oxidation testing, and at 450 C for the initial 300h testing, and at 500 C for the initial 50h testing. However, the parabolic rate constants for the pre-crystallised samples were greater than for the amorphous alloy, i.e. the pre-crystallised Fe₇₈Si₉B₁₃ had a poorer oxidation resistance at ≤ 400 C. As shown in Fig.5-4, amorphous Fe₇₈Si₉B₁₃ had a mass gain 1.5-2 times smaller than the pre-crystallised alloy after 500h oxidation at 350 and 400 C. At 450 C, the mass gain of amorphous samples was only 20% smaller than pre-crystallised samples after 300h oxidation since the amorphous samples crystallised during oxidation annealing. The mass gains of amorphous and pre-crystallised samples were very similar after 50h oxidation at 500 C, since at this temperature, crystallisation took place very early after 0.3-2.0h of oxidation annealing.

Fig.5-5 shows the comparison of oxidation resistance between amorphous Fe₇₈Si₉B₁₃ and industrial crystalline Fe₉₄Si₆ silicon steel. The parabolic rate constants for Fe₉₄Si₆ are also included in Table 5-1. Amorphous Fe₇₈Si₉B₁₃ exhibited a better oxidation resistance than the silicon steel and the oxidation mass gains of amorphous Fe₇₈Si₉B₁₃ were 5-10 times smaller than those of silicon steel after 500h oxidation in air at 350-400 C.

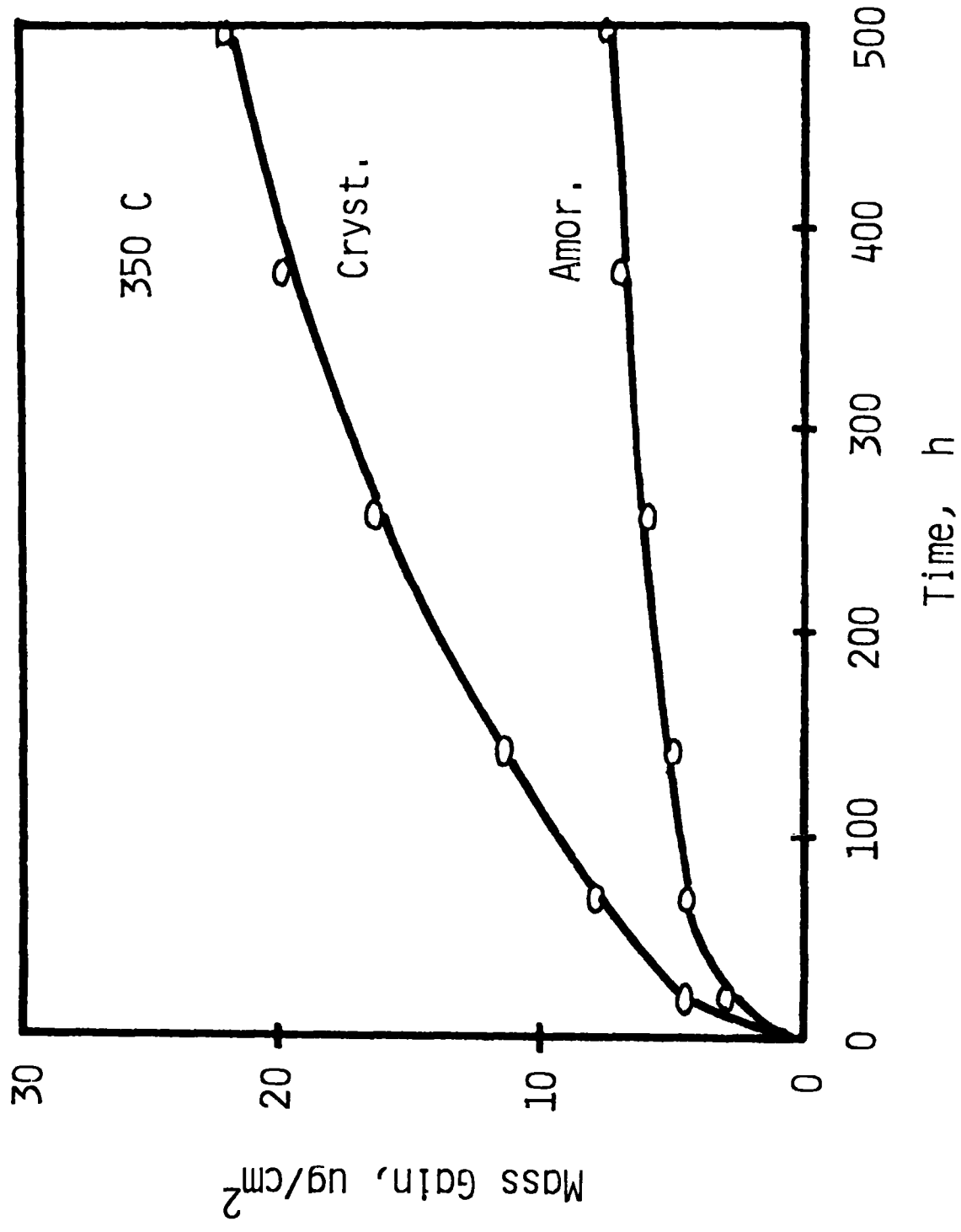


Fig.5-4 Mass gain Y versus oxidation time t for amorphous and pre-crystallised Fe78Si9B13 at (a) 350, (b) 400 and (c) 450°.

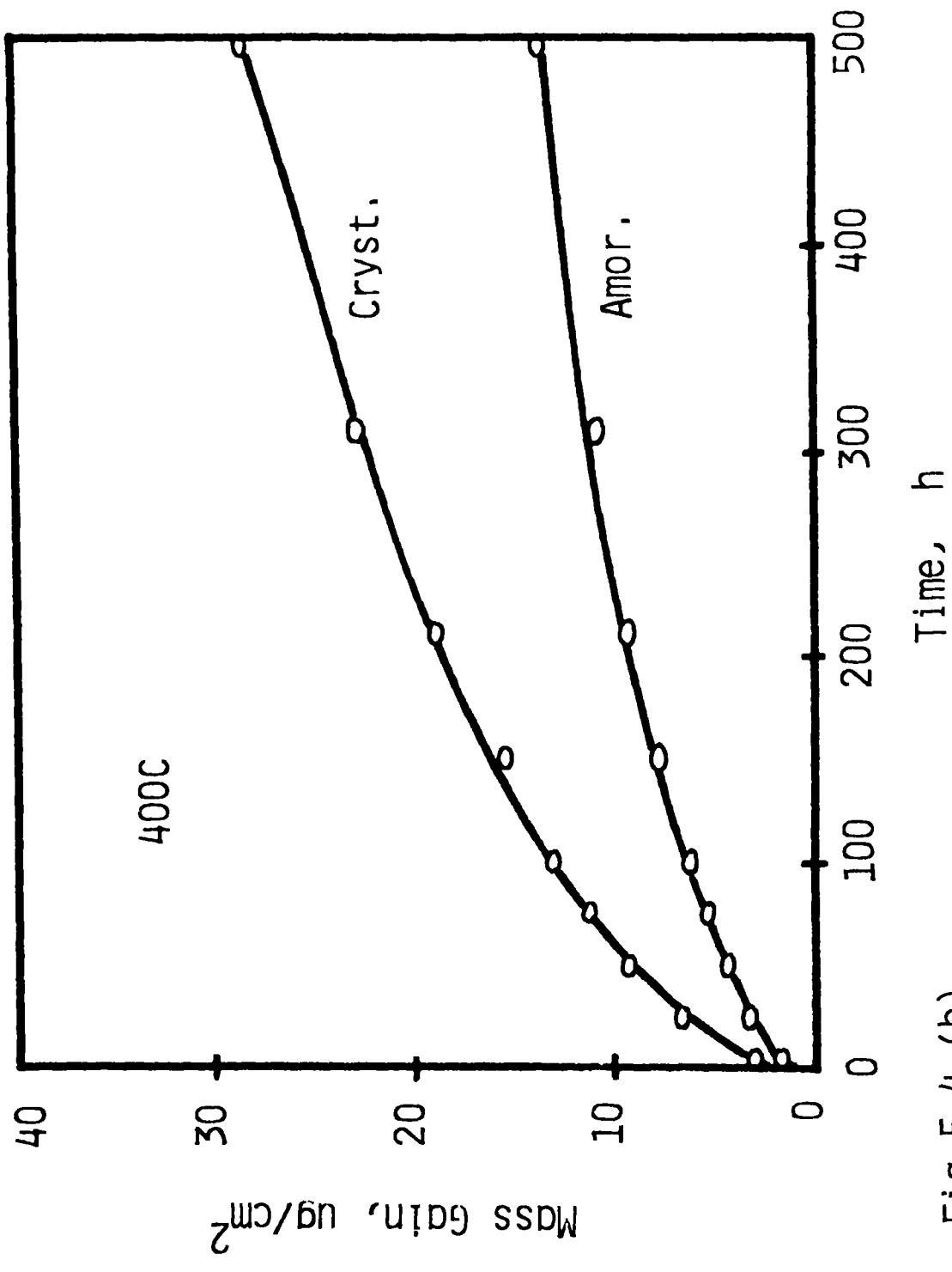


Fig.5-4 (b)

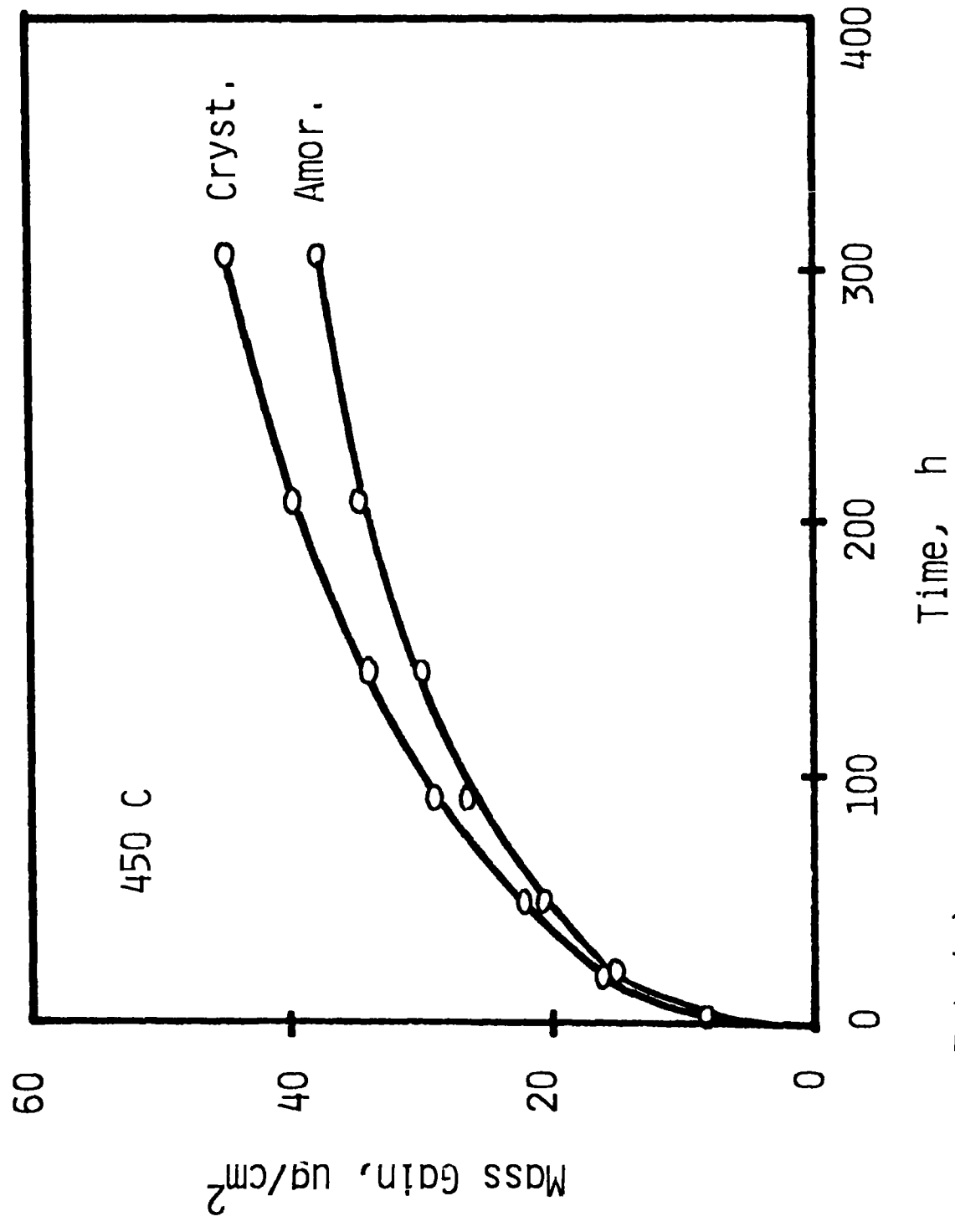


Fig.5-4 (c)

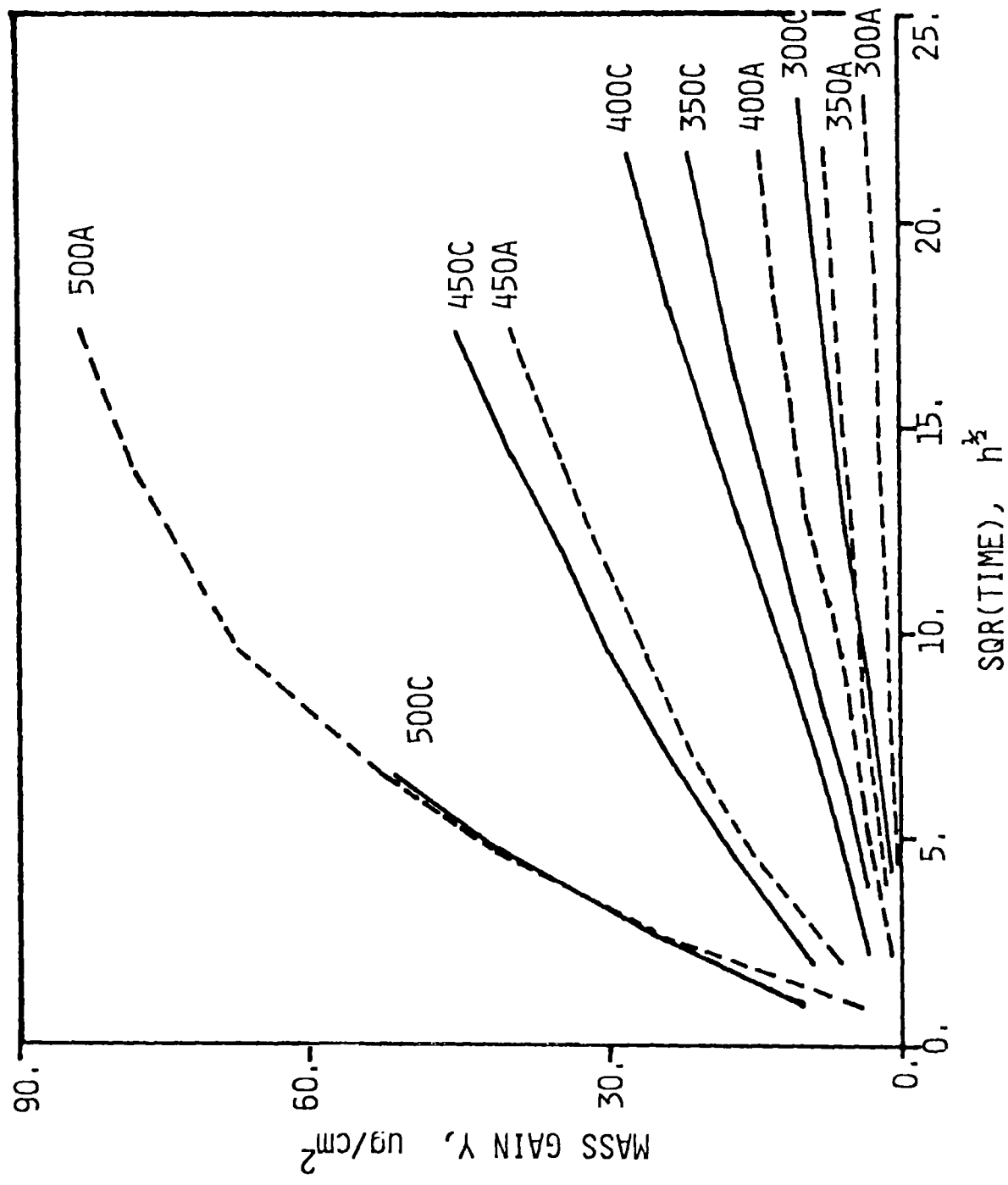


Fig.5-4 (d) (d) Mass gain Y versus square root of oxidation time t for pre-crystallised Fe78Si9B13 over the temperature range 300-500°C in air, together with the equivalent results for amorphous Fe78Si9B13 from Fig.5-1 (dashed lines).

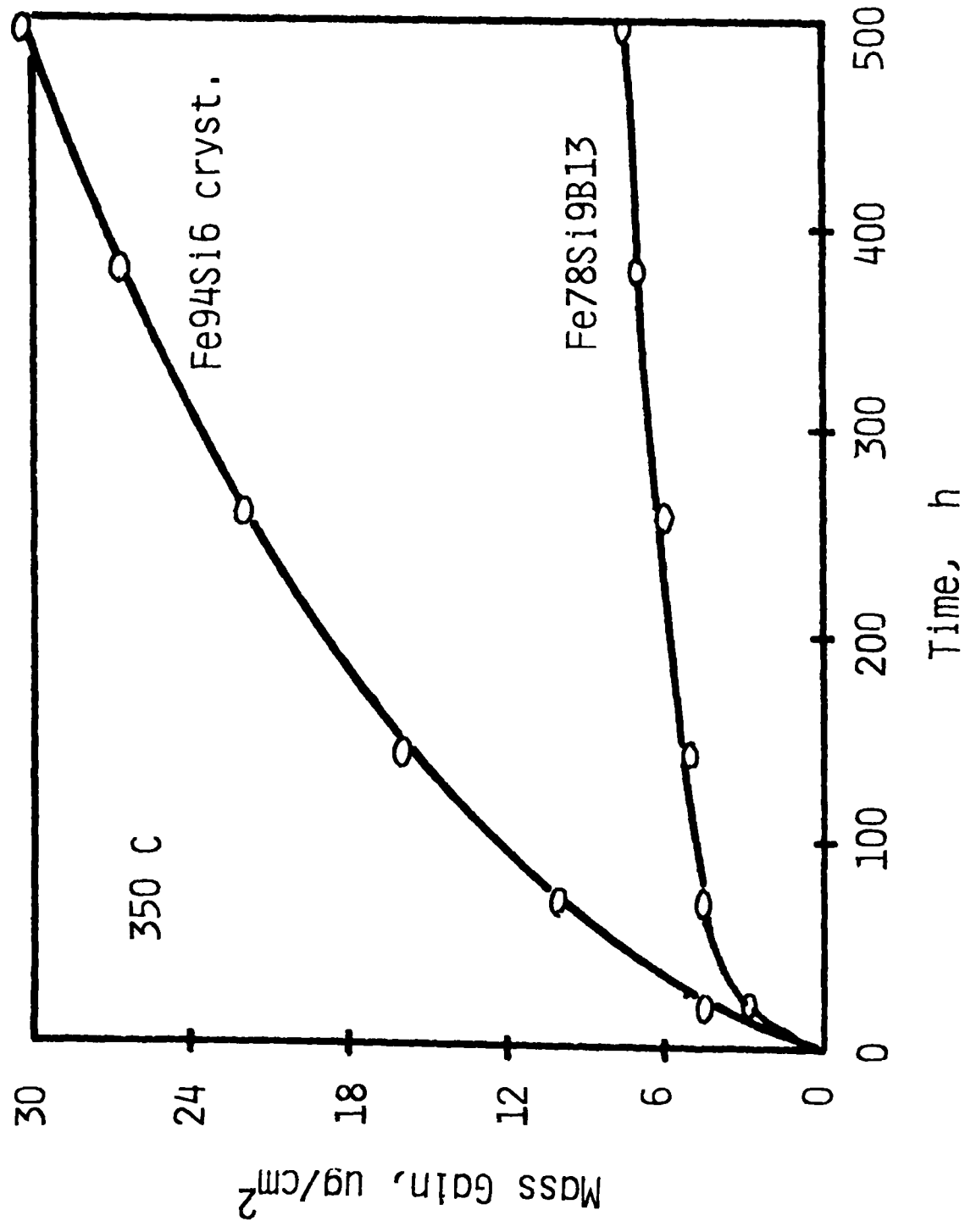


Fig.5-5 Mass gain Y versus oxidation time t for amorphous Fe78Si9B13 and oriented crystalline silicon steel Fe94Si6 at temperatures of (a) 350°C, and (b) 400°C.

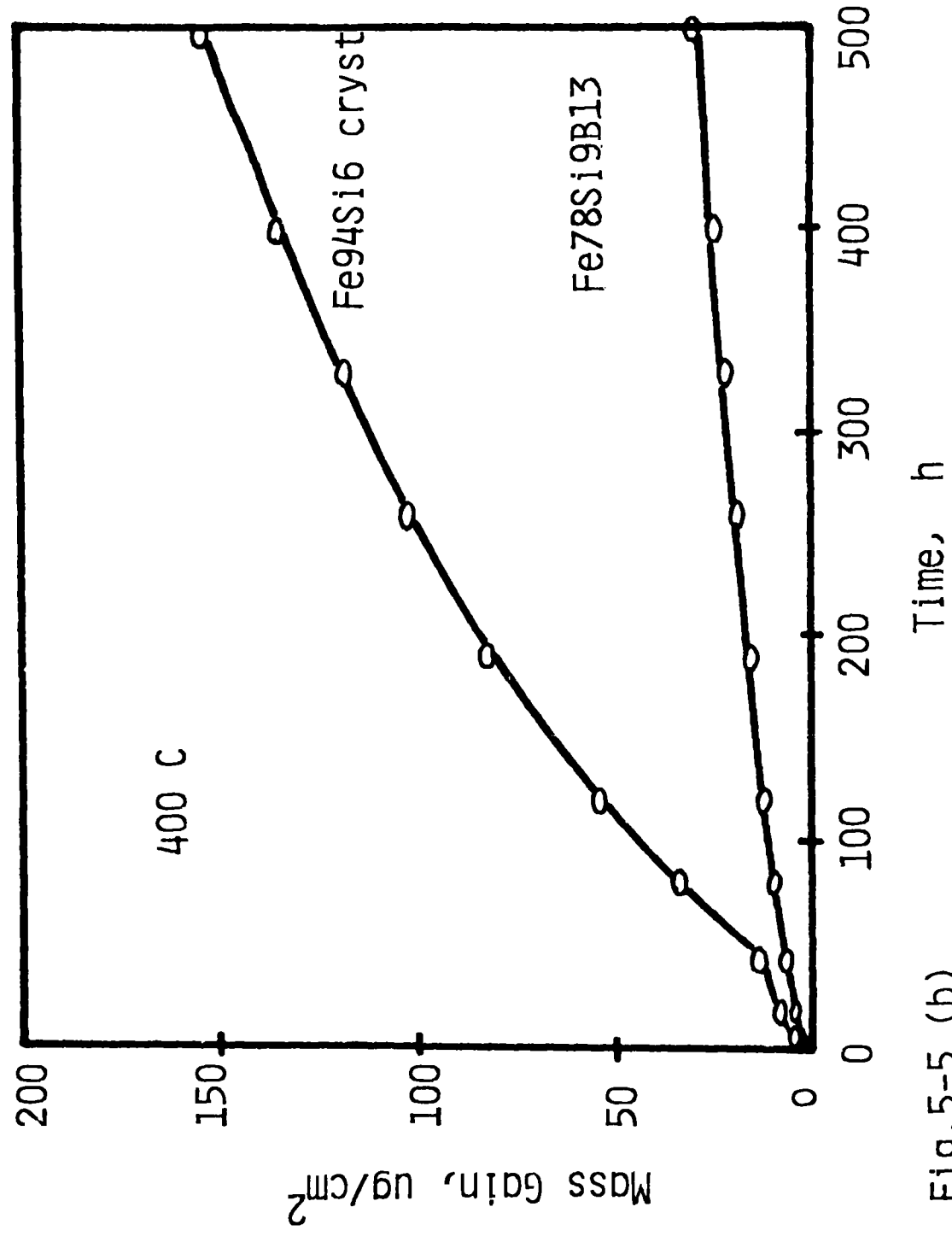


Fig.5-5 (b)

5.2.2 Oxide morphology, microstructure and microcomposition

Figs.5-6 and 5-7 show typical SEM micrographs of the oxide morphology on both amorphous and pre-crystallised Fe₇₈Si₉B₁₃ after oxidation for different times and temperatures in the temperature range 300 - 500 C. Fig.5-8 shows SEM micrographs for crystalline Fe₉₄Si₆ silicon steel after 120h oxidation at 400 C. Figs.5-9 and 5-10 show bright field TEM micrographs of the oxide films stripped from amorphous and pre-crystallised Fe₇₈Si₉B₁₃ oxidised for 500h at 300 and 350 C. As shown in Figs.5-6 and 5-9, the oxide scale formed on the amorphous alloy was mainly polycrystalline, consisting of many oxide particles, embedded in a thin layer of oxide matrix. In TEM images such as Fig.5-9, the larger particles correspond to the dark areas, which are considerably thicker than the bright areas of oxide matrix. The size of the larger oxide particles was found to increase with increasing oxidation temperature and exposure time as shown in Figs.5-6 and 5-9, and Table 5-3. The morphology and microstructure of the oxide scale formed on pre-crystallised Fe₇₈Si₉B₁₃ was different from the amorphous alloy, with a larger size and greater irregularity in shape of the oxide particles, as shown particularly well in Figs.5-7 and 5-10.

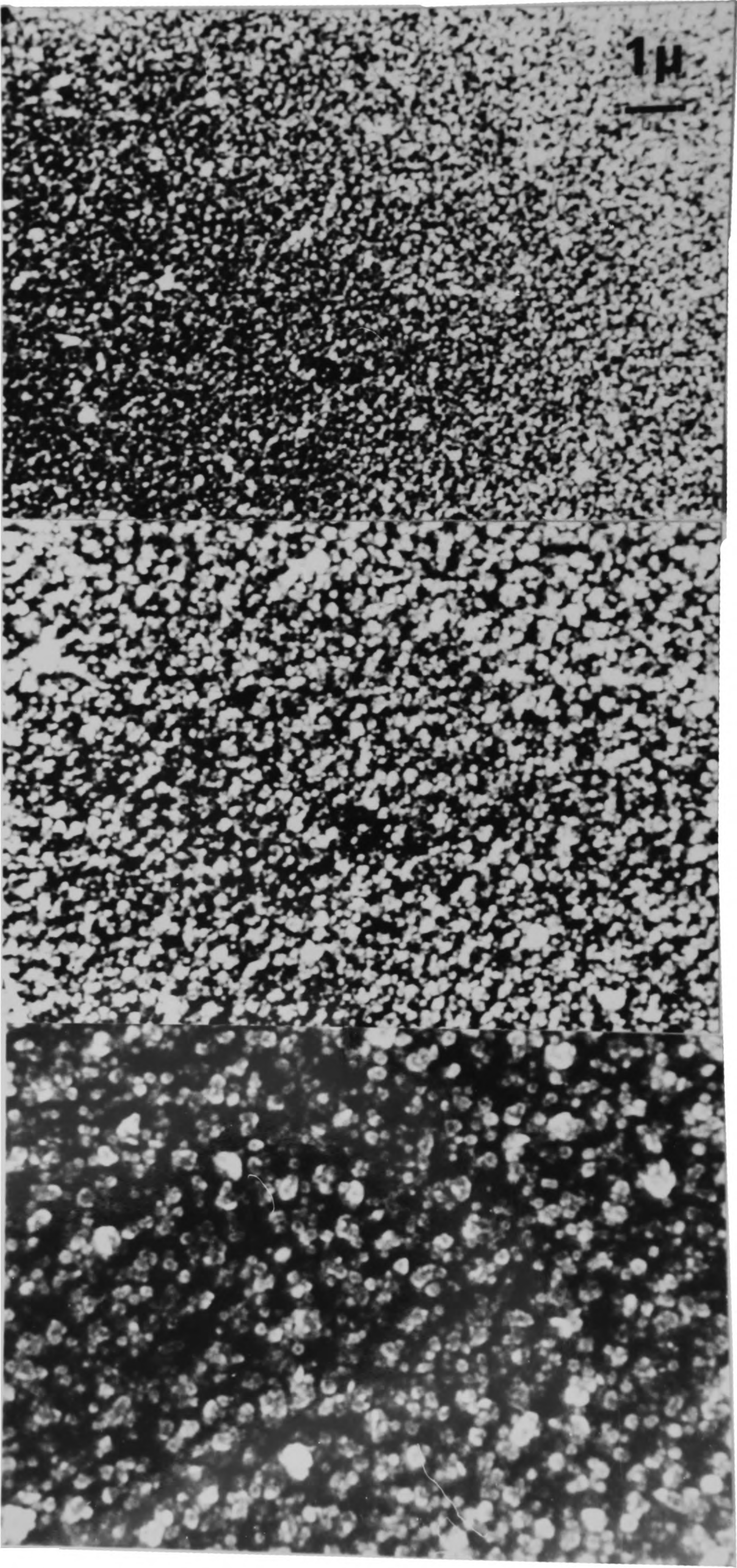
Figs.5-11 and 5-12 show high magnification TEM bright field images and corresponding SAED patterns from the same specimens shown in Figs.5-9(b) and 5-10(b), i.e. the stripped oxide films from amorphous and pre-crystallised samples after 500h oxidation at 350 C. As shown in Figs.5-11 and 5-12, the larger oxide particles and the thin oxide matrix both consist of many grains. For instance, Fig.5-11(b) shows that a 100nm oxide particle contains hundreds of very fine grains. Typical SAED patterns from both particle and matrix areas on the oxide films are shown in Figs.5-11(c), 5-11(d), and Figs.5-12(b), 5-12(c). The results of

Fig.5-6

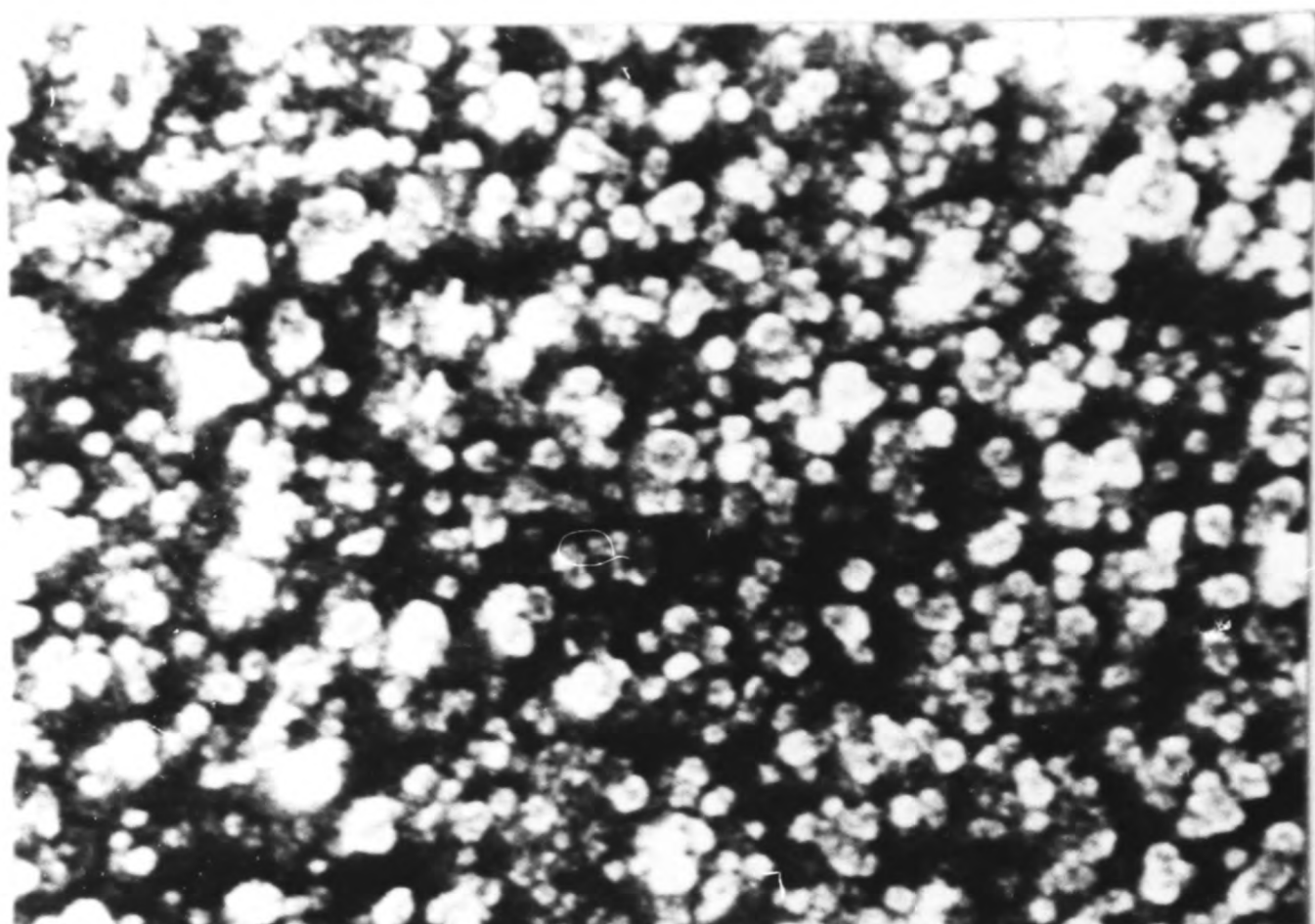
(a)

(b)

(c)



(d)



(e)

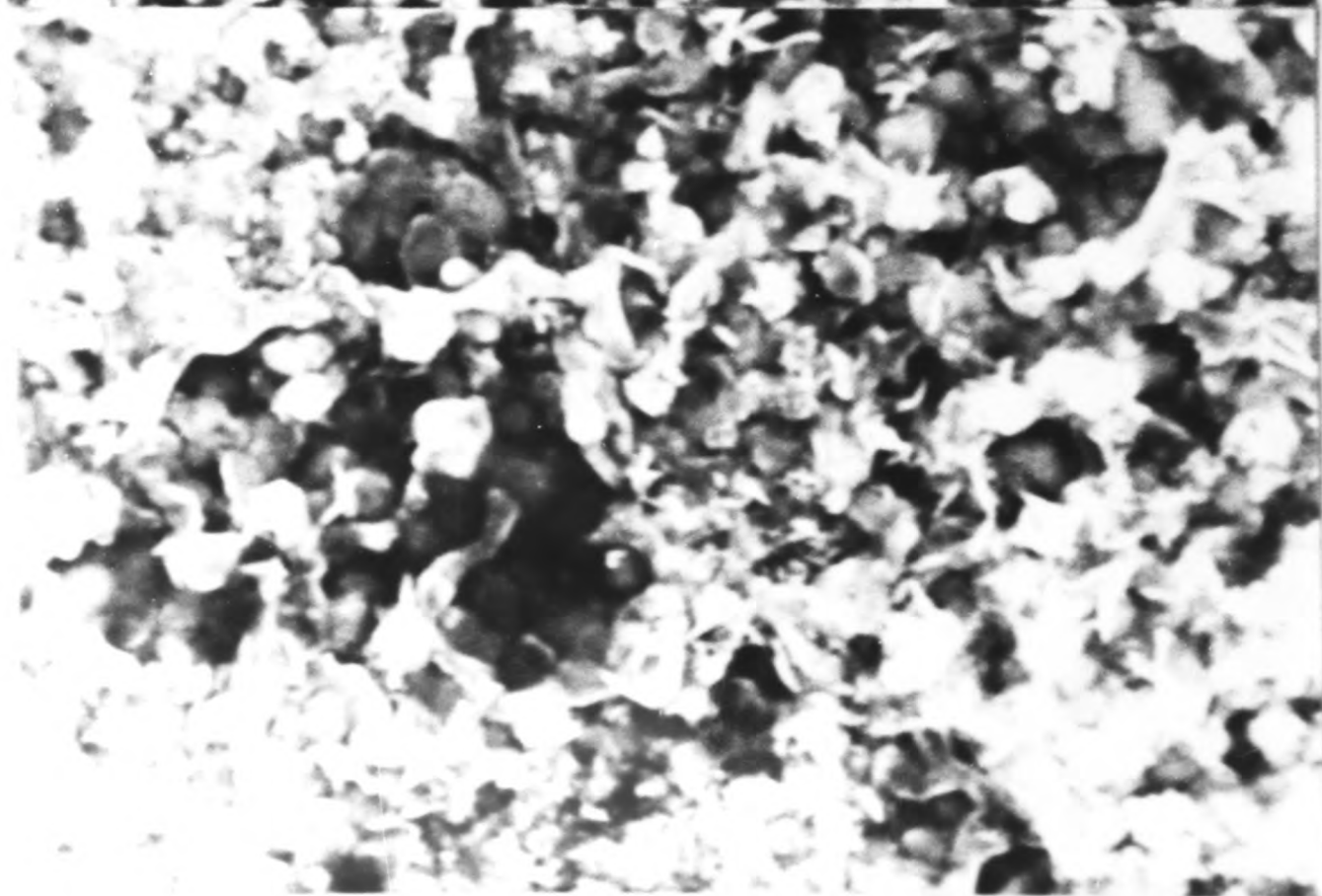
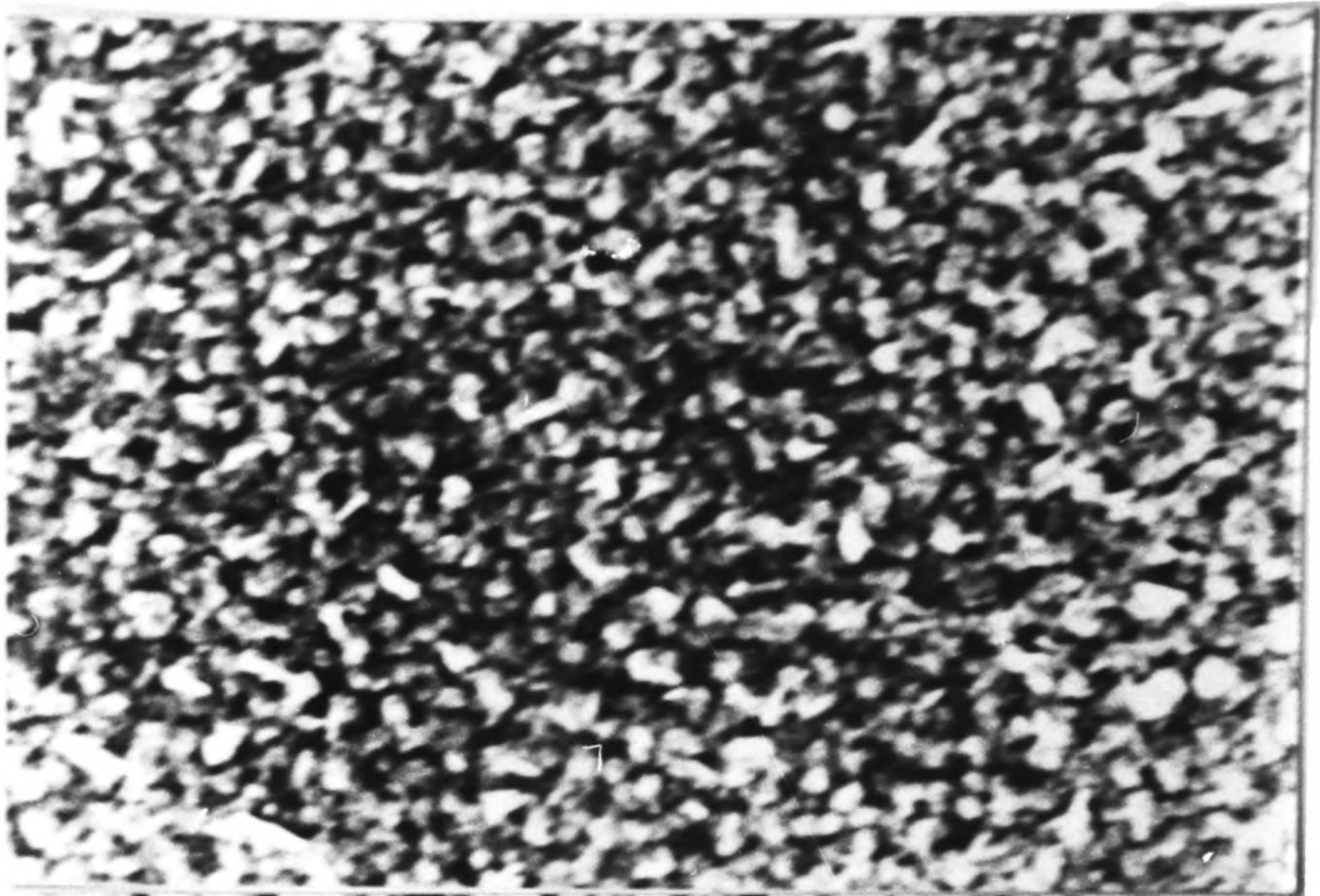


Fig.5-6 SEM micrographs of the oxide scale surfaces formed on amorphous $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ oxidised in air over the temperature range $300\text{--}500^\circ\text{C}$: (a) 300°C 500h, (b) at 350°C for 500h, (c) at 400°C for 310h, (d) at 450°C for 250h, and (e) at 500°C for 250h.

(a)



(b)

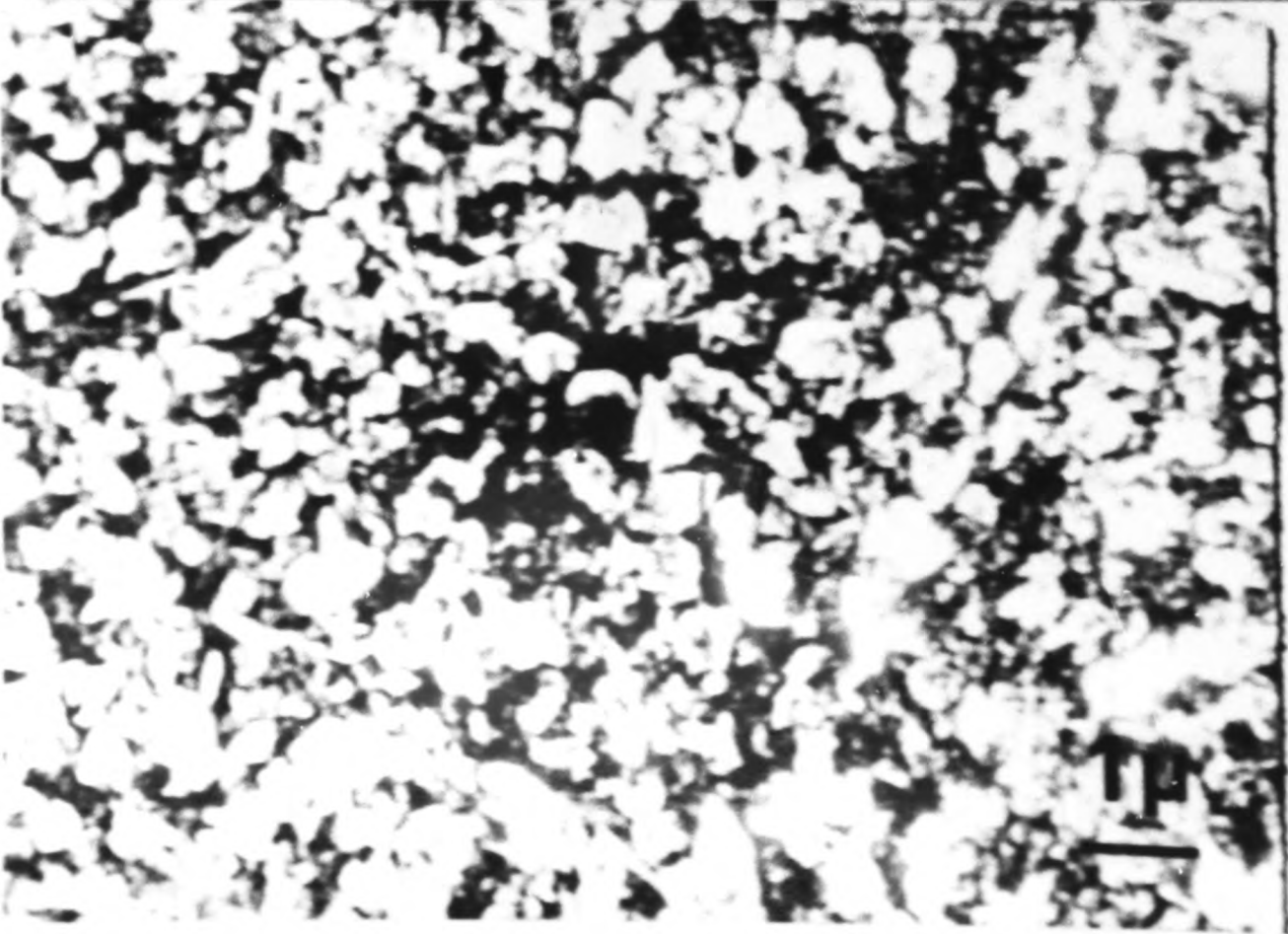
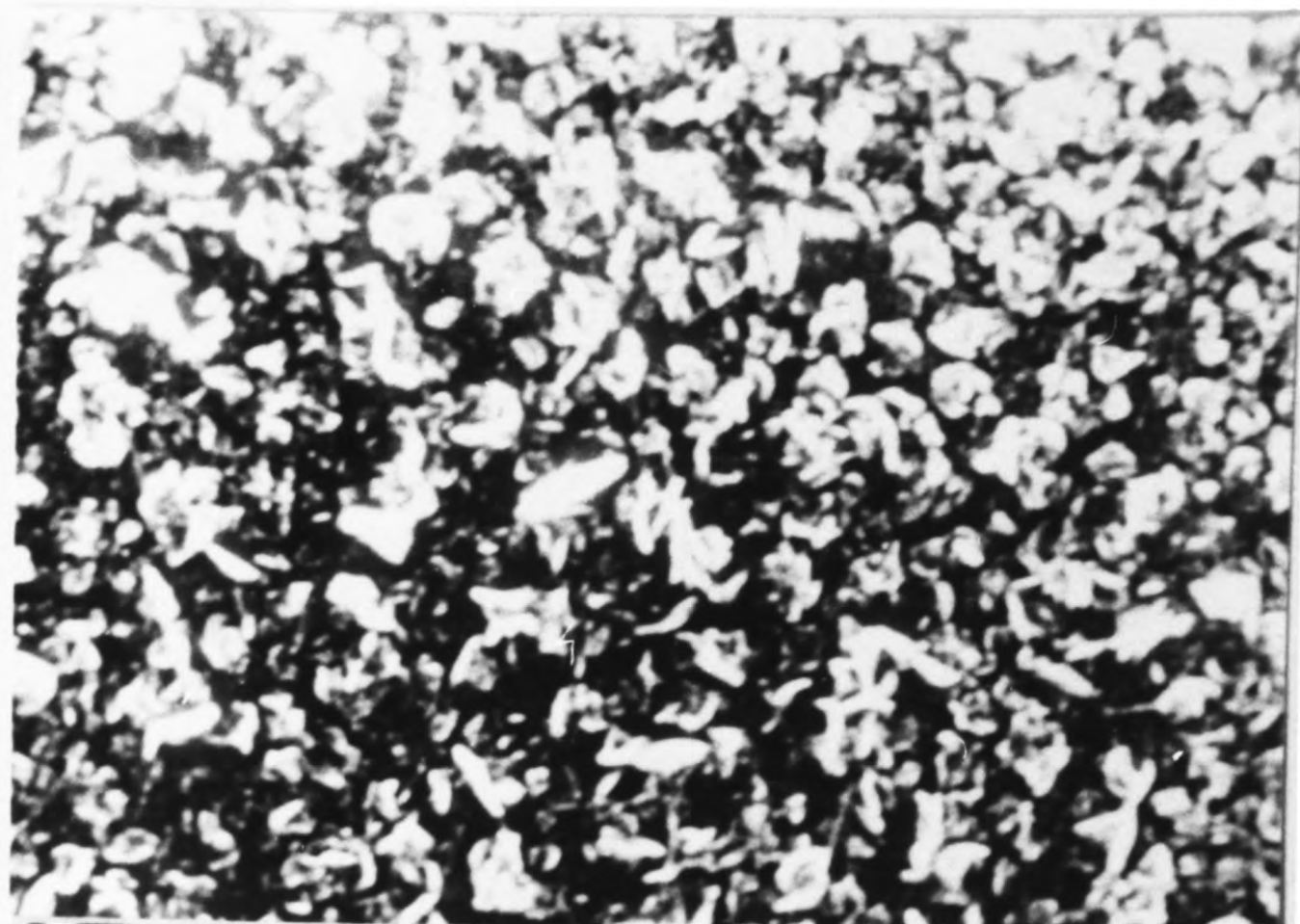


Fig.5-7 SEM micrographs of the oxide scale surfaces formed on pre-crystallised Fe₇₈Si₉B₁₃ oxidised in air at the temperature range 300–450°C. (a) at 300°C for 500h, (b) at 350°C for 500h, (c) at 400°C for 310h, and (d) at 450°C for 250h.

Fig.5-7

(c)



(d)



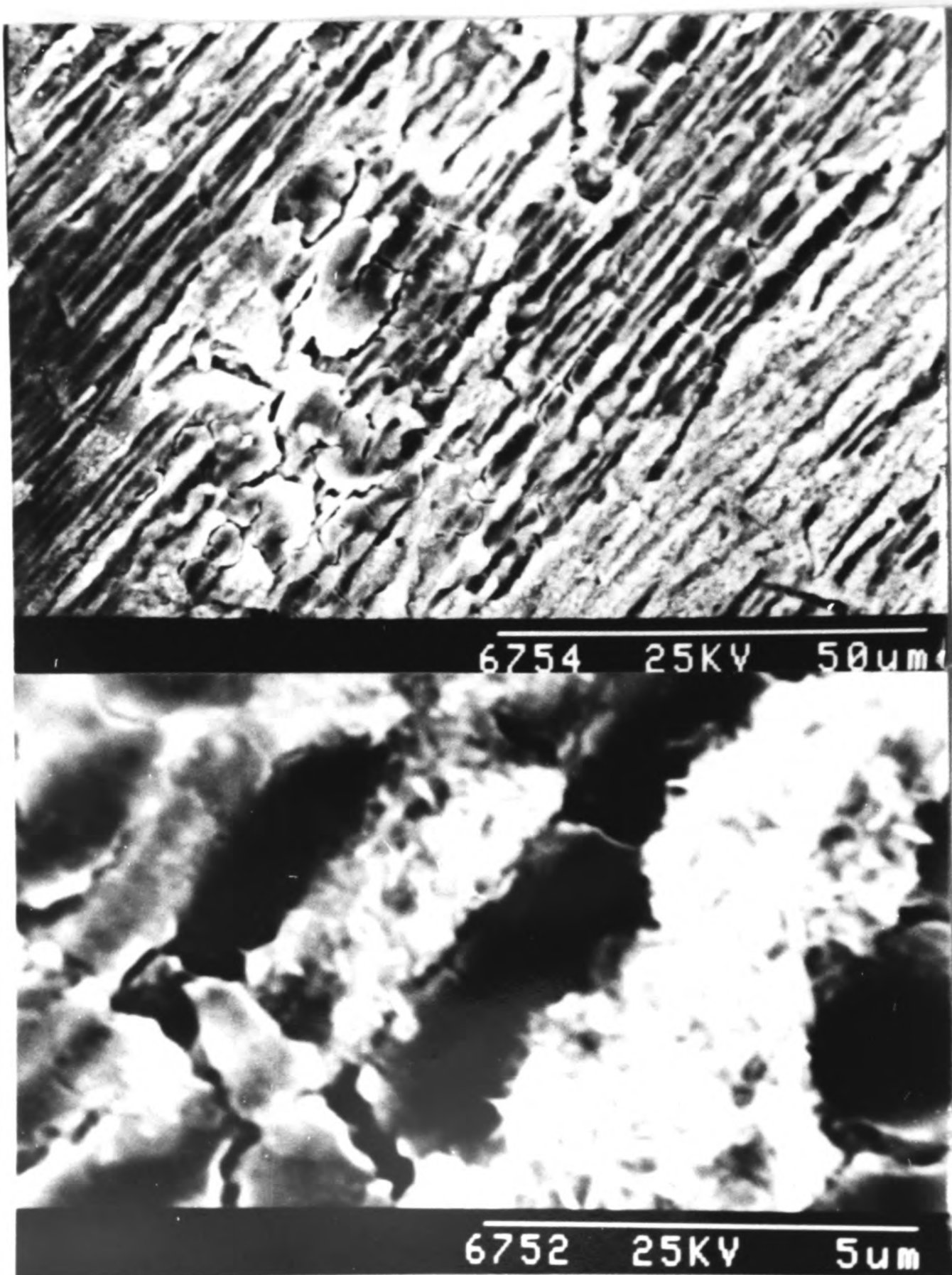


Fig.5-8 SEM micrographs of the oxide scale surfaces formed on crystalline Fe₉₄-Si₆ silicon steel after 120h oxidation at 400°C.

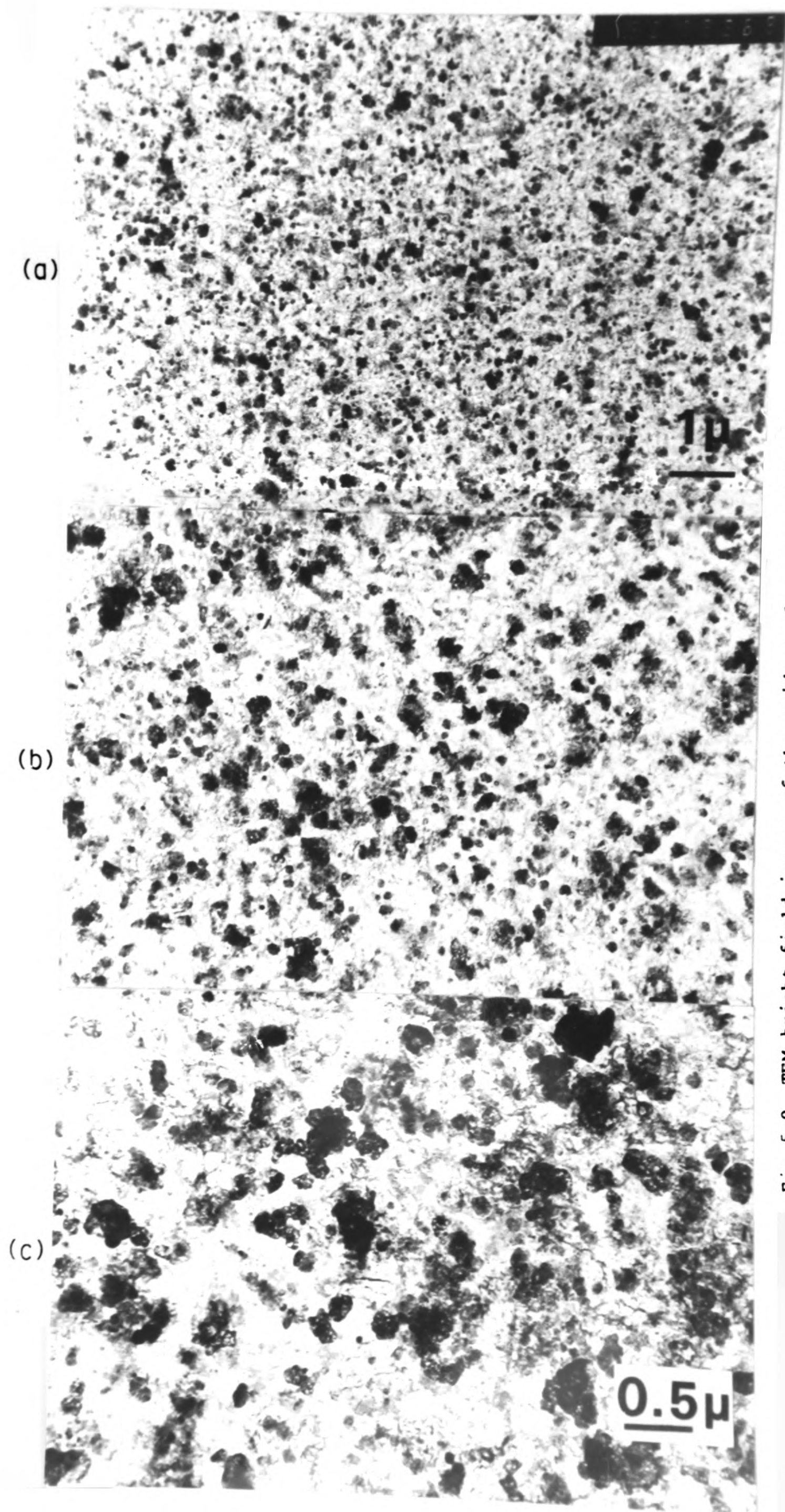


Fig.5-9 TEM bright field images of the oxide scales removed from amorphous Fe₇₈Si₉B₁₃ oxidised in air (a) at 300°C for 500h, (b) and (c) at 350°C for 500h.

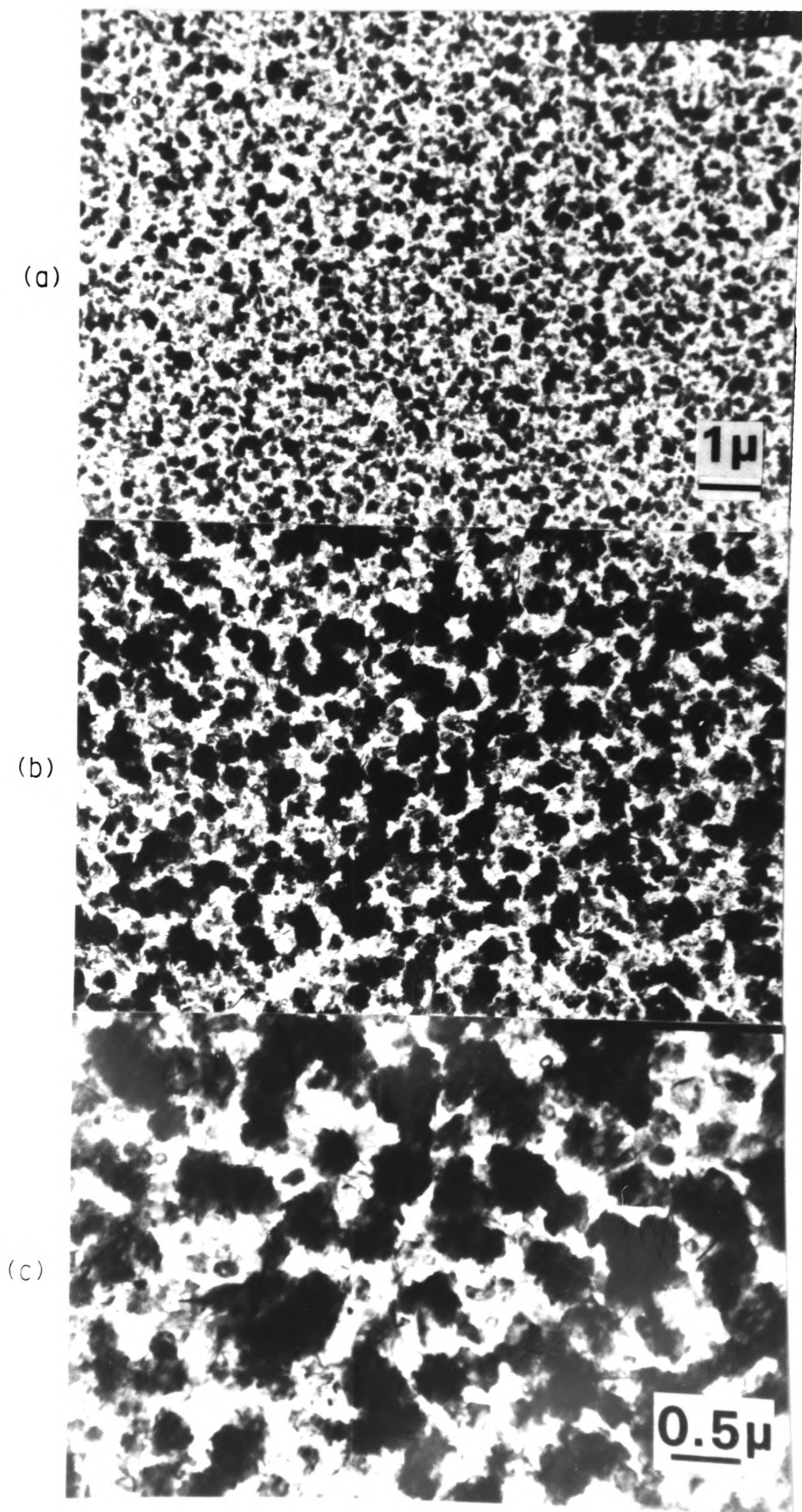
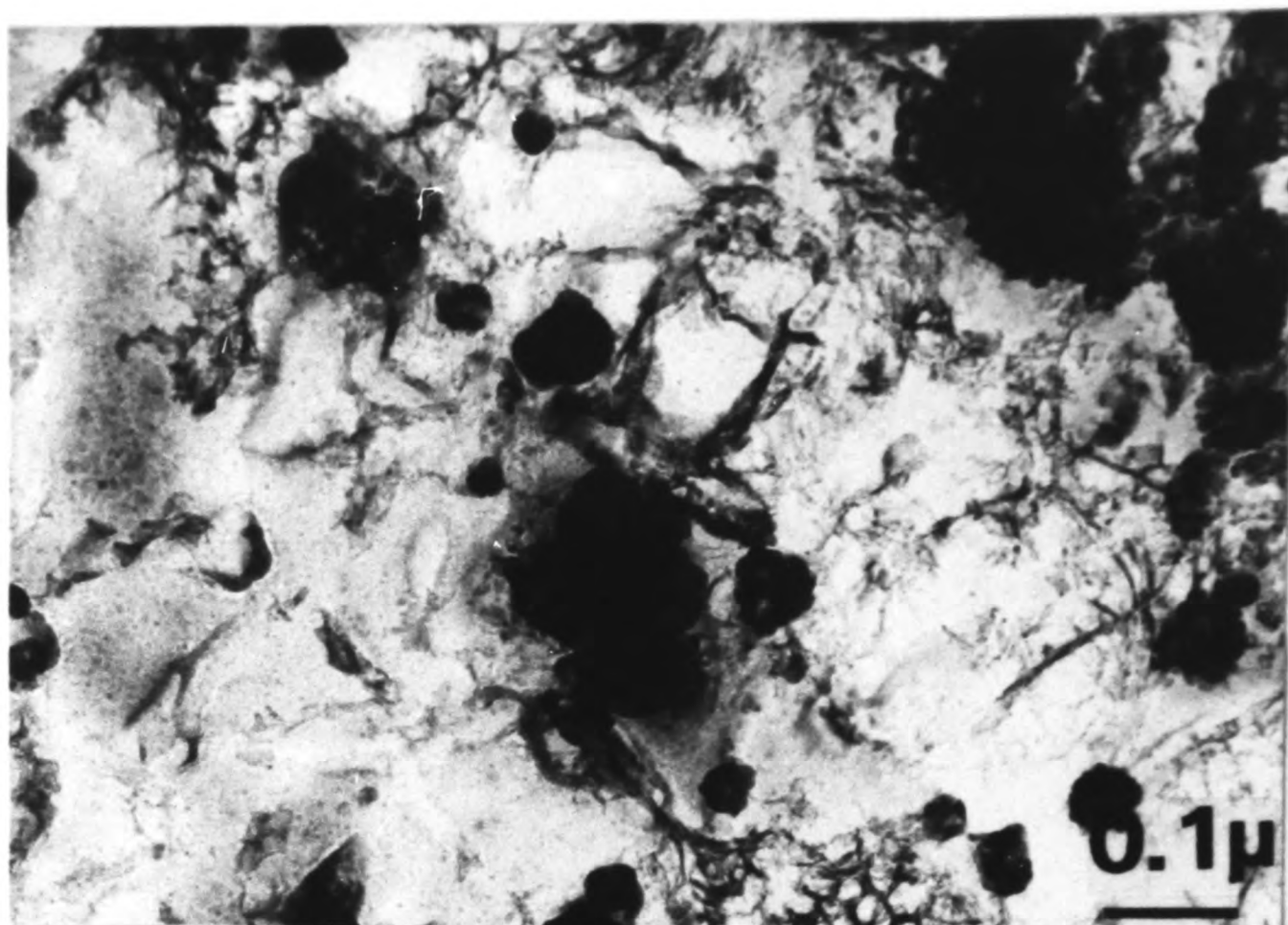


Fig. 5-10 TEM bright field images of the oxide scales removed from pre-crystallised Fe78Si9B13 oxidised in air (a) at 300°C for 500h, (b) and (c) at 350°C for 500h.

(a)



(b)

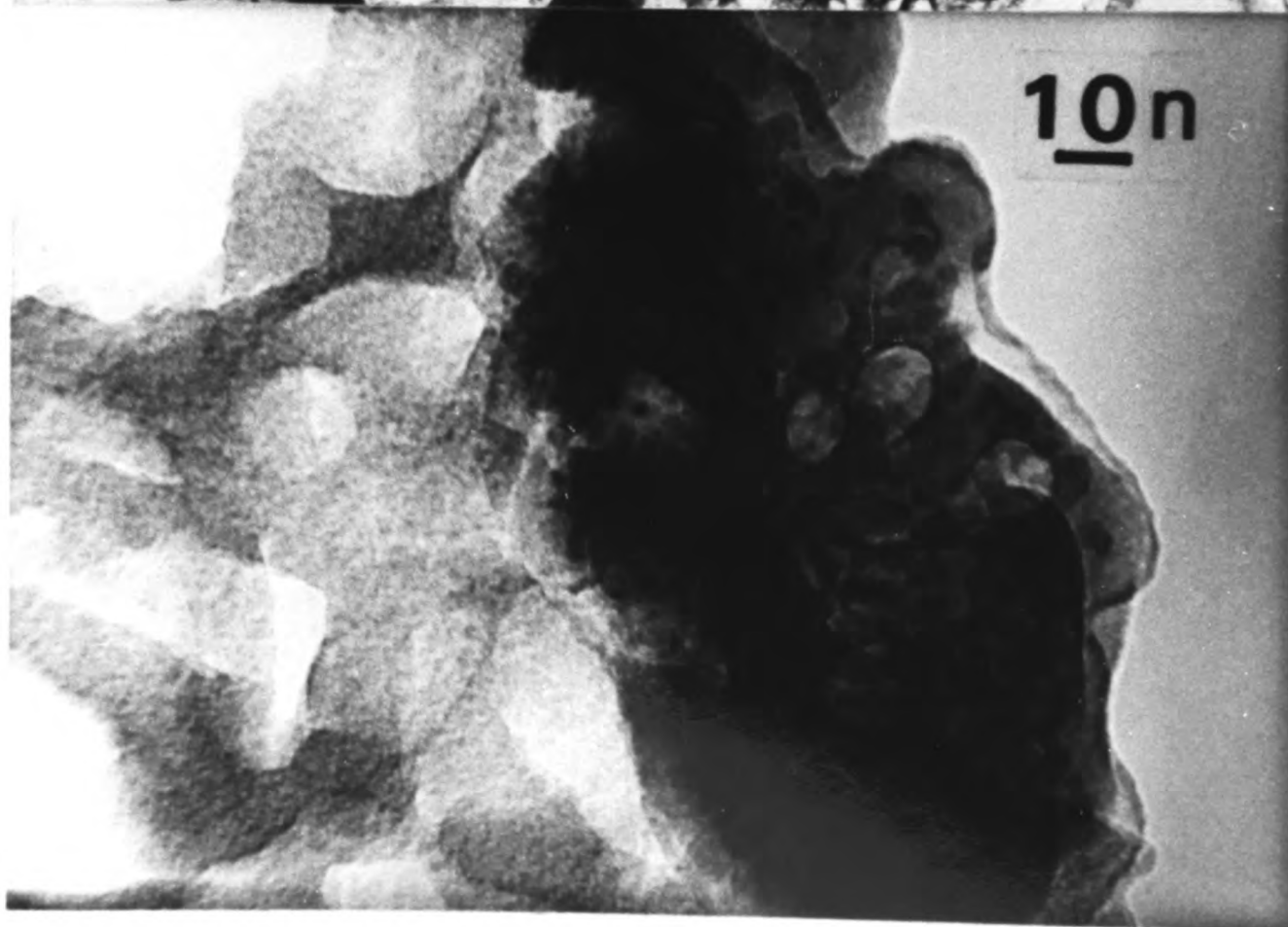
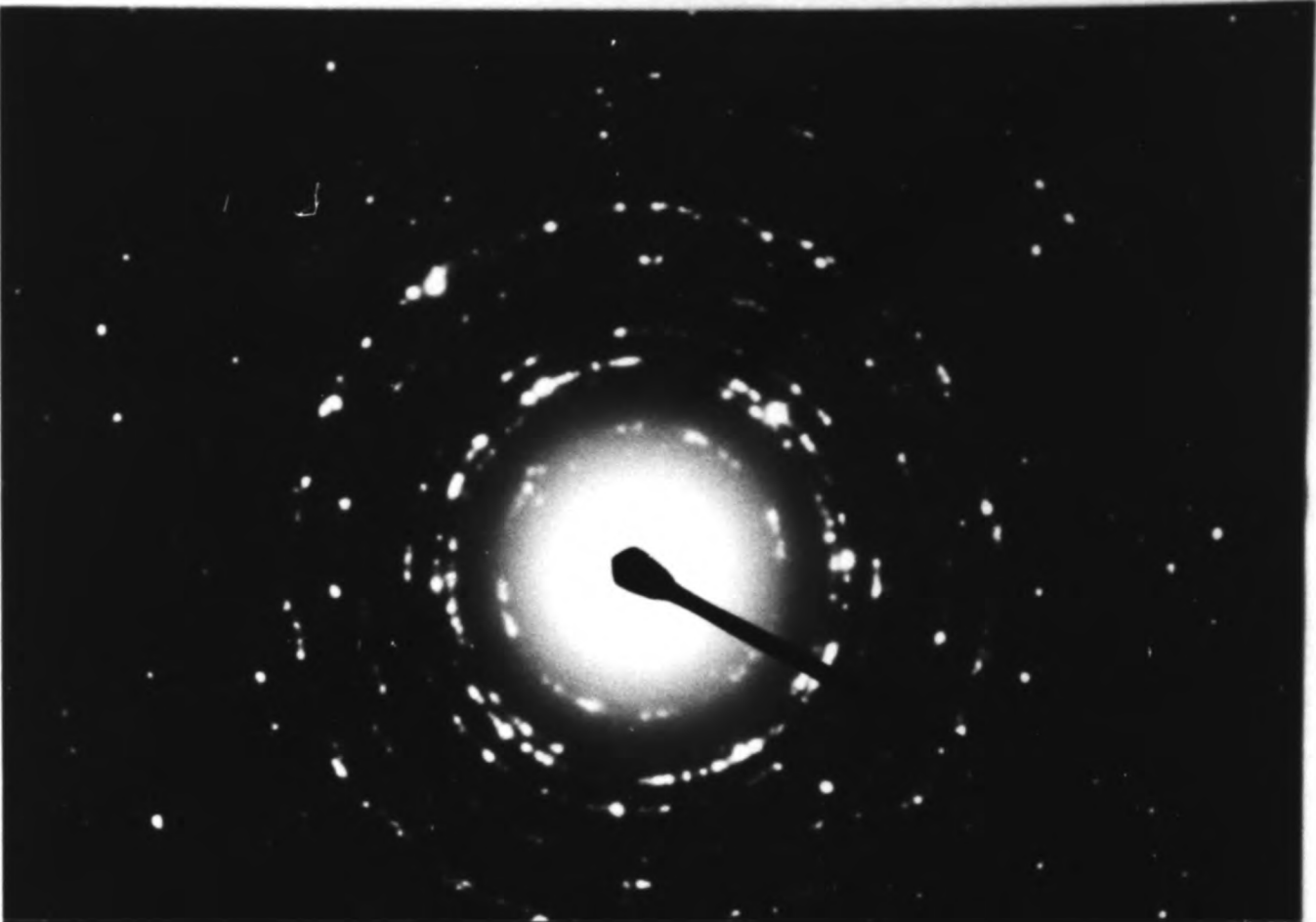


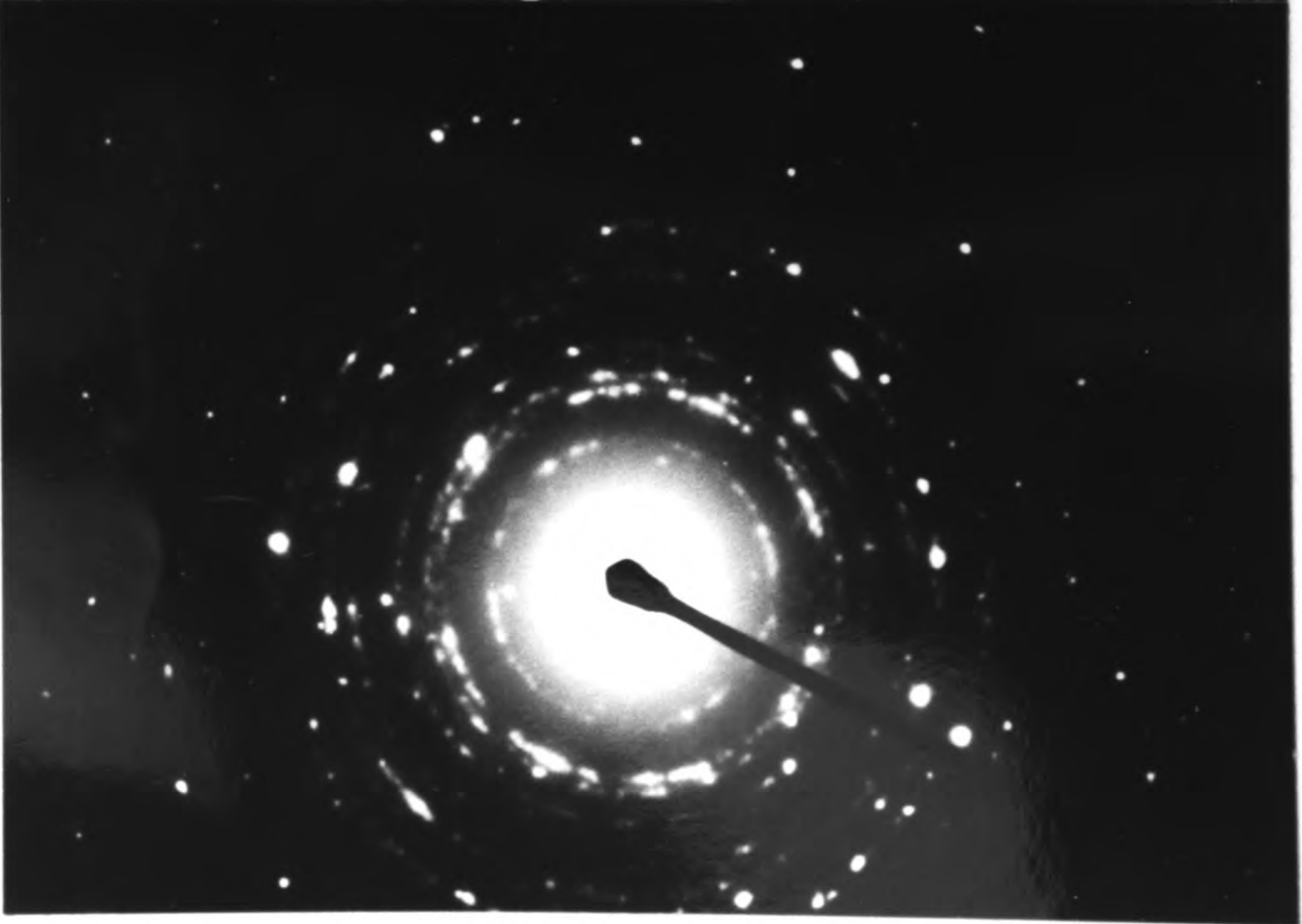
Fig.5-11 (a) (b) High magnification TEM micrographs of oxide scale removed from amorphous Fe₇₈Si₉B₁₃ oxidised in air at 350°C for 500h; (c)(d) SAED patterns from the bright and dark areas in Fig.5-11(a) respectively.

Fig.5-11

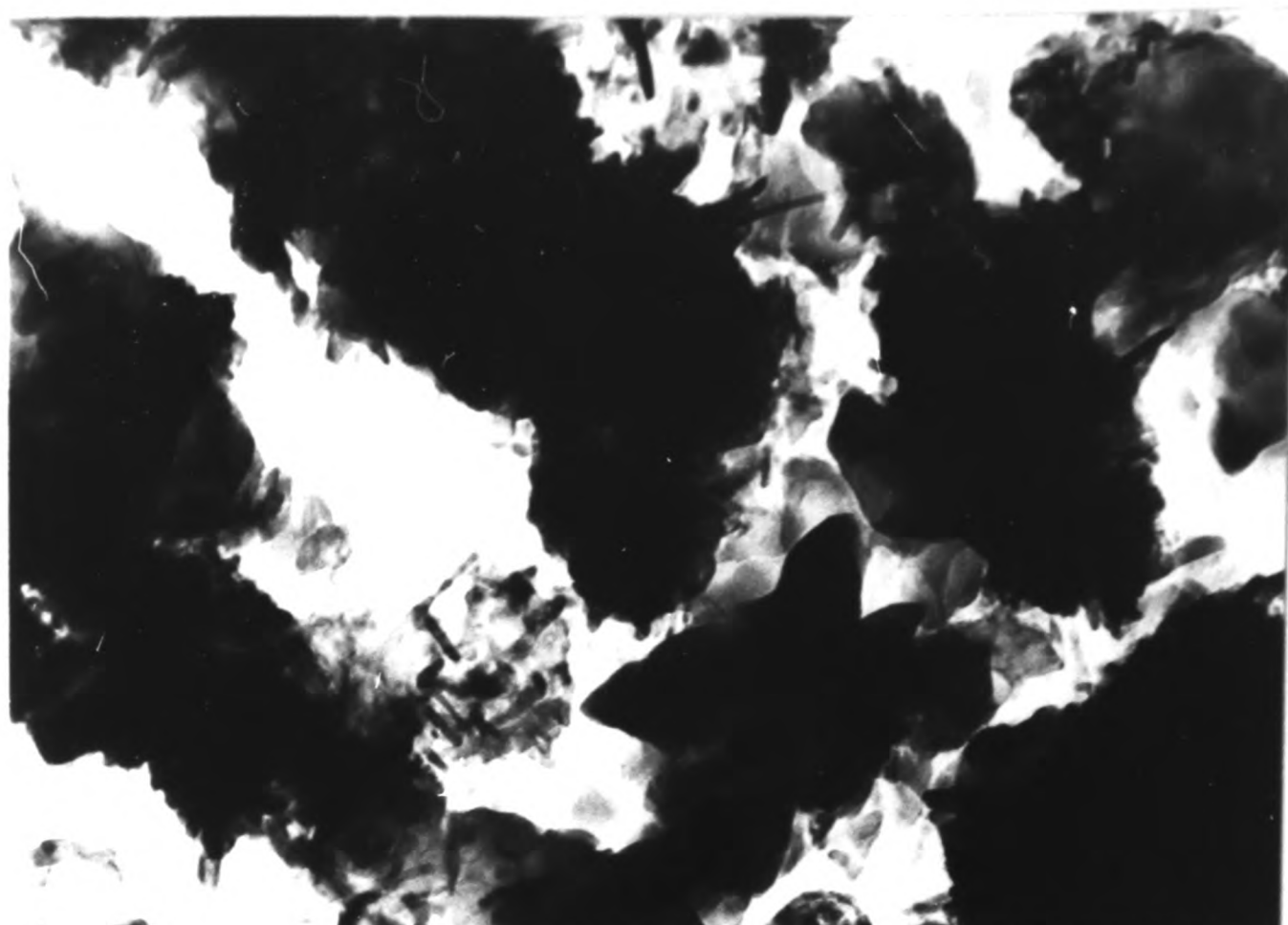
(c)



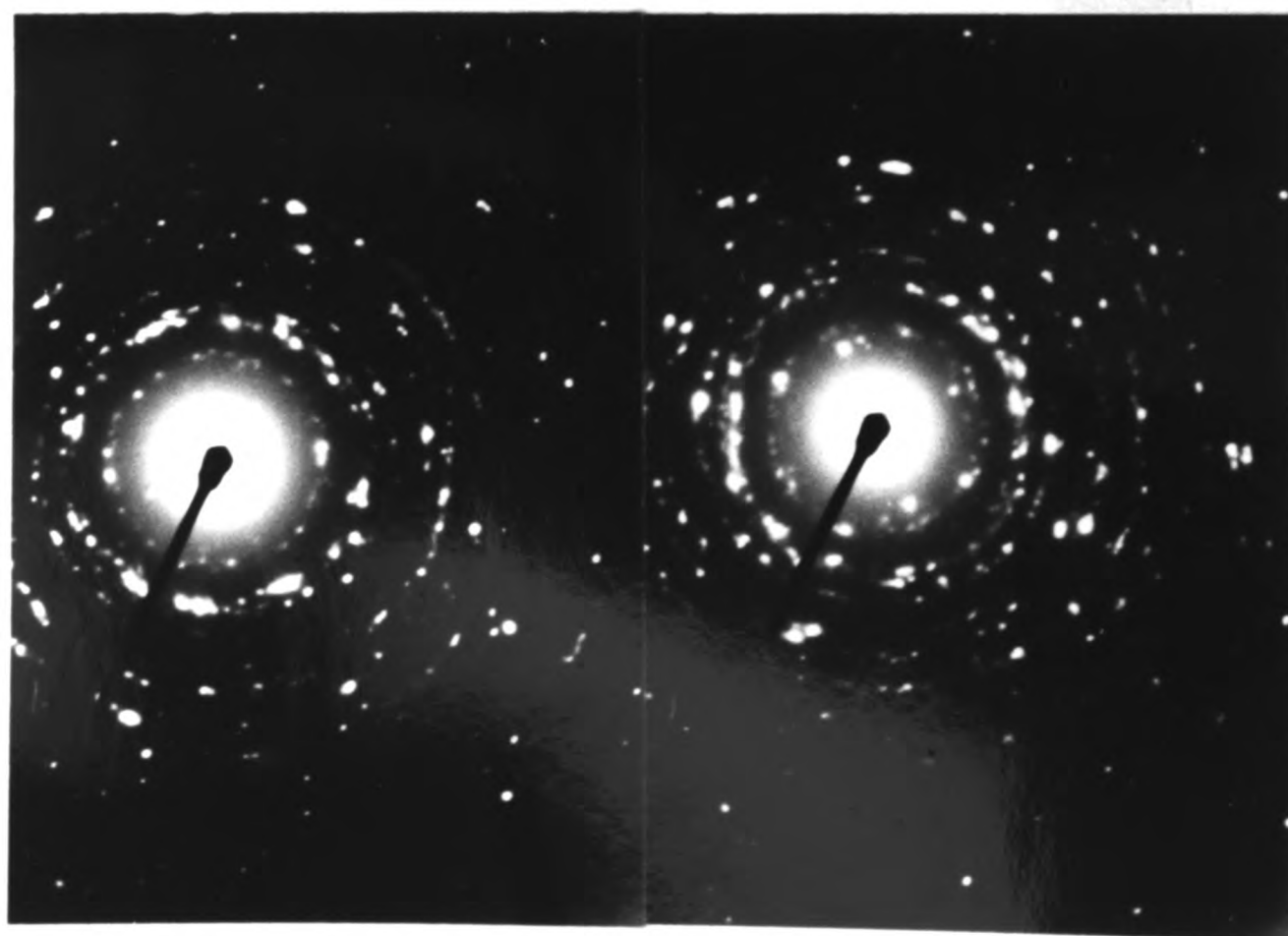
(d)



(a)



0.1 μ



(b)

(c)

Fig.5-12 (a) High magnification TEM micrograph of oxide scale removed from pre-crystallised Fe₇₈Si₉B₁₃ oxidised in air at 350°C for 500h; (b)(c) SAED patterns from the bright and dark areas in Fig.5-12(a) respectively.

Table 5-3

Mean size of the oxide particles formed on amorphous and pre-crystallized $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ over a range of oxidation temperature from 300 to 500°C

Oxidation temperature, °C	300	350	400	450	500
Oxidation time, h	500	500	500	300	300
Mean size of the particles for amor. $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$, μm	0.08	0.15	0.26	0.40	0.60
Mean size of the particles for pre-crystallised $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$, μm	0.16	0.28	0.36	0.52	0.68

indexing the different SAED patterns are shown in Table 5-4, and the resulting crystal structures are given in Table 5-5. The oxide matrixes on both amorphous and pre-crystallised Fe78Si9B13 contained β -quartz SiO_2 , amorphous SiO_2 , and Fe_3O_4 ; the oxide particles in the amorphous specimens contained Fe_2O_3 , Fe_3O_4 and tridymite SiO_2 ; and the particles in the pre-crystallised specimens contained mainly Fe_3O_4 .

Fig.5-13 shows typical EDS spectra for oxide matrix and particle areas on the oxide films removed from amorphous and pre-crystallised Fe78Si9B13. In both cases, the oxide matrix contained more silicon than the particle areas, while the oxide particles mainly contained iron. Composition measurements such as those in Figs.5-11 and 5-12 are summarised in Table 5-5, and agreed well with the SAED results.

Quantitative metallography by point counting was performed with TEM micrographs to calculate the percentage of bright matrix and dark particle areas in the oxide scales formed on both amorphous and pre-crystallised samples. These results are also included in Table 5-5.

Fig.5-14 shows typical TEM micrographs and corresponding SAED patterns from thin foil alloy specimens of amorphous and crystalline Fe78Si9B13 respectively. Amorphous Fe78Si9B13 exhibited a featureless bright field image and an electron diffraction pattern consisting only of two broad haloes, as expected for an amorphous atomic structure. Pre-crystallised Fe78Si9B13, however, exhibited a much more complicated multiphase microstructure, as can be seen in Fig.5-14(c). The SAED patterns consist of many spots and polycrystalline rings as shown in Fig.5-14(d) due to the very small grain size. Indexing of these SAED patterns showed that crystallised Fe78Si9B13 consisted mainly of α -Fe, Fe_2B and Fe_3Si , as shown in Table 5-6. The different grains in the pre-crystallised structure had various silicon contents ranging from 5 to 15%at as shown by the typical EDX

Table 5-4

Calculated d spacings for typical diffraction patterns obtained from both bright and dark areas on oxide films removed from amorphous and pre-crystallized $\text{Fe}_{7.8}\text{Si}_{1.3}\text{B}_{1.3}$ oxidized at 350°C for 500h, together with ASTM powder card index d spacings for several relevant oxides

DP from amor.		DP from pre-cryst.		$\beta\text{-SiO}_2$	SiO_2	Fe_3O_4	Fe_2O_3
bright areas	dark areas	bright areas	dark areas	(7-346)	tridymite (14-260)	(11-614)	(13-534)
		4.85	4.84			4.85	
		4.42		4.43			
			4.26		4.268		
			4.04		4.075		
			3.82		3.832		
	3.66	3.55	3.64		3.609		3.66
3.43	3.42	3.42	3.47	3.42	3.432		
2.97	2.95	2.98	2.96		2.955	2.966	
	2.69						2.69
2.53	2.50	2.54	2.53	2.55	2.534	2.530	2.51
	2.42	2.43	2.45		2.454	2.419	
2.29	2.30	2.29		2.30	2.303		
2.22	2.20	2.22		2.22			
	2.10		2.09		2.111	2.096	
2.05		2.05		2.05			
1.86	1.84	1.87		1.85	1.8705		1.838
1.72	1.70	1.71	1.71	1.71		1.712	
1.62	1.61	1.61	1.61			1.614	1.596
1.57	1.58	1.57		1.57			
1.47	1.48	1.48	1.48			1.483	1.484
1.42		1.41		1.421			
1.39	1.40	1.39		1.393			
1.33	1.34		1.33			1.327	
1.30		1.29		1.292			
1.28	1.26		1.28	1.277		1.279	1.258
1.23	1.23	1.24		1.225			1.226
1.20	1.19	1.19	1.22	1.196		1.2112	1.213
1.12	1.13	1.11	1.114	1.113		1.1214	1.141
1.09	1.10	1.08	1.085	1.105		1.0922	1.102
1.05	1.06		1.045	1.044		1.0489	1.055
0.985	0.980					0.9890	0.9890
.963	.955					.9692	.9601
.885	.890					.8794	.9080

Table 5-5 Crystal structure obtained by indexing SAED patterns, and compositions obtained ce by EPMA from the oxide scales removed from amorphous and pre-crystallised Fe78Si9B13 after oxidation in air at 350 C for 500h

Sample			Oxide structure	Oxide composition, at%*		
Alloys	Area	Percentage in whole oxide film		Fe	Si	Si/Fe
Amorphous	matrix	80	SiO2(β -quartz)+	30+-10	70+-10	1.5-4.0
			SiO2(amor.)+ Fe3O4			
Fe78Si9B13	particles	20	Fe2O3 + Fe3O4 + SiO2(β -quartz)	83+-7	17+-7	0.11-0.32
Pre-cryst.	matrix	45	SiO2(β -quartz)+	30+-25	70+-25	0.8-19
			Fe3O4 + SiO2(amor.)			
Fe78Si9B13	particles	55	Fe3O4 + SiO2(tridymite)	95+-2	5+-2	0.03-0.07

* 10 poiⁿt analyses for each measurement; elements with atomic number < 11 not detected by EDX.

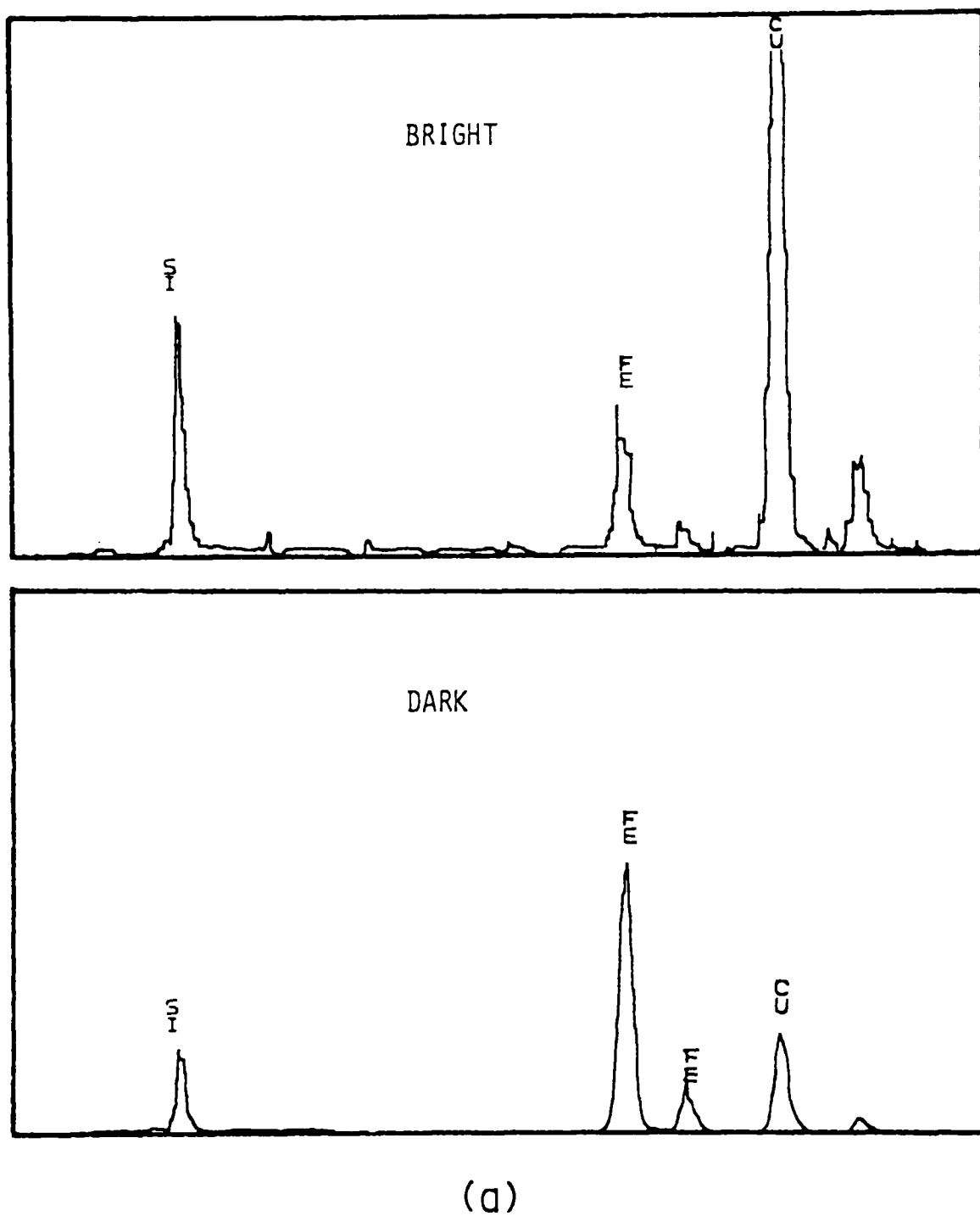


Fig.5-13 Typical EDS spectra from the bright and dark areas of the oxide scales removed from (a) amorphous and (b) pre-crystallised Fe₇₈Si₉B₁₃ oxidised in air at 350°C for 500h. The extraneous Cu peaks are from the support grid and sample holder.

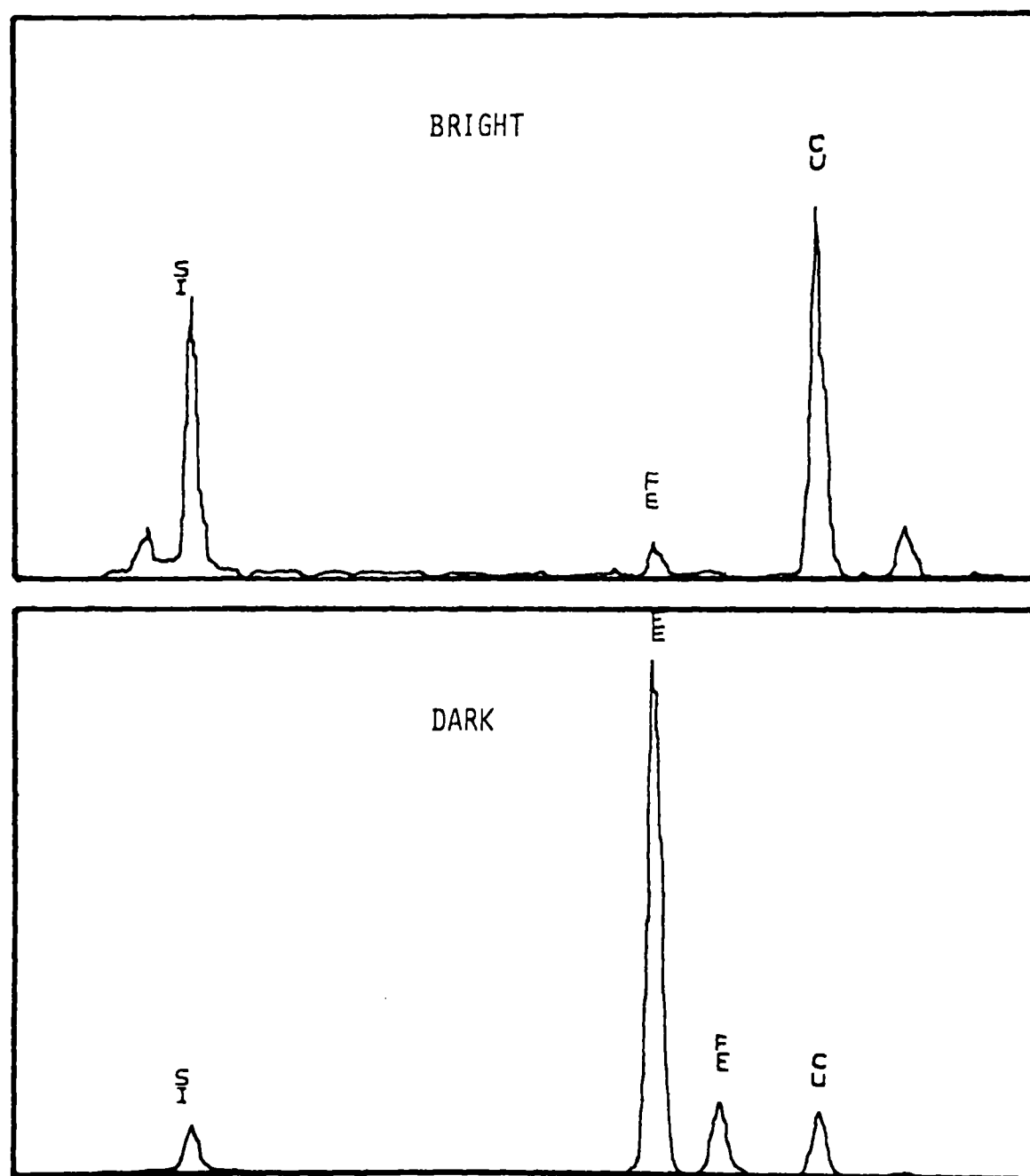


Fig.5-13 (b)

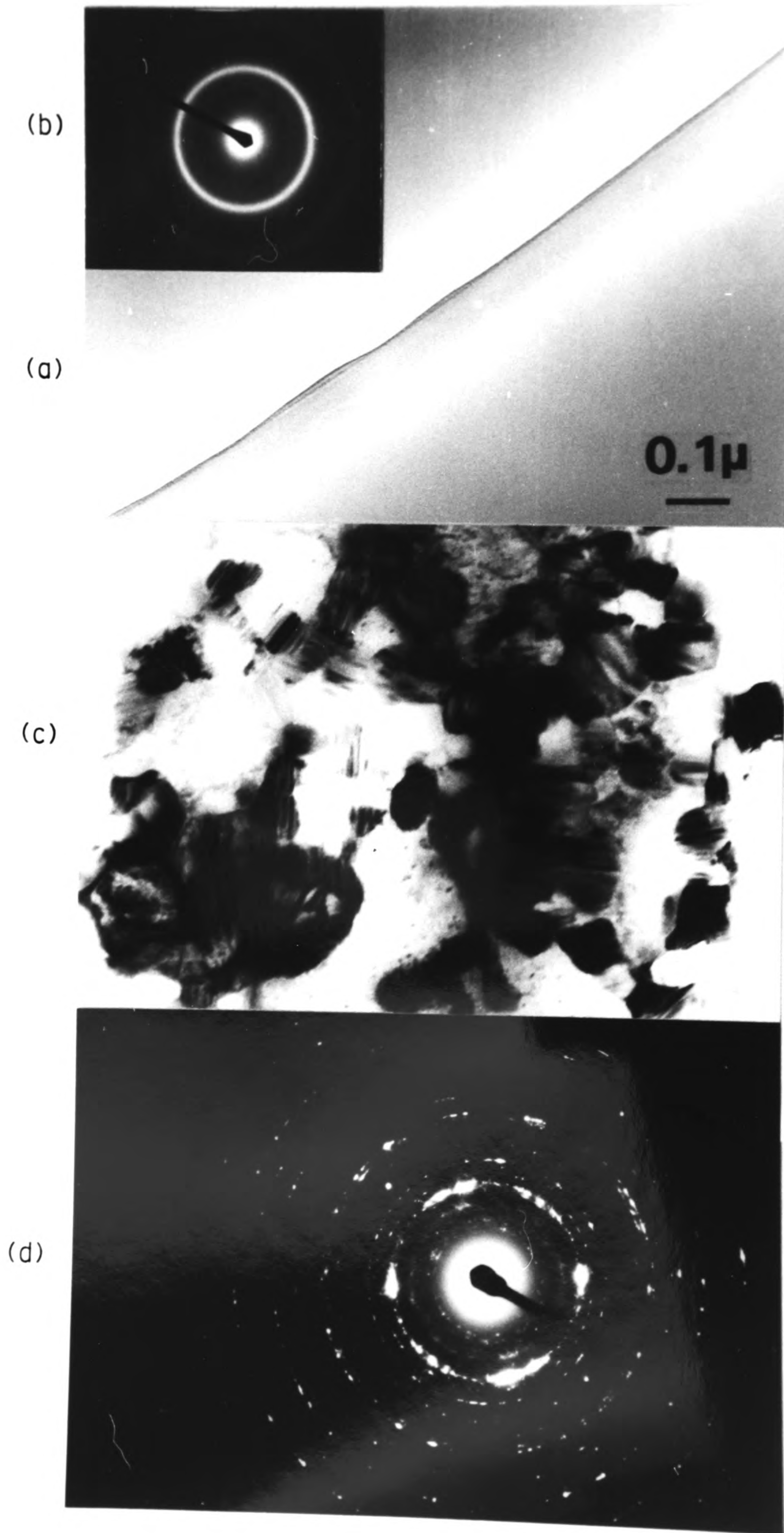


Fig.5-14 TEM micrographs of thin foil samples of (a) amorphous and (c) pre-crystallised Fe₇₈Si₉B₁₃ before oxidation, (b) and (d) are selected area electron diffraction patterns from (a) and (c) respectively.

Table 5-6

Calculated d spacing for Fig.5-14(d), together with
ASTM powder card index d spacings of some relevant compounds

d(A)	α -Fe 6-696	Fe ₃ Si 11-616	Fe ₂ B 3-1053
3.60			3.61
3.26		3.25	
3.21			
2.92			
2.83		2.83	
2.57			2.56
2.27			
2.12			2.12
2.02*	2.0268		2.01
1.99*		1.99	
1.82			1.83
1.71		1.70	
1.63			1.63
1.62*		1.62	
1.43*	1.4332		
1.41*		.41	
1.36			1.37, 1.35
1.29			1.29
1.28			
1.25			
1.20			1.20, 1.19
1.17*	1.1702		
1.15		1.145	1.14
1.09			1.09
1.05			1.05
1.04			
1.01	1.0134		
0.993		0.995	
0.930			0.930
0.898	0.9064		0.907, 0.885
0.827	0.8275		

*Shows a very strong spot occurs in that position

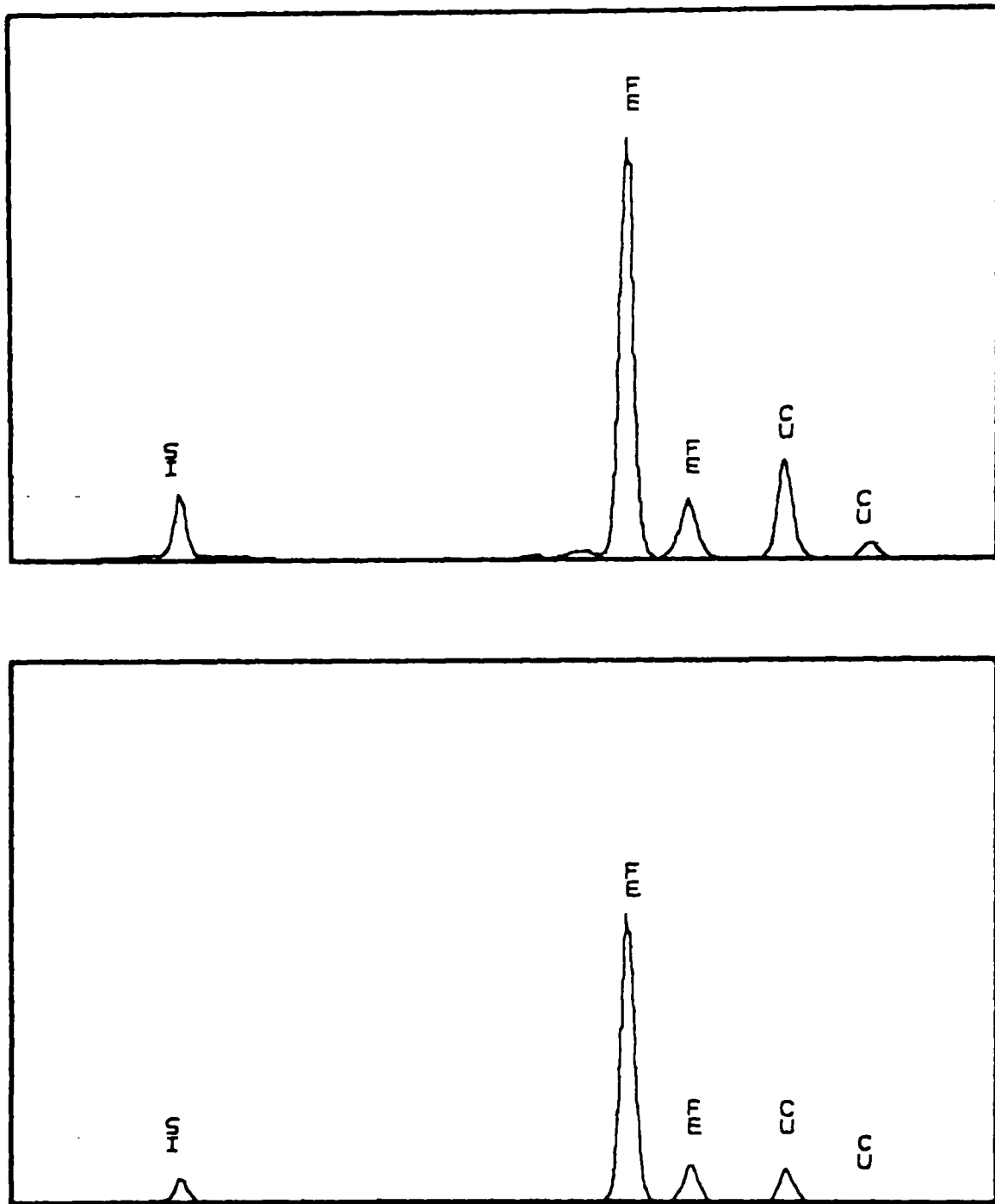


Fig.5-15 Typical EDS spectra from different grains in pre-crystallised Fe₇₈Si₉B₁₃ before oxidation, with silicon content varying from 5 to 15at.%. The extraneous Cu peaks are from the support grid and sample holder.

spectra in Fig.5-15.

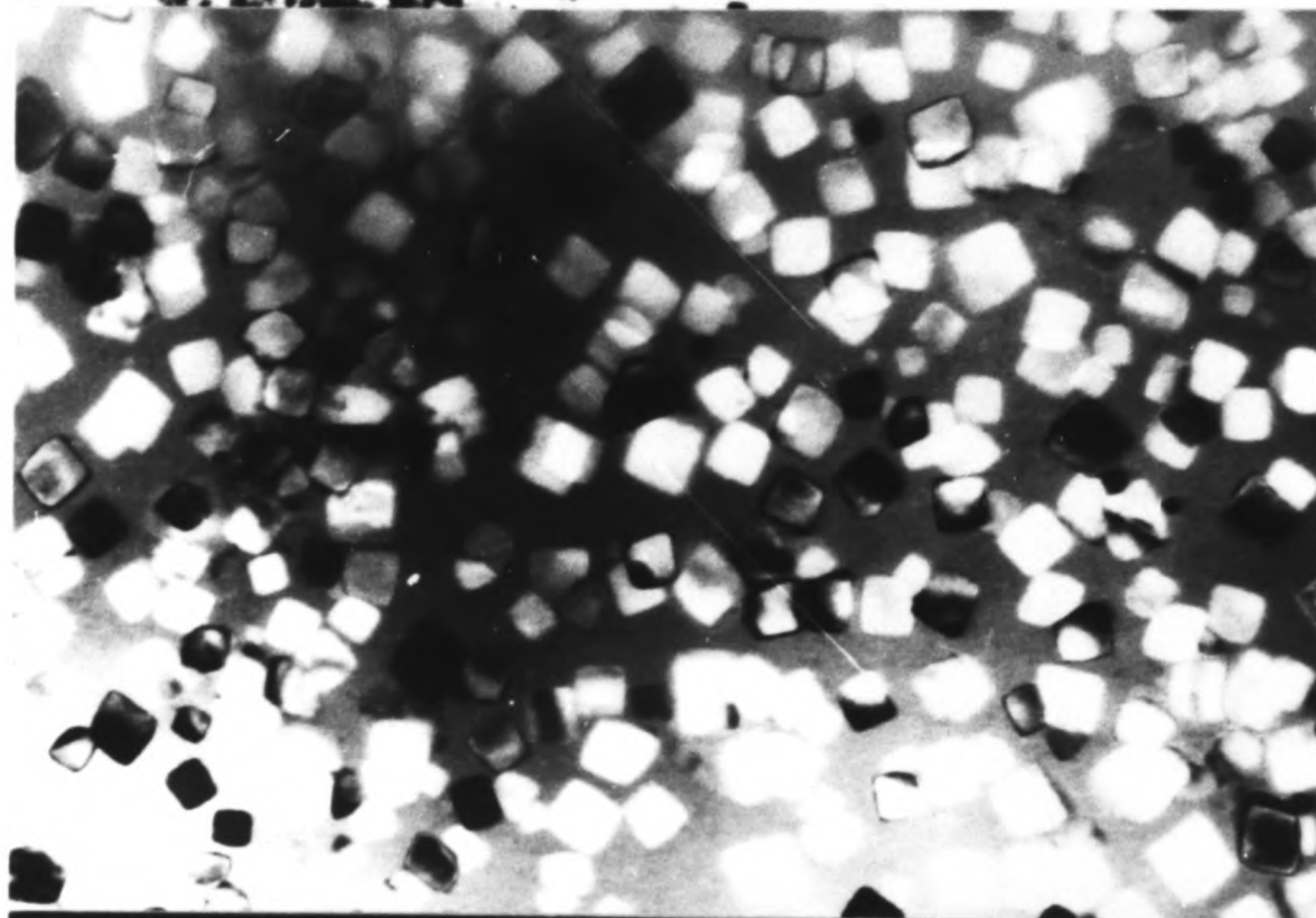
Typical TEM bright field images from amorphous Fe₇₈Si₉B₁₃ thin foils after 2 and 20h oxidation at 350 C are shown in Figs.5-16(a) and (b). Oxide grains which formed in the first stage of oxidation at 350 C had a well defined, square shape, with a mean size of 15nm after 0.5h, 25nm after 2h and 40nm after 20h oxidation. The square oxide grains were distributed quite uniformly, and apparently randomly over the surface of the thin foil amorphous samples, and covered only about 5% of the surface area after 2h of oxidation. With further oxidation annealing, oxide coverage of the amorphous alloy surface progressively increased, reaching approximately 50% after 20h of oxidation. This increase in oxide coverage was caused by a combination of two effects, growth of the square oxide grains and further nucleation of new square grains. Fig.5-16(c) shows the SAED pattern from the area in Fig.5-16(a), consisting of two broad haloes from the amorphous matrix, many spots and several narrow polycrystalline rings. Table 5-7 gives the results of indexing Fig.5-16(c). The diffraction spots were from the square oxide particles and were found to be Fe₃O₄, while the narrow diffraction rings were from fine grains of β -quartz SiO₂. These results were in good agreement with those obtained from the stripped oxide films shown in Table 5-5.

Figs.5-17(a) and (b) show typical TEM micrographs of pre-crystallised thin foil specimens after 2 and 20h oxidation at 350 C respectively. The oxide morphology is not so distinct as in the oxidised amorphous foil specimens, because of additional complex contrast contributed by the underlying crystalline matrix. However, it can clearly be seen in Fig.5-17(a) and (b) that many oxide grains had nucleated on the surface after 2h of oxidation, and had grown quite large after 20h oxidation. The different oxide morphology in amorphous and crystalline Fe₇₈Si₉B₁₃ agreed

(a)



(b)



(c)



Fig.5-16 TEM micrographs of amorphous Fe₇₈Si₉B₁₃ foils oxidised at 350°C for (a) 0.5h and (b) 20h; (c) SAED pattern from (a).

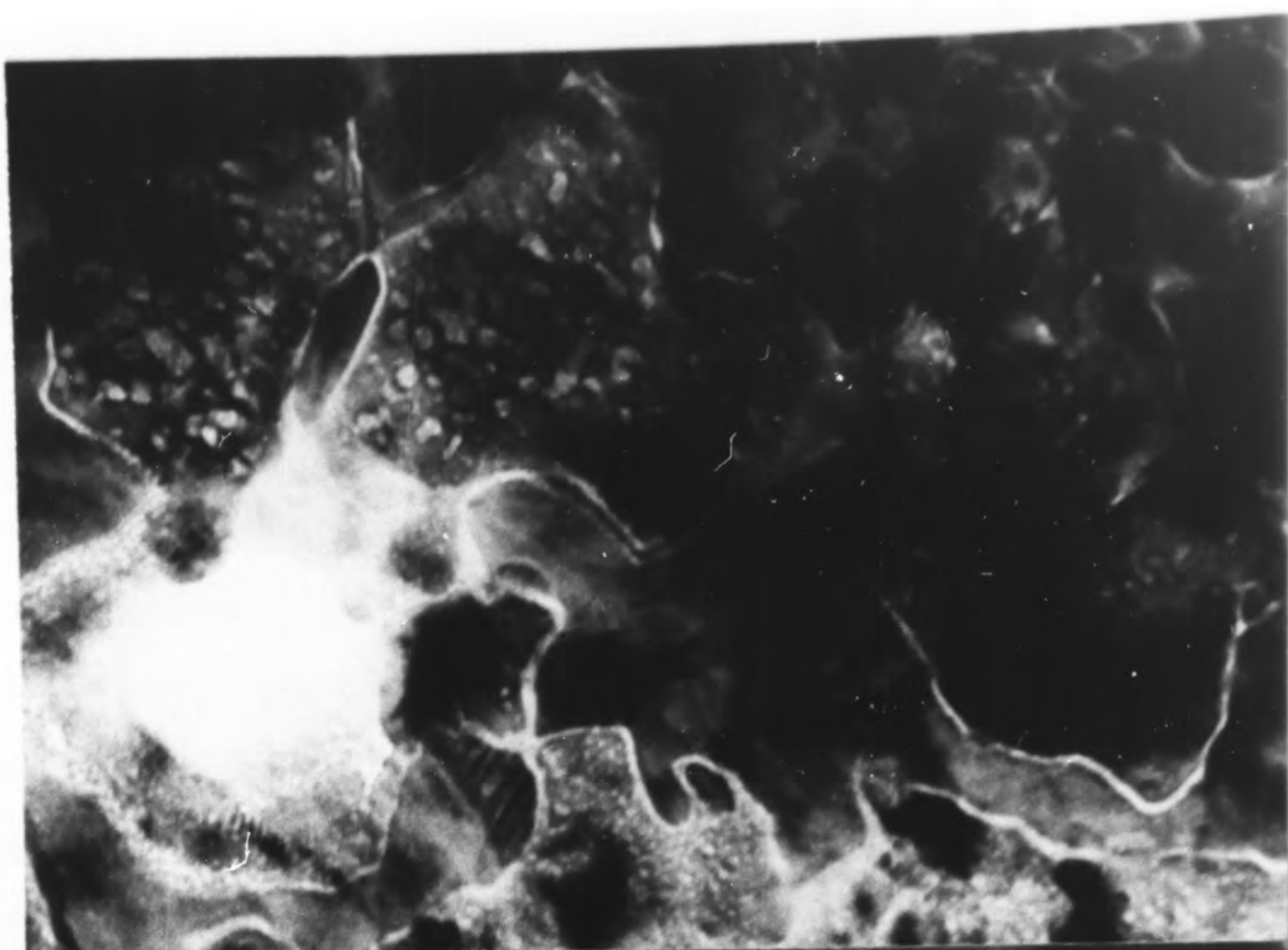
Table 5-7

Calculated d spacings for Fig.5-16(c), together with
 ASTM powder card index d spacings of β -SiO₂ and Fe₃O₄

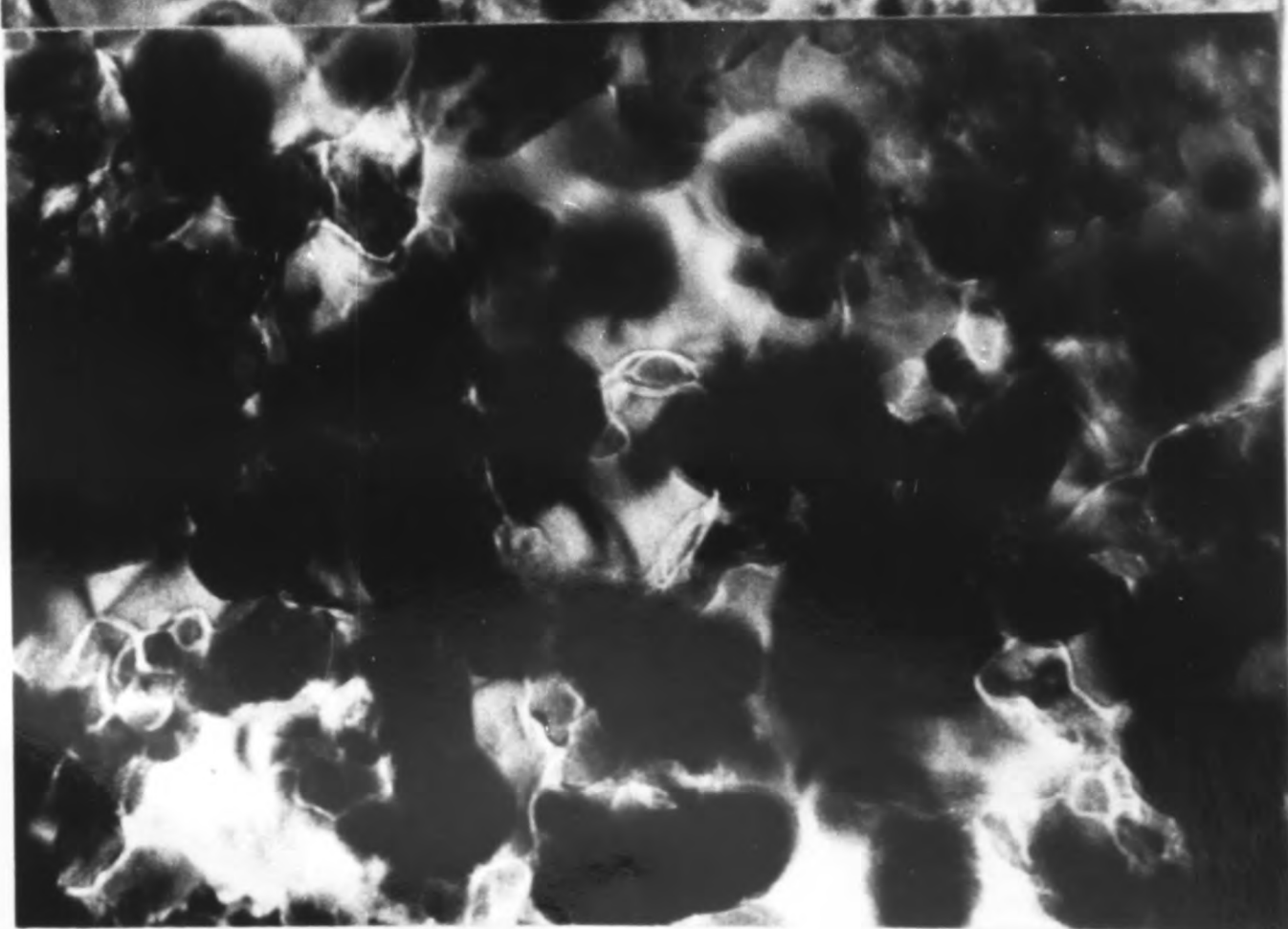
d (Å)	SiO ₂ , β -quartz (7-346)		Fe ₃ O ₄ (11-614)
	d (Å)	relative intensity (%)	d (Å)
3.45*	3.42	100	
2.96			2.966
2.54	2.55	60	2.530
2.39			2.419
2.30*	2.30	40	
2.10*	2.05, 2.22	60, 60	2.096
1.92			
1.86*	1.85	90	
1.71	1.71	40	1.712
1.61			1.614
1.59	1.57	80	
1.50			1.483
1.40*	1.421	80	
1.38*	1.393	80	
1.33			1.327
1.27	1.277, 1.292	60, 60	1.279, 1.264
1.23*	1.225	40	1.211
1.20*	1.190, 1.196	60, 40	
1.10	1.105, 1.113	20, 20	1.092, 1.121
1.04	1.044	20	1.049
0.98*			0.9692, 0.9890
0.940			0.9386

*Shows a polycrystalline ring occurs in that position

(a)



(b)



0.1μ
—

Fig.5-17 TEM micrographs of pre-crystallised Fe₇₈Si₉B₁₃ foils oxidised at 350°C for (a) 0.5 and (b) 20h.

with the thermogravimetry results, in showing that the oxide growth mechanism depended on the alloy microstructure.

5.3 Discussion

5.3.1 Oxidation kinetics

Figs.5-1 and 5-4 show that the oxidation kinetics of both amorphous and crystalline Fe₇₈Si₉B₁₃ obey a parabolic rate law at temperatures of 300-400 C over 500h oxidation, at 450 C over the initial 300h oxidation, and at 500 C over the initial 50h oxidation. This suggests that for these times and temperatures, the oxidation reactions controlling process is diffusion of ions through the oxide scale brought about by a concentration gradient across the oxide scale (32,33). As in Chapter 4, the parabolic constant K is given by an Arrhenius equation:

$$K = K_0 \exp(-Q/RT) \quad (5-2)$$

Fig.5-18 shows the parabolic rate constant plotted versus inverse temperature ($\ln K - 1/T$) for both amorphous and crystallised Fe₇₈Si₉B₁₃. The data for pre-crystallised Fe₇₈Si₉B₁₃ show good linear behaviour from 300 to 450 C, in agreement with the Arrhenius eqn.(5-2). At temperatures below 400 C, the data for amorphous Fe₇₈Si₉B₁₃ also show good linear behaviour in agreement with the Arrhenius eqn.(5-2), with a steeper slope and therefore higher activation energy than the crystalline alloy. Because the alloy does not remain amorphous and crystallises during oxidation annealing at 450 and 500 C, there is a change in oxidation mechanism, and the points at 450 and 500 C are rather higher than expected from the lower temperature results of amorphous alloys.

Activation energies for the two curves in Fig.5-18 were calculated by using linear regression analysis. The results are given in Table 5-8, together with other relevant diffusion data taken from the literature

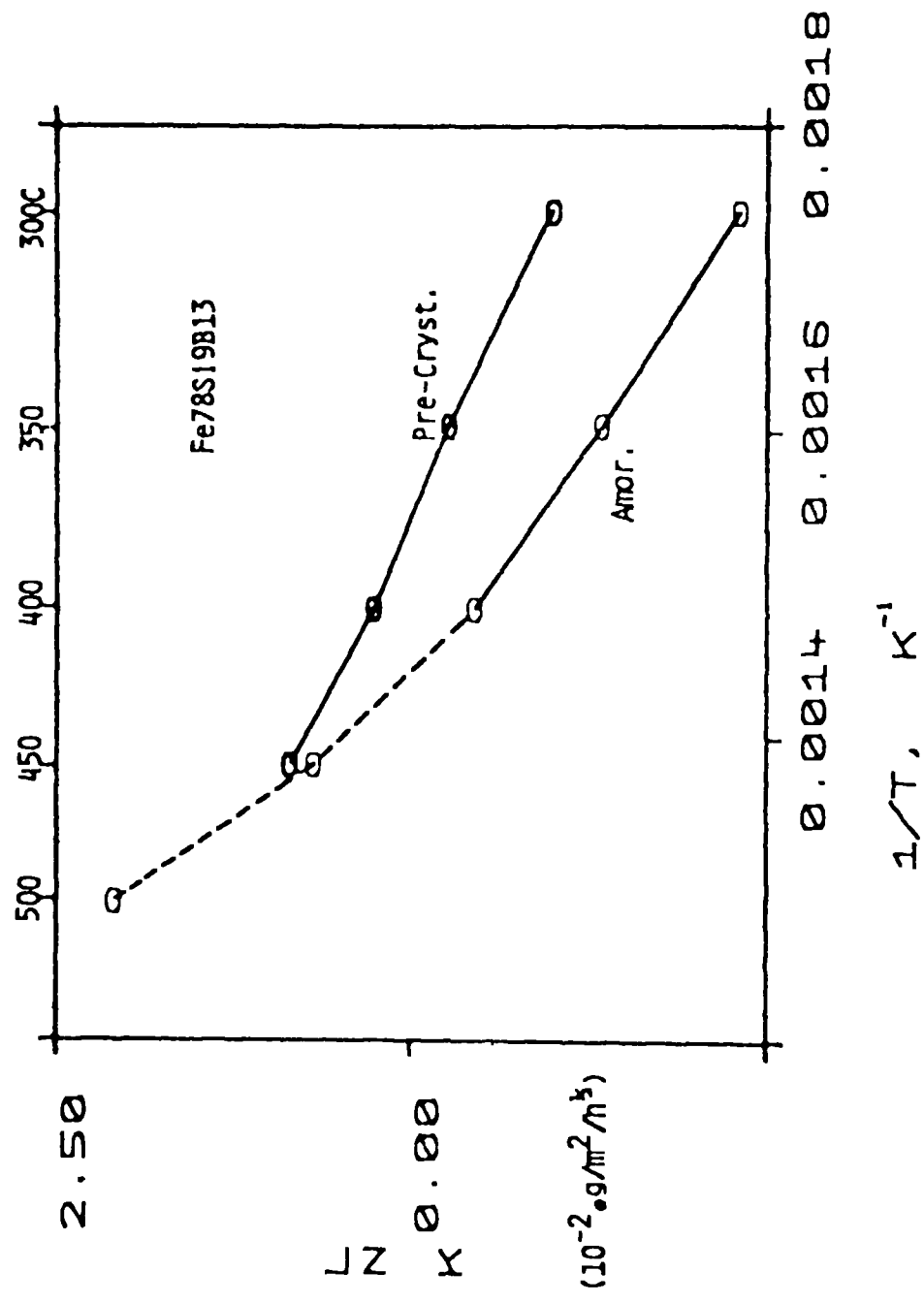


Fig.5-18 The Arrhenius variation of $\ln$ parabolic rate constant versus inverse absolute temperature ($\ln K - 1/T$) for amorphous and pre-crystallised Fe78Si9B13.

Table 5-8 Activation energies for oxidation of amorphous and crystalline Fe78Si9B13 together with other relevant diffusion data obtained from the literature (34-36)

Diffusion ions	Diffusion matrix	Temperature range C	Activation energy (kJ/mol)	Correlation coefficient	Data source
Fe + Si	Fe3O4 + Fe2O3 + SiO2	300 - 400	120	0.999	amorphous Fe78Si9B13
Fe + Si	Fe3O4 + SiO2	300 - 450	86	0.998	pre-cryst. Fe78Si9B13
Fe	FeO	690 - 1010	126.4		(34)
Fe	Fe3O4	750 - 1000	230		(34)
Fe	Fe2O3	930 - 1270	469 390 - 470		(34) (36)
O	Fe2O3		330 - 610		(36)
O	SiO2	1200 - 1360	180 148		(35) (36)

(34-36). The measured activation energies for both amorphous and crystalline Fe₇₈Si₉B₁₃ are considerably smaller than those measured previously⁽³⁴⁻³⁶⁾ for Fe ions in Fe₃O₄ or Fe₂O₃, and oxygen ions in SiO₂. The low activation energies for oxidation can be explained as a consequence of the very small oxide grains which were found in both types of oxide scale, so that the rate controlling process for oxidation is likely to be diffusion of ions along the oxide grain and interphase boundaries instead of through the bulk oxide crystal lattice (37).

As reviewed in section 2.2.2, diffusion of ions along grain boundaries or other defects in the oxide scale has been reported as the rate controlling process in a number of cases for metallic oxidation⁽³⁶⁻⁴⁰⁾. For instance, Atkinson et al⁽⁴⁰⁾ have indicated that oxidation of nickel is controlled by diffusion of Ni ions along NiO grain boundaries at temperatures below 1100 C, and similar results have been reported for the growth of Fe₂O₃, Fe₃O₄ and Cr₂O₃ (36). In the present case, the oxide scales on amorphous and pre-crystallised Fe₇₈Si₉B₁₃ are very complex, consisting of Fe₂O₃ and Fe₃O₄ particles embedded in a thin matrix layer of crystalline and amorphous SiO₂. Thus, ion diffusion may take place along various different types of grain and interphase boundaries, including β-SiO₂ grain boundaries in the oxide matrix, Fe₂O₃ and Fe₃O₄ grain boundaries in the oxide particles, and the interphase boundaries between the oxide particles and oxide matrix. This makes quantitative analysis of the diffusion process very difficult.

The oxidation rate decreased from parabolic at 450 C after about 300h oxidation and at 500 C after 50h oxidation, as shown in Figs.5-1 and 5-4. Several possible effects may contribute to this decrease. Firstly, as the reaction proceeds, the contact between scale and metal can be lost at certain areas due to growth stresses within the oxide scale. This reduces

the area through which the ions migrate outwards, and therefore reduces the reaction rate. This effect is usually more significant at higher oxidation temperatures and/or longer oxidation times. Secondly, oxide grain growth may take place during oxidation annealing, reducing the total area of grain boundaries available for ion migration. However, the mass gains on amorphous and crystallised Fe₇₈Si₉B₁₃ are concentrated in the iron oxide particles, and little evidence was found for iron oxide grain growth within the particles. Thirdly, the iron oxide particle size does increase during oxidation annealing, as shown in Table 5-3, which again can increase the area of oxide particle-matrix interphase boundary available for ion diffusion. At the same time, however, the interphase boundary area is reduced by oxide particle coarsening, and the observed microstructures indicated that neither effect would strongly influence the oxidation rate. A detailed quantitative analysis of oxidation kinetics in amorphous and crystalline Fe₇₈Si₉B₁₃ is clearly very difficult to achieve.

The oxidation kinetics of industrial crystalline Fe₉₄Si₆ silicon steel at 350 C also obeys a parabolic rate law as shown in Fig.5-5(a), with a higher rate constant of $1.38 \times 10^{-2} \text{ gm}^{-2} \text{ h}^{-1/2}$. At 400 C, however, the oxidation exhibited a two stages of parabolic growth with different rate constants of $2.02 \times 10^{-2} \text{ gm}^{-2} \text{ h}^{-1/2}$ for 0-44h and $8.70 \times 10^{-2} \text{ gm}^{-2} \text{ h}^{-1/2}$ for 44-500h oxidation. This suggested that the oxide scales formed on Fe₉₄Si₆ were different before and after 44h oxidation at 400 C. In fact, SEM observation of the oxide morphology in Fig.5-8(a) shows many cracks on the oxide scale on Fe₉₄Si₆ silicon steel after 120h oxidation at 400 C, with a fresh non-protective oxide under the cracked oxide scales (Fig.5-8(b)). In comparison, the oxide scales formed on amorphous and crystalline Fe₇₈Si₉B₁₃ showed no evidence of breakdown at oxidation temperatures up to 450 C, as shown in Figs.5-6 and 5-7. Comparing Fig.5-6 with Fig.5-8, amorphous

Fe₇₈Si₉B₁₃ has a more protective oxide scale than Fe₉₄Si₆ silicon steel, and therefore exhibits better oxidation resistance. The reasons for this probably include (a) amorphous Fe₇₈Si₉B₁₃ contains a higher Si concentration, and (b) Si distributes homogeneously in the amorphous alloy.

These two factors help to develop a Si-rich protective scale and result in better oxidation resistance, as will be described for amorphous Fe₇₈Si₉B₁₃ below.

5.3.2 Oxide growth mechanism

There is a big difference in oxidation behaviour between amorphous and crystalline Fe₇₈Si₉B₁₃. As discussed in Chapter 4, there is also a big difference in oxidation behaviour between amorphous and crystalline Fe₄₀Ni₄₀P₁₄B₆. However, the effects of crystallisation on the oxidation behaviour of these two alloys are different: Amorphous Fe₇₈Si₉B₁₃ has a better oxidation resistance than crystalline Fe₇₈Si₉B₁₃, while amorphous Fe₄₀Ni₄₀P₁₄B₆ has a poorer oxidation resistance than crystalline Fe₄₀Ni₄₀P₁₄B₆. Evidence showed again that the microstructure and microchemistry of the amorphous and crystalline alloys affected the oxide growth mechanism. A suggested mechanism for oxide growth on amorphous and crystallised Fe₇₈Si₉B₁₃ can be given as follows.

Amorphous Fe₇₈Si₉B₁₃ has a homogeneous chemical composition which can supply silicon to build up a thin layer of SiO₂ over the whole alloy surface. At the same time, iron oxide nucleates and grows within the thin SiO₂ film, as shown by the SAED and EPMA results in Tables 5-4, 5-5, and 5-7, and Figs. 5-6, 5-9, 5-11 and 5-16. Even the dark areas in the oxide scale on the amorphous alloy contained 10-20at.%Si (Fig. 5-13), and showed quite strong SiO₂ diffraction patterns or rings. It has been reported previously ^(35,36) that the growth rate of SiO₂ is slow, with oxygen as the dominant diffusing species. The diffusion of Fe³⁺ in SiO₂ has also been

measured⁽⁴¹⁾, and the results suggest that a continuous thin SiO_2 film is effective in reducing the oxidation rate of ferrous alloys. This is the reason for good oxidation resistance in some conventional Fe alloys which contain silicon^(42,43). There is a similar effect in oxidation of amorphous $\text{Fe}_{78}\text{Si}_{9}\text{B}_{13}$, where iron oxides grow relatively slowly, probably because of the formation of a continuous thin SiO_2 layer, which slows down outward diffusion of iron ions.

Crystallised $\text{Fe}_{78}\text{Si}_{9}\text{B}_{13}$ has a fine scale multiphase crystalline structure. Chang and Marti⁽¹³⁾ have reported that crystalline $\text{Fe}_{80}\text{Si}_8\text{B}_{12}$ contains dendritic bcc $\alpha\text{-Fe}(\text{Si})$ and cylindrical particles of bct Fe_3B ; and Bhatti and Cantor⁽¹⁴⁾ have reported that the crystallised structure in $\text{Fe}_{78}\text{Si}_{9}\text{B}_{13}$ consists of a mixture of dendritic bcc $\alpha\text{-Fe}(\text{Si})$, some epitaxial Fe_3Si , and spherulites of a mixture of bcc $\alpha\text{-Fe}(\text{Si})$ and Fe_3B . In the present work, pre-crystallised samples were heat treated with longer time, higher temperature crystallisation anneals compared with the heat treatments used previously by Chang and Marti (13) and Bhatti and Cantor (14). The diffraction patterns in Fig.5-14(d) show that this leads to a crystalline structure consisting mainly of $\alpha\text{-Fe}$, Fe_2B and Fe_3Si , and the electron probe microanalysis results in Fig.5-15 show that Si contents vary locally from approximately 5at.% below the overall alloy Si concentration to approximately 5at.% above. The variation in Si content seems to prevent an SiO_2 layer from building up continuously, so that microanalysis of the oxide films removed from the pre-crystallised samples shows almost complete SiO_2 in some of the matrix areas, but almost no SiO_2 in most of the oxide particles. Compared with the amorphous alloy, Si depleted regions in the oxide scale allow Fe_3O_4 to grow faster on crystalline $\text{Fe}_{78}\text{Si}_{9}\text{B}_{13}$, leading to a faster oxidation rate. Another possible explanation for the higher oxide growth rate on crystalline $\text{Fe}_{78}\text{Si}_{9}\text{B}_{13}$ is that epitaxial relationships

between oxide and alloy crystals may promote oxide growth on crystalline Fe₇₈Si₉B₁₃ (45), but it is difficult to investigate this further because of the very small grain size in both the alloy matrix and oxide film.

Fig.5-19 shows schematically the oxide growth mechanism in amorphous and crystalline Fe₇₈Si₉B₁₃ described above.

5.4 Conclusions

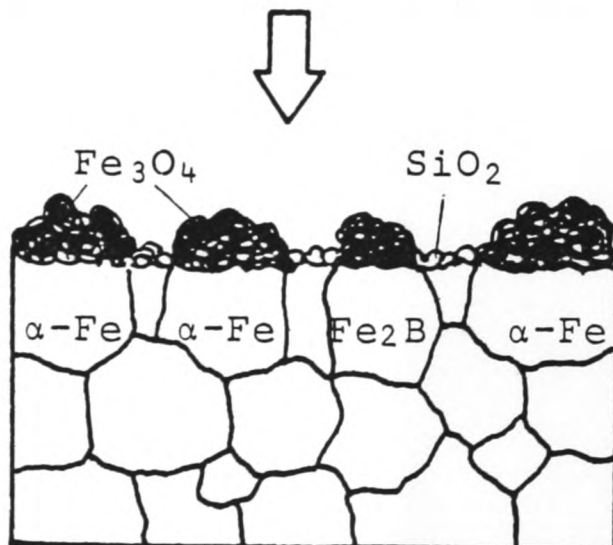
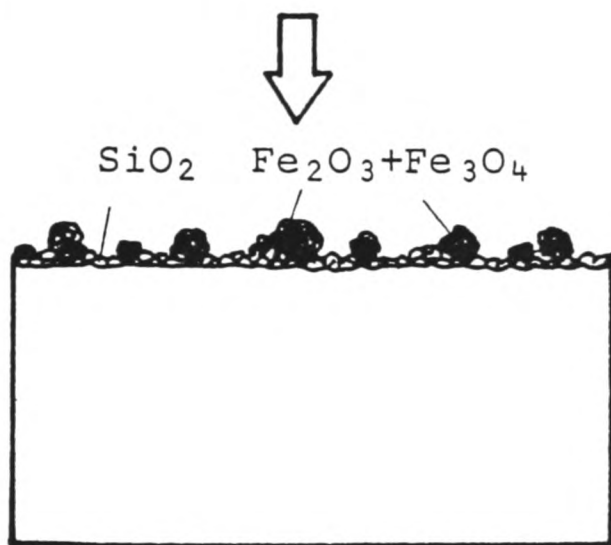
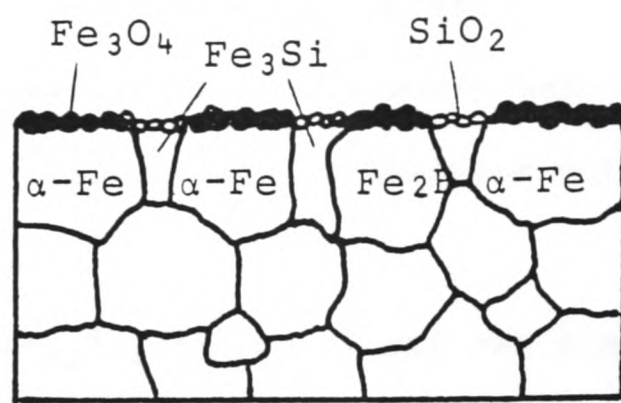
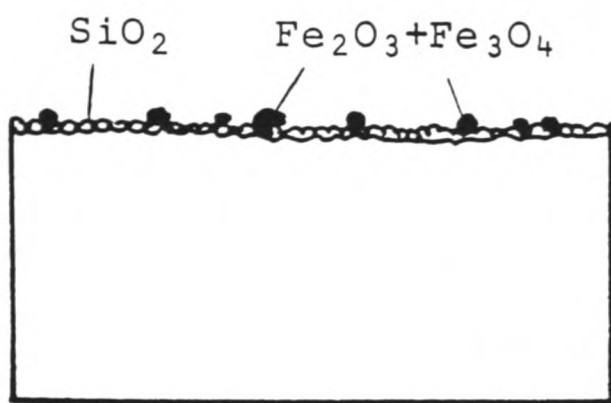
From the present investigation, the following conclusions can be drawn.

1. Oxidation of amorphous Fe₇₈Si₉B₁₃ in air obeys a parabolic rate law over the temperature range 300-400 C. The parabolic rate constant increases with the oxidation temperature according to an Arrhenius law, with an activation energy of 120 kJ/mol. Above 400 C, the amorphous alloy crystallises quickly so that the oxidation behaviour is more characteristic of the crystalline alloy.

2. The oxide scale formed on amorphous Fe₇₈Si₉B₁₃ consists of a thin, continuous layer of SiO₂ in which larger particles of Fe₂O₃ and Fe₃O₄ are embedded. The oxide scale grows relatively slowly and the rate controlling process is probably diffusion of ions along grain and interphase boundaries.

3. Oxidation of crystalline Fe₇₈Si₉B₁₃ in air also obeys a parabolic rate law over the temperature range of 300-450 C, but with higher parabolic rate constants than amorphous Fe₇₈Si₉B₁₃. The parabolic rate constant increases with the oxidation temperature and again obeys an Arrhenius law, with a lower activation energy of 86kJ/mol.

4. The oxide scale formed on crystalline Fe₇₈Si₉B₁₃ consists of Fe₃O₄ and SiO₂, but unlike the amorphous alloy, the SiO₂ is not continuous. Because of this, the Fe₃O₄ grains grow more rapidly and the overall oxidation rate is therefore higher than for amorphous Fe₇₈Si₉B₁₃. The rate



Amorphous Fe₇₈Si₉B₁₃

Crystalline Fe₇₈Si₉B₁₃

(a)

(b)

Fig.5-19 Schematic oxide growth on (a) amorphous and (b) crystallised Fe₇₈Si₉B₁₃ alloys.

controlling process is again probably diffusion of ions along grain and interphase boundaries.

5. Different oxidation kinetics and oxide growth mechanisms in amorphous and crystalline Fe₇₈Si₉B₁₃ are caused by different alloy microstructures. Microsegregation of Si within the multiphase crystalline structure of Fe₇₈Si₉B₁₃ inhibits the formation of a continuous layer of SiO₂, and eventually leads to an oxide structure and composition different from amorphous Fe₇₈Si₉B₁₃.

6. Industrial oriented crystalline Fe₉₄Si₆ silicon steel has a poorer oxidation resistance than amorphous Fe₇₈Si₉B₁₃ in the temperature range 350–450 C because of the formation of a non-protective oxide scale.

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Chapter 6 The Oxidation Behaviour of Amorphous and Crystalline

Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ and Some Other Co-based Alloys

6.1 Introduction

Co-based metal-metalloid amorphous alloys with low or zero magnetostriction are of particular interest for applications in the area of electronics (1-3). For soft magnetic materials the magnetisation process is affected by induced magnetic and magnetoelastic anisotropy. The magnetoelastic interaction is proportional to the product of effective local stress and magnetostriction, and can be reduced either by stress relief annealing or by choosing an alloy with a small magnetostriction. Amorphous alloys in the Co-Ni-Fe-Si-B system have almost zero magnetostriction and therefore are insensitive to external as well as internal stresses (3-4). There have been several studies of the magnetic properties and applications of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ (5-8). Investigations of the magnetic properties (9,10,19), manufacturing techniques (11,12), structural relaxation (13,14), mechanical and joining properties (15,16) and technological applications (17,18) of some other Co-Fe-Si-B amorphous alloys with similar chemical compositions have also been reported, showing the technological value of amorphous alloys in this system.

The main application of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ is for manufacturing audio and video recording heads (3,17). The required properties for magnetic head materials include high magnetic saturation, high permeability, low magnetostriction, small coercivity, relatively high electrical resistivity, low wear loss, good formability and thermal stability. Amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ possesses most of the required properties mentioned above (3,17). However, there has been very little

previous investigation of the thermal degradation of Co-Ni-Fe-Si-B alloys by either crystallisation or oxidation ((20,21) and also see section 2.6.2). Understanding the crystallisation and oxidation behaviour is essential to prevent such thermal degradation effects during alloy manufacture, heat treatment and service.

The present work has concentrated on the oxidation behaviour of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ (Vitrovac 6010). Two other Co based amorphous alloys, Co₆₆Ni₁Fe₄Si₁₅B₁₄ (Metglas 2714A) and Co₇₆Mn₄Fe₂Si₆B₁₂ (Metglas 2705MN), have also been studied to achieve a more general view of the oxidation behaviour of amorphous Co alloys (22). Crystallisation kinetics and the resulting crystal structure in amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ has also been investigated, with particular attention to the effect of crystallisation on the oxidation behaviour (23). As in the previous Chapters on amorphous Fe₄₀Ni₄₀P₁₄B₆ and Fe₇₈Si₉B₁₃, pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ have been used for comparison purpose. The effect of surface oxidation on the magnetic properties has also been studied and will be published elsewhere (24).

6.2 Experimental results

6.2.1 Oxidation kinetics

Fig.6-1 shows the measured mass gain of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ as a function of (a) the oxidation time, and (b) the square root of oxidation time over a temperature range of 300-500 C. The mass gain was found to be approximately proportional to the square root of oxidation time at temperatures of 300, 350 and 400 C over the whole 500h period of oxidation testing. This showed that at these temperatures the oxidation reaction obeyed a parabolic rate law:

$$y^2 = Kt$$

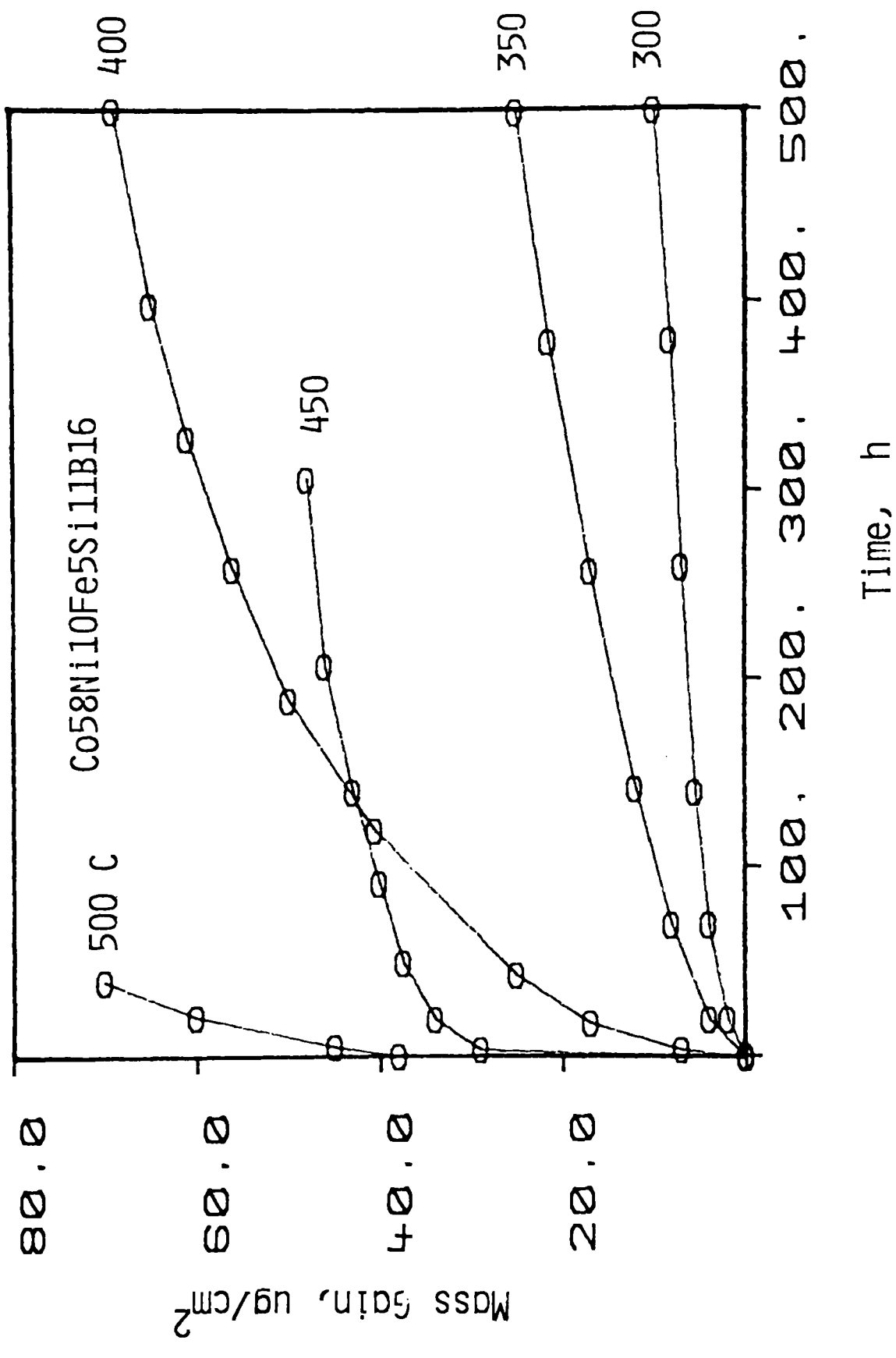


Fig.6-1 Mass gain Y versus (a) oxidation time t, (b) square root of oxidation time t for amorphous Co58Ni10Fe5Si11B16 over the temperature range 300-500°C.

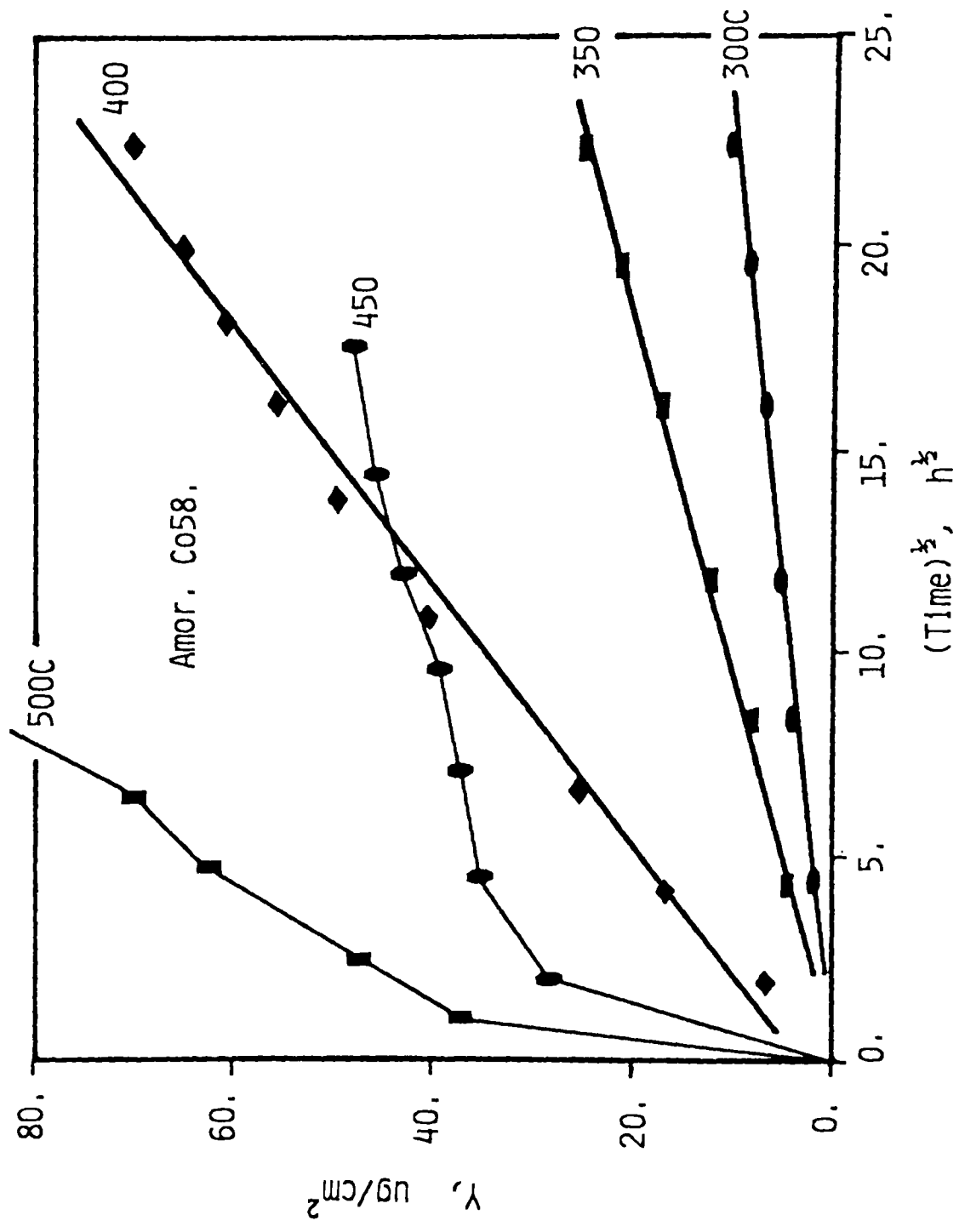


Fig. 6-2(b)

$$Y = K't^{1/2} \quad (6-1)$$

Table 6-1 shows best fit values of K' and the corresponding correlation coefficients obtained by fitting the experimental data to eqn.(6.1). The parabolic rate constant for amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ increased from 0.45 to $3.15 \text{ ug/cm}^2/\text{h}^{1/2}$ as the temperature increased from 300 to 400 C. At 450 and 500 C, the oxidation rate decreased more sharply than expected for a parabolic rate law as can be seen in Fig.6-1, so that the mass gain at 450 C was smaller than at 400 C after 140h oxidation. As found for the oxidation of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ and $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ in Chapter 4 and 5, this again suggested that the oxidation reaction of amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ underwent a change in mechanism as the temperature range increased above 400 C.

The observed change from parabolic to non-parabolic oxidation behaviour for amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ was again found to be related to the onset of crystallisation during oxidation annealing. Fig.6-2(a) shows an isothermal DSC trace from as-supplied amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ at 500 C, indicating that crystallisation was completed after approximately 6h heat treatment. Thus, the oxidation results at 500 C in Fig.6-1 corresponded to the fully crystallised alloy. Fig.6-2(b) shows continuous heating DSC traces from amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ samples which had previously been oxidised at 450 and 400 C for various periods of time. The exothermic crystallisation peak began to decrease after about 50h oxidation at 450 C, and had virtually disappeared after about 250h at 450 C. Thus the onset of crystallisation at 450 C corresponded reasonably well with the decline from parabolic oxidation kinetics in Fig.6-1. However, Fig.6-2(b) shows no change in the exothermic crystallisation peak after 500h oxidation at 400 C, so that the parabolic oxidation kinetics in Fig.6-1 corresponded to a fully amorphous material over the whole period of oxidation testing.

Table 6-1: Best fit linear slopes and correlation coefficients in eqns.(6-1) and (6-2) for the oxidation kinetic curves of amorphous and crystalline Co58Ni10Fe5Si11B16.

Sample	Oxidation Temp. ^o C	Oxidation Time	Slope Kp* and K _L **	Intercept A _P * and A _L **	Correlation coefficient
Amor.	300	0-500h	0.20	-2.8	0.992
	350	0-500h	1.28	-24.7	0.998
	400	0-500h	9.95	279.2	0.990
Cryst.	300	20-500h	0.93	1.50	0.994
	350	20-500h	1.77	-1.30	0.985
	400	4-400h	3.49	-0.75	0.985
	450	4-308h	5.40	8.14	0.988

* K_p in units of 10⁻⁴ x g²/m⁴/h, and A_p in units of 10⁻⁴ x g²/m⁴

** with Y in units of ug/cm² and t in units of h in eqn.(2)

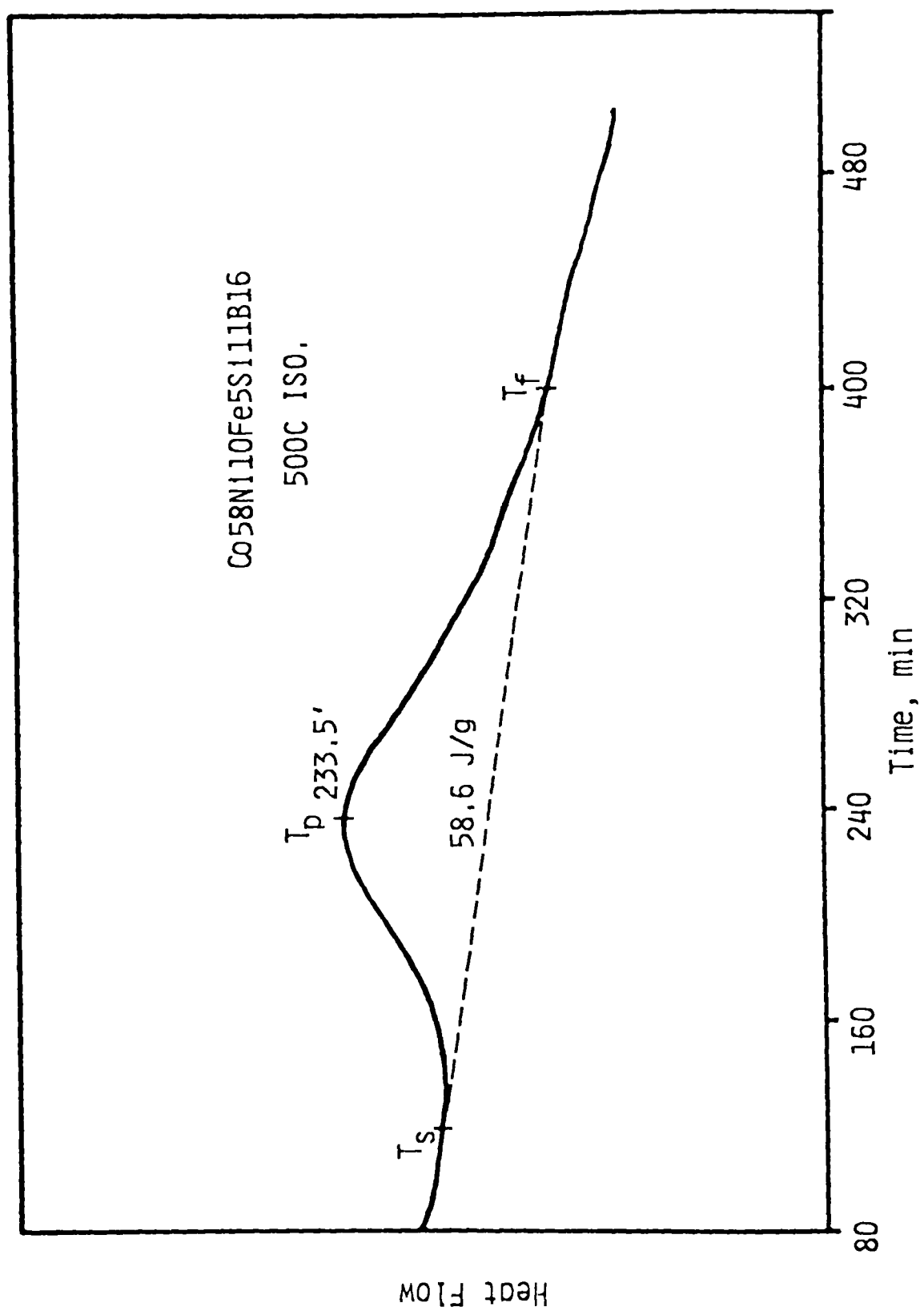


Fig.6-2 (a) Isothermal DSC trace from amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ at 500°C, showing exothermic crystallisation peak between 2.3 and 6h. (b) Continuous heating DSC traces from amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, showing exothermic crystallisation peak as a function of prior oxidation time at 400 and 450°C.

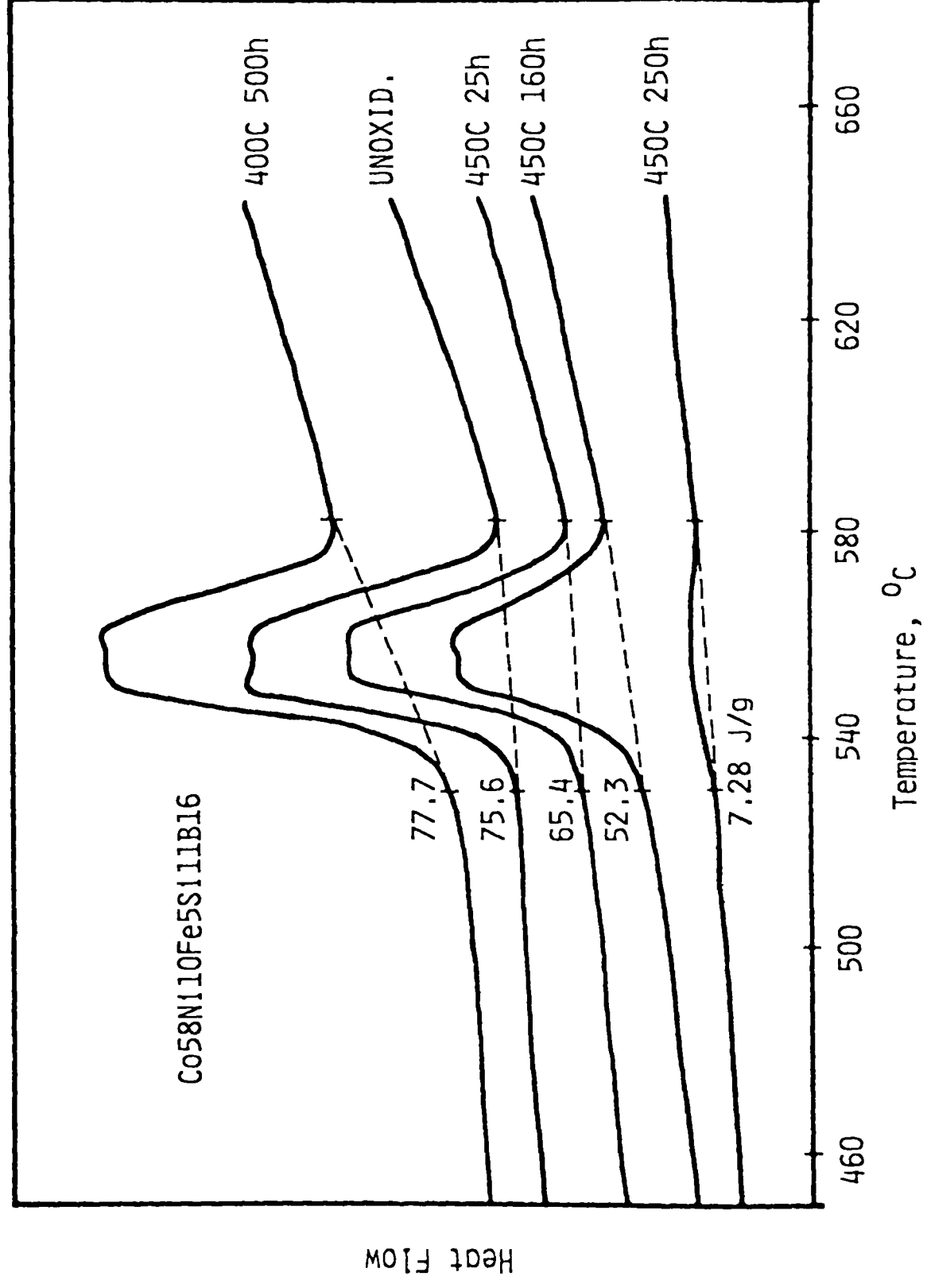


Fig.6-2 (b)

In summary, therefore, the amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ crystallised during oxidation annealing at 450 and 500 C, leading to a change of oxidation mechanism and a decrease in reaction rate.

Comparison oxidation tests were performed on amorphous and pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ in order to investigate further the effect of crystallisation on the oxidation behaviour, and typical results of mass gain versus time are shown in Figs.6-3(a)-(c) for oxidation at 300, 400 and 450 C respectively. Comparing the oxidation kinetics of amorphous and crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ in Fig.6-3 (a) and (b), the amorphous alloy had mass gains 1.5 and 2.3 times greater than the pre-crystallised alloy after 500h oxidation at 350 and 400 C respectively. At the higher temperature of 450 C, the average mass gain of amorphous samples was only about 20% greater than pre-crystallised samples after 310h oxidation as shown in Fig.6-3(c), since the amorphous samples crystallised during oxidation annealing. Fig.6-3(d) shows the measured oxidation mass gains of pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ versus $\ln$ oxidation time $Y-\ln t$, indicating that the mass gains were not only smaller than the amorphous alloy at the same oxidation conditions, but also obeyed a different oxidation rate law. Oxidation of pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ over the temperature range 300-450 C obeyed logarithmic rather than parabolic kinetics:

$$Y = K_L \ln t + A_L \quad (6-2)$$

where K_L and A_L are constants, which are given in Table 6-1. This indicated that amorphous and crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ have different oxidation mechanisms, as was found for amorphous Fe₄₀Ni₄₀P₁₄B₆ and Fe₇₈Si₉B₁₃ in Chapter 4 and 5.

Fig.6-4(a) shows the mass gain versus square root of oxidation time at 400 C in air for the other two Co based alloys Co₆₆Ni₁Fe₄Si₁₅B₁₄ and

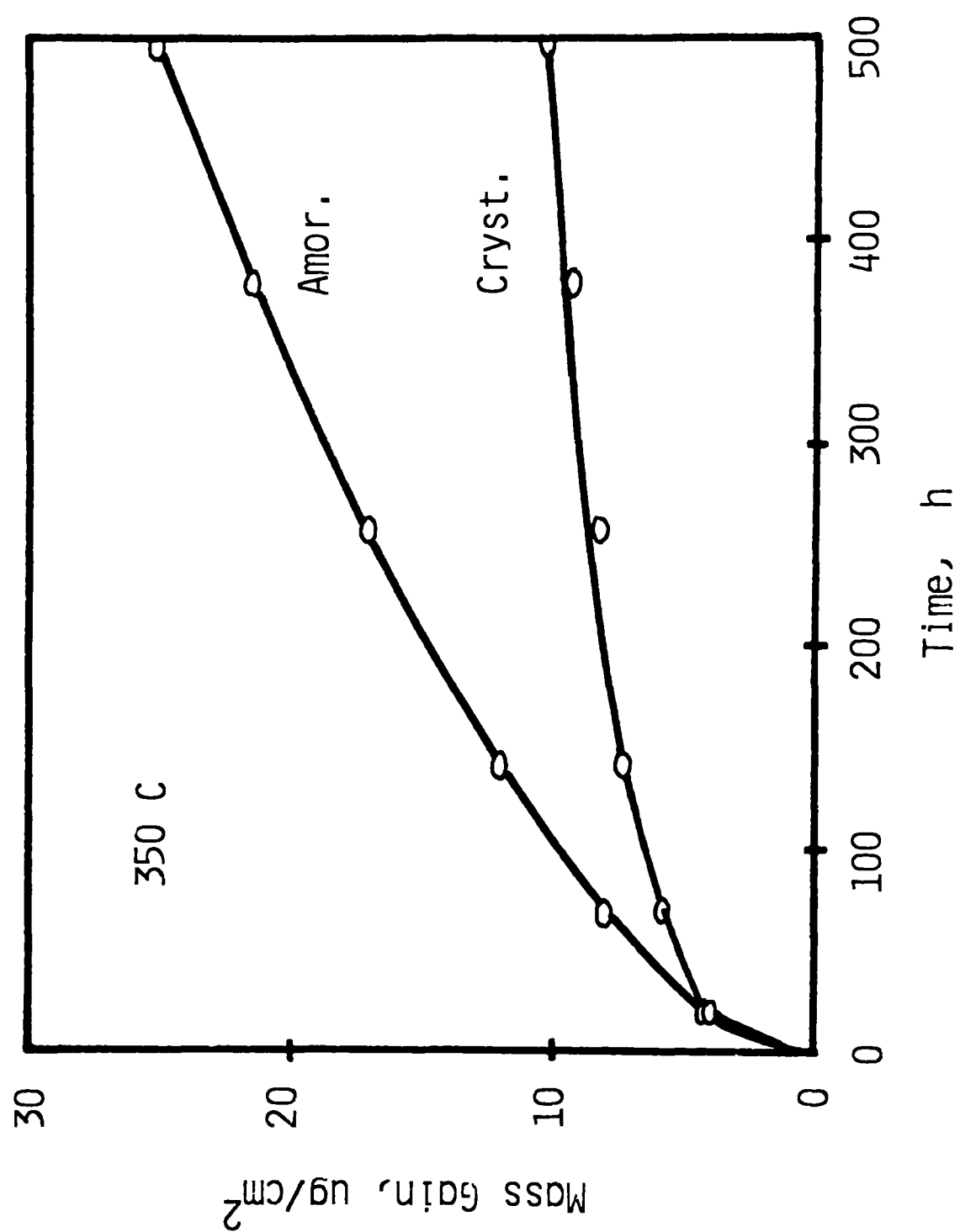


Fig.6-3 Mass gain Y versus oxidation time t for amorphous and pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ at (a) 350°C , (b) 400°C and (c) 450°C , showing the comparison of the amorphous and crystalline alloys under the identical oxidation conditions. (d) Mass gain Y versus $\ln t$ for pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ over the temperature range $300\text{--}450^\circ\text{C}$ in air.

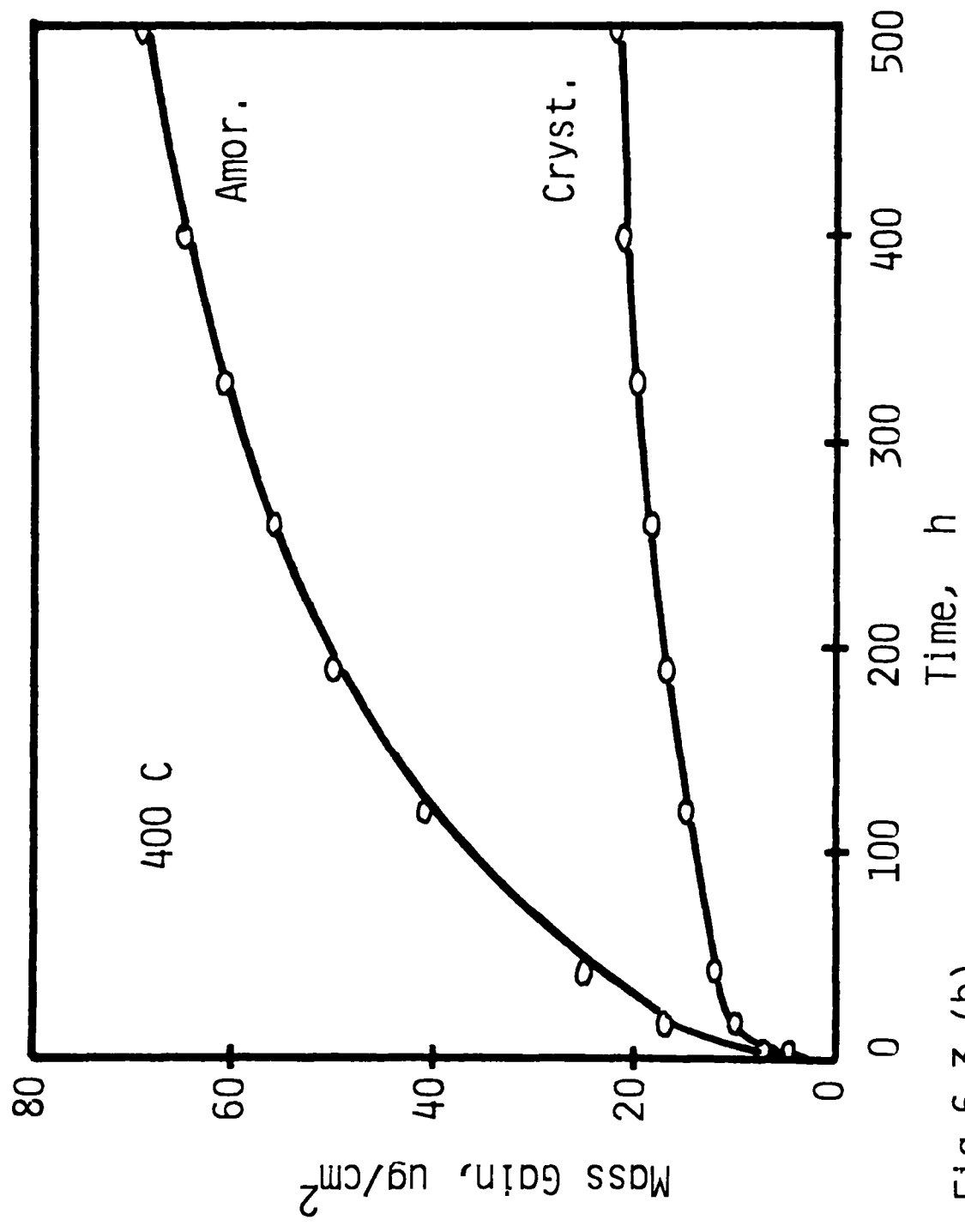


Fig.6-3 (b)

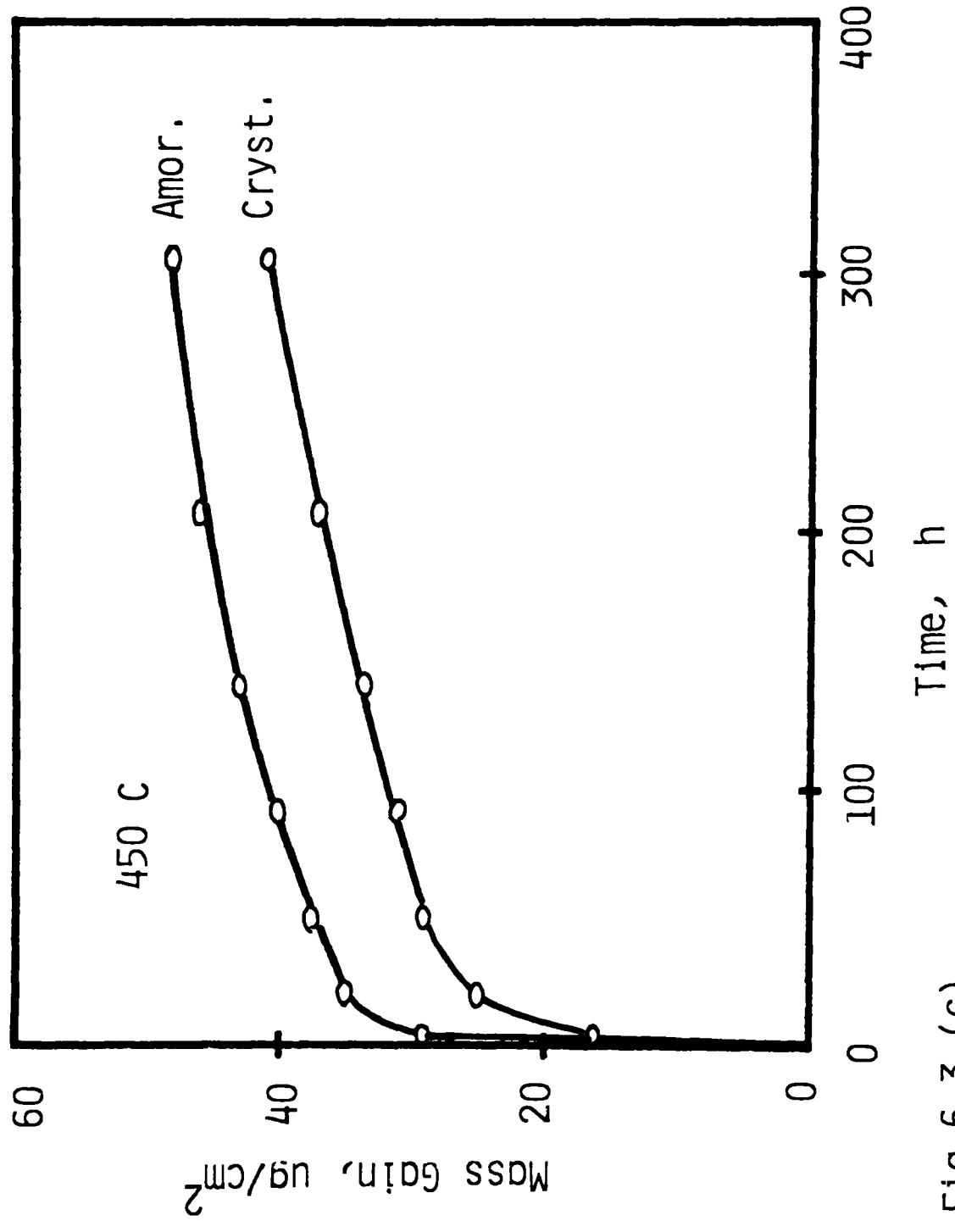


Fig. 6-3 (c)

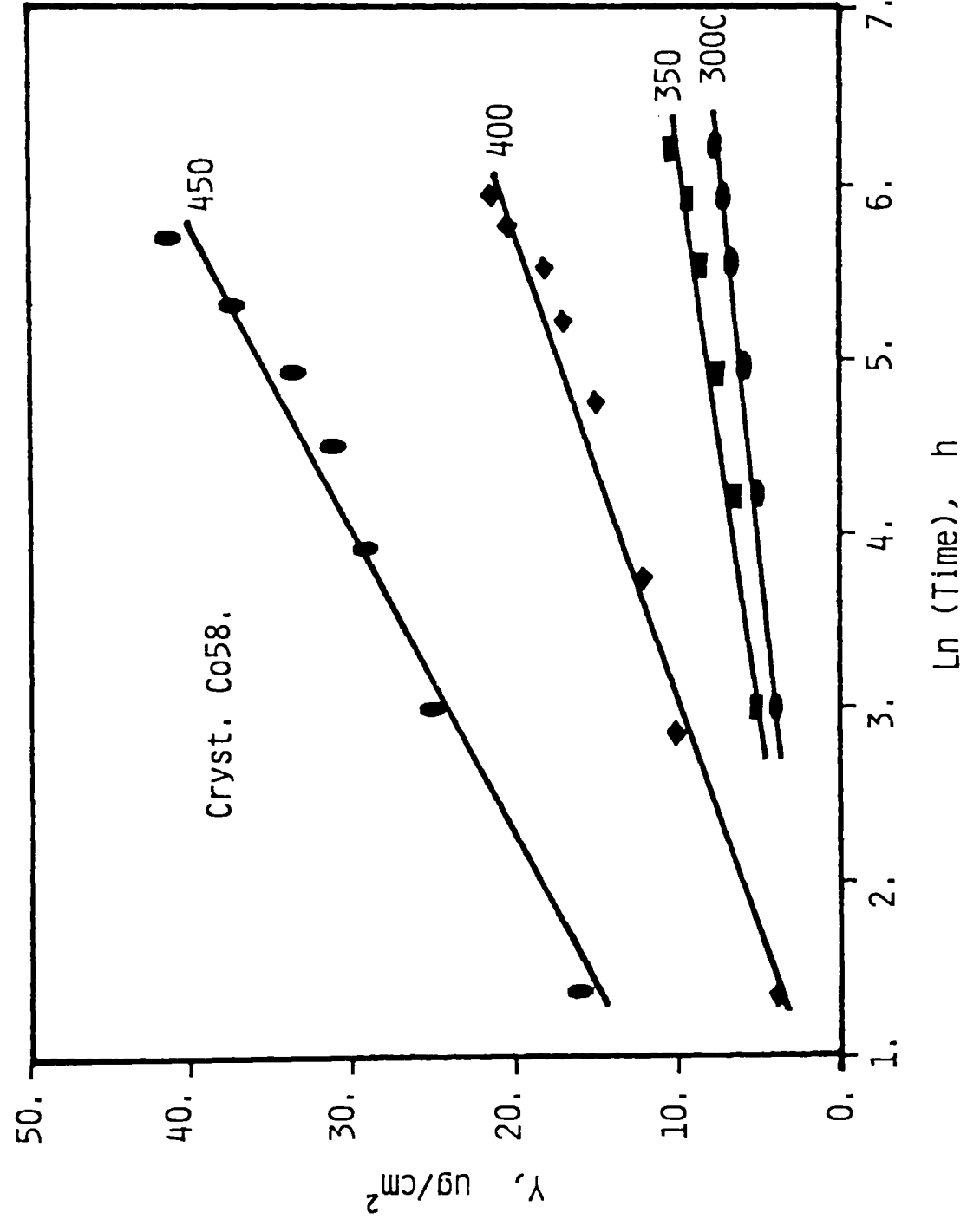


Fig.6-3 (d)

Co₇₆Mn₄Fe₂Si₆B₁₂ in both amorphous and crystallised states. Fig.6-4(b) shows the same oxidation kinetics of the crystallised alloys plotted as mass gain versus ln(time). Amorphous Co₆₆Ni₁Fe₄Si₅B₁₄ and Co₇₆Mn₄Fe₂Si₆B₁₂ again obeyed a parabolic oxidation rate law, similar to amorphous Fe₅₈Ni₁₀Fe₅Si₁₁B₁₆. Amorphous Co₆₆Ni₁Fe₄Si₅B₁₄ had an average oxidation rate slightly greater than amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, while amorphous Co₇₆Mn₄Fe₂Si₆B₁₂ had a lower average oxidation rate than amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, as shown in Fig.6-4(a). As with crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, crystallised Co₆₆Ni₁Fe₄Si₅B₁₄ and Co₇₆Mn₄Fe₂Si₆B₁₂ both obeyed logarithmic rate laws with smaller mass gains than the equivalent amorphous alloys, as shown in Fig.6-4(b). Crystallised Co₇₆Mn₄Fe₂Si₆B₁₂ had an average oxidation rate slightly greater than crystallised Co₆₆Ni₁Fe₄Si₅B₁₄.

6.2.2 Oxide morphology, microstructure and microcomposition

Figs.6-5 and 6-6 show typical SEM micrographs of the oxide morphology on both amorphous and pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ after 500h oxidation at 350 C respectively. Figs.6-7 and 6-8 show bright field TEM micrographs of the oxide films stripped from amorphous and pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ respectively after the same oxidation treatment. As shown in Figs.6-5 to 6-8, the oxide scales formed in all cases were complex, fine-scale multiphase structures. For amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, relatively large 0.1-3µm oxide particles were embedded in a thin matrix layer of 20-40nm oxide grains. The larger 0.5-3µm particles imaged as bright areas in the SEM micrograph in Fig.6-5, and as dark areas in the TEM micrograph, indicating their relative thickness compared with the underlying matrix of 20-40nm oxide grains in Fig.6-7. The microstructure of the oxide scale on pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ was in general quite similar to the amorphous alloy, as

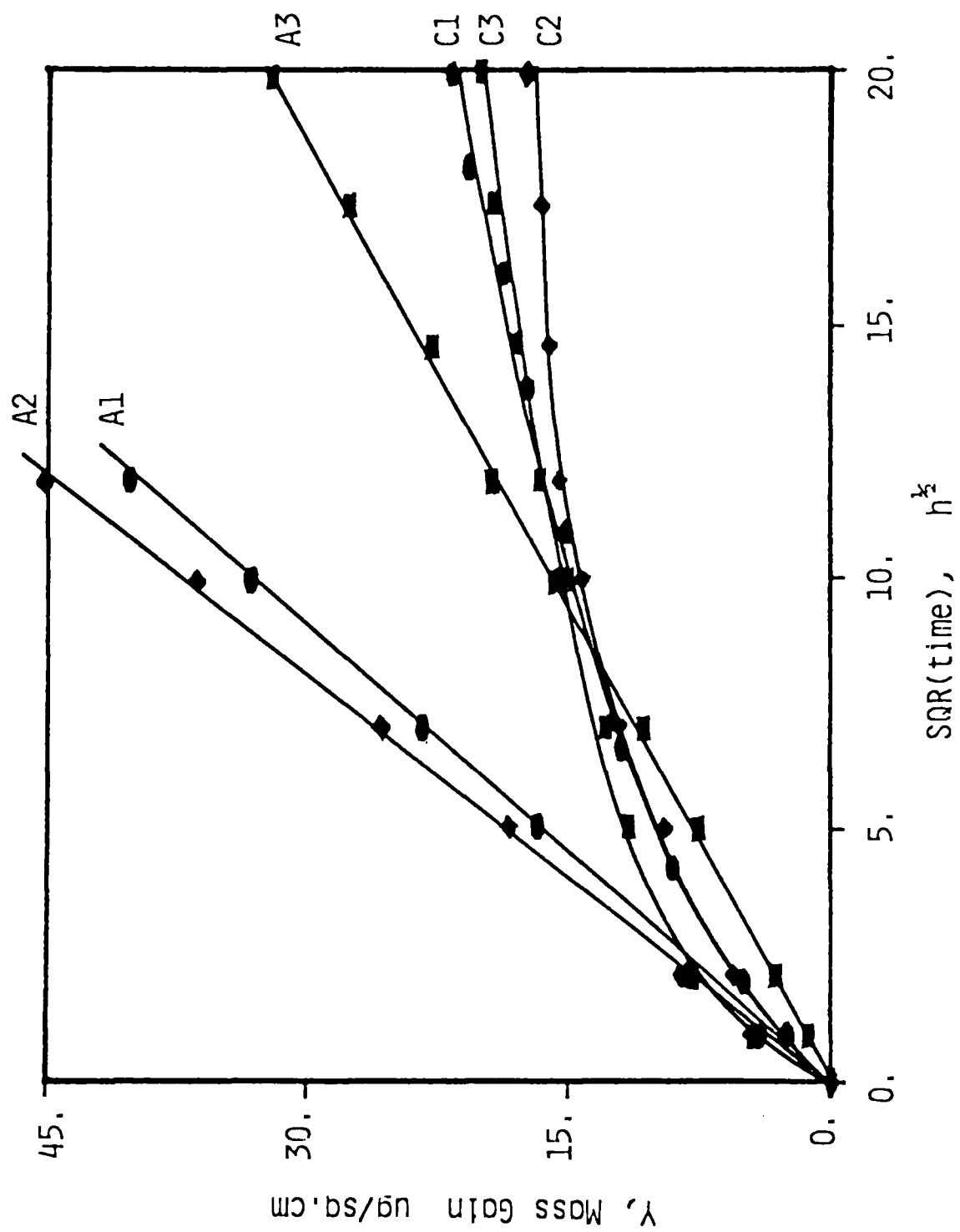


Fig.6-4(a) Mass gain Y versus square root of oxidation time t for amorphous and pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, $\text{Co}_{66}\text{Ni}_{10}\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$ at 400°C in air. A1, A2, A3 and C1, C2, C3 are for amorphous and pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, $\text{Co}_{66}\text{Ni}_{10}\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$ respectively.

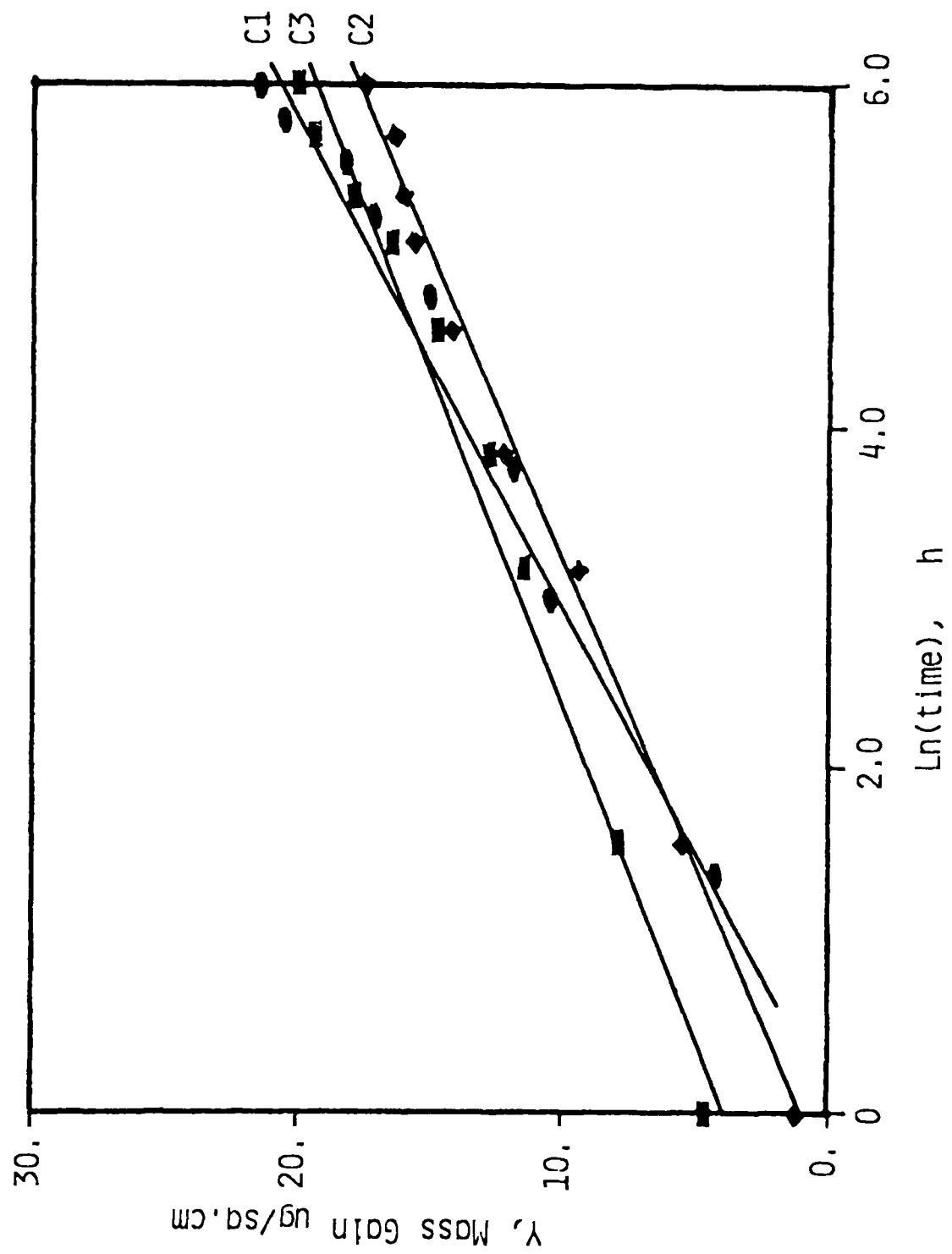


Fig.6-4(b) Mass gain Y versus $\ln t$ for pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, $\text{Co}_{66}\text{Ni}_{1}\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$ at 400°C in air.

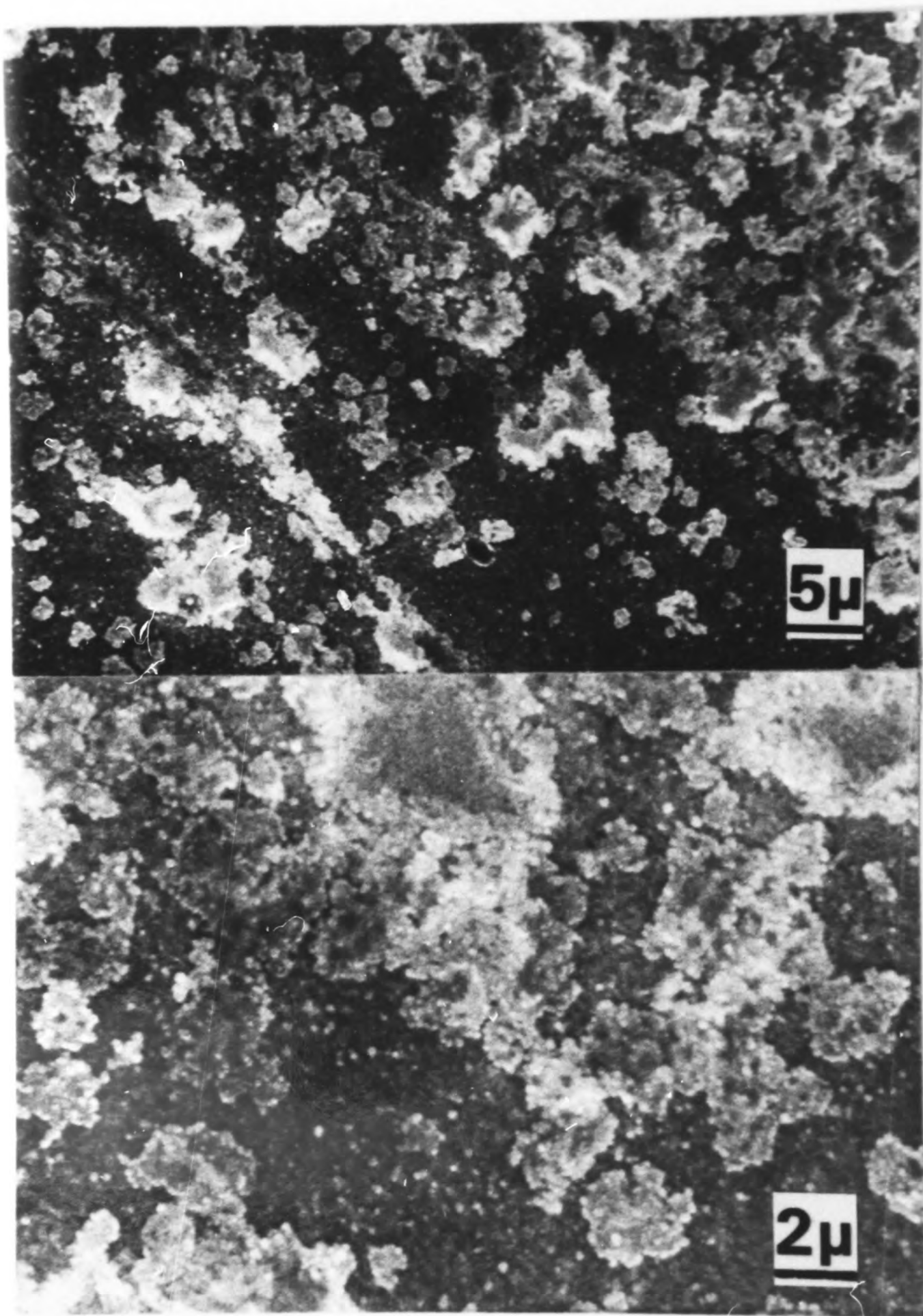


Fig.6-5 SEM images of the oxide scale surfaces formed on amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, oxidised in air at 350°C for 500h.

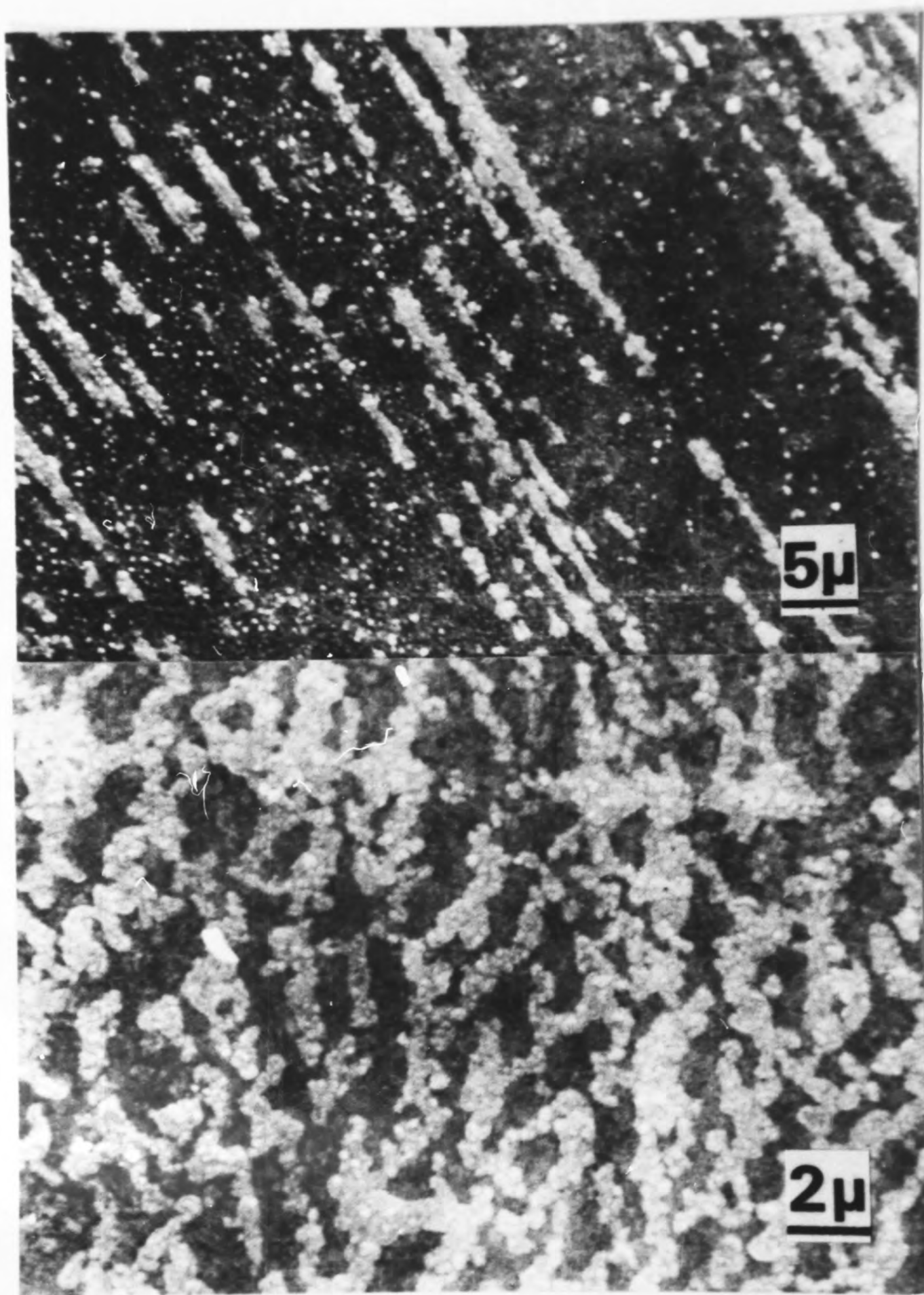


Fig.6-6 SEM images of the oxide scale surfaces formed on pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, oxidised in air at 350°C for 500h.

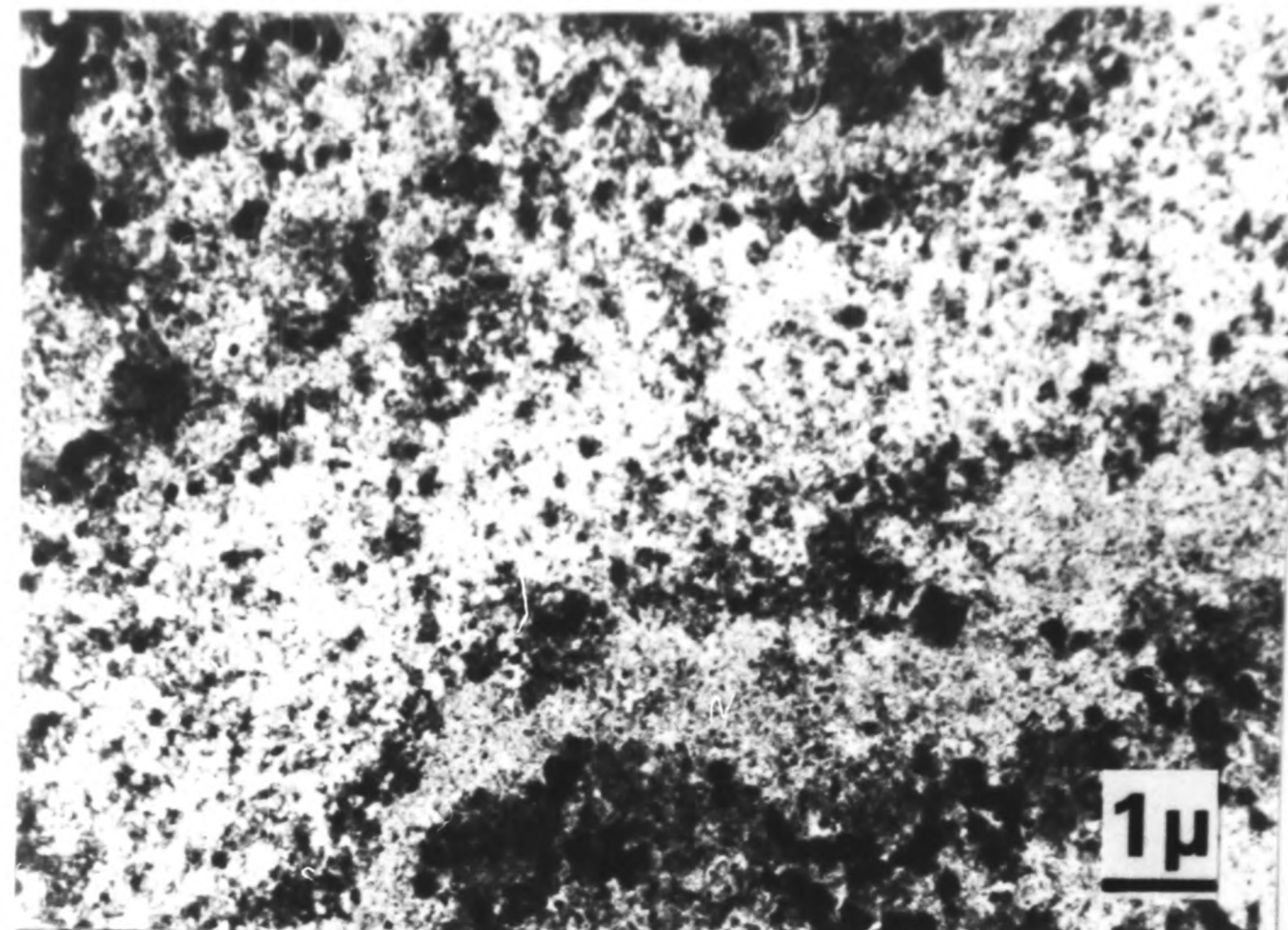
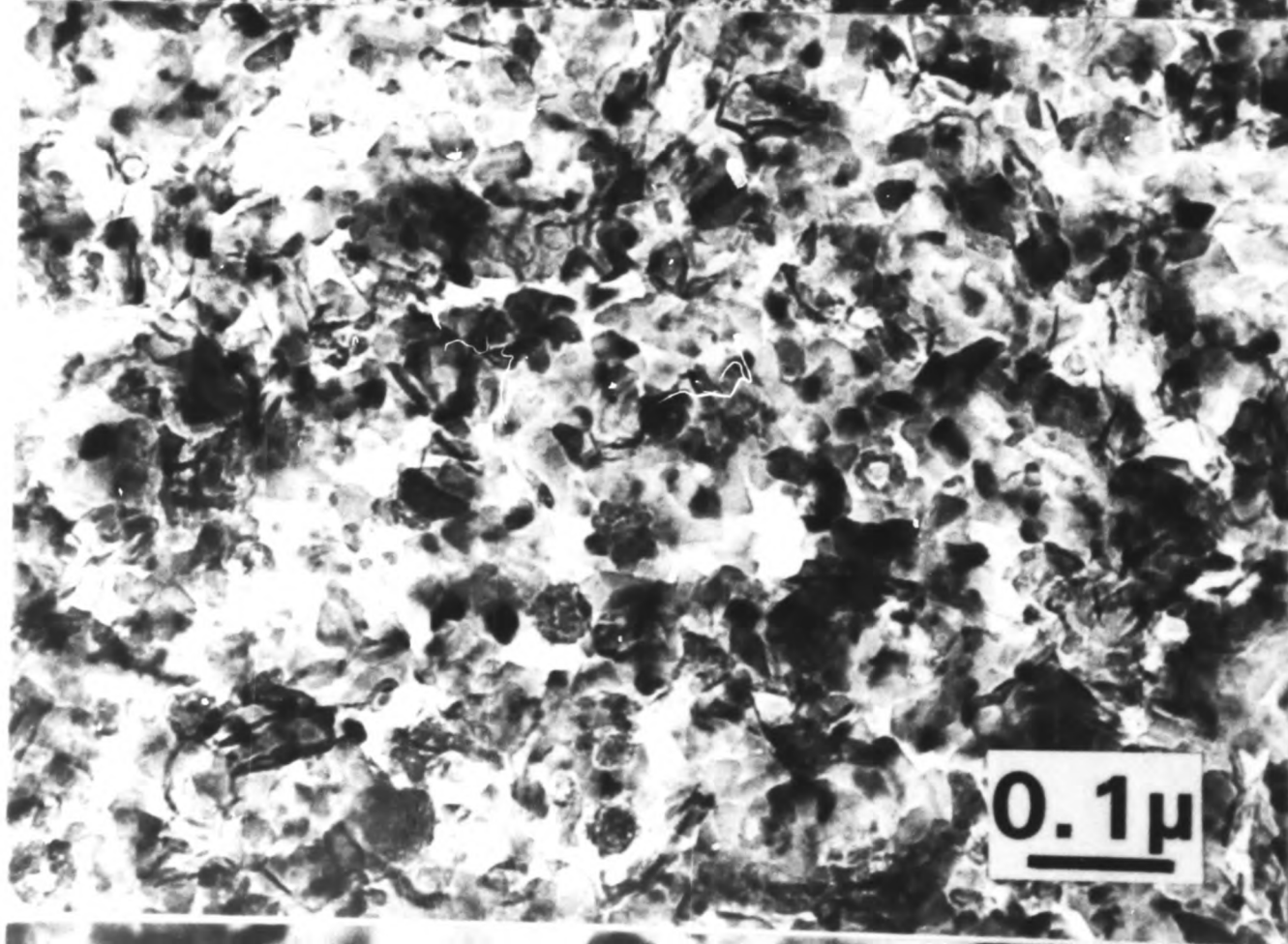
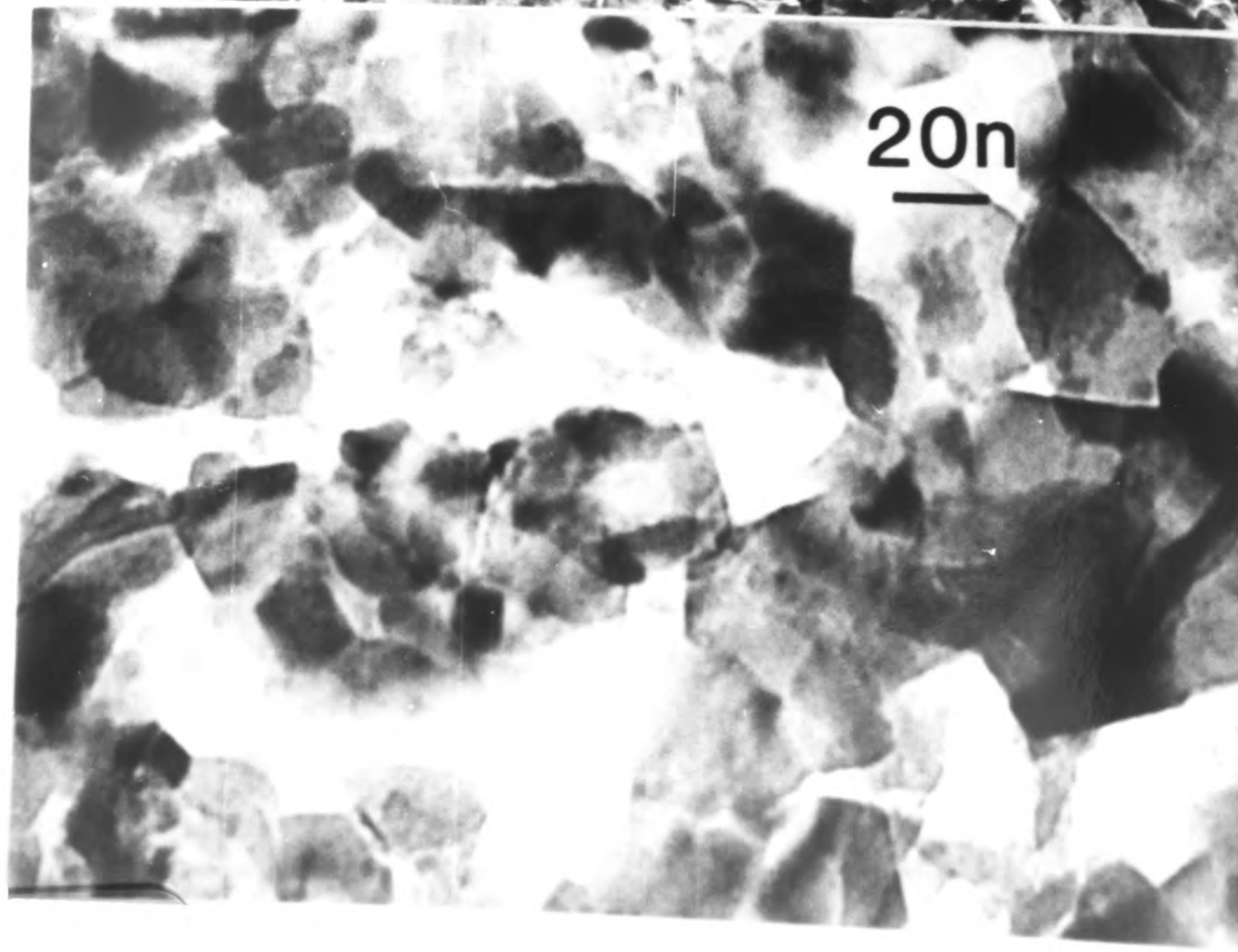


Fig.6-7 TEM bright field images of the oxide scales removed from amorphous Co58Ni10Fe5Si11B16 oxidised in air at 350°C for 500h, showing small particles embedded in fine grained matrix.

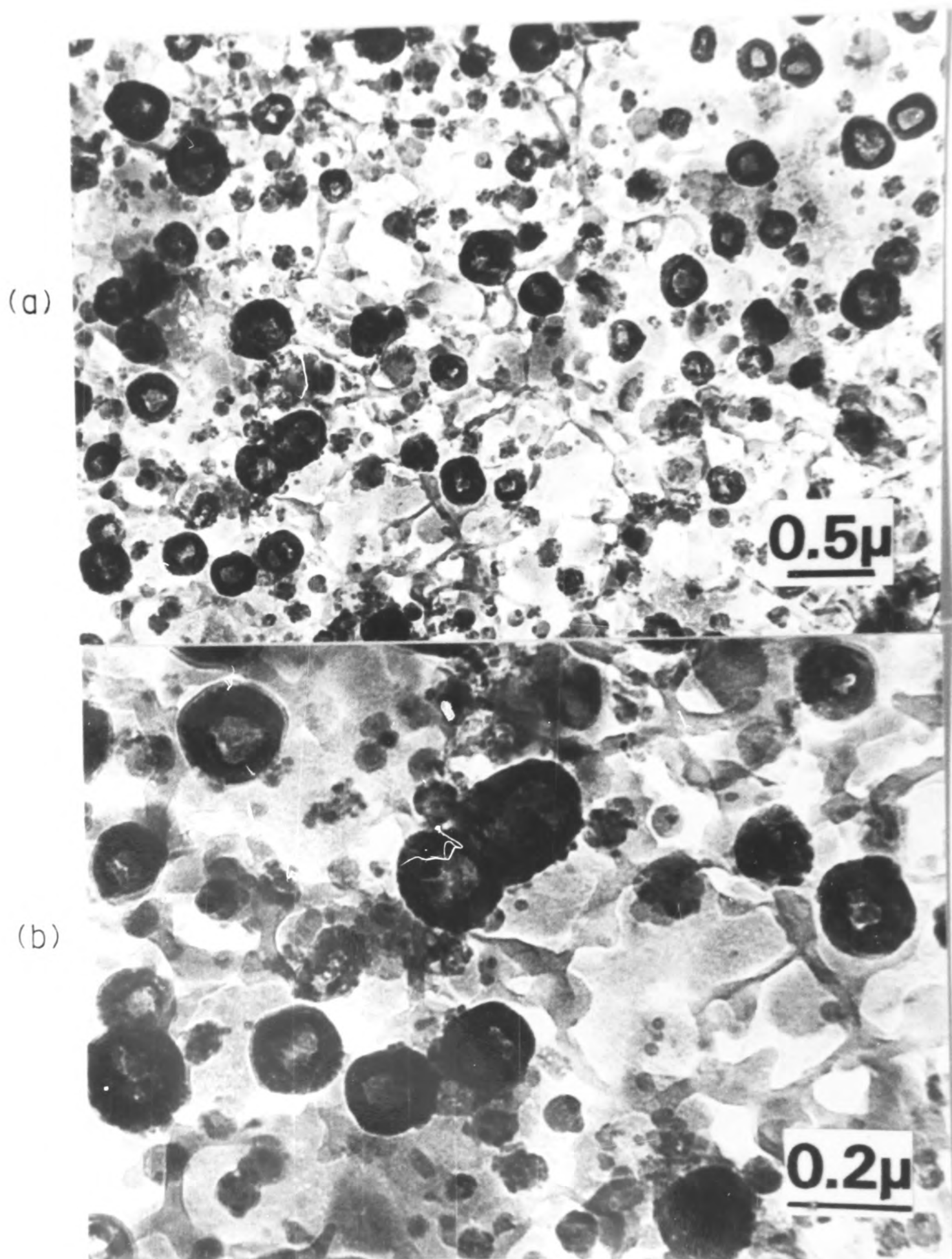


Fig.6-8 TEM bright field images of the oxide scales removed from pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ oxidised in air at 350°C for 500h, showing small round particles embedded in fine scale matrix. (c) and (d) show the thin matrix area consisting of amorphous silica (marked A).

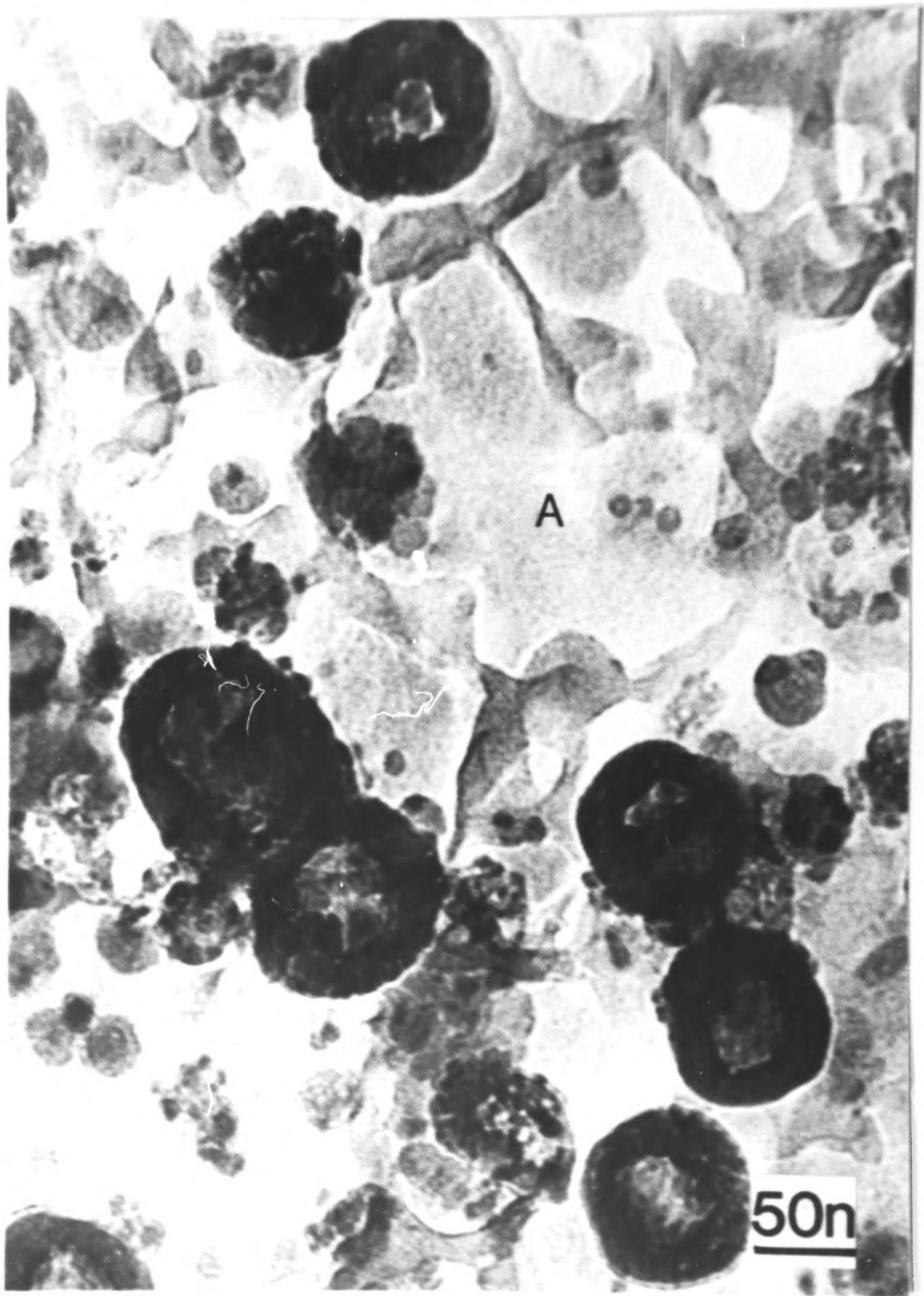


Fig.6-8 (c)

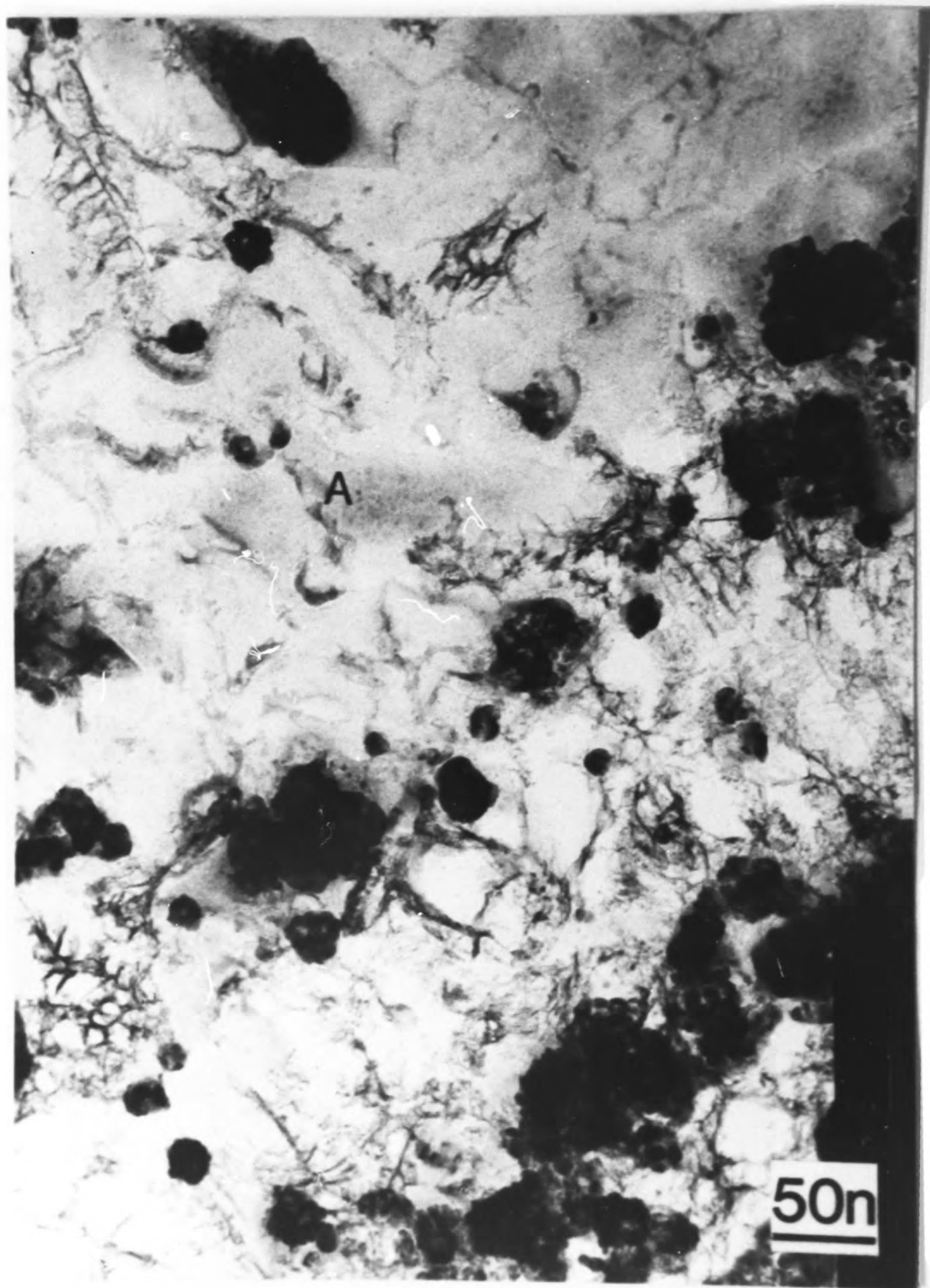
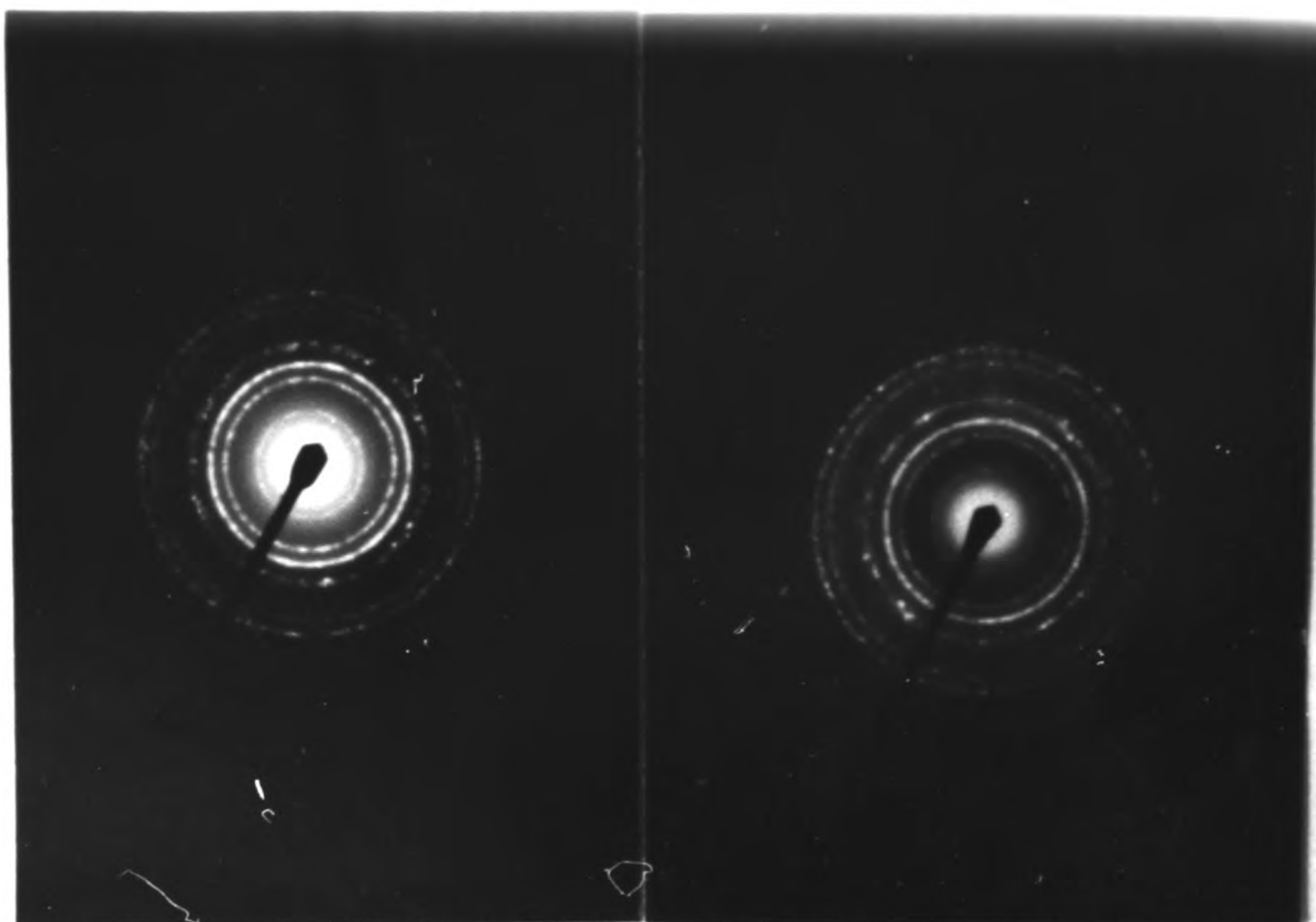


Fig.6-8 (d)

shown in Figs.6-6 and 6-8. Once again, relatively large oxide particles were embedded in a thin oxide matrix layer, similar to the oxide on amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆. Comparing Fig.6-8 with 6-7, however, there were more matrix areas on the oxide of the crystallised alloy than on the oxide of the amorphous alloy after same oxidation treatment. This is shown in many areas on the TEM micrographs in Fig.6-8(c) and (d).

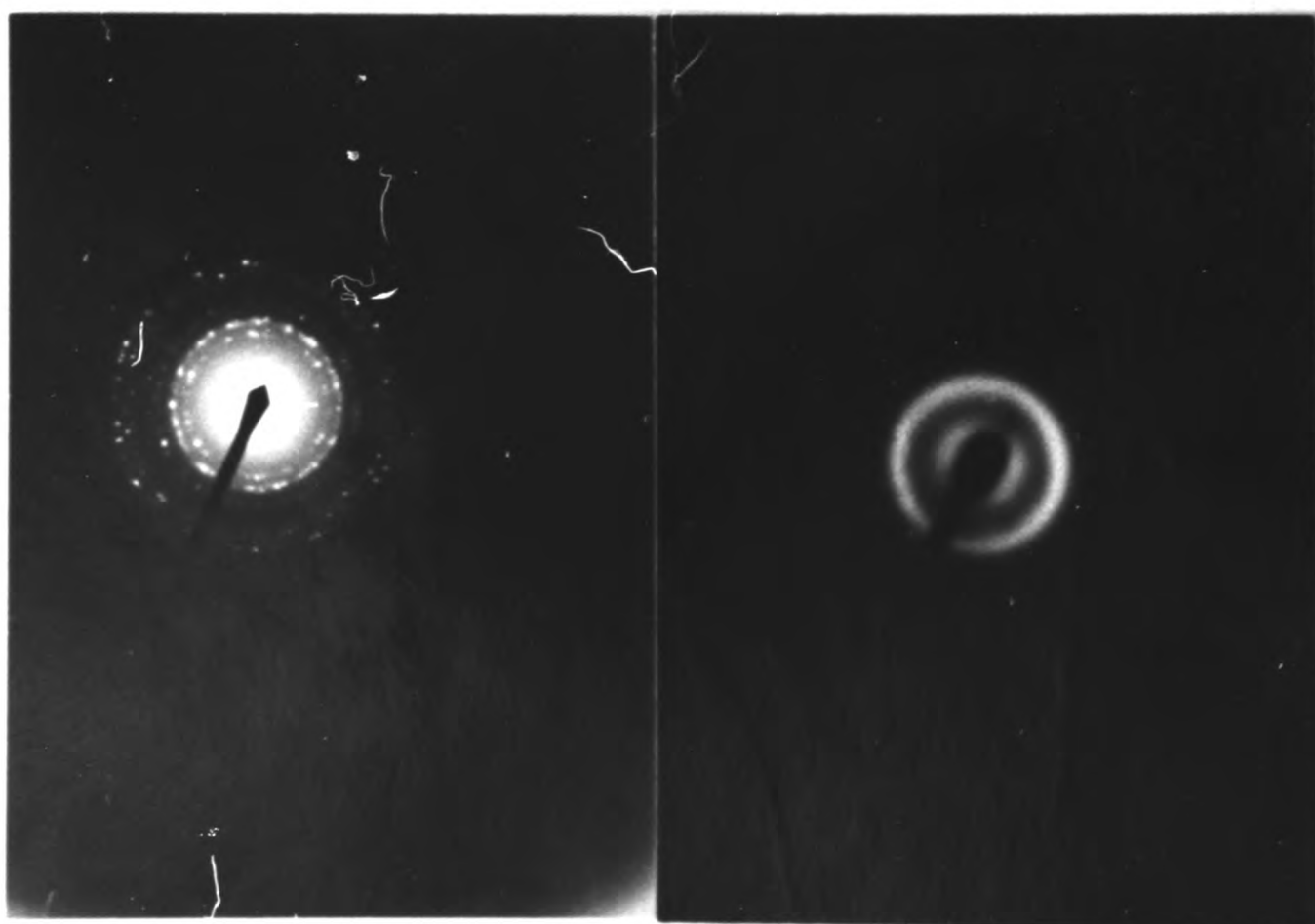
Fig.6-9 shows typical SAED patterns from different regions of the oxide scale on amorphous and pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆. In general, indexing the SAED patterns showed little difference between the amorphous and crystallised samples, with the oxide particles consisting of a mixture of Co₂SiO₄, Co₃O₄, CoO, Fe₂SiO₄ and Fe₃O₄ as listed in Table 6-2. Figs.6-9(a) and (b), for instance, show the similar SAED patterns from the larger oxide particles on amorphous and crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ respectively. However, SAED patterns from the fine scale oxide matrix showed some difference between the two types of alloy sample. For pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Fig.6-9(d) shows an SAED pattern from a bright area marked A in Fig.6-8(c), which contains a broad halo from amorphous SiO₂, which was not detected in the oxide scales formed on the amorphous alloy. SAED patterns from typical thin oxide matrix regions on the amorphous alloy again corresponded to a broad spinel structure, as shown in Fig.6-9(c), indicating that the oxide matrix had a similar composition to the oxide particles.

Fig.6-10 shows typical EDS spectra from different areas of the oxide films removed from amorphous and pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆. It can clearly be seen that in both cases the larger oxide particles contained more Co and Fe than the fine-scale thin oxide matrix areas. In addition, the oxide scales formed on the amorphous alloy contained more Fe than on the crystalline alloy. Composition measurements are summarised in Table



(a)

(b)



(c)

(d)

Fig.6-9 Typical SAED patterns from oxide scales removed from amorphous and pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$: (a) oxide particles on amorphous alloy; (b) oxide particles on pre-crystallised alloy; (c) oxide matrix on amorphous alloy; (d) oxide matrix on pre-crystallised alloy (from the area marked A in Fig.6-8(d)).

Table 6-2. Calculated d spacings for oxide particles formed on amorphous and crystalline Co58Ni10Fe5Si11B16 together with d spacings of some relevant compounds

d amr.	d cry.	d(Co ₃ O ₄) (9-418)	d(Co ₂ SiO ₄) (15-497)	d(CoO) (9-402)	Fe ₂ SiO ₄ (12-284)	Fe ₃ O ₄ (11-614)
4.70*	4.65*	4.67	4.64		4.75	4.85
	4.10					
2.87*	2.85*	2.86	2.85		2.91	2.966
2.46*	2.44*	2.44	2.443	2.460	2.48	2.530
2.34	2.34	2.33			2.37	
2.13	2.13			2.130		
2.04*	2.03*	2.02	2.024		2.05	2.096
1.86	1.85	1.851			1.888	
1.66	1.65	1.65	1.650			
1.56*	1.56*	1.55	1.560		1.583	1.614
1.50	1.51			1.5062		
1.44*	1.44*	1.43	1.434		1.454	1.483
1.37	1.36	1.372				
1.24*	1.23	1.233	1.238		1.255/1.241	1.279
1.06	1.055	1.053	1.058		1.072	1.092/1.049
0.94	0.945	0.9335	0.9401			0.969/0.939

* Rings are strong and broad in these positions.

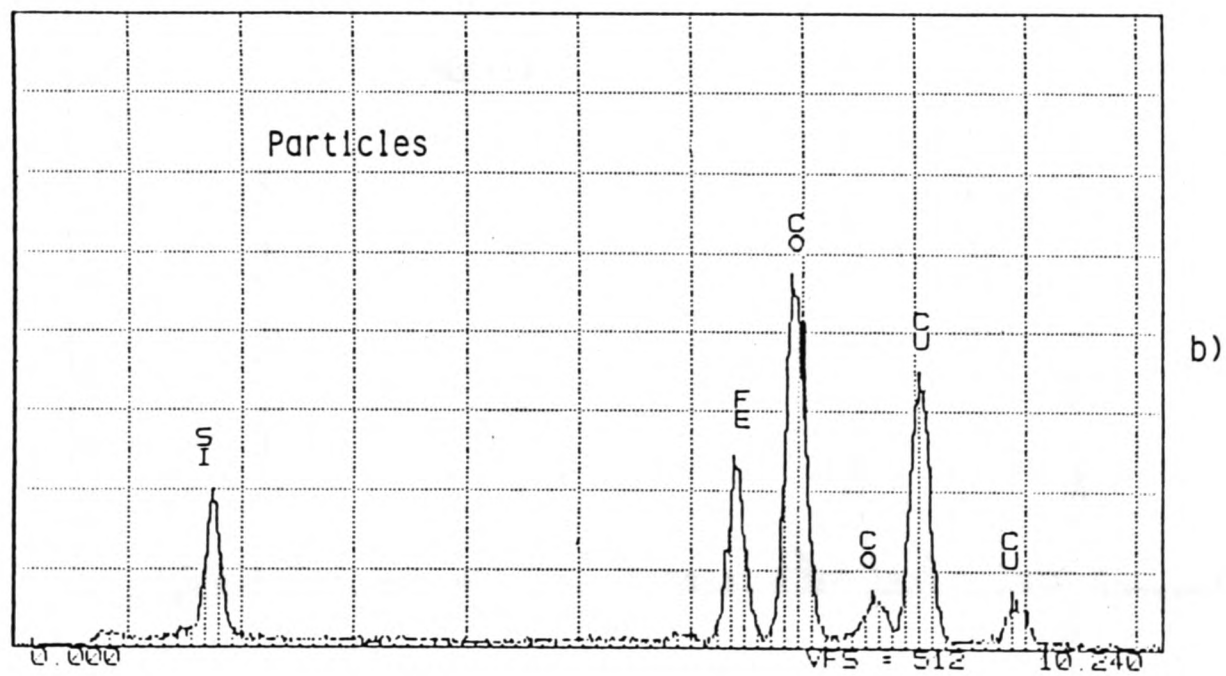
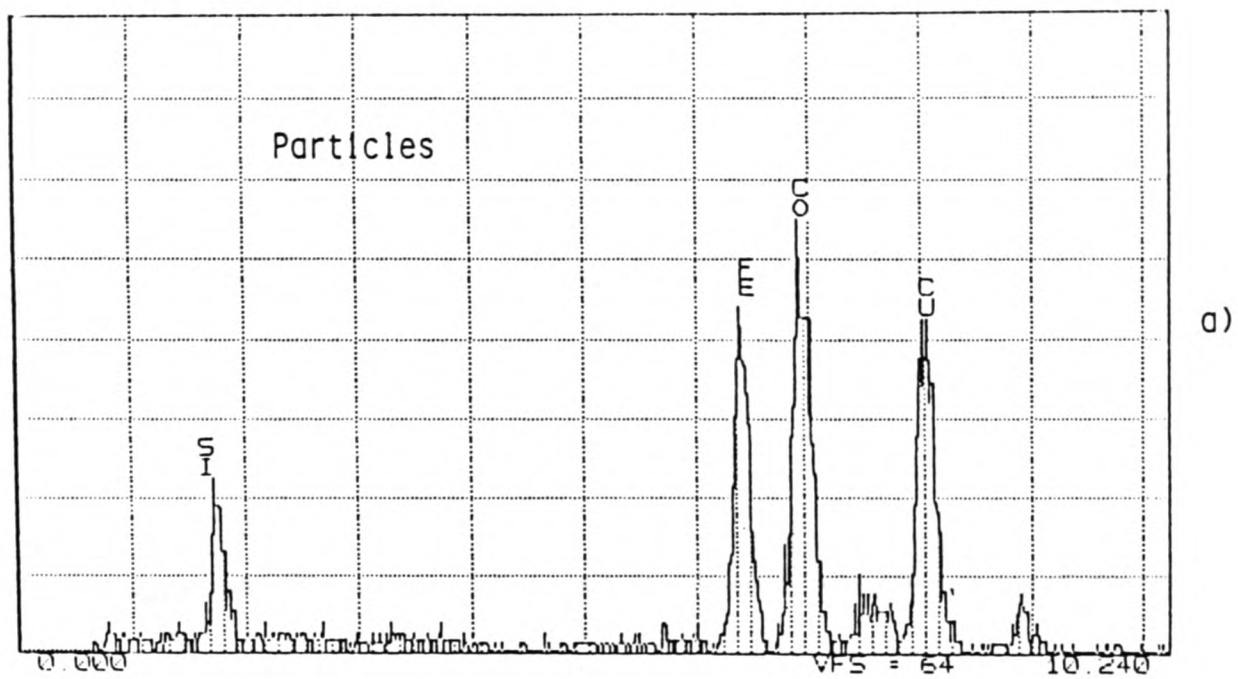
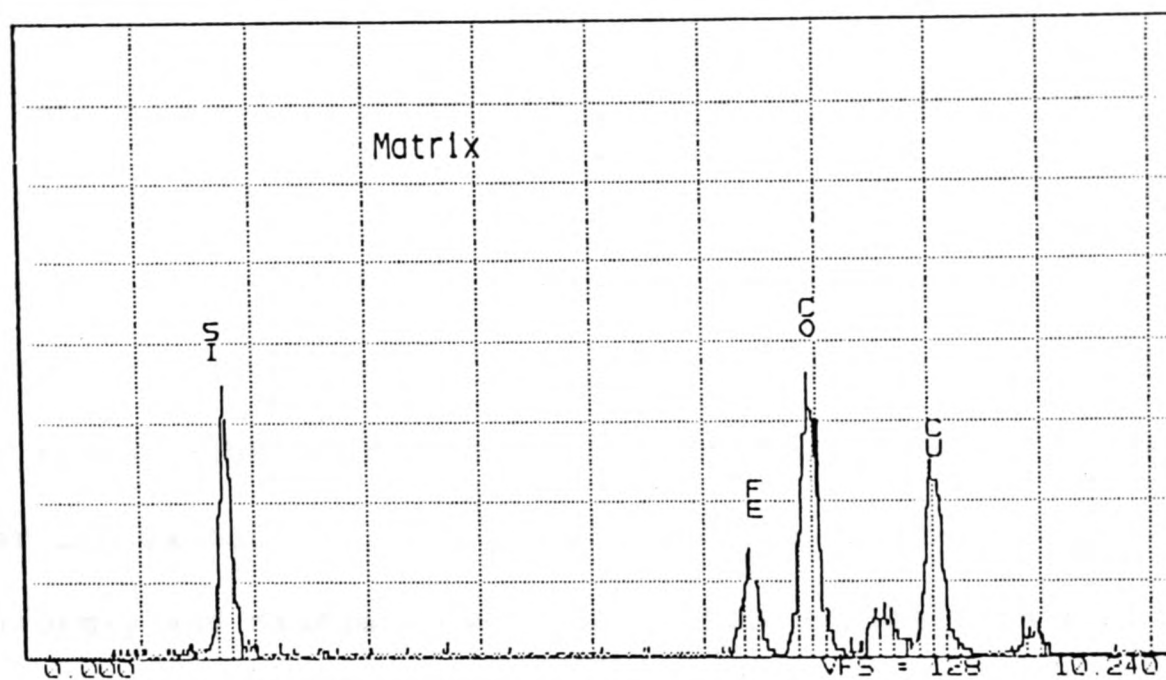
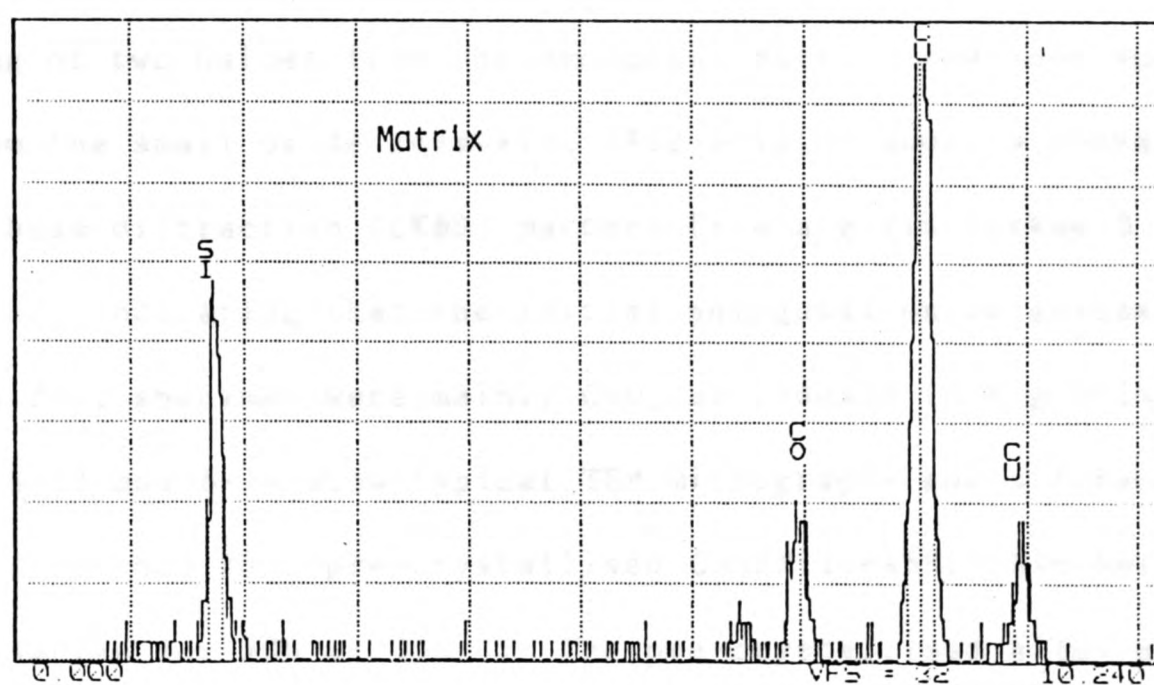


Fig.6-10 Typical EDS spectra from oxide scales removed from amorphous and pre-crystallised Co58Ni10Fe5Si11B16: (a) oxide particles on amorphous alloy; (b) oxide particles on pre-crystallised alloy; (c) oxide matrix on amorphous alloy; and (d) oxide matrix on pre-crystallised alloy. The Cu peaks are from the the Cu support grids and sample holder.



c)



d)

Fig.6-10

6-3, and agreed well with the results of indexing SAED patterns.

Figs.6-11 and 6-12 show typical TEM micrographs and diffraction patterns from thin foil amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ specimens before and after oxidation annealing for 20h at 350 C. The amorphous alloy exhibited a featureless bright field image (Fig.6-11(a)) and an electron diffraction pattern consisting only of two broad haloes (Fig.6-12(a)), as expected for an amorphous atomic structure. Figs.6-11(b) and (c) show that the oxide grains formed in early stage of oxidation at 350 C had a well defined, polygonal shape. The mean size of the oxide grains was 15nm after 2h and 20nm after 20h oxidation. The polygonal oxide grains were distributed quite uniformly and randomly over the surface of the thin foil amorphous samples. Fig.6-12(b) shows a SAED pattern from the area in Fig.6-11(b), consisting of two haloes from the amorphous matrix, and many spots and rings from the small oxide crystals. Fig.6-12(c) shows a convergent electron beam diffraction (CEBD) pattern from a grain marked B in Fig.6-11(c), indicating that the initial polygonal oxide grains on the amorphous foil specimen were mainly CoO , as indexed in Fig.6-14(d).

Figs.6-13 and 6-14 show typical TEM micrographs and diffraction patterns from thin foil pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ before and after oxidation for 20h at 350 C. The pre-crystallised alloy exhibited a relatively complex polycrystalline microstructure, as can be seen in Figs.6-13(a), and 6-14(a), with many spots and rings from the very small multiphase grains. Indexing the pre-crystallised alloy SAED patterns showed that crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ mainly consisted of $\alpha\text{-Co}(\text{Ni, Fe})$, Co_2Si and Co_2B as listed in Table 6-4. CEBD patterns from some of the larger grains showed clearly the hcp structure of $\alpha\text{-Co}$, as can be seen for instance in Fig.6-14(b). Typical EDS spectra from the different grains in the pre-crystallised structure are shown in Fig.6-15. The results

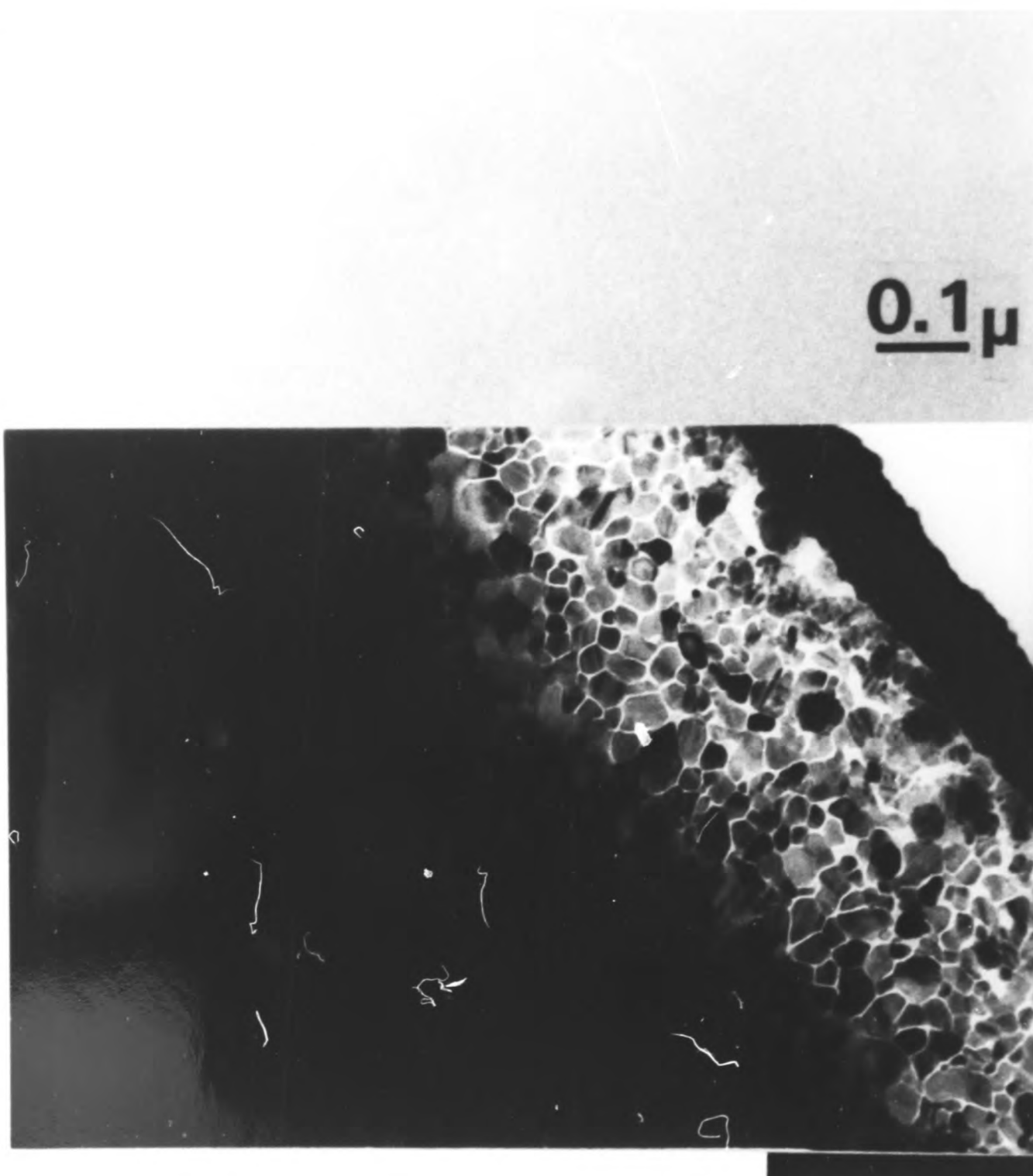
Table 6-3: Oxide structures and compositions* for amorphous and crystalline Co58Ni10Fe5Si11B16

Alloy & area	oxide structure	oxide composition (at.%)
Am. matrix	Co ₂ SiO ₄ , Fe ₂ SiO ₄ , Co ₃ O ₄ , Fe ₃ O ₄	Si39+-5, Co34+-5, Fe26+-6, Ni:1
Am. particle	Co ₃ O ₄ , Fe ₂ SiO ₄ Co ₂ SiO ₄ , CoO, Fe ₃ O ₄	Si20+-10, Co44+-10, Fe34+-10, Ni:2
Am. average		Si:35, Co:35, Fe:29, Ni:1
Cry. matrix	SiO ₂ (amor.), Co ₂ SiO ₄ ...	Si76+-10, Co18+-7, Fe6+-3
Cry. particle	Co ₃ O ₄ , Co ₂ SiO ₄ , CoO Fe ₂ SiO ₄ , Fe ₃ O ₄	Si18+-5, Co58+-12, Fe18+-8, Ni:6
Cry. average		Si:34, Co:48, Fe:14, Ni:4

* Elements with Z < 11 cannot be measured by EPMA.

d)

(b)



(c)

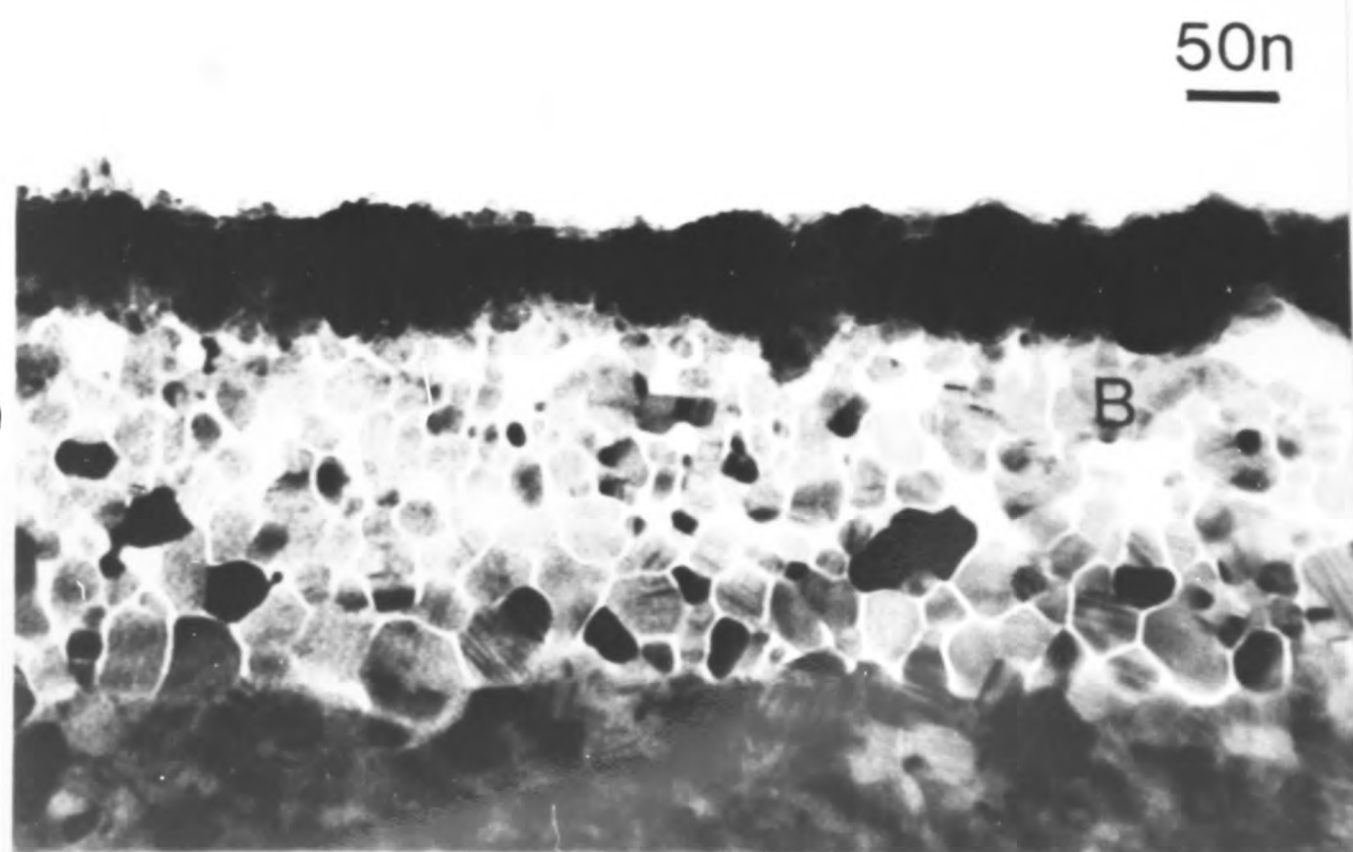
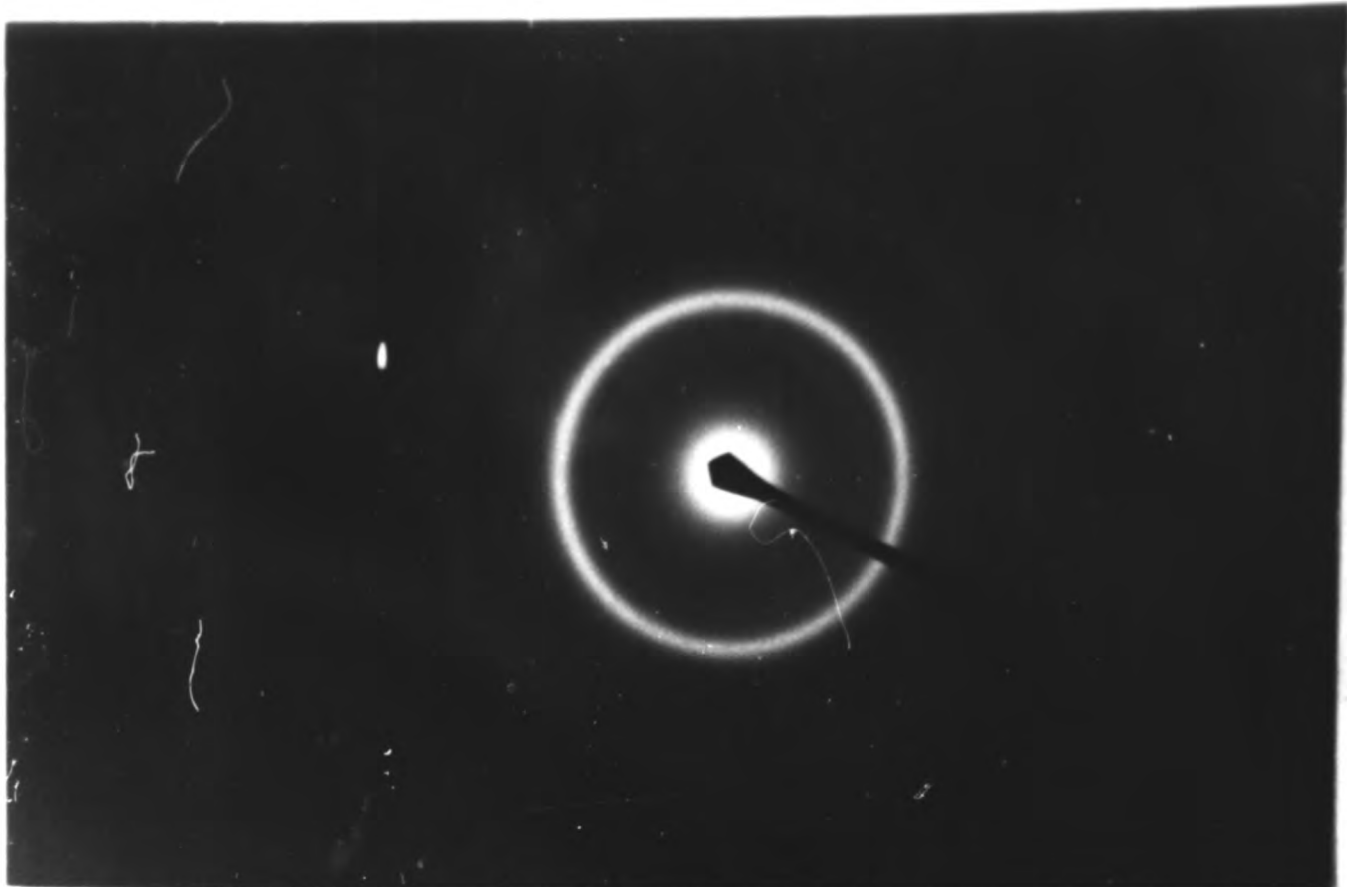
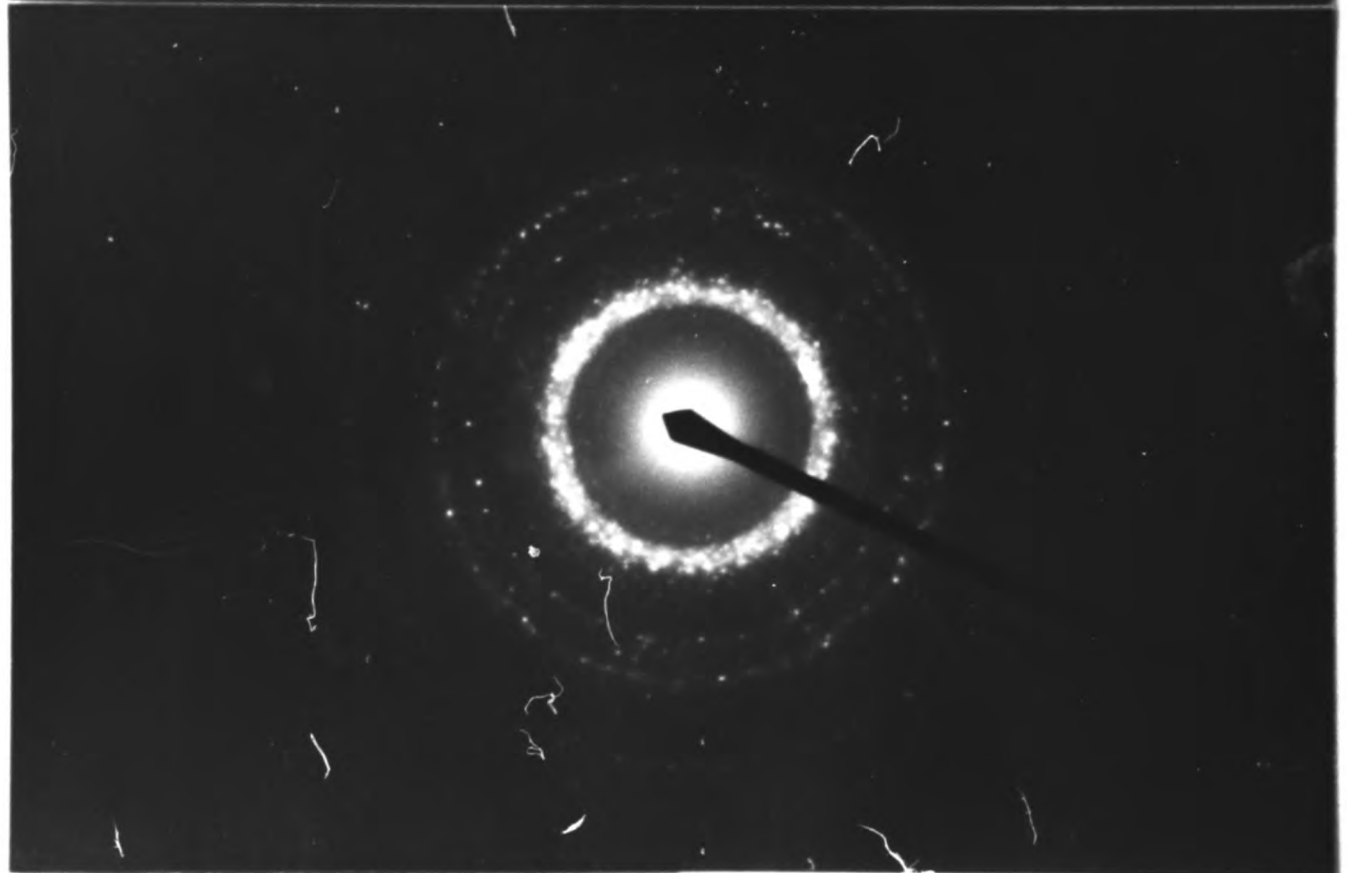


Fig.6-11 TEM micrographs of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ thin foils: (a) before oxidation; (b) and (c) after oxidation at 350°C for 20h.

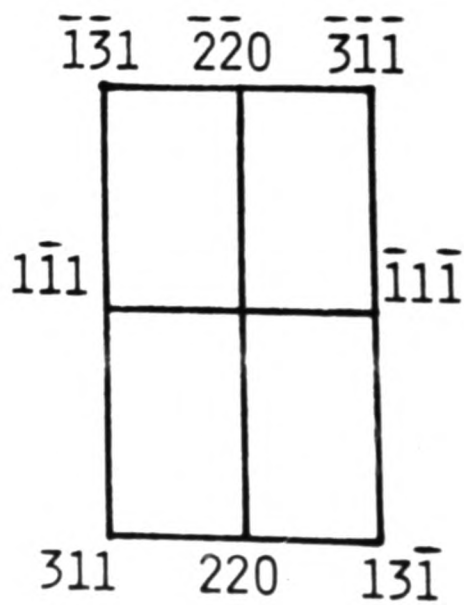
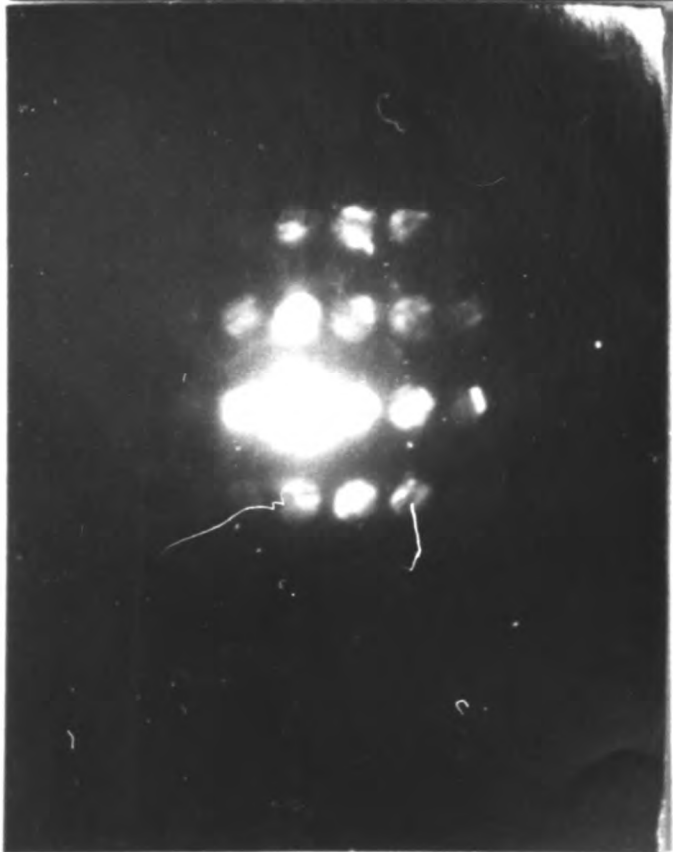
(a)



(b)



(c)



CoO $\langle \bar{1}12 \rangle$

Fig.6-12 Electron diffraction patterns from amorphous Co58Ni10Fe5Si11B16 thin foils: (a) SAED patterns before oxidation; (b) SAED patterns after 20h at 350°C; (c) CEED patterns after 20h at 350°C from the grain marked B in Fig.6-11(c); (d) indexing of (c) as CoO $\langle \bar{1}12 \rangle$ zone.

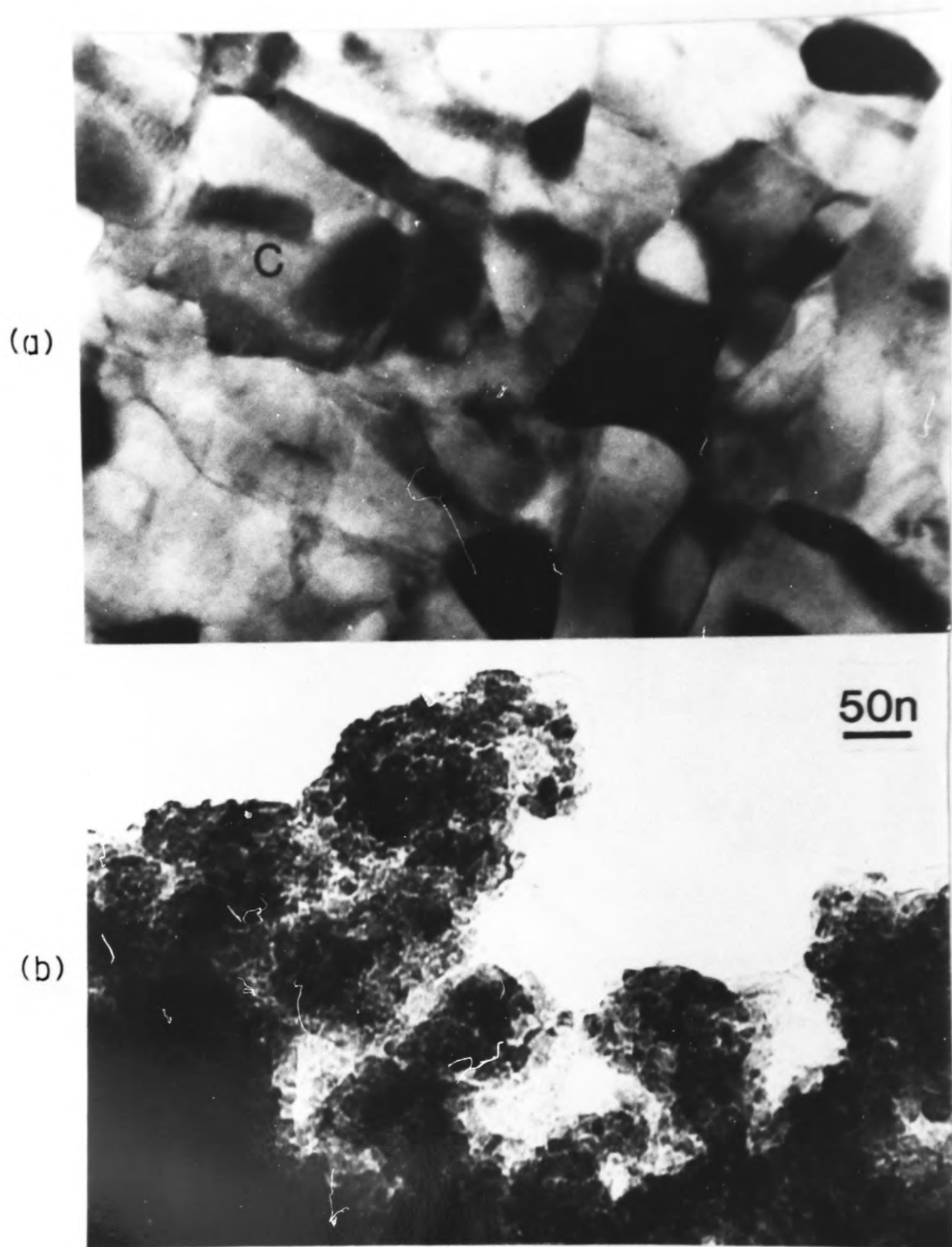
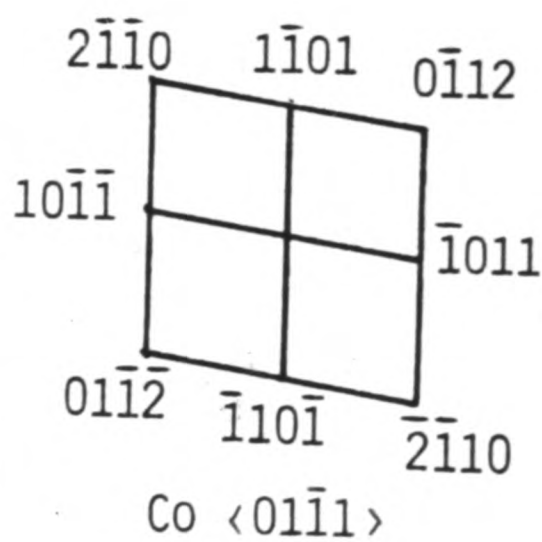
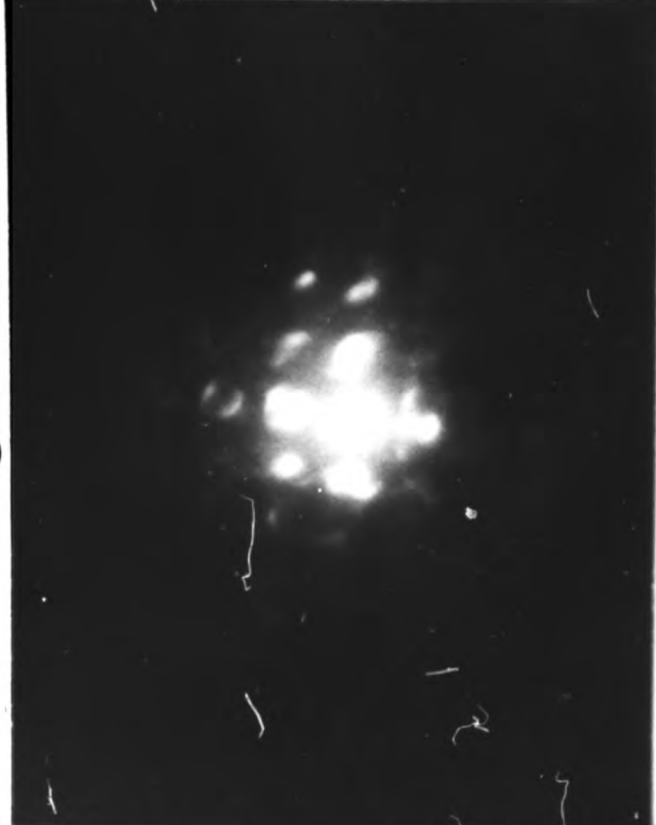


Fig.6-13 TEM micrographs of pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ thin foils: (a) before oxidation and (b) after oxidation at 350°C for 20h.

(a)



(b)/
(c)



(d)

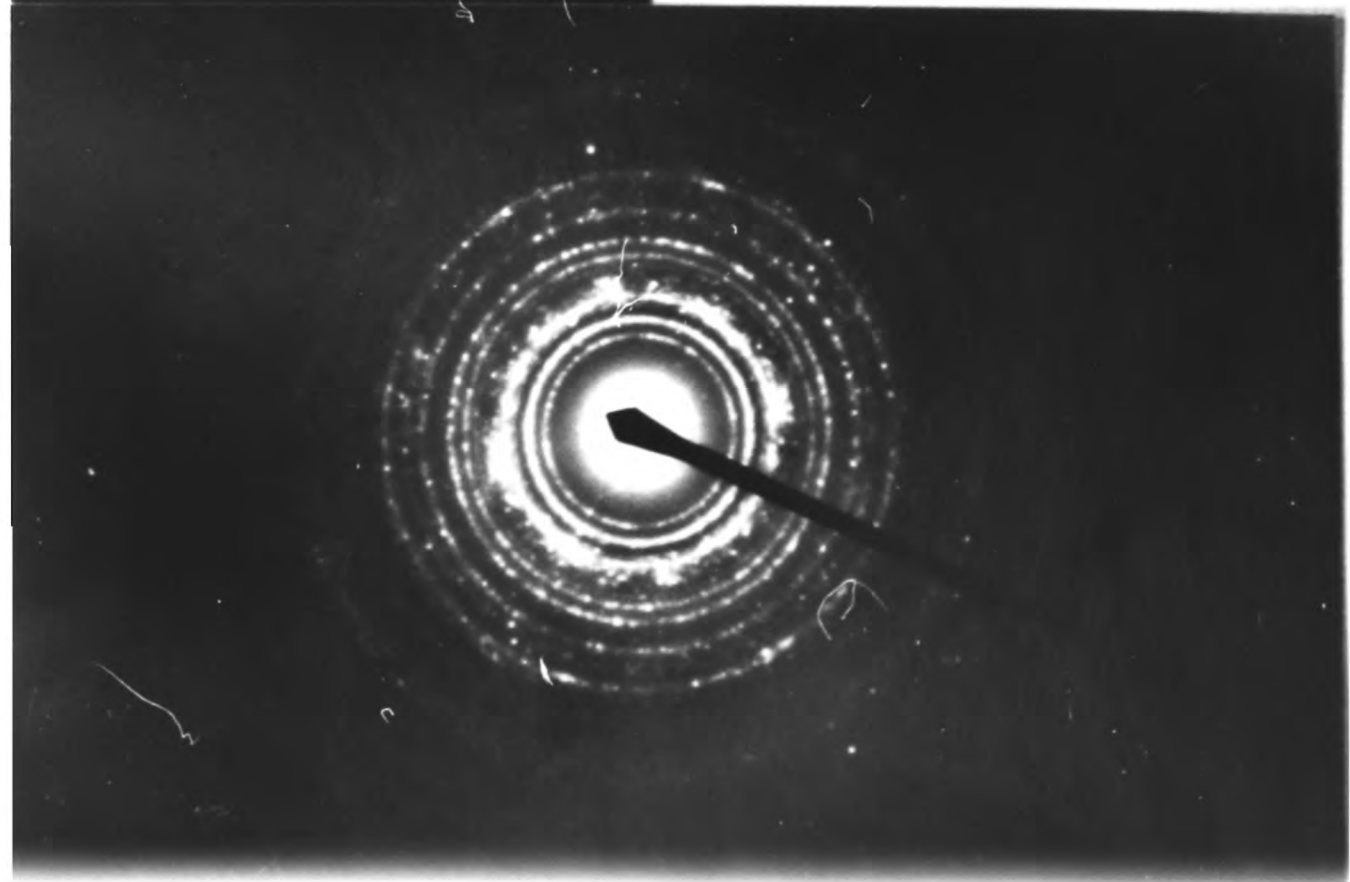
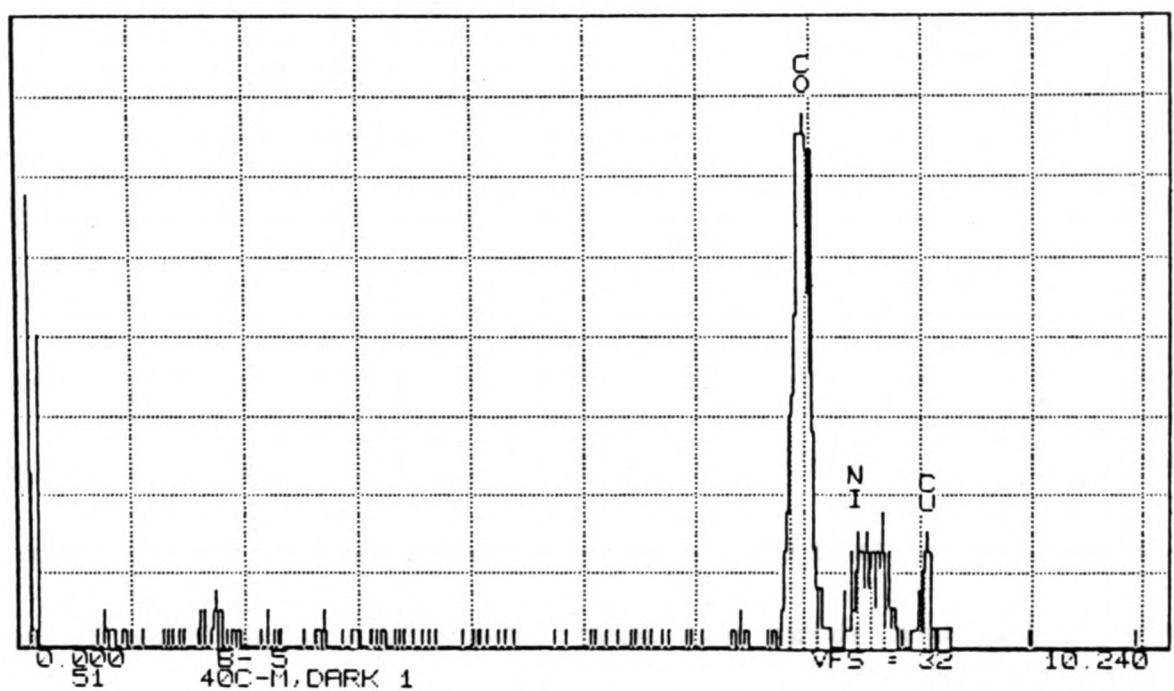


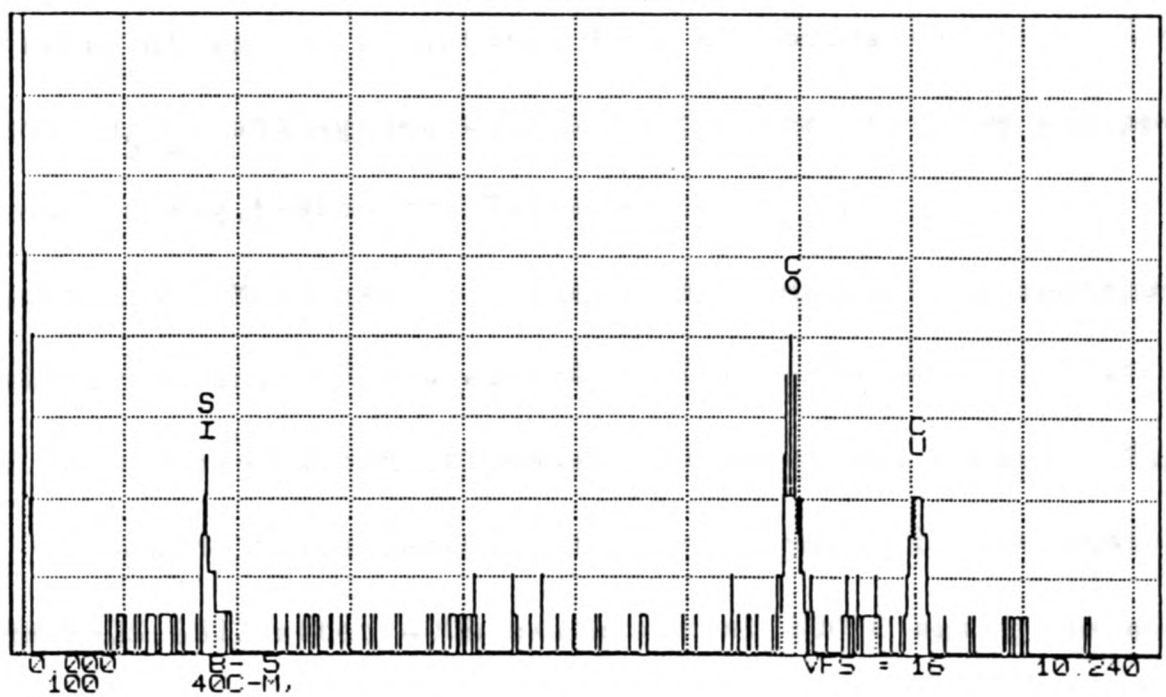
Fig.6-14 Electron diffraction patterns from pre-crystallised Co58Ni10Fe5Si11B16 thin foils: (a) SAED patterns before oxidation; (b) CEED patterns before oxidation from the grain marked C in Fig.6-13(a); (c) indexing of (b) as hcp Co $\langle 01\bar{1}1 \rangle$ zone; (d) SAED patterns after 20h at 350°C.

Table 6-4. Calculated d spacings for crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ together with d spacings of some relevant compounds

d (Å)	α -Co (5-727)	Co ₂ Si (4-847)	Co ₂ B (25-241)
2.2		2.88	
2.75		2.75	
2.49			2.51
2.31		2.28	
2.14	2.165	2.13	2.113
2.05		2.05	
2.00	2.023	2.02/2.00	
1.96		1.97	
1.90	1.910	1.87/1.85	
1.72		1.71/1.70/1.67	
1.59		1.60	1.616/1.588
1.54		1.53	
1.49		1.49	
1.39		1.44/1.41/1.37	
1.24	1.252	1.27/1.26/1.25	1.268
1.21		1.21	
1.18		1.19	1.192
1.15	1.149	1.17-1.14	1.169
1.12		1.11/1.10	
1.088	1.083/1.066	1.08/1.05	
1.021	1.015	1.03/1.02/1.00	1.032



a)



b)

Fig.6-15 Typical EDS spectra from different grains in pre-crystallised $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ thin foils before oxidation. Si varies from 2 to 30% and Co varies from 70 to 86%. (a) Co rich grain of hcp $\text{Co}(\text{Ni}, \text{Fe})$; (b) Si rich grain of Co_2Si . The Cu peaks are from the Cu support grids and sample holder.

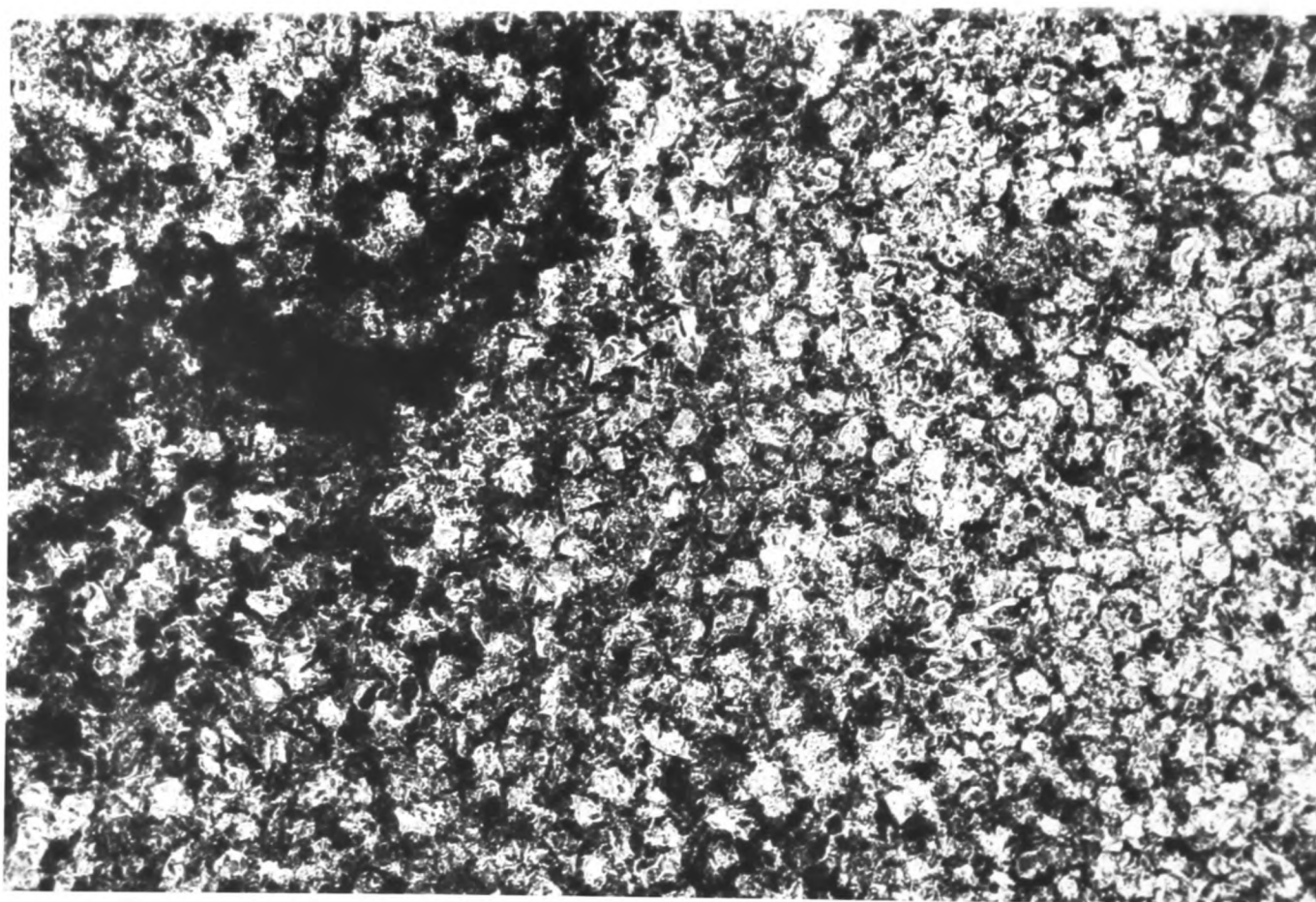
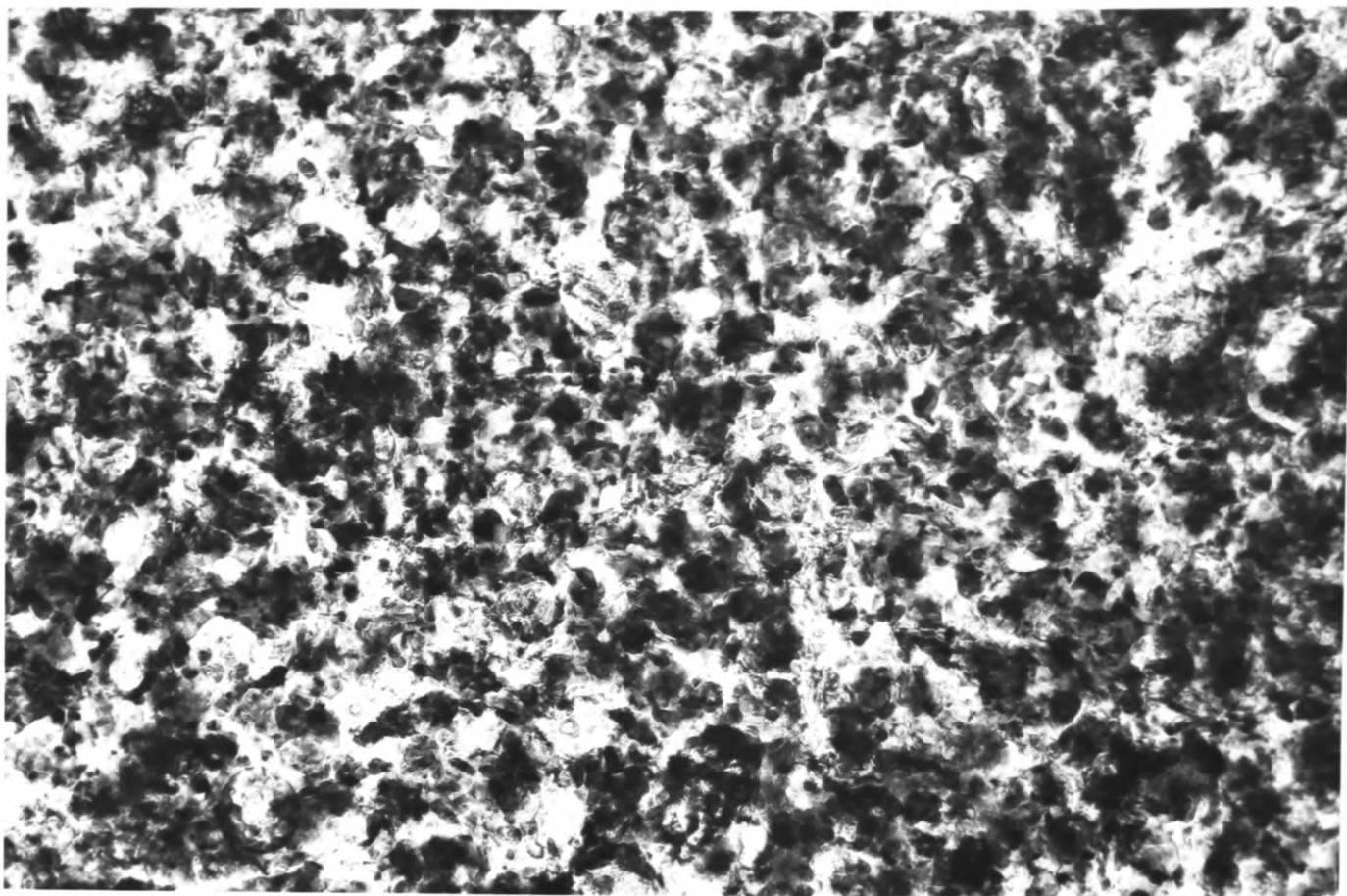
indicated that the different grains in the crystallised structure contained different cobalt and silicon contents, ranging from 70-86at.%Co and 2-30at.%Si. The Co rich grains typically contained about 10at.%Ni and a small amount of Fe (Fig.6-15(a)), while the Si rich grains contained virtually no Ni or Fe (Fig.6-15(b)), corresponding to a-Co(Ni, Fe) and Co₂Si respectively. Fig.6-13(b) shows a typical TEM micrograph of pre-crystallised thin foil specimens after 20h oxidation at 350 C. The oxide morphology was less distinct than for the oxidised amorphous thin foils, because of additional complex contrast contributed by the underlying crystalline matrix. SAED patterns were also relatively complex because of the mixing of diffraction patterns from the oxide and matrix crystals, as shown in Fig.6-14(d). The continuous rings in the SAED patterns were again characteristic of spinel structures from a combination of Co₂SiO₄, Co₃O₄, Fe₂SiO₄ and Fe₃O₄, and agreed well with the results from stripped oxide scales shown in Fig.6-9(b) and Table 6-3.

Bright field TEM images of oxide films removed from amorphous Co₆₆Ni₁Fe₄Si₁₅B₁₄ and Co₇₆Mn₄Fe₂Si₆B₁₂ after 400h oxidation at 400 C again exhibited very fine-scale multiphase structures, as shown in Figs.6-16 (a) and (b). The oxide films removed from pre-crystallised Co₆₆Ni₁Fe₄Si₁₅B₁₄ and Co₇₆Mn₄Fe₂Si₆B₁₂ after 400h oxidation at 400 C again contained amorphous SiO₂ in the thin matrix areas, as shown in Figs.6-17(a) and (b).

6.3. Discussion

6.3.1 Oxidation chemistry

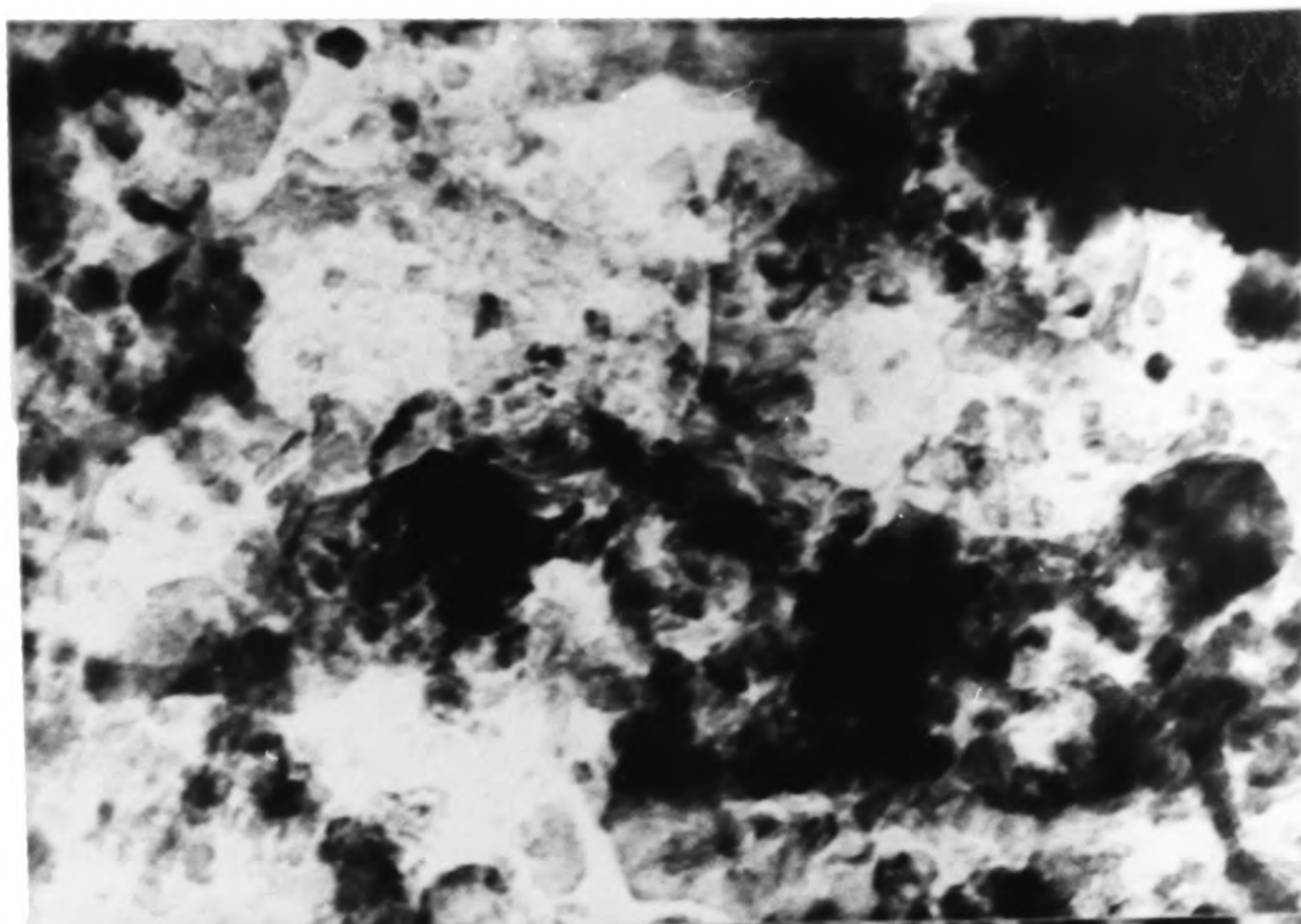
The present results clearly establish the overall oxidation chemistry of amorphous and crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆. From the EDS results in Table 6-3, the oxide scales formed on both amorphous and crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ contain mostly Co, Si and Fe, with very little Ni.



(a)/(b)

Fig.6-16 TEM bright field images of the oxide scales removed from amorphous (a) $\text{Co}_{66}\text{Ni}_1\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and (b) $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$, oxidised for 400h at 400 C in air.

(a)



(b)

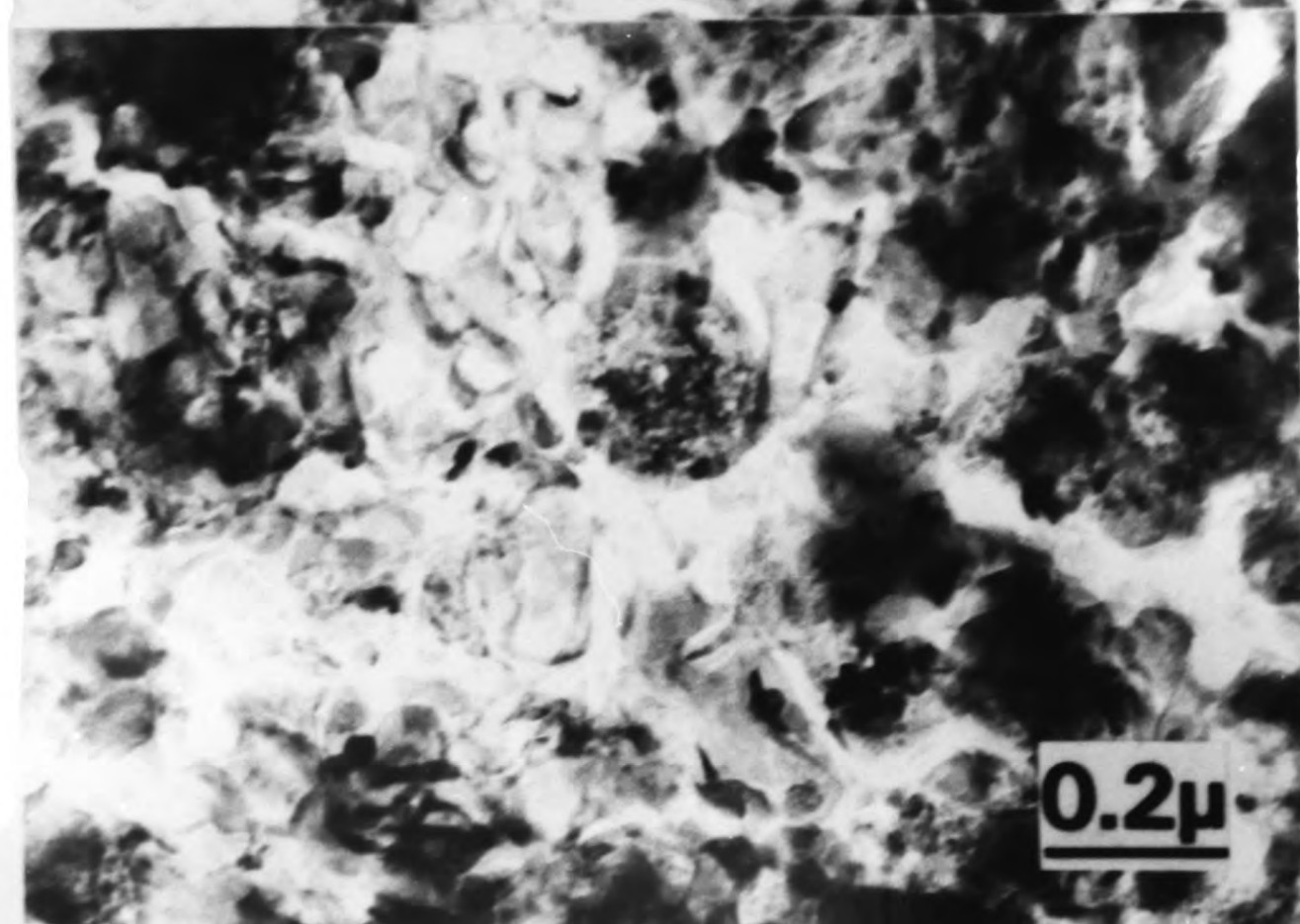


Fig.6-17 TEM bright field images of the oxide scales removed from pre-crystallised (a) $\text{Co}_{66}\text{Ni}_1\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and (b) $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$, oxidised in air at 400°C for 400h.

Average concentrations of Si(about 35%) and Fe(14-29%) are more than 3 times greater than in the alloy matrix, as expected since silicon is the least noble element, followed by iron, cobalt and nickel. The SAED results in Tables 6-2 and 6-3 show strong diffraction rings from the oxide scales which can be indexed as corresponding to the complex oxide Co_3O_4 , Fe_3O_4 , Co_2SiO_4 and Fe_2SiO_4 . The overall oxidation process can therefore be represented by the following reactions:



The oxides Co_3O_4 , Fe_3O_4 , Co_2SiO_4 and Fe_2SiO_4 exhibit similar spinel crystal structures, with some degree of mutual solubility ((25), also see Chapter 2). This, together with the small grain size in the oxide scales shown in Figs.6-7 and 6-8, makes it extremely difficult to determine the exact stoichiometry of the oxide grains.

6.3.2 Oxidation mechanisms

The present results do not establish clearly the detailed mechanisms for evolution of the complex oxide scale microstructures which form on amorphous and crystallised Co58Ni10Fe5Si11B16. SiO_2 is expected to form first, since Si is the most oxidisable element present. As shown in Figs.6-11 and 6-12, however, the initial oxidation of amorphous alloy thin foils is dominated by the growth of small grains of CoO, with no evidence for the formation of SiO_2 , although it may have been present in small quantities and finely divided form. Diffraction from the initial oxidation product on crystalline thin foils is masked by the complex microstructure of the underlying matrix, as shown in Figs.6-13 and 6-14, but the detectable oxide has the spinel structure of Co_3O_4 , Fe_3O_4 , Co_2SiO_4 and

Fe_2SiO_4 . However, amorphous SiO_2 is clearly present in the thin matrix regions of the oxide scale after longer oxidation annealing times, as shown in Figs.6-8(c) and (d).

In general, SiO_2 has good protective ability against oxidation, since it grows very slowly by diffusion of oxygen ions inwards through the SiO_2 scale ((26-28), also see section 2.5.3). High Si regions of the oxide scales stripped from amorphous and crystallised Co58Ni10Fe5Si11B16 are all therefore very thin, even after long oxidation annealing times. Fe and Co oxidise differently from Si, by the much faster process of metal ion diffusion through the oxide scale (see sections 2.4.1 and 2.4.3). Thus, Figs.6-5 to 6-8 and Table 6-3 show that Fe and Co oxides on amorphous and crystalline Co58Ni10Fe5Si11B16 become concentrated in the form of relatively thick, fast growing particles embedded in a thin, slow growing, Si rich matrix. Mass gain measurements such as those in Figs.6-1, 6-3 and 6-4 are then dominated by fast growth of Co and Fe rich oxide particles, with the overall oxidation kinetics controlled by Co and Fe oxidation rates.

6.3.3 Oxidation kinetics

Figs.6-1 and 6-3 show clearly different oxidation kinetics for amorphous and crystalline Co58Ni10Fe5Si11B16. The amorphous alloy obeys a parabolic rate law, indicating that the oxidation reaction obeys Wagner's theory ((29,30), also see section 2.3.3). For a diffusion process, the parabolic constant K is given by an Arrhenius equation:

$$K = K_0 \exp(-Q/RT) \quad (6-7)$$

Fig.6-18 shows $\ln$ parabolic rate constant plotted versus inverse absolute oxidation temperature, $\ln K - 1/T$, for amorphous Co58Ni10Fe5Si11B16. The data show linear behaviour over the temperature range 300 to 400 C, in agreement with the Arrhenius eqn.(6-7). The activation energy Q was

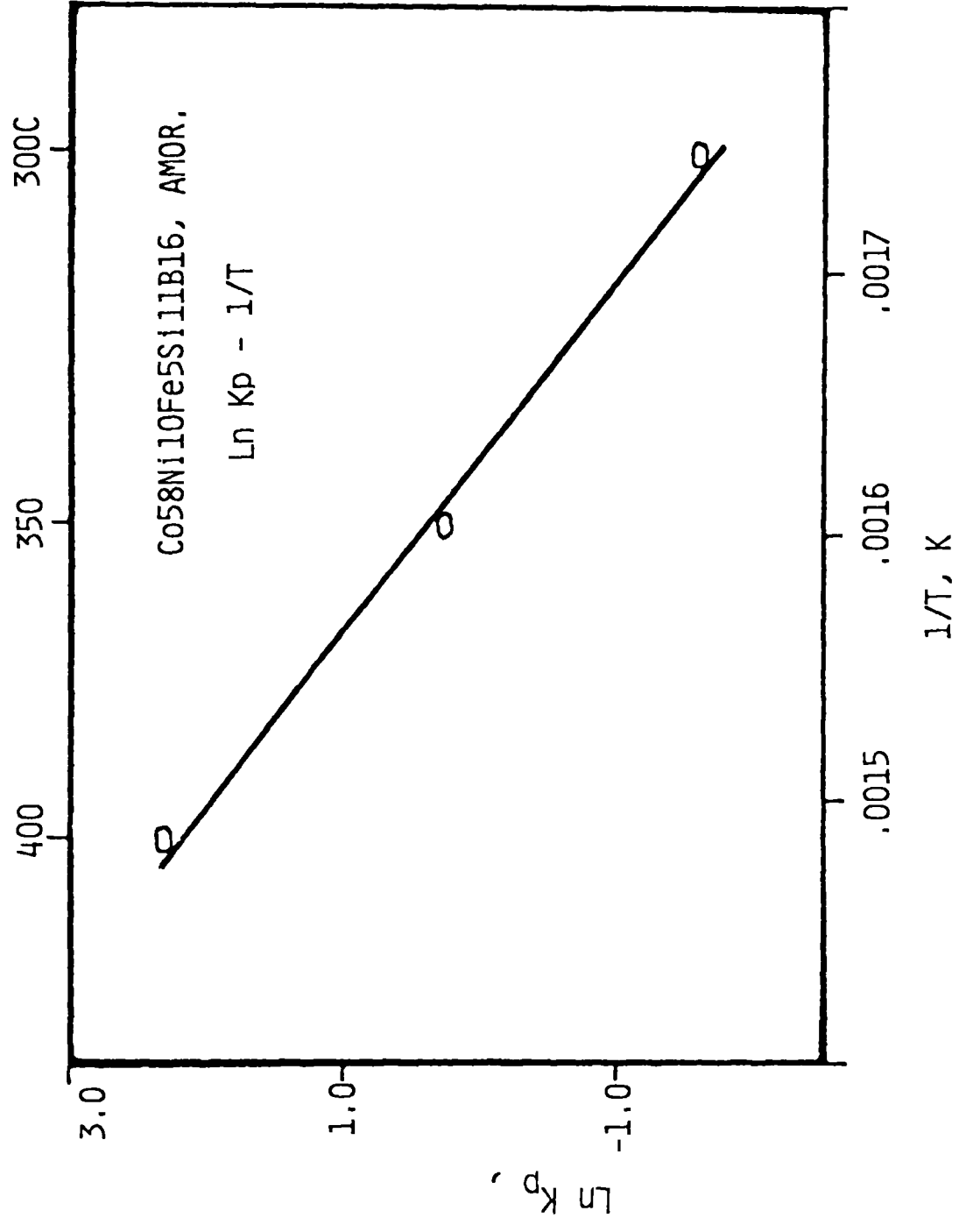


Fig.6-18 Arrhenius variation of $\ln$ parabolic rate constant versus inverse absolute temperature ($\ln K' - 1/T$) for amorphous Co58Ni10Fe5Si11B16.

calculated by applying linear regression analysis to the data in Fig.6-1 and Table 6-1, giving a value of 130 +/- 10 kJ/mol.

Previous direct measurements of diffusion activation energy have given values of 140-170, 390-470, and 190-230kJ/mol respectively for Co in CoO, Fe in Fe₂O₃ and Fe in Fe₃O₄ over the temperature range 500-1300 C (31,27). In comparison, activation energies calculated from parabolic oxidation rate constants give corresponding values of 184+/-20, 194+/-30, and 150+/-15kJ/mol for growth of CoO, Fe₂O₃ and Fe₃O₄ in air (27,32-36). The two sets of CoO data agree within experimental error, indicating that Co oxidation in air follows Wagner's ion diffusion model. However, the Fe₂O₃ and Fe₃O₄ measurements imply a more complex oxide growth mechanism, perhaps by diffusion through faster short-circuit paths such as grain boundaries (37,27). The oxide scale on amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ consists of a complex multiphase, fine scale mixture of several Co, Fe and Si oxides, so that a complex rate controlling oxidation process might also be expected. However, the activation energy of 130 +/- 10 kJ/mol calculated from the Arrhenius temperature variation of parabolic oxidation rate constant in Fig.6-18 agrees reasonably well with the previously measured diffusion activation energy of 140-170 kJ/mol for Co in CoO. Thus, the overall oxidation reaction for amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ is dominated by oxidation of Co, probably with a rate controlling process of Co ion diffusion through the complex oxide scale.

Unlike amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, the crystalline alloy obeys a logarithmic rather than parabolic oxidation rate law, which suggests a more complicated oxide growth mechanism. As reviewed in 2.3.4, there are several different interpretations of logarithmic oxidation kinetics, based on progressive blocking of low resistance diffusion paths, adsorption of reactive species, electric fields across the oxide scale, and

non-isothermal conditions in the oxide layer (38-41). Logarithmic oxidation kinetics are usually found at relatively low temperatures. The present understanding of logarithmic oxidation kinetics is still rather poor. Based on the present experimental results, however, a tentative explanation for logarithmic oxidation kinetics in pre-crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ can be given as follows. TEM observations such as in Figs.6-8(c) and (d) and indexing of SAED patterns in Fig.6-9(d) show that the fine scale thin layer of oxide formed on crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ contains amorphous silica, which is not present in the oxide scale on the amorphous alloy. Amorphous silica possesses good stability, and is an efficient barrier to ion diffusion (42,26,28). As amorphous silica forms progressively in the oxide scale on crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, the effective area available for ion transport is reduced, and the overall oxidation rate decreases quickly. This type of blocking effect on ion diffusion by the growing second phase oxide amorphous SiO₂ leads to a logarithmic oxidation rate law (41), as discussed in section 2.3.4.

Fig.6-19 shows the Arrhenius variation of $\ln K_L - 1/T$ for the oxidation of crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ over the temperature range 300-450 C. The data again show very good linear behaviour in agreement with the Arrhenius eqn.(6-7), indicating that the oxidation reaction was also controlled by a thermally activated process.

6.3.4 The effect of alloy structure on oxide growth mechanism

Amorphous and crystallised Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ have identical chemical composition, but different microstructure and microchemistry, leading to significant differences in oxidation kinetics and oxide structure. Amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ has a homogeneous Si concentration, which during oxidation is absorbed into small crystals of the mixed spinel oxides

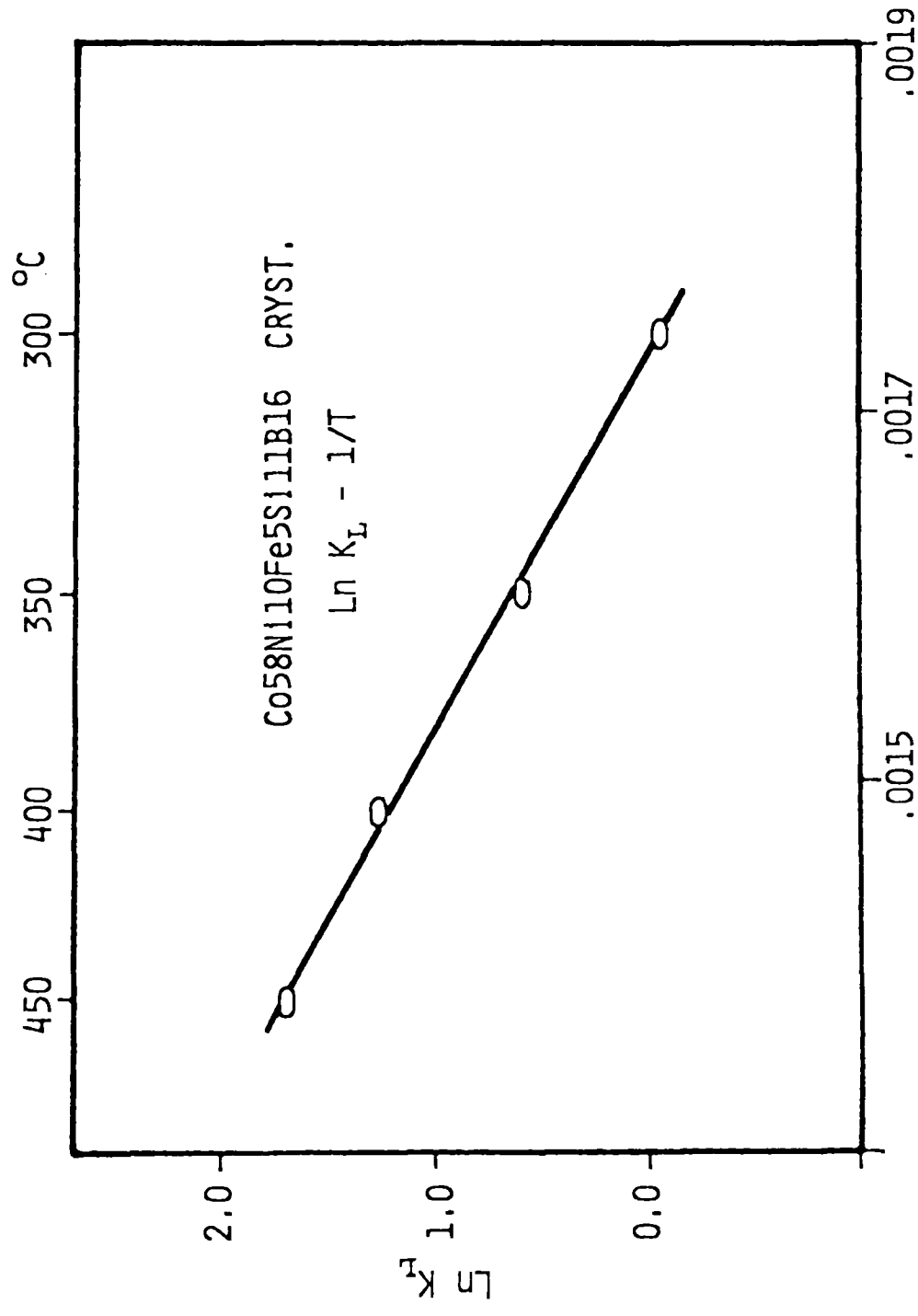


Fig.6-19 Arrhenius variation of $\ln$ logarithmic rate constant versus inverse absolute temperature ($\ln K_L - 1/T$) for crystalline $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$.

Co_2SiO_4 and Fe_2SiO_4 , resulting in parabolic oxidation growth. In contrast, crystallised Co58Ni10Fe5Si11B16 contains a Si-rich phase Co_2Si . Local regions of high Si concentration seem to stimulate the formation of amorphous silica, leading to the logarithmic oxidation kinetics shown in Fig.6-3, and a reduction in the overall oxidation rate relative to the homogenous amorphous alloy.

Another possible explanation for the different oxide growth rates on amorphous and crystalline Co58Ni10Fe5Si11B16 is that an epitaxial relationship is established between the oxide and matrix crystal phases, which slows down the growth of the Co and Fe oxides formed on crystalline Co58Ni10Fe5Si11B16 (43).

6.3.5 Oxidation at higher temperatures

At the higher temperatures of 450 and 500 C, the oxidation behaviour of amorphous Co58Ni10Fe5Si11B16 is more complicated than at lower temperatures, as shown in Fig.6-1. Several factors can contribute to this change in oxidation behaviour. Firstly, the amorphous alloy crystallises during oxidation annealing. Microstructural and microchemical changes in the underlying alloy during crystallisation can affect the metal-oxide interface, the diffusion conditions and the oxide growth mechanism. Secondly, the adhesion between scale and metal also affects the oxidation kinetics. As the reaction proceeds, contact between the oxide scale and underlying metal can be lost at certain areas due to oxide growth stresses within the scale (44,45). Partial loss of oxide/metal contact again reduces the area through which ions migrate outwards and therefore causes the oxidation rate to decrease. If, however, the oxide scale becomes cracked, the underlying metal is freshly exposed to the oxidising atmosphere, and the oxidation rate increases (45). All these effects become increasingly significant at higher oxidation temperatures and longer

oxidation times, making quantitative prediction or explanation of oxidation kinetics difficult. In the present study, alloy crystallisation and partial alloy-scale decohesion are dominant effects during oxidation of the amorphous alloy at 450 C, when the oxidation rate decreases from the initial parabolic rate law; whereas oxide cracking has a strong influence after 40h oxidation at 500 C, when the oxidation rate increases from the parabolic rate law, as shown in Fig.6-1.

6.4 Conclusions

From the present investigation, the following conclusions can be drawn.

1. Oxidation of amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ in air obeys a parabolic rate law over the temperature range 300-400 C. The parabolic rate constant increases with oxidation temperature according to an Arrhenius law, with an activation energy of 130 +/- 10kJ/mol. Above 400 C, the amorphous alloy crystallises quickly, and the oxidation rate decreases more sharply than expected from the parabolic rate law.

2. Oxide scales formed on amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ consist of a complex, fine grained, multiphase oxide mixture, containing Co₃O₄, Fe₃O₄, Co₂SiO₄, Fe₂SiO₄ and CoO in a microstructure of relatively large, Co and Fe rich particles, embedded in a relatively thin, Si rich matrix. Oxidation of Co and Fe dominates the rate of oxidation mass gain, and the rate controlling process is probably Co ion diffusion through the oxide scale.

3. Oxidation of crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ in air obeys a logarithmic rate law over the temperature range of 300-450 C. The crystalline alloy is more resistant to oxidation than the amorphous alloy over this range of testing temperatures.

4. Oxide scales formed on crystalline Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ are in general similar to those found on the amorphous alloy, and again consist of a

complex, fine grained, multiphase oxide mixture. Unlike the amorphous alloy, the thin oxide matrix layer contains amorphous SiO_2 , which progressively reduces the extent of Co and Fe ion diffusion, leading to a logarithmic oxidation rate law.

5. Different oxidation kinetics and oxide growth mechanisms for amorphous and crystalline $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ are caused by different alloy microstructures. Microsegregation of Si within the multiphase crystalline structure of $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$ stimulates the formation of amorphous silica, and eventually leads to a logarithmic oxidation rate law and a lower reaction rate than amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$.

6. As with amorphous $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, oxidation of amorphous $\text{Co}_{66}\text{Ni}_{10}\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$ also obeys a parabolic rate law in air at 400 C, with parabolic constants of 3.1 and 3.5 $\text{ug}/\text{cm}^2/\text{h}^{1/2}$ respectively. As with crystalline $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$, oxidation of crystalline $\text{Co}_{66}\text{Ni}_{10}\text{Fe}_4\text{Si}_{15}\text{B}_{14}$ and $\text{Co}_{76}\text{Mn}_4\text{Fe}_2\text{Si}_6\text{B}_{12}$ also obeys a logarithmic rate law, with rate constants slightly smaller than crystalline $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{Si}_{11}\text{B}_{16}$.

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Chapter 7 The Oxidation Behaviour of Amorphous Fe₄₀Ni₄₀B₂₀ and

Fe₃₂Ni₃₆Cr₁₄P₁₂B₆

7.1 Introduction

Amorphous Fe₄₀Ni₄₀B₂₀ (VITROVAC 0040) is another soft ferromagnetic amorphous alloy, which has been investigated in great detail, covering almost all aspects of structure and properties (1,2). Studies of the structure and formation of amorphous Fe₄₀Ni₄₀B₂₀ include the manufacturing process (3,4), microstructure (5), atomic structure (6-8), electronic states (9), structural relaxation (10-16), diffusion and self-diffusion (17-20), viscosity (21), internal friction (22) and radiation effects (23).

Properties of amorphous Fe₄₀Ni₄₀B₂₀ which have been studied include embrittlement (24-27), fatigue and fracture (28), hardness (29), thermal properties (30), electronic properties (31), and corrosion and catalytic behaviour (32-34). As expected for a magnetic amorphous alloy, studies of the applications of amorphous Fe₄₀Ni₄₀B₂₀ have concentrated on the soft ferromagnetic properties and relevant applications in electrical and electronic devices (36-43). This Chapter and Chapter 8 describe the oxidation and crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀ respectively.

Amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ (METGLAS 2826A) is also a ferromagnetic amorphous alloy, which contains Cr and therefore has excellent corrosion resistance. Studies of the structure and properties of amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ can be found in references (44)-(51).

7.2 Oxidation behaviour of amorphous and crystalline Fe₄₀Ni₄₀B₂₀

7.2.1 Oxidation kinetics

Fig.7-1 shows oxidation mass gain versus (a) oxidation time and (b) square root of oxidation time for Fe₄₀Ni₄₀B₂₀ in air over the temperature

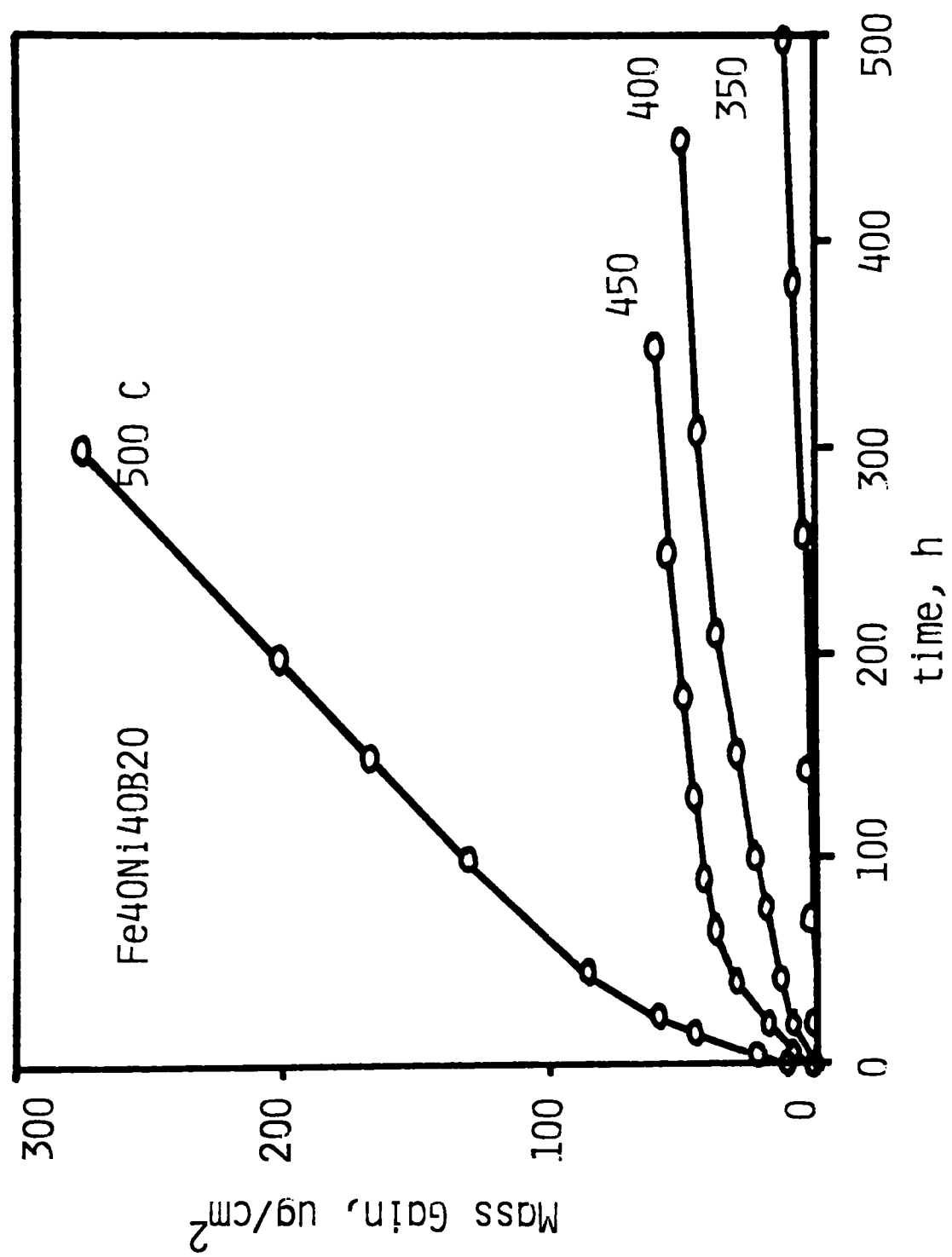


Fig.7-1 (a)

Fig.7-1 Mass gain Y versus (a) oxidation time t , and (b) square root of oxidation time t for Fe₄₀Ni₄₀B₂₀ over the temperature range 350-500°C in air.

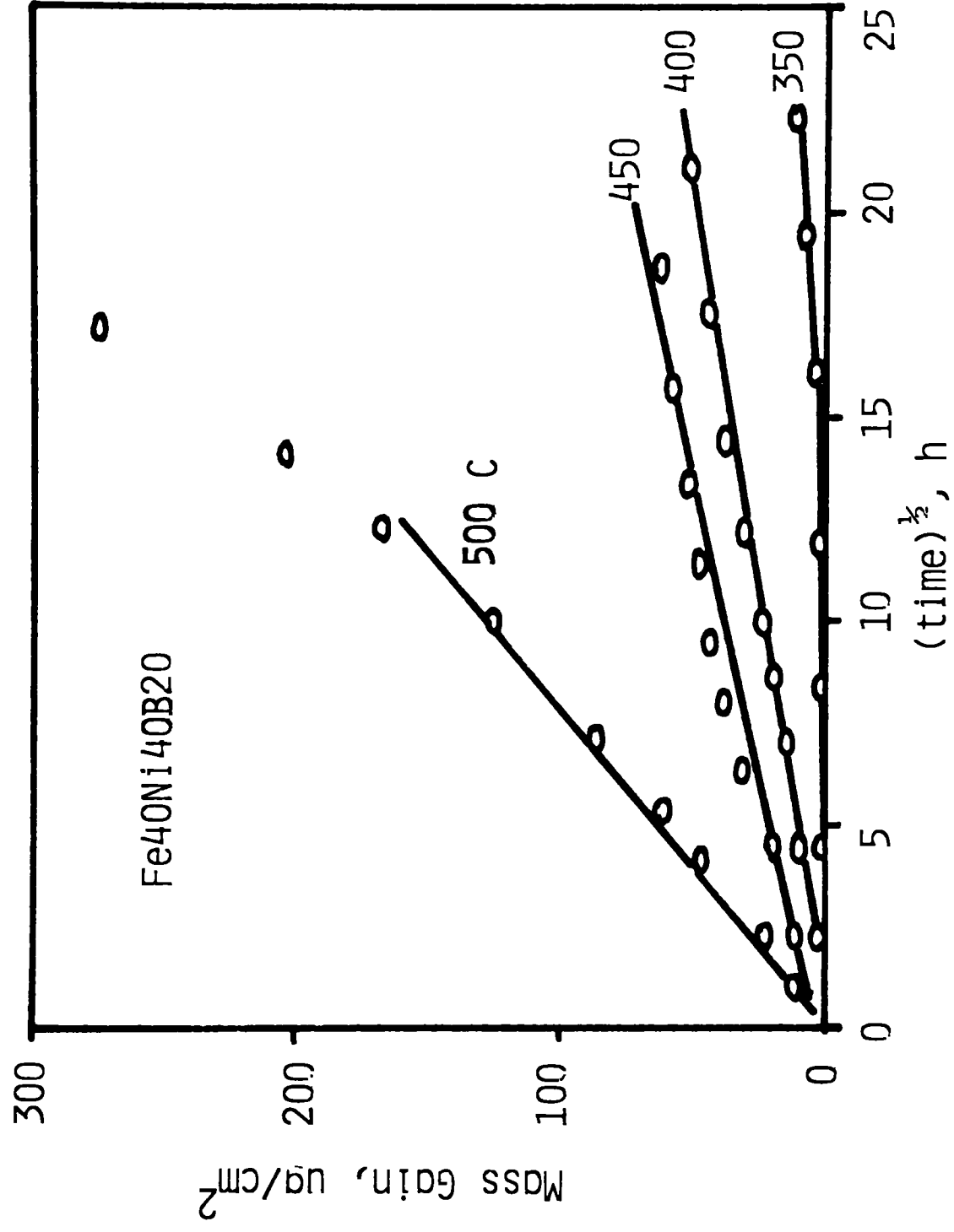


Fig.7-1 (b)

range 350-500 C. Fig.7-2 shows oxidation mass gain versus (a) oxidation time and (b) square root of oxidation time for amorphous and crystallised Fe₄₀Ni₄₀B₂₀, and Fig.7-2(c) shows oxidation mass gain versus ln oxidation time for pre-crystallised Fe₄₀Ni₄₀B₂₀, all in air at 350 C. The oxidation kinetics of amorphous Fe₄₀Ni₄₀B₂₀ are rather complicated. At temperatures of 400 and 450 C, the oxidation kinetics obeyed approximately a parabolic rate law of $Y = Kt^{1/2}$, as shown in Fig.7-1(b), with best fit K values of 2.55 and 3.30 ug/cm²/h^{1/2} respectively. At 500 C, the oxidation kinetics of Fe₄₀Ni₄₀B₂₀ obeyed a parabolic rate law during the first 25h oxidation, then gradually changed into a linear rate law, as shown in Figs.7-1(a) and (b). At 350 C, the oxidation kinetics also obeyed a parabolic rate law at the first 150h oxidation, then changed sharply into another parabolic rate law, as shown in Fig.7-2. The parabolic rate constants calculated from Fig.7-2(b) are 0.14 and 1.15 ug/cm²/h^{1/2} for oxidation at 350 C from 0 to 140h and 260 to 500h respectively. On the other hand, Fe₄₀Ni₄₀B₂₀ pre-crystallised by vacuum-annealing at 500 C for 20min, obeyed a logarithmic rate law during oxidation at 350 C, as shown in Fig.7-2(c). However, mass gains on amorphous and crystallised Fe₄₀Ni₄₀B₂₀ were too small to determine detailed oxidation kinetics at the lower temperatures of 250 and 300 C. The oxidation kinetics of Fe₄₀Ni₄₀B₂₀ over the temperature range 350-500 C are summarised in Table 7-1.

7.2.2 Oxide morphology, structure and composition

Fig.7-3 shows SEM micrographs of surface morphology of amorphous Fe₄₀Ni₄₀B₂₀ oxidised in air over the temperature range 350-500 C for times of up to 500h. After oxidation at for 140h at 350 C, the top surface of oxidised amorphous Fe₄₀Ni₄₀B₂₀ had a slight yellow colour, and SEM micrographs showed small grains of oxide distributed uniformly on the surface (Fig.7-3(a)). After oxidation for a longer time of 500h at 350 C,

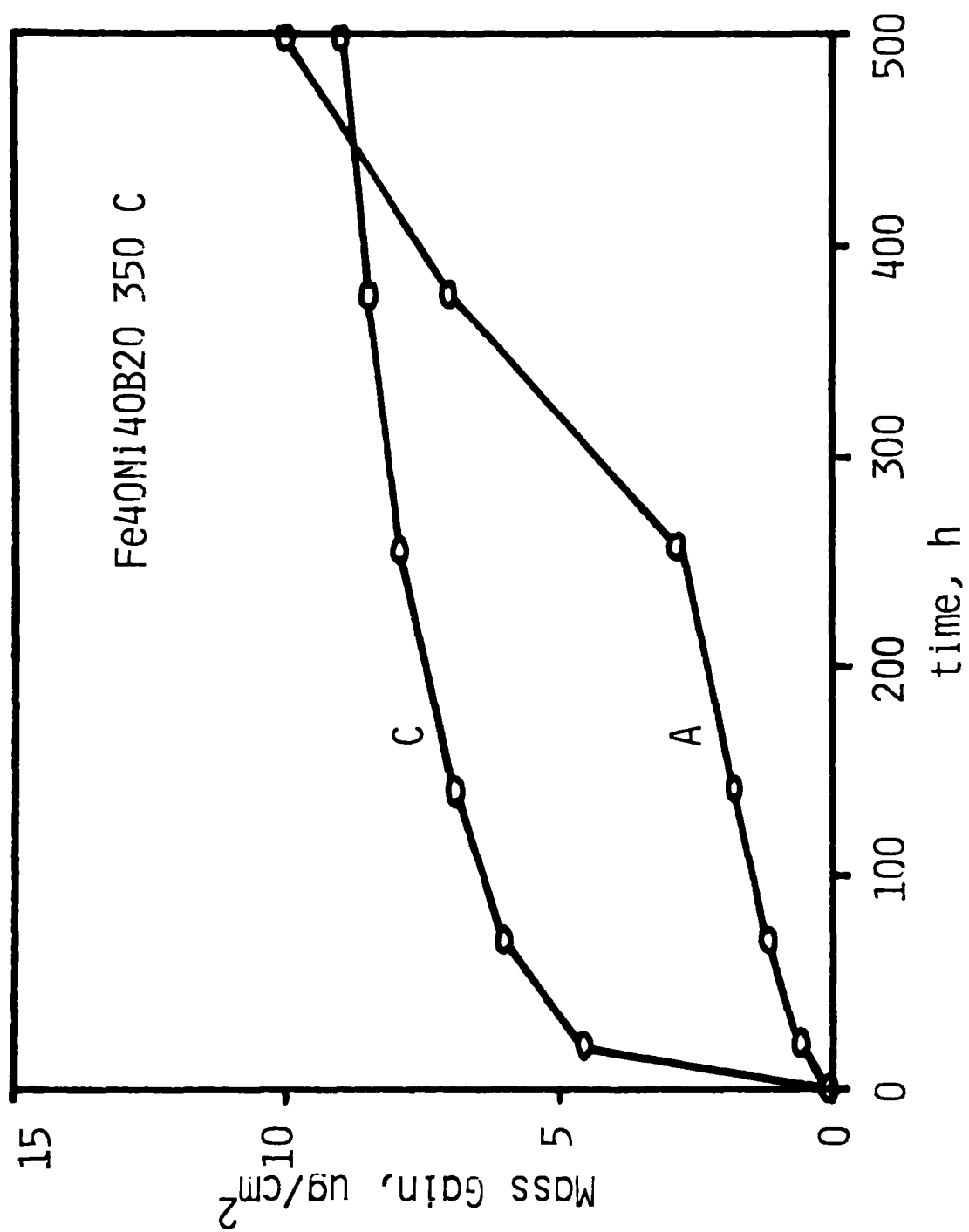


Fig.7-2 (a)

Fig.7-2 Mass gain Y versus (a) oxidation time t , (b) square root of oxidation time t and (c) $\ln$ oxidation time t for amorphous (A) and pre-crystallised (C) Fe₄₀Ni₄₀B₂₀ at 350°C in air.

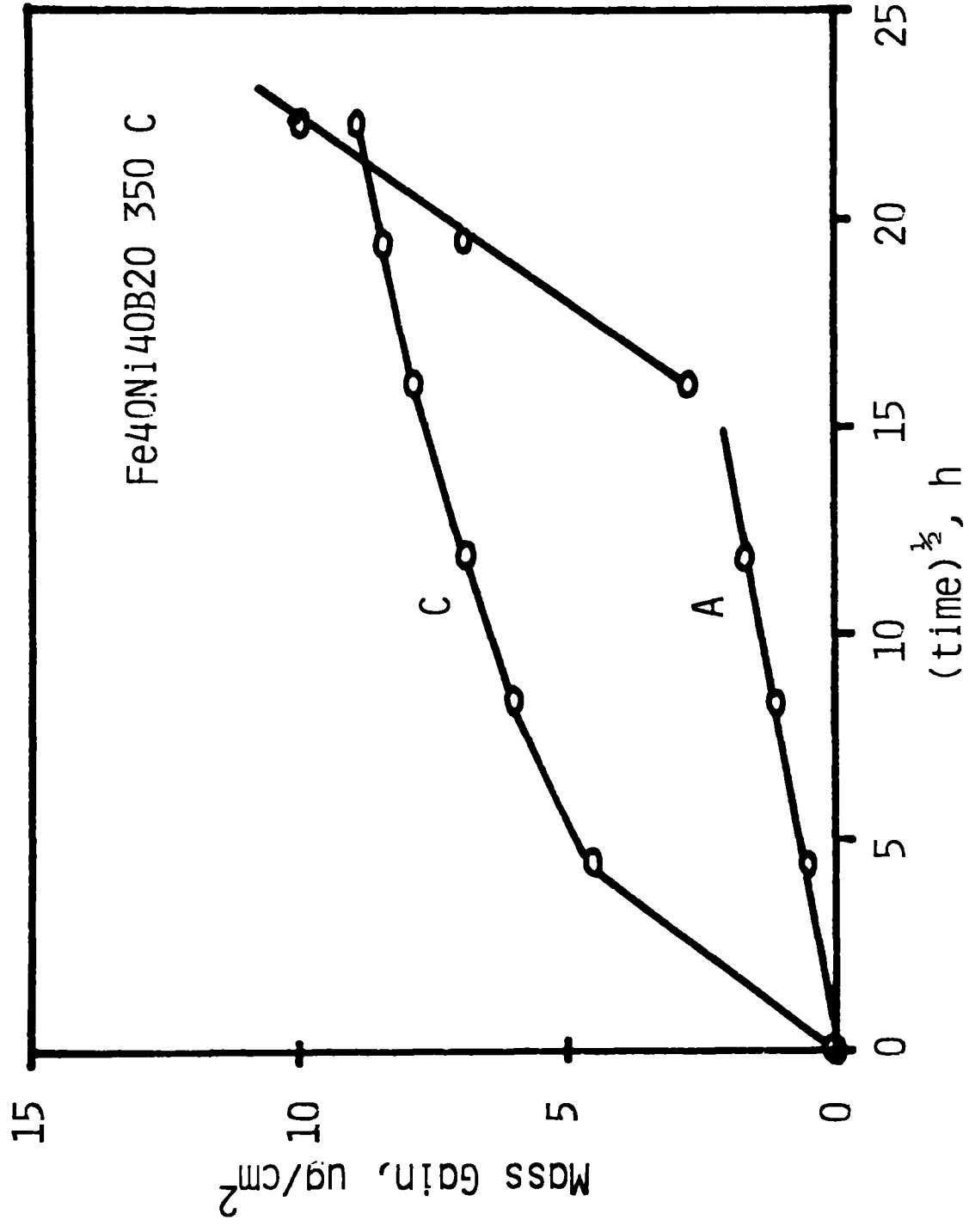


Fig.7-2 (b)

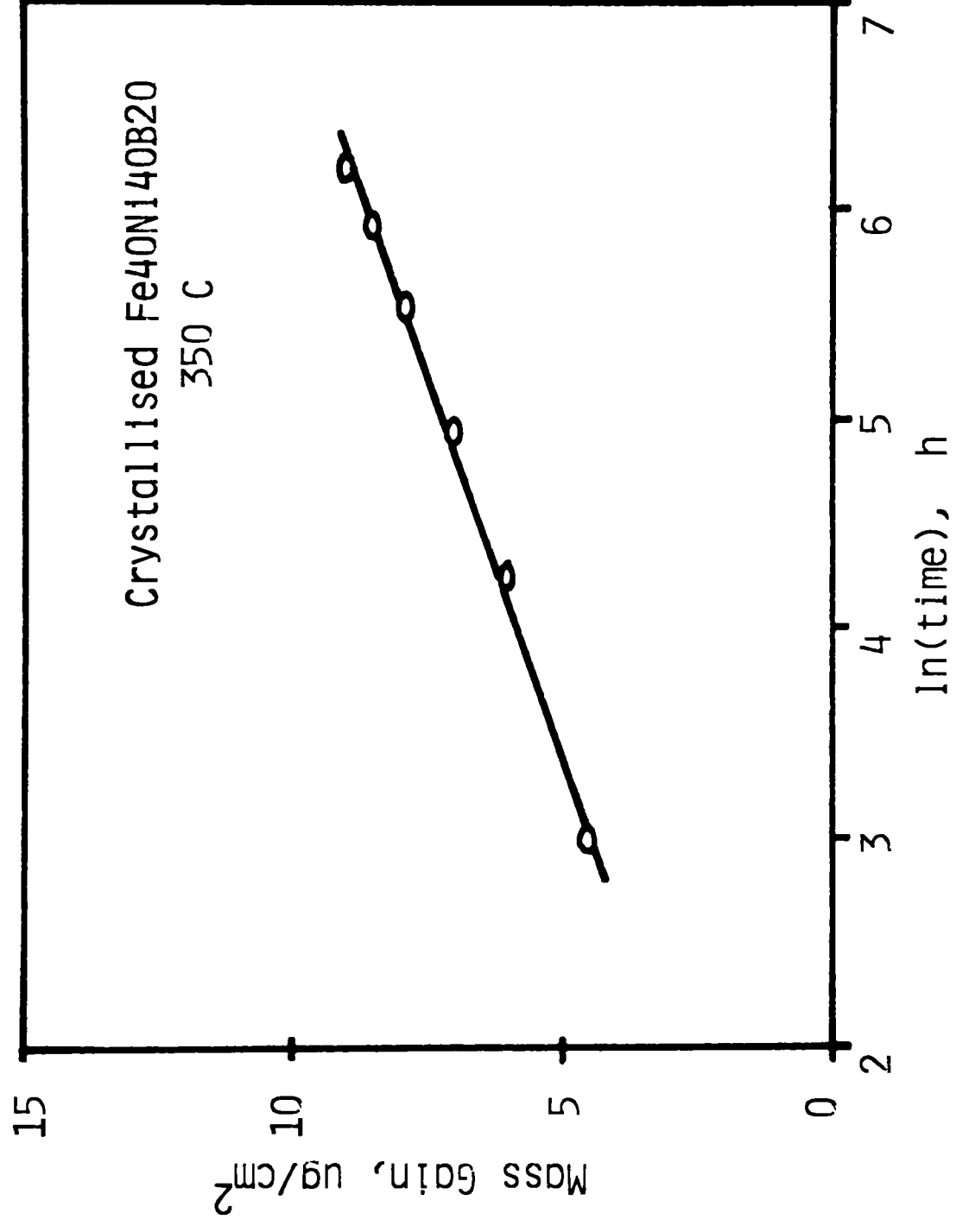


Fig.7-2 (c)

Table 7-1 The oxidation kinetics of amorphous and crystallised Fe₄₀Ni₄₀B₂₀ in air at temperature range 350 - 500 C

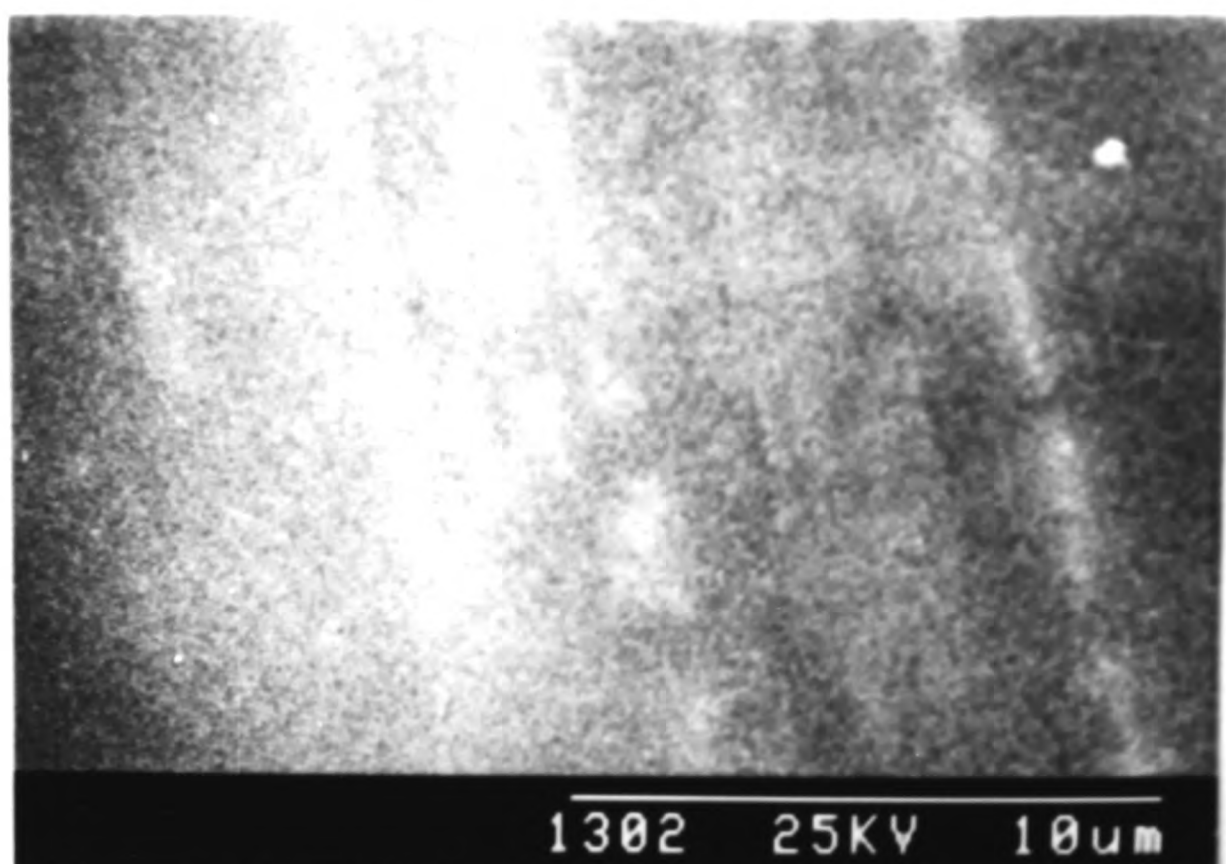
Oxidation temperature	Oxidation time	Oxidation rate law	Constant** K	A	Correlation coefficient R
350 C	0-140h	$Y = K t^{1/2} + A$	0.14	-0.1	0.996
350 C*	260-500h	$Y = K t^{1/2} + A$	1.15	-15.5	0.999
350 C crys-tallised	20-500h	$Y = K \ln t + A$	1.40	0.2	0.997
400 C*	0-450h	$Y = K t^{1/2} + A$	2.55	-2.6	0.995
450 C*	0-350h	$Y = K t^{1/2} + A$	3.30	4.3	0.980
500 C*	0-30h	$Y = K t^{1/2} + A$	10.4	-1.3	0.994
500 C*	100-300h	$Y = K t + A$	0.72	59.7	0.999

* Amorphous Fe₄₀Ni₄₀B₂₀ were crystallised during oxidation at this temperatures.

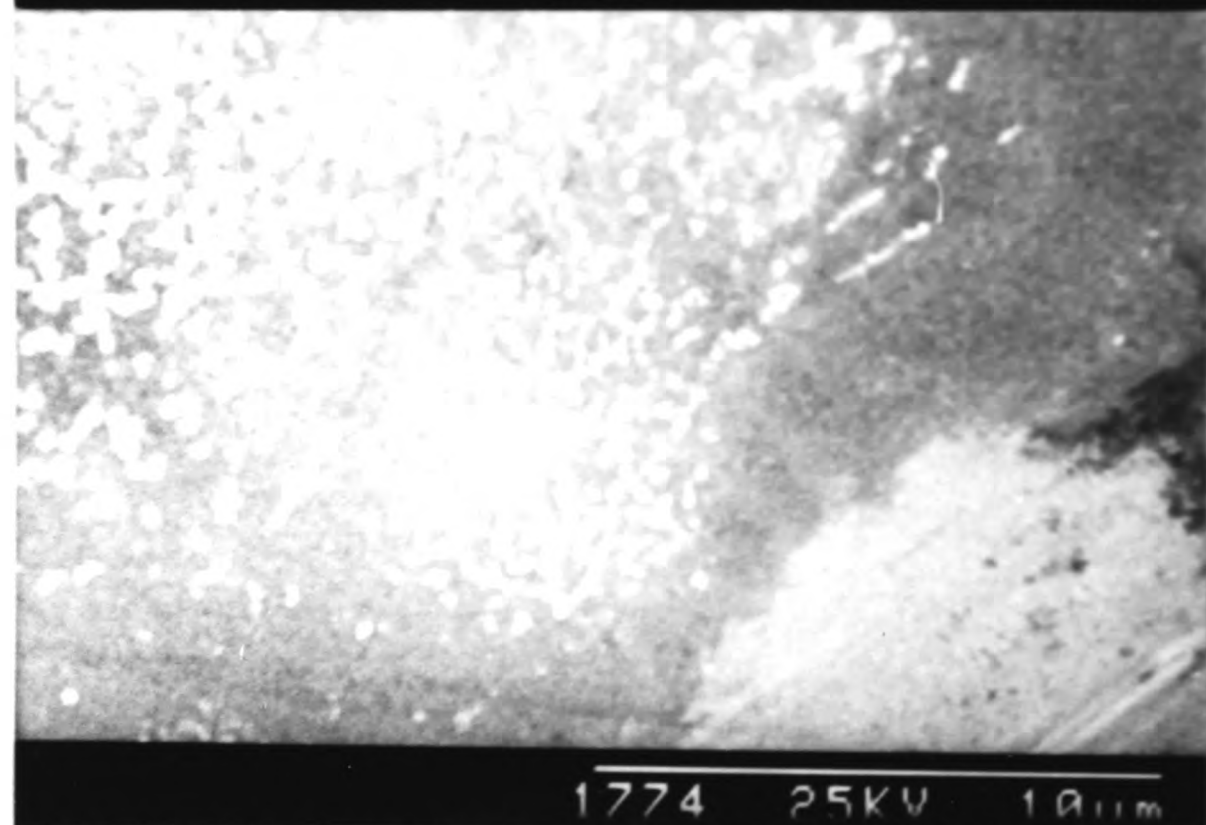
**K and A calculated with the mass gain in ug/cm² and time in hour.

Fig.7-3

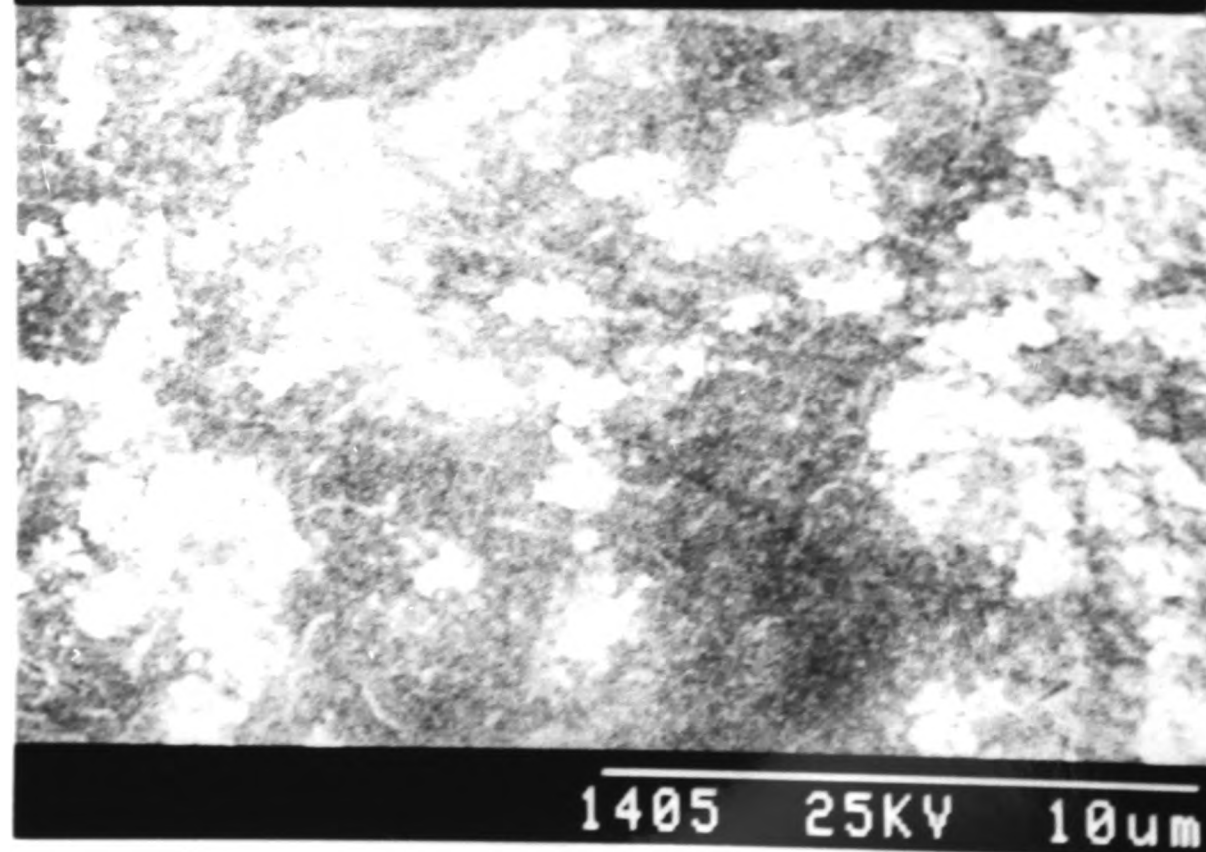
(a)



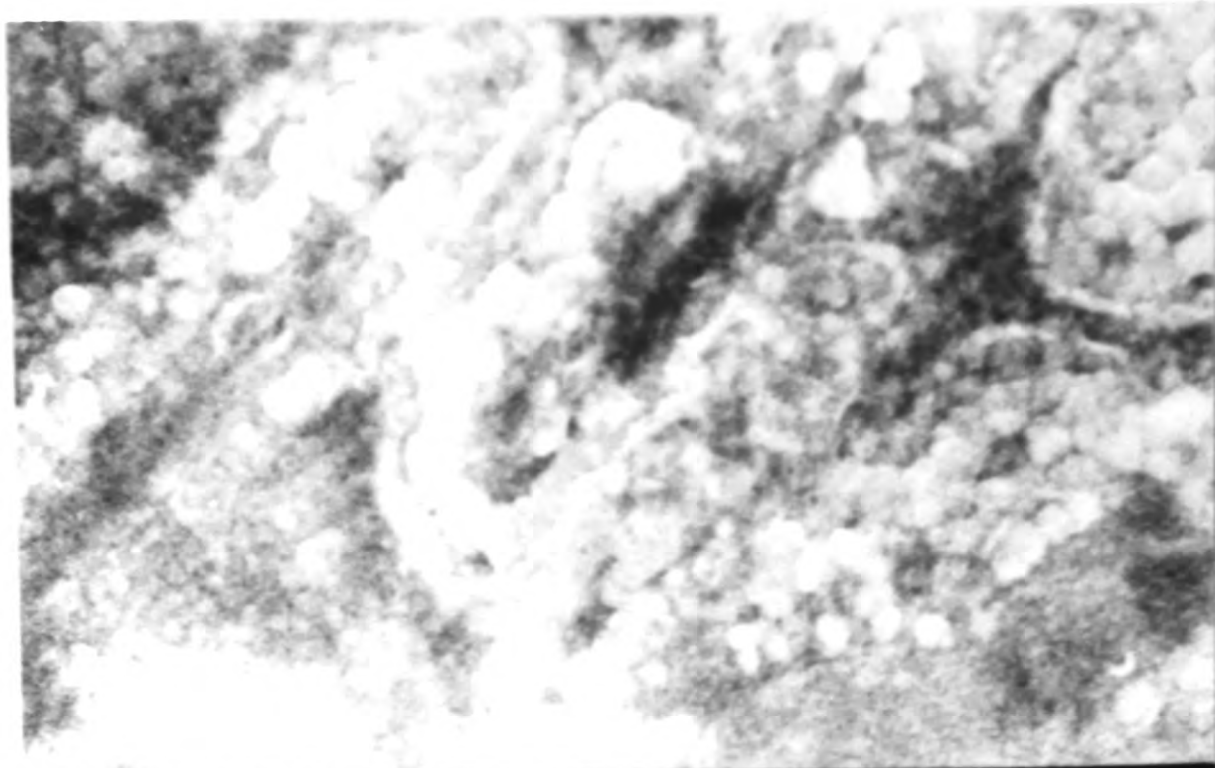
(b)



(c)

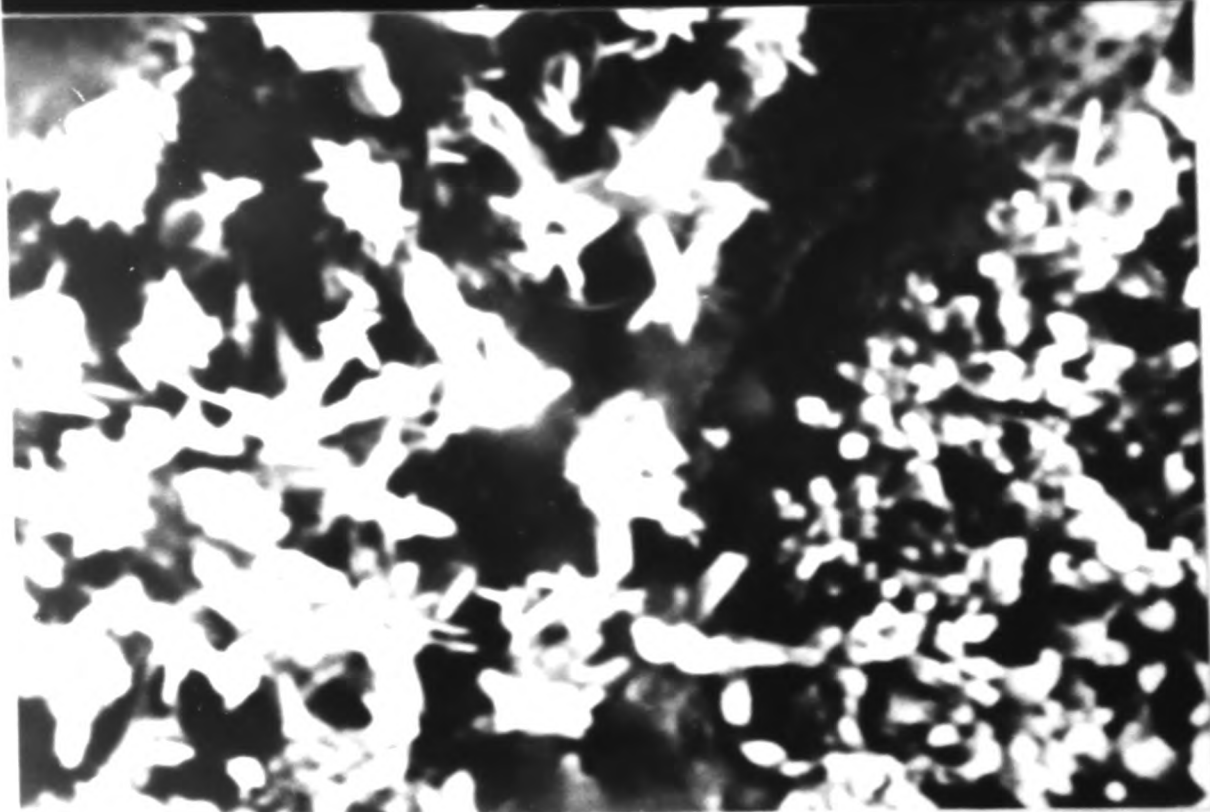


(d)



1908 25KV 10μm

(e)



1μ

Fig.7-3 SEM micrographs of the morphology of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ oxidised in air over the temperature range $350\text{--}500^{\circ}\text{C}$ for times of up to 500h: (a) at 350°C for 140h, (b) at 350°C for 500h, (c) at 400°C for 450h, (d) at 450°C for 350h, and (e) at 500°C for 300h.

the top surface had a light yellow colour with some darker yellow strips, and SEM micrographs showed larger oxide grains, especially on the darker yellow areas (Fig.7-3(b)). After oxidation for 450h at 400 C and for 350h at 450 C, the top surface had a dark grey colour, and SEM micrographs showed even larger oxide grains with a more irregular distribution on the surface (Figs.7-3(c) and (d)). However, at the highest temperature of 500 C, a multilayer, non-protective and irregular-shaped oxide formed, as shown in Fig.7-3(e).

Figs.7-4 and 7-5 show TEM micrographs of oxide films stripped from amorphous Fe₄₀Ni₄₀B₂₀ oxidised in air at 350 C for 140h and 500h respectively. The oxide film formed after oxidation for 140h at 350 C consisted of many oxide particles, with sizes ranging from 10 to 50nm, embedded in a thin oxide matrix as shown in Figs.7-4(a) and (b). The oxide film formed after oxidation for 500h at 350 C also consisted of many oxide particles with sizes ranging from 10 to 100nm, as well as many clusters of particles with size ranging from 500 to 1000nm, as shown in Figs.7-5(a) and (b). STEM micrographs in Fig.7-6 show similar features for oxide films removed from amorphous Fe₄₀Ni₄₀B₂₀ oxidised for 500h at 350 C, in agreement with the SEM and TEM micrographs in Figs.7-3(b) and 7-5. Figs.7-7(a) and (b) show typical SAED patterns from the oxide films in Figs.7-4 and 7-5 respectively. The oxide films formed in both cases, ie after 140 and 500h oxidation at 350 C, consisted mainly of Fe₃O₄ and Fe₂O₃, as indexed in Table 7-2. EDS microanalysis of the oxide films in Figs.7-4 and 7-5 are shown in Fig.7-8 and Table 7-3. The oxide films in both cases contained ~95 at.%Fe and ~5 at.%Ni, distributed homogeneously over the particle and matrix. The small amount of Ni detected by EDS probably corresponded to NiFe₂O₄, which is difficult to detect by SAED because of a similar crystal structure to Fe₃O₄. The microanalysis results agreed reasonably well with

Table 7-2 Calculated d spacings for typical diffraction patterns obtained from oxide films removed from amorphous and pre-crystallised Fe₄₀Ni₄₀B₂₀ oxidised at 350 C for 140h, together with ASTM powder card index d spacings for Fe₃O₄ and Fe₂O₃

d1	d2	d Fe ₃ O ₄ (hkl) 11-614	d Fe ₂ O ₃ (hkl) 13-534
4.83		4.85 (111)	
3.70	3.69		3.66 (012)
3.00	3.01	2.966 (220)	
2.71	2.70		2.69 (104)
2.53	2.52	2.530 (311)	2.51 (110)
	2.40	2.419 (222)	
2.29	2.27		2.285 (006)
2.19			2.201 (113)
2.12	2.10	2.096 (400)	
1.86			1.838 (024)
1.72		1.712 (422)	
	1.69		1.690 (116)
1.62	1.61	1.614 (333,511)	1.596 (018)
1.49	1.50	1.483 (440)	1.484 (214)
			1.452 (300)
1.32	1.31	1.327 (620)	1.310 (119)
1.27		1.279 (533)	
	1.24	1.264 (622)	1.258 (220)
1.19	1.21	1.2112 (444)	1.189 (128)
1.10	1.11	1.0922 (553,731)	1.102 (226)
1.05		1.0489 (800)	1.055 (2,1,10)
0.955	0.960	0.9692 (555,751)	0.9601 (324)
...	...	0.9386 (840)	0.9512 (140)
		...	...

d1 - from the oxide film removed from amorphous Fe₄₀Ni₄₀B₂₀ oxidised at 350 C for 140h;

d2 - from the oxide film removed from pre-crystallised Fe₄₀Ni₄₀B₂₀ oxidised at 350 C for 140h.

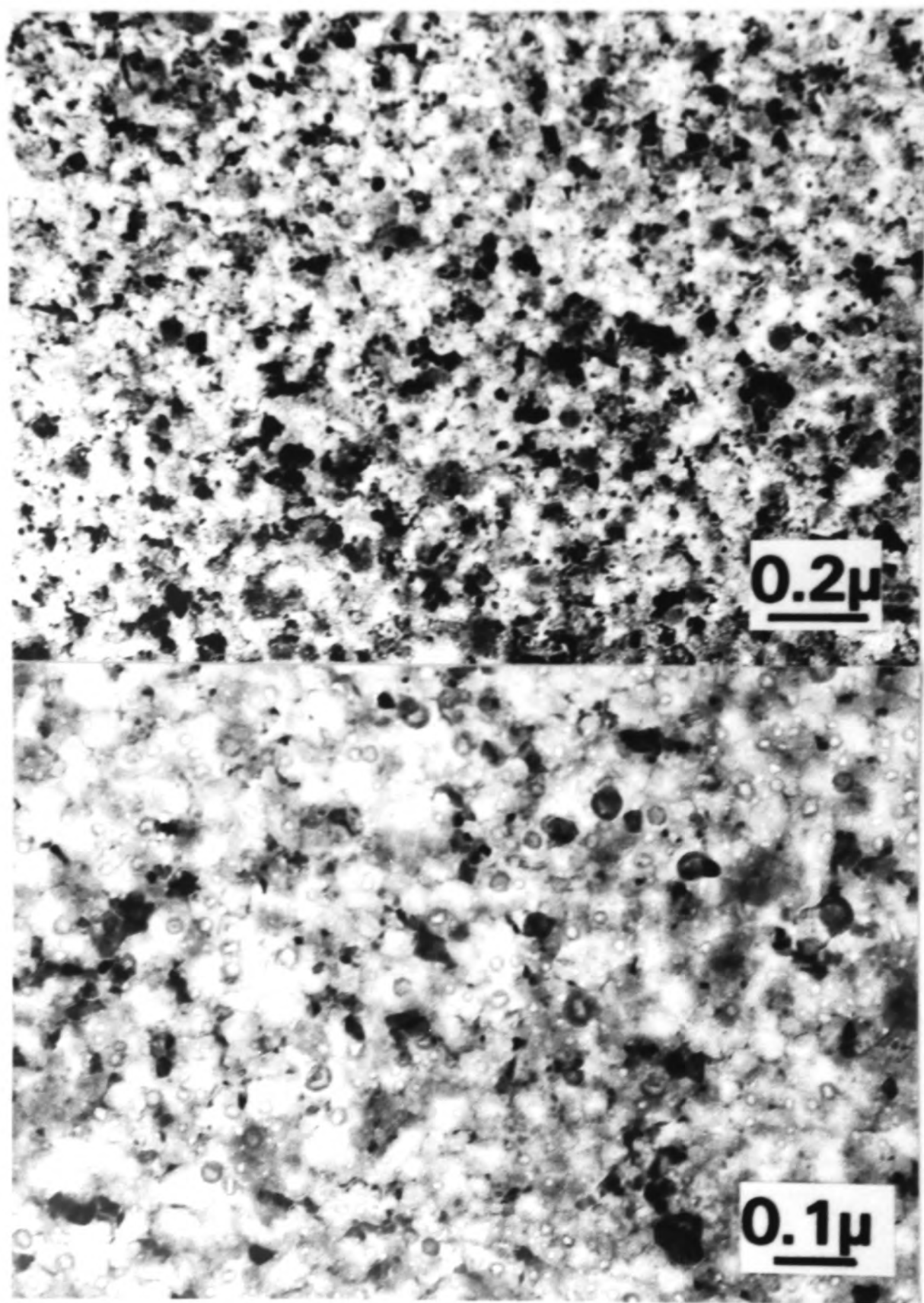
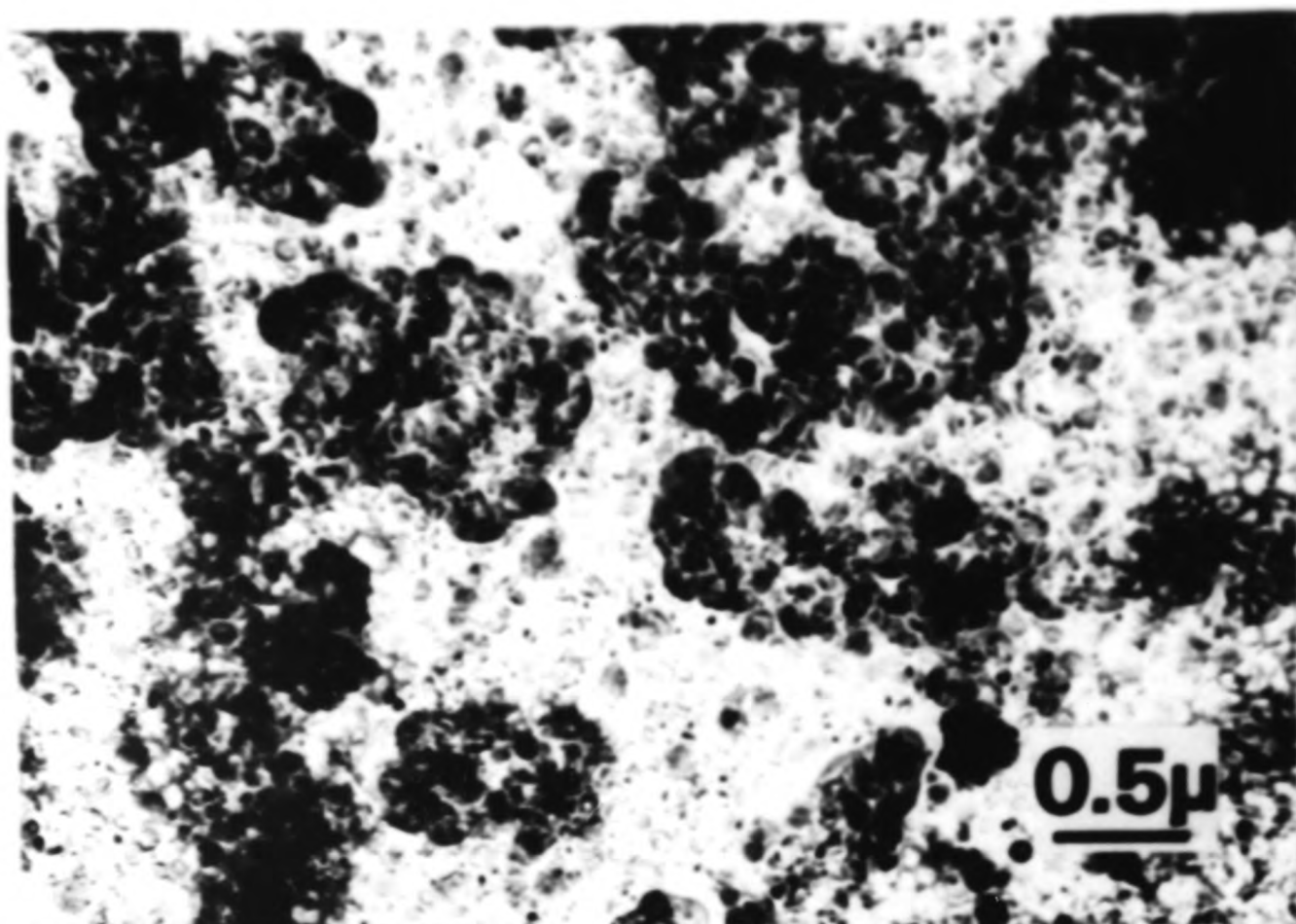


Fig.7-4 TEM bright field images of the oxide film removed from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ oxidised in air at 350°C for 140h.

а)



б)

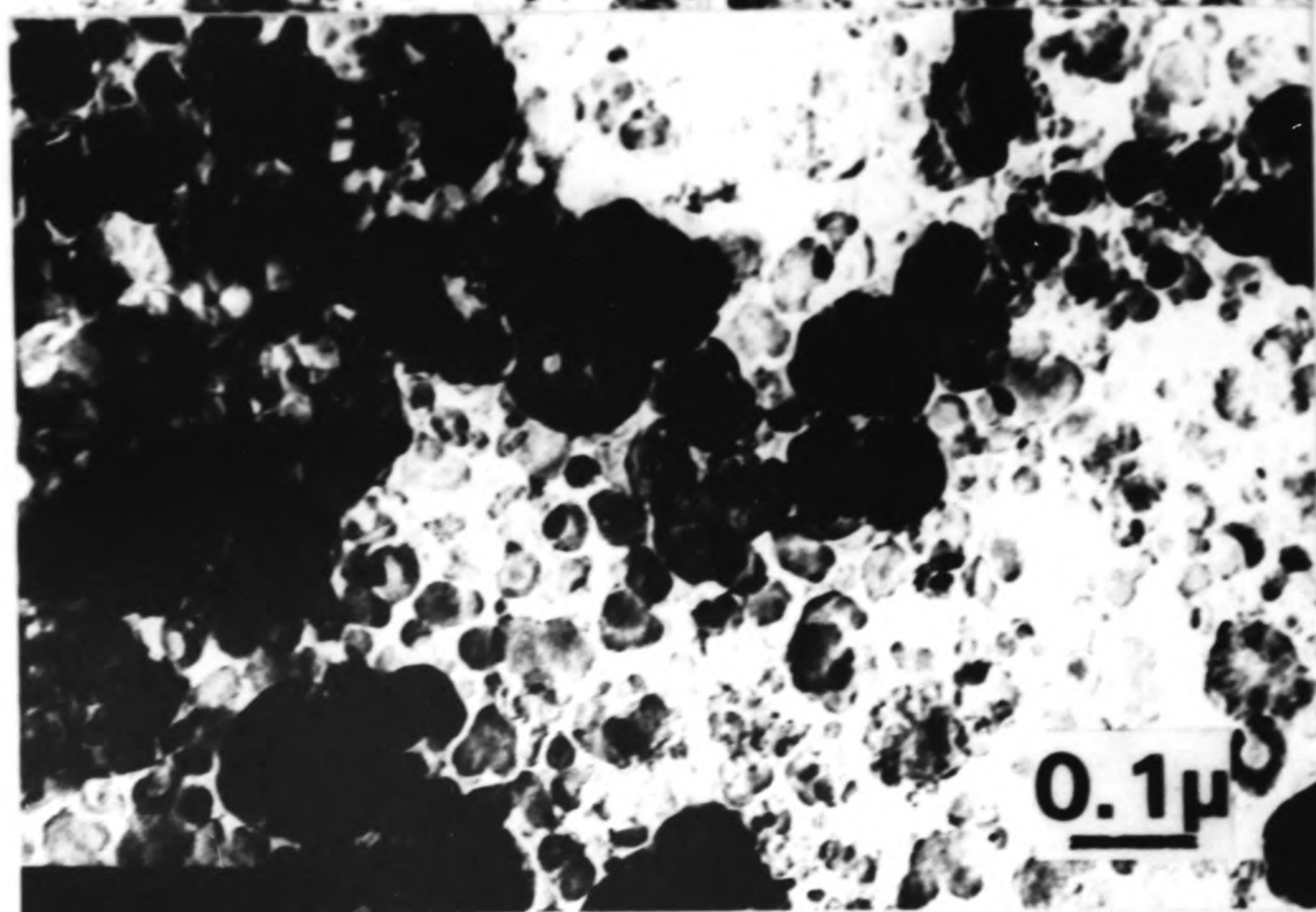


Fig.7-5 TEM bright field images of the oxide film removed from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ oxidised in air at 350°C for 500h.

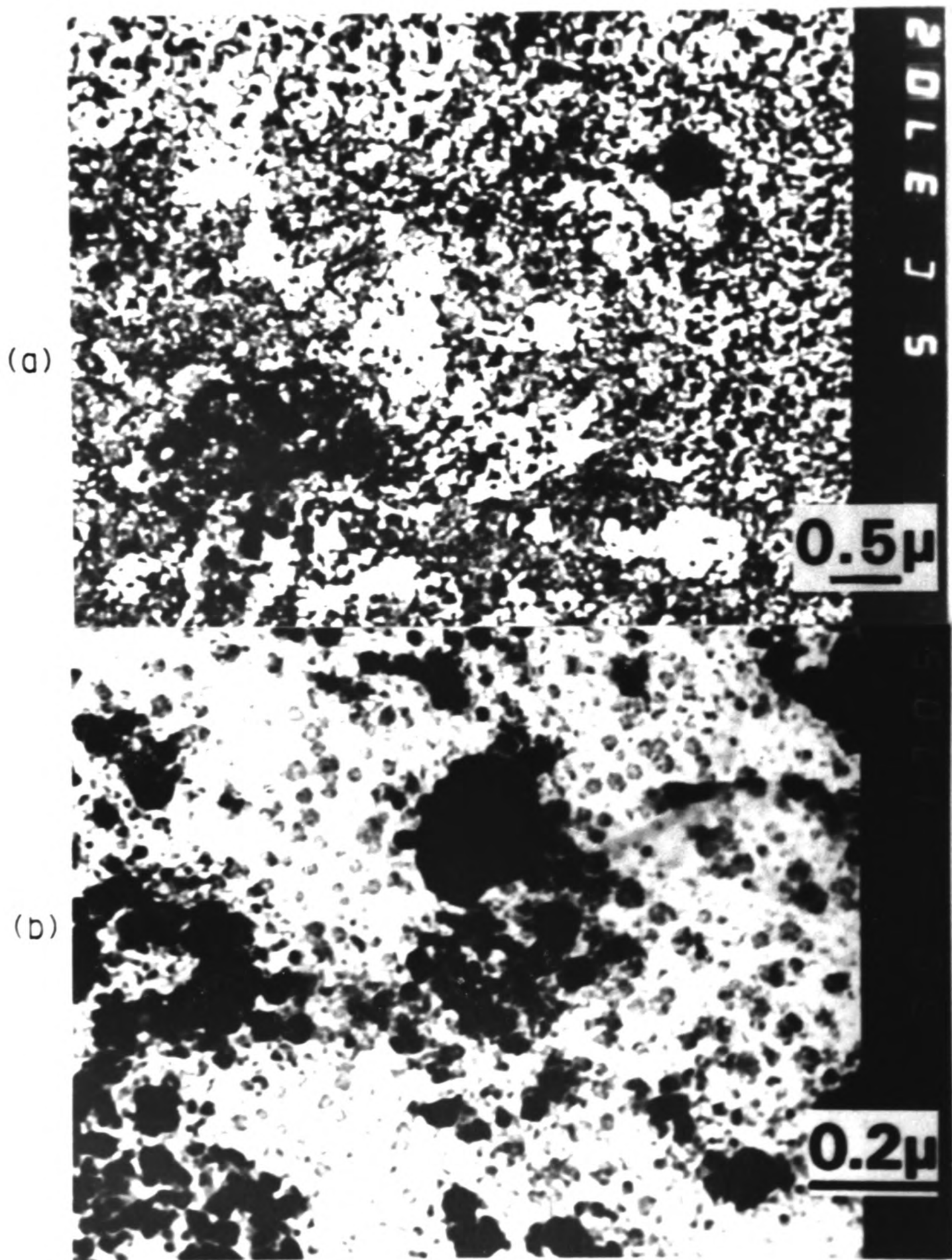


Fig.7-6 STEM micrographs of the oxide film removed from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ oxidised in air at 350°C for 500h, showing the similar feature as the TEM micrographs in Fig.7-5.

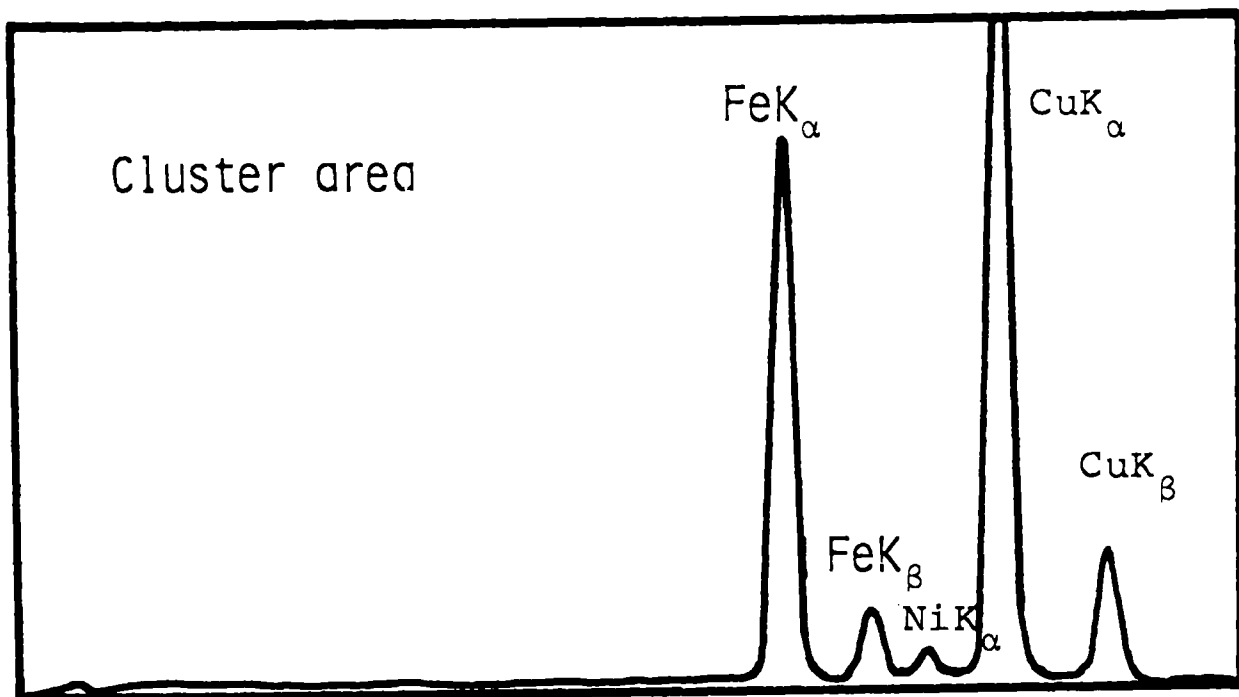
(a)



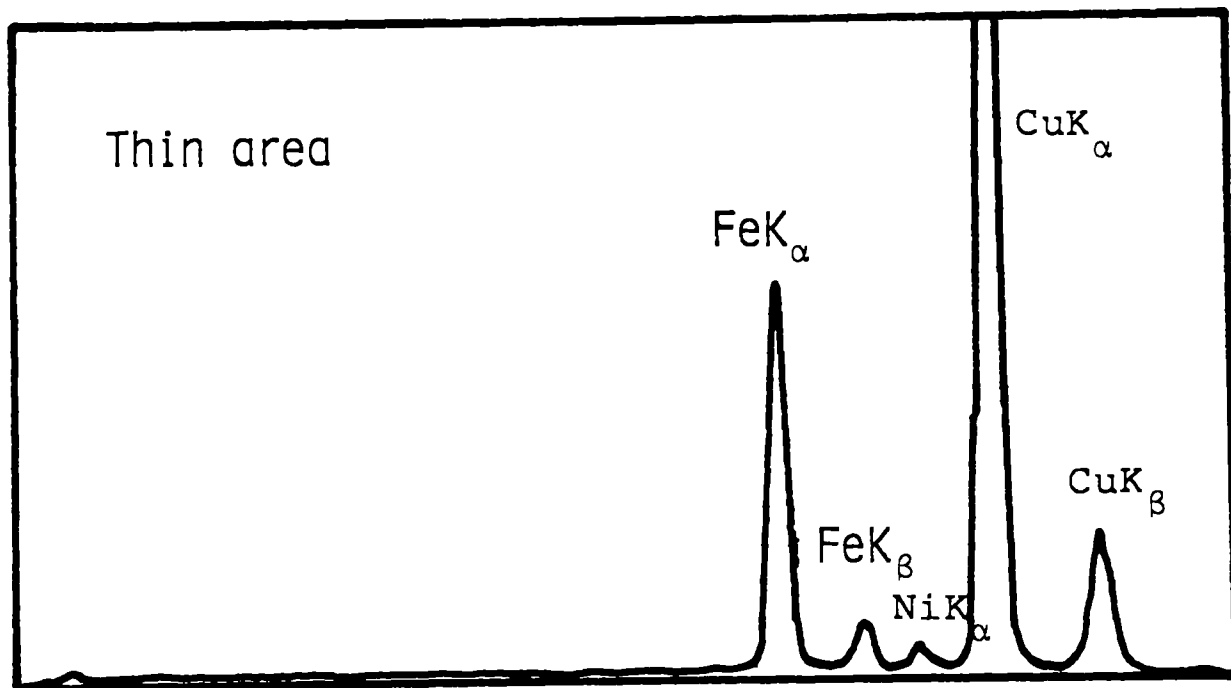
(b)



Fig.7-7 Typical SAED patterns from the oxide films removed from amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (a) after 140h oxidation at 350°C and (b) after 500h oxidation at 350°C .



(a)



(b)

Fig.7-8 Typical EDS spectra from (a) the clusters of thick oxide particles and (b) thin matrix areas of the oxide scales removed from amorphous Fe₄₀Ni₄₀B₂₀ oxidised in air at 350°C for 500h. The extraneous Cu peaks are from the support grid and sample holder.

Table 7-3 Crystal structure obtained by indexing SAED patterns and compositions obtained by EPMA from the oxide films removed from amorphous and crystallised Fe40Ni40B20 oxidised for 140h at 500 C

Sample		Oxide structure	Oxide composition* (at.%)	
Alloy	Oxide area		Fe	Ni
Amorphous	thick area	Fe3O4 + Fe2O3	94.4	5.6
Fe40Ni40B20	thin area	Fe3O4 + Fe2O3	95.5	4.5
Crystallised	thick area (cluster)	Fe3O4 + Fe2O3	94.6	5.4
Fe40Ni40B20	thin area	Fe3O4 + Fe2O3	95.0	5.0

* 6 poitⁿ analyses for each measurement;
elements with atomic number < 11 not detected.

the SAED results, as shown in Table 7-3.

7.2.3 Discussion

The oxidation kinetics of amorphous and crystallised Fe₄₀Ni₄₀B₂₀ are more complicated than the other amorphous alloys discussed in Chapters 4, 5 and 6. Several factors may have affected the oxidation kinetics:

1. Alloy structure influences the oxidation behaviour, as shown for amorphous Fe₄₀Ni₄₀P₁₄B₆, Fe₇₈Si₉B₁₃ and Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ in Chapters 4-6.

Fig.7-9(a) shows continuous heating DSC traces for amorphous Fe₄₀Ni₄₀B₂₀ oxidised for 30, 50, 80, 120 and 170h at 350 C, indicating that crystallisation takes place in amorphous Fe₄₀Ni₄₀B₂₀ between 30 to 170h at 350 C. Thus the sharp change in the oxidation kinetics of amorphous Fe₄₀Ni₄₀B₂₀ at 200-300h, shown in Figs.7-2(a) and (b), corresponds to a change in the Fe₄₀Ni₄₀B₂₀ alloy structure from amorphous to crystalline. According to Fig.7-2, amorphous and pre-crystallised Fe₄₀Ni₄₀B₂₀ exhibit different oxidation kinetics. At 350 C, amorphous Fe₄₀Ni₄₀B₂₀ obeys a parabolic oxidation rate law from 0-140h, while pre-crystallised Fe₄₀Ni₄₀B₂₀ obeys a logarithmic rate law with a higher initial reaction rate than the amorphous alloy.

2. Crystallisation also takes place in amorphous Fe₄₀Ni₄₀B₂₀ during oxidation at 400, 450 and 500 C. Fig.7-9(b) shows a typical isothermal DSC trace at 400 C for amorphous Fe₄₀Ni₄₀B₂₀, with crystallisation start, peak and finish times of 8, 37 and 56 min respectively. Fig.7-9(c) shows a crystallisation TTT diagram calculated from the isothermal DSC traces like that in Fig.7-9(b). The DSC traces and TTT diagram in Fig.7-9 show that amorphous Fe₄₀Ni₄₀B₂₀ undergoes crystallisation between 30 to 170h at 350 C and 8 to 56 min at 400 C, and is finished almost immediately at 450 C and 500 C. As shown in Fig.7-1 and 7-2, however, the amorphous alloy oxidation kinetics obey an approximate parabolic rate law at 400 and 450 C and a

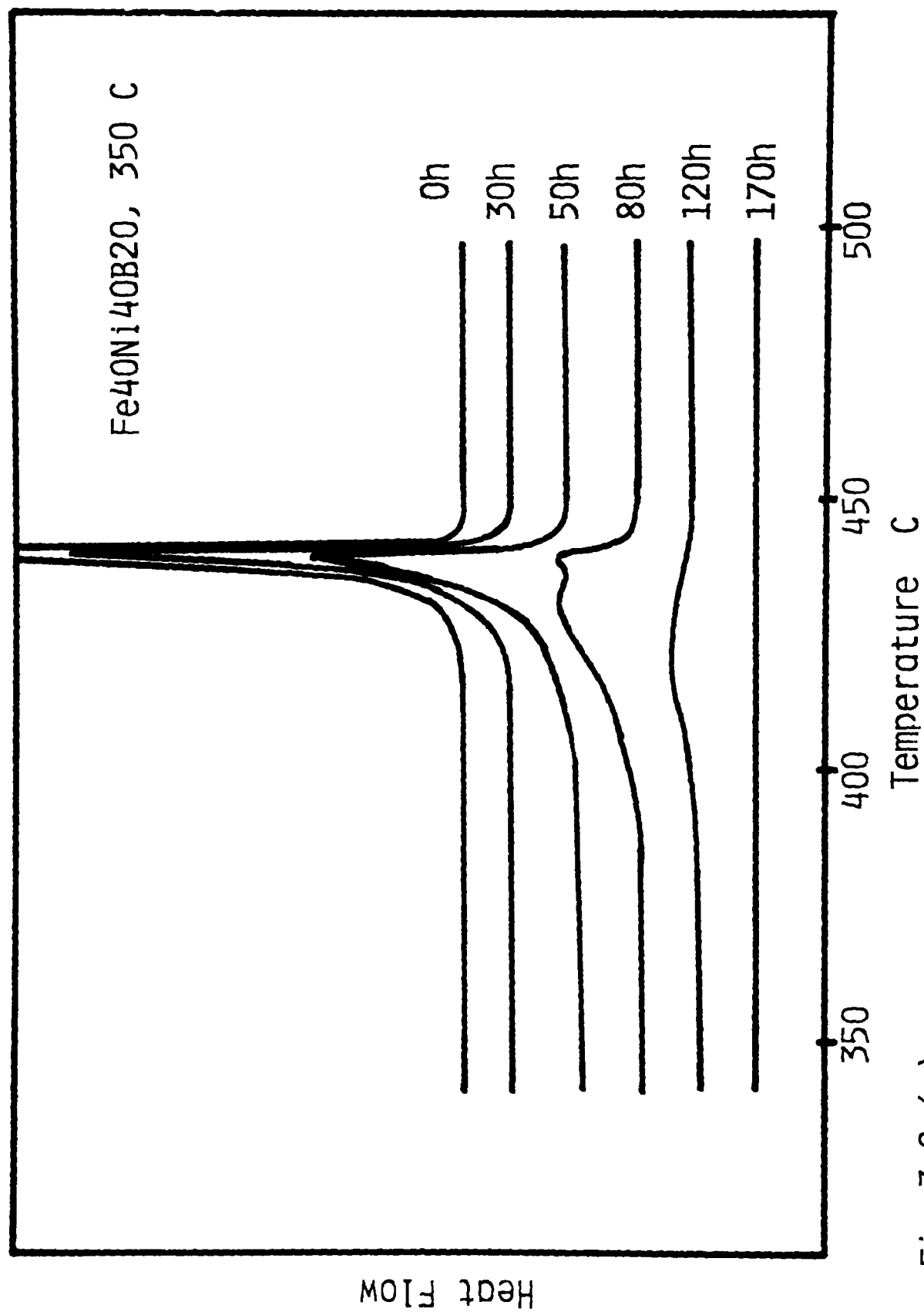


Fig.7-9 (a)

Fig.7-9 (a) Continuous heating DSC traces of amorphous Fe40Ni40B20, showing exothermic crystallisation peak as a function of prior oxidation time at 350°C; (b) isothermal heating DSC curve of amorphous Fe40Ni40B20 at 400°C; (c) crystallisation TTT diagram calculated from the isothermal DSC results. t_s , t_p and t_f are the crystallisation start, peak and finish times respectively.

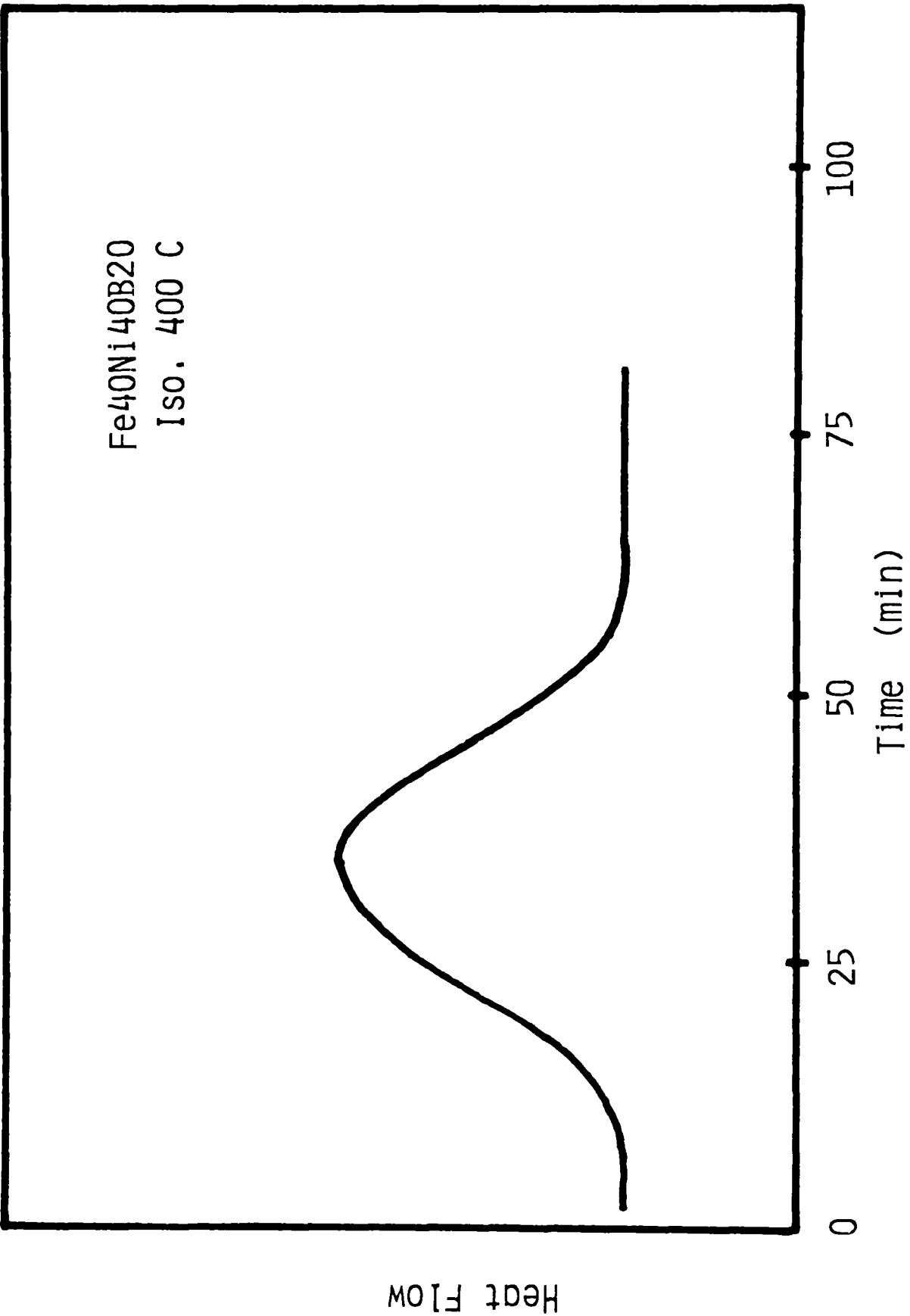


Fig.7-9(b)

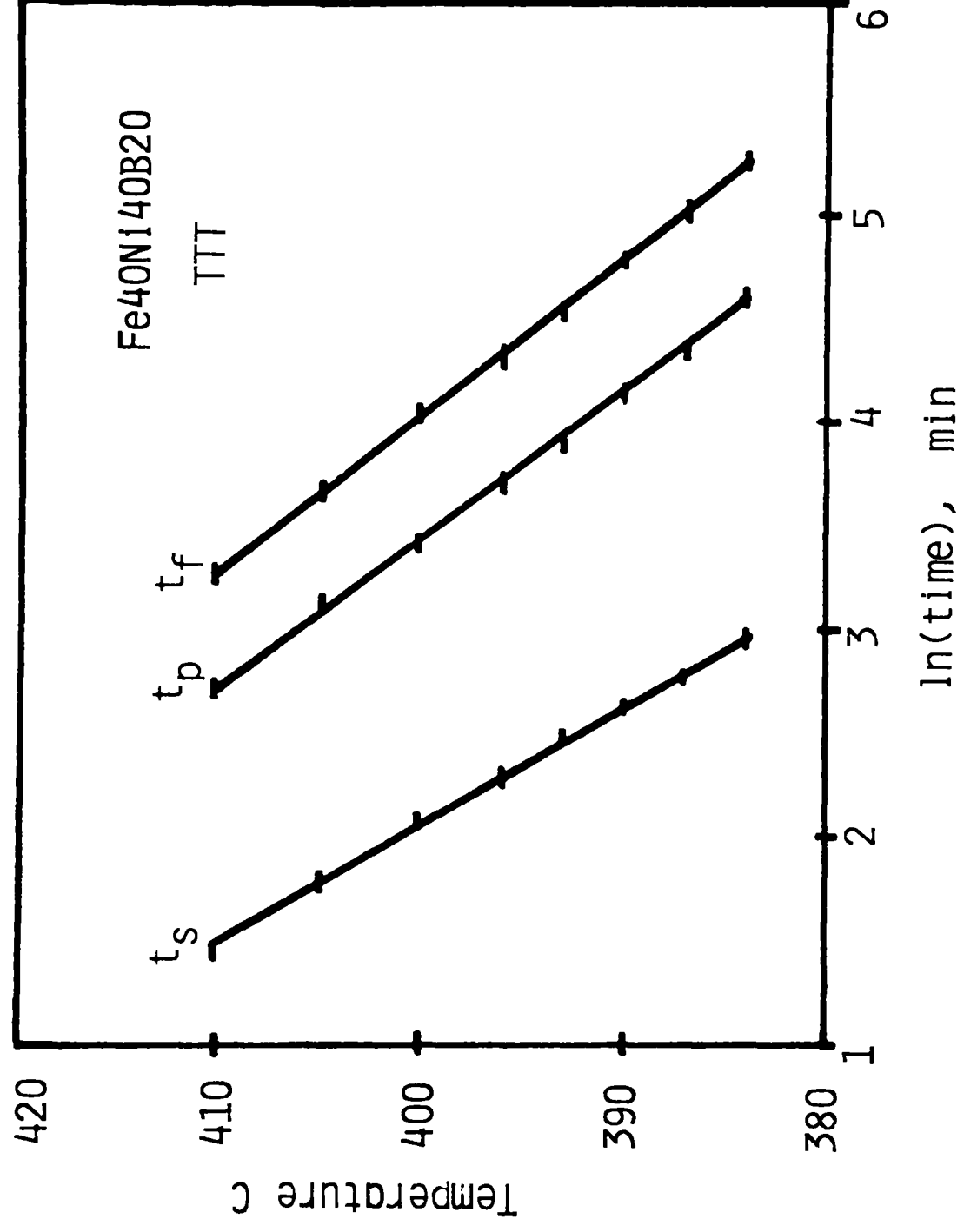


Fig.7-9 (C)

linear rate law at 500 C, whereas the pre-crystallised alloy obeys a logarithmic rate law. This shows that the initial stages of oxidation when alloy is amorphous strongly influence the subsequent oxide growth mechanism after the alloy has crystallised.

3. Crystallised Fe₄₀Ni₄₀B₂₀ has an oxidation mass gain four times greater than amorphous Fe₄₀Ni₄₀B₂₀ after 140h oxidation at 350 C, as shown in Fig.7-2. This can be explained as a result of the formation of clusters of the thick oxide particles in the oxide films formed on crystallised Fe₄₀Ni₄₀B₂₀. The clusters of thick oxide particles on crystallised Fe₄₀Ni₄₀B₂₀ are probably caused by micro-segregation in the crystalline matrix, while a layer of smaller oxide grains can grow uniformly on the homogeneous amorphous matrix.

4. At the higher temperature of 500 C, a non-protective oxide scale is formed on Fe₄₀Ni₄₀B₂₀, resulting in near-linear oxidation kinetics. Scale cracking is found at 500 C, as shown in Fig.7-3(e), indicating that the oxide layer is no longer protective against further oxidation.

7.3 Oxidation behaviour of amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆

Amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ (METGLAS 2826A) has a rather high oxidation resistance, better in fact than all the other amorphous alloys investigated in the present work. However, the crystallisation temperature of amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ is not particularly high, 407 C during continuous heating at 10K/min, as shown in Table 3-4 and Fig.3-7. The surface of amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ showed no visual change after oxidation annealing for times of up to 500h at temperatures of up to 450 C, with no detectable mass gain. At 500 C, however, the alloy surface exhibited a light yellow colour after 300h exposure in air. Fig.7-10 shows mass gain versus (a) oxidation time and (b) square root of oxidation time for Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ at 500 C,

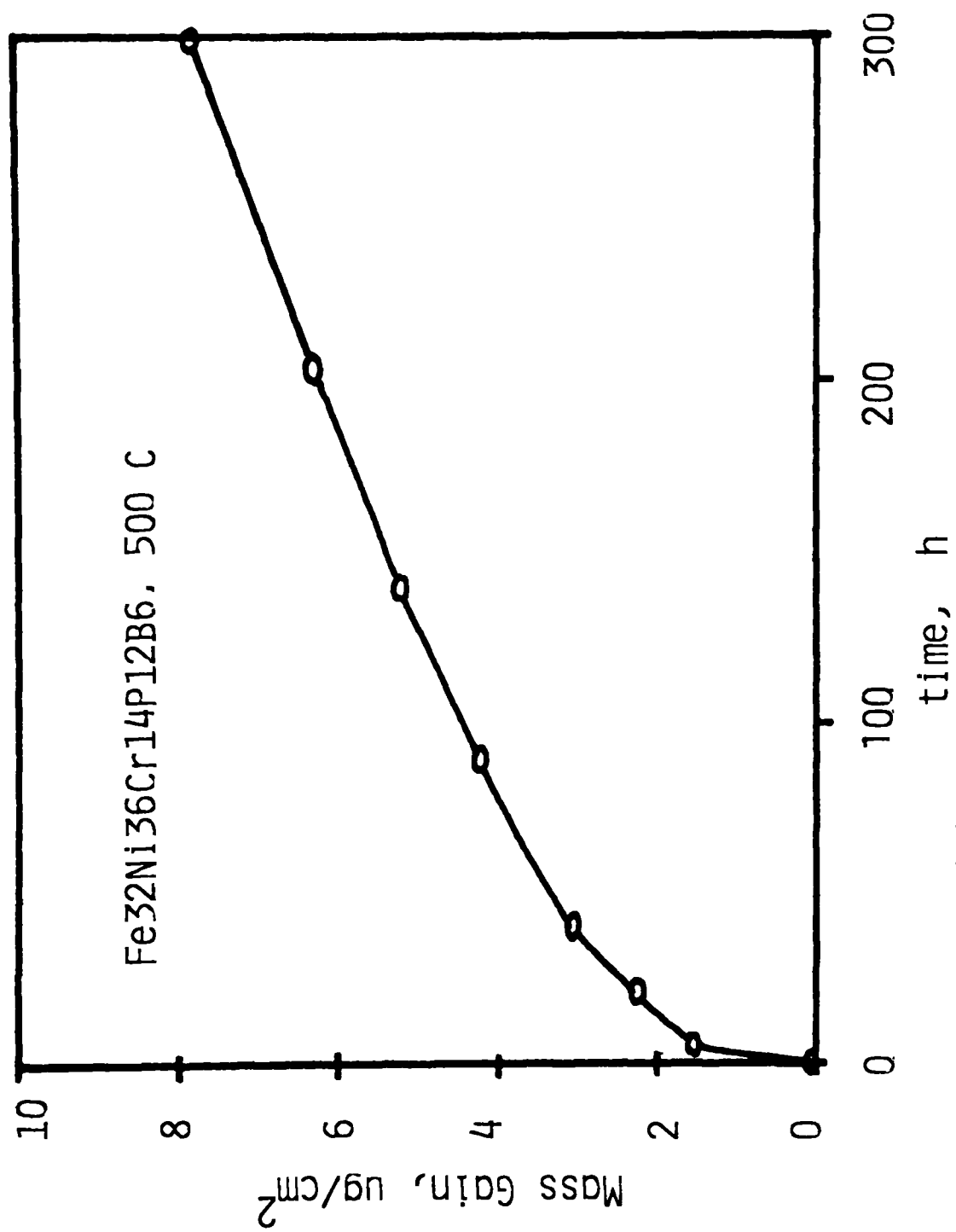


Fig.7-10 (a)

fig.7-10 Mass gain Y versus (a) oxidation time t, and (b) square root of oxidation time t for Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ at 500°C in air.

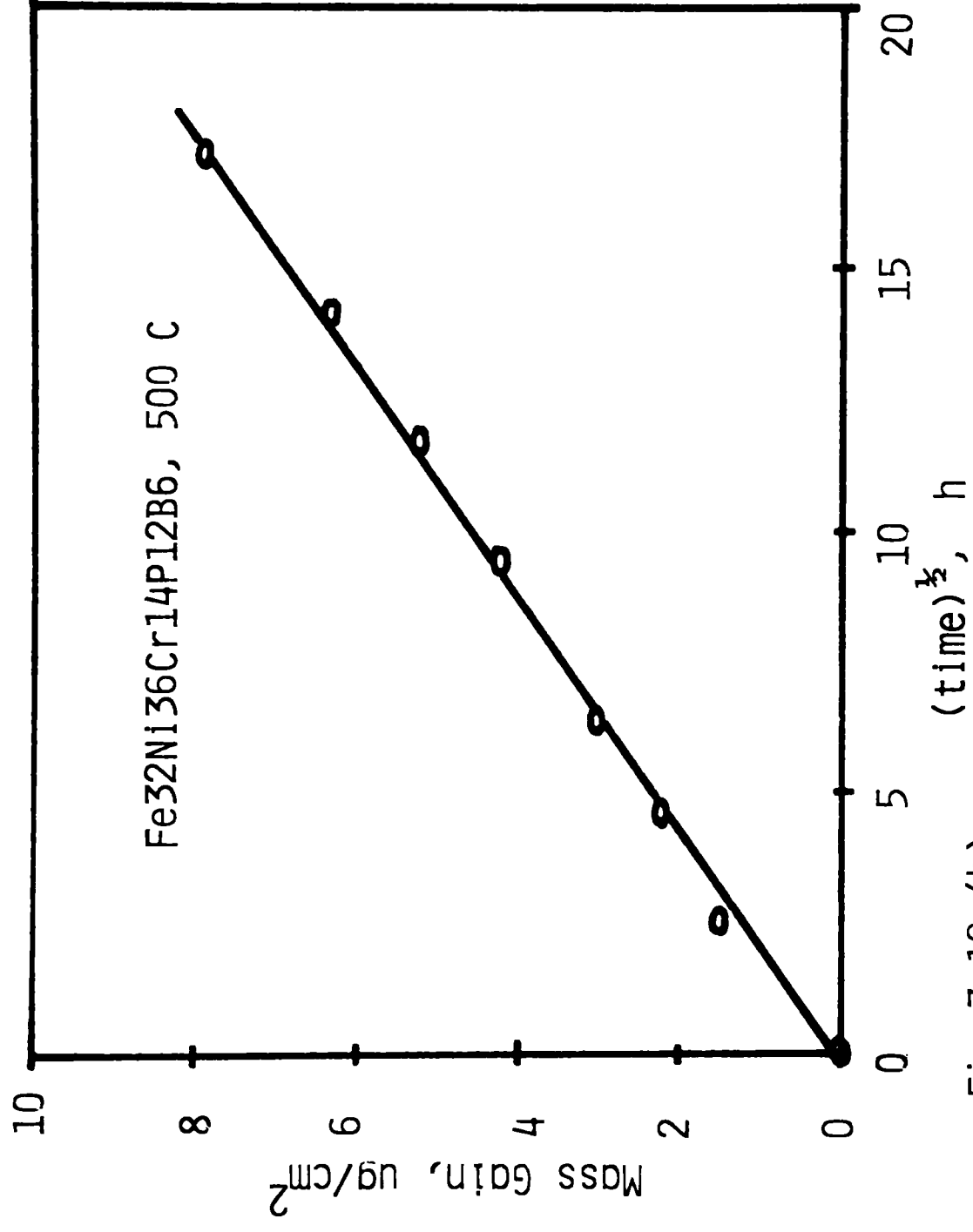


Fig.7-10 (b)

indicating that the oxidation process followed parabolic kinetics.

Fig.7-11 shows a TEM micrograph and typical SAED pattern from the oxide film stripped from Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ after oxidation for 300h at 500 C.

Indexing the SAED pattern from the oxide film in Fig.7-11(b) gave the characteristic diffraction lines of Cr₂O₃, as listed in Table 7-4.

Fig.7-12 shows a typical EDS spectrum from the same oxide film as in

Fig.7-11. After 300h oxidation at 500 C, the oxide scale on

Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ contained mainly Cr, in good agreement with SAED patterns such as in Fig.7-11(b). As formed in crystalline Fe-Cr and Fe-Ni-Cr alloys ((52,53) also see section 2.5.2), the Cr₂O₃ scale on Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ has good protective ability, and slows down further oxidation.

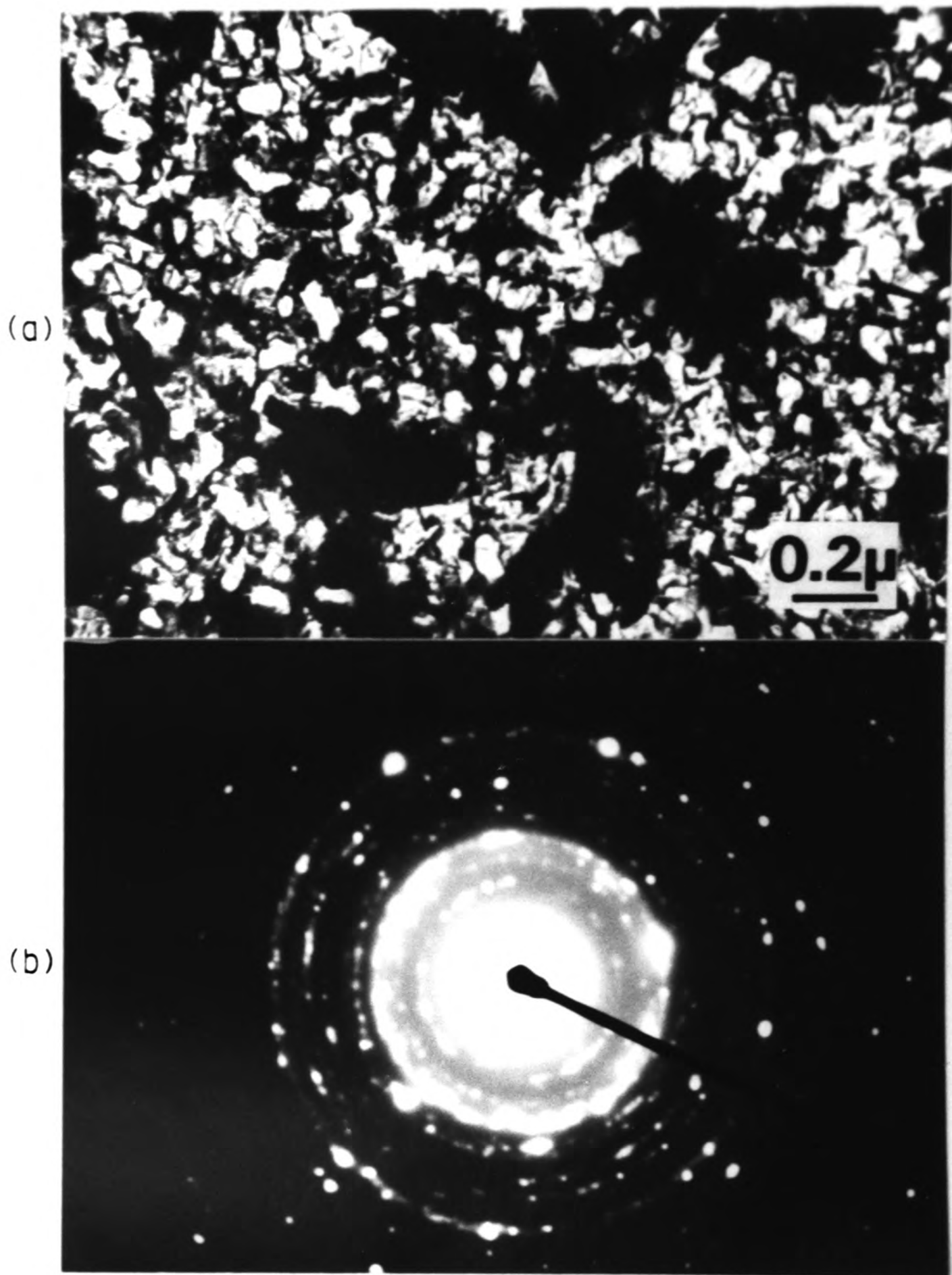


Fig.7-11 (a) A typical TEM bright field image of the oxide film removed from Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ oxidised for 300h at 500°C in air and (b) typical SAED patterns from (a).

Table 7-4 Calculated d spacings for typical diffraction patterns
obtained from oxide films removed from Fe₃₂Ni₃₆Cr₁₄Pl₂B₆
oxidised at 500 C for 300h, together with ASTM
powder card index d spacings for Cr₂O₃

d	d Cr ₂ O ₃	(hkl)	d Fe ₂ O ₃	(hkl)
	6-504		13-534	
3.61	3.633	(012)	3.66	(012)
2.66*	2.666	(104)	2.69	(104)
2.49*	2.480	(110)	2.51	(110)
2.29	2.264	(006)	2.285	(006)
2.20*	2.176	(113)	2.201	(113)
2.06	2.048	(202)		
1.83	1.816	(024)	1.838	(024)
1.68*	1.672	(116)	1.690	(116)
1.43*	1.4314	(300)	1.452	(300)
1.28	1.2961	(1,0,10)	1.310	(1,0,10)
1.24	1.2398	(220)	1.258	(220)
1.18	1.1731	(128)	1.189	(128)
1.07	1.0874	(226)	1.102	(226)
0.935	0.9462	(324)	0.9601	(324)
	0.9370	(410)		
...	...		...	

* Lines are strong in these positions.

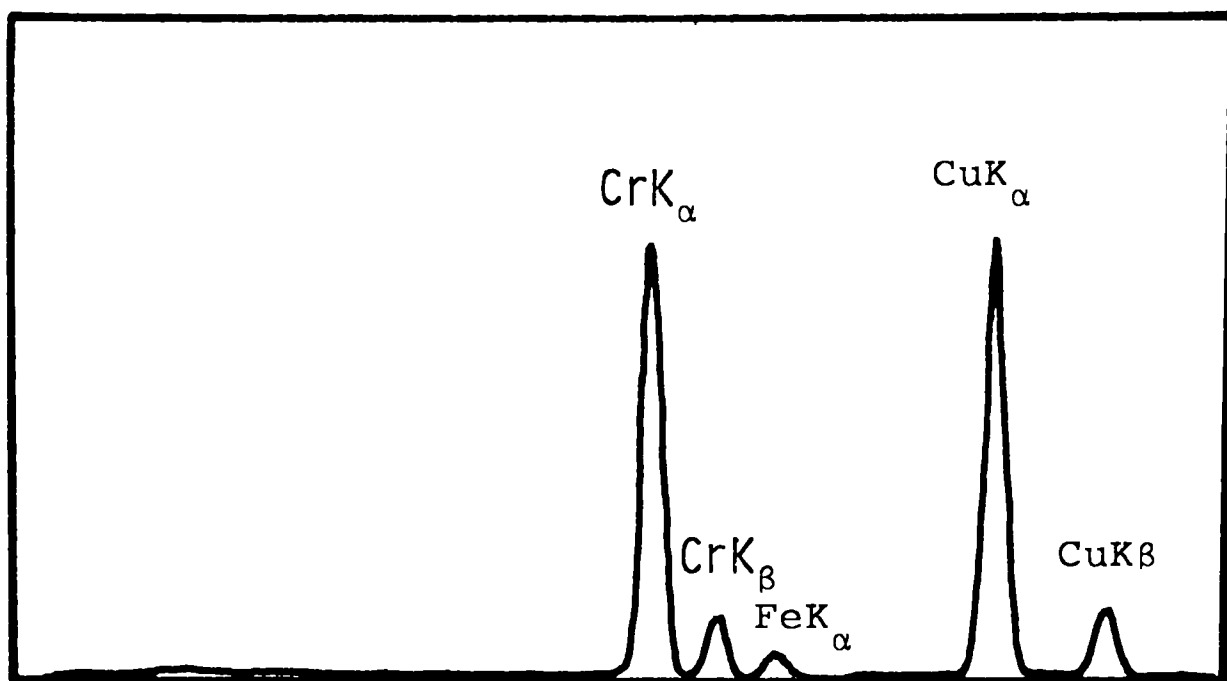


Fig.7-12 Typical EDS spectra from the oxide film removed from $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ oxidised for 300h at 500 C in air.

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Chapter 8 The Effect of Heat Treatment and Surface Treatment on the Crystallisation Behaviour of Amorphous Fe₄₀Ni₄₀B₂₀

8.1 Crystallisation of amorphous Fe₄₀Ni₄₀B₂₀

The crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀ has also been studied by a number of researchers (1-8), for both scientific and technological reasons. Crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ has been found to proceed by nucleation and growth processes in the bulk or at the surface (3,6,8), and is often sensitive to minor variations in heat treatment. A variety of different crystallisation mechanisms have been reported for amorphous Fe₄₀Ni₄₀B₂₀, including (a) eutectic fcc (Fe,Ni) + orthorhombic (Fe,Ni)₃B (6,9); eutectic fcc (Fe,Ni) + tetragonal (Fe,Ni)₃B (3,6,9); eutectic fcc (Fe,Ni) + fcc (Fe,Ni)₂₃B₆ (3); polymorphic tetragonal (Fe,Ni)₃B (6,9); and primary fcc (Fe,Ni) (3,6,9). Surface treatments such as grinding (3), electropolishing, electroplating and oxidation (3,8,10) have been reported to influence the crystallisation mechanism in amorphous Fe₄₀Ni₄₀B₂₀, but the results are conflicting and too limited to draw clear and detailed conclusions.

In the present work, a combination of DSC, optical microscopy, TEM and X-ray diffractometry has been used to investigate the separate and combined effect of heat treatment and surface treatment on the crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀.

8.2 Experimental techniques

Amorphous Fe₄₀Ni₄₀B₂₀ (VITROVAC 0040) samples were subjected to various combinations of surface treatment and pre-annealing, followed by testing in DSC to monitor the subsequent crystallisation kinetics, and a combination of optical microscopy, TEM and X-ray diffractometry to determine the

crystallisation structure.

8.2.1 Pre-annealing and surface treatment

Pre-annealing treatments were performed under different atmospheres: (a) in ambient atmosphere, (b) in sealed silica tubes evacuated to less than 10^{-7} torr and (c) in sealed silica tubes evacuated to less than 10^{-7} torr and then backfilled with 99.995% pure Ar to 200 torr. Pre-annealing treatments were performed at five temperatures in the range 300 to 350 C for times ranging from 1 to 500h. The pre-annealing temperatures and times were selected to ensure that no crystallisation took place during the pre-anneal, so as to monitor the effect of pre-annealing on subsequent crystallisation.

Amorphous alloy samples were subjected to several different surface treatments either before or after pre-annealing: (a) mechanical polish with either 320 SiC, 1200 SiC, 6 μ m diamond, or 1200 SiC followed by 6 μ m diamond; (b) electropolishing in 5% HClO_4 + 95% CH_3OH at 20 C and 50mA/cm², and (c) nickel plating in 180g NiSO_4 + 12.5g NH_4Cl + 15.0g H_3BO_4 + 500ml distilled water at 40 C and 20mA/cm² (11). The amorphous alloy samples were weighed before and after surface treatment in a Perkin-Elmer AD2 microbalance, to determine the average thickness removed by mechanical or electrolytic polishing, and the average thickness of Ni plating.

8.2.2 Crystallisation kinetics and crystal structure determination

Crystallisation kinetics were monitored with a DSC as a function of pre-annealing and surface treatment. As-supplied, pre-annealed and surface treated amorphous samples were heated under a dynamic 99.995%Ar atmosphere, either (a) isothermally in the temperature range 381-396 C, or (b) continuously at 10K/min from 400 to 470 C. The resulting exothermic crystallisation peaks were recorded to compare peak shapes and to analyse the crystallisation kinetics. For each test, three samples were used and

the average was taken as the results for crystallisation onset, peak and finish times and temperatures.

The crystal structures of the specimens which were crystallised after various combinations of pre-annealing and surface treatments have been observed in optical microscope and TEM. Taper cross section samples for optical microscopy were prepared by nickel plating both sides of the ribbon samples, followed by mounting in epoxy resin, and then mechanical polishing with a specimen-surface to polishing-surface angle of about 10 degrees. With this technique, the thin ribbons had a visual thickness in the microscope approximately 5 times greater than the true thickness (also see section 3.2). The TEM samples were prepared by ion beam thinning from either one side or both sides, so as to observe surface or bulk crystal structures respectively.

8.3 Results

8.3.1 The effect of surface treatment

8.3.1.1 Different surface treatments without pre-annealing

Fig.8-1 shows isothermal DSC traces at 390 C for a series of amorphous Fe₄₀Ni₄₀B₂₀ specimens, which were subjected to different surface treatments without any pre-annealing treatment. The DSC traces in Fig.8-1 correspond to specimens in the following conditions: (a) as-supplied; (b) mechanically polished with 320 SiC, 1200 SiC and 6µm diamond; (c) electropolished to remove 20 and 50% of the amorphous alloy ribbon thickness; and (d) electropolished to remove 20% of the ribbon thickness followed by mechanical polishing with 1200 SiC. The crystallisation kinetics were independent of mechanical surface polishing when no pre-annealing was applied, and the isothermal DSC traces from as-supplied and mechanically polished specimens all showed similar broad exothermic peaks, with

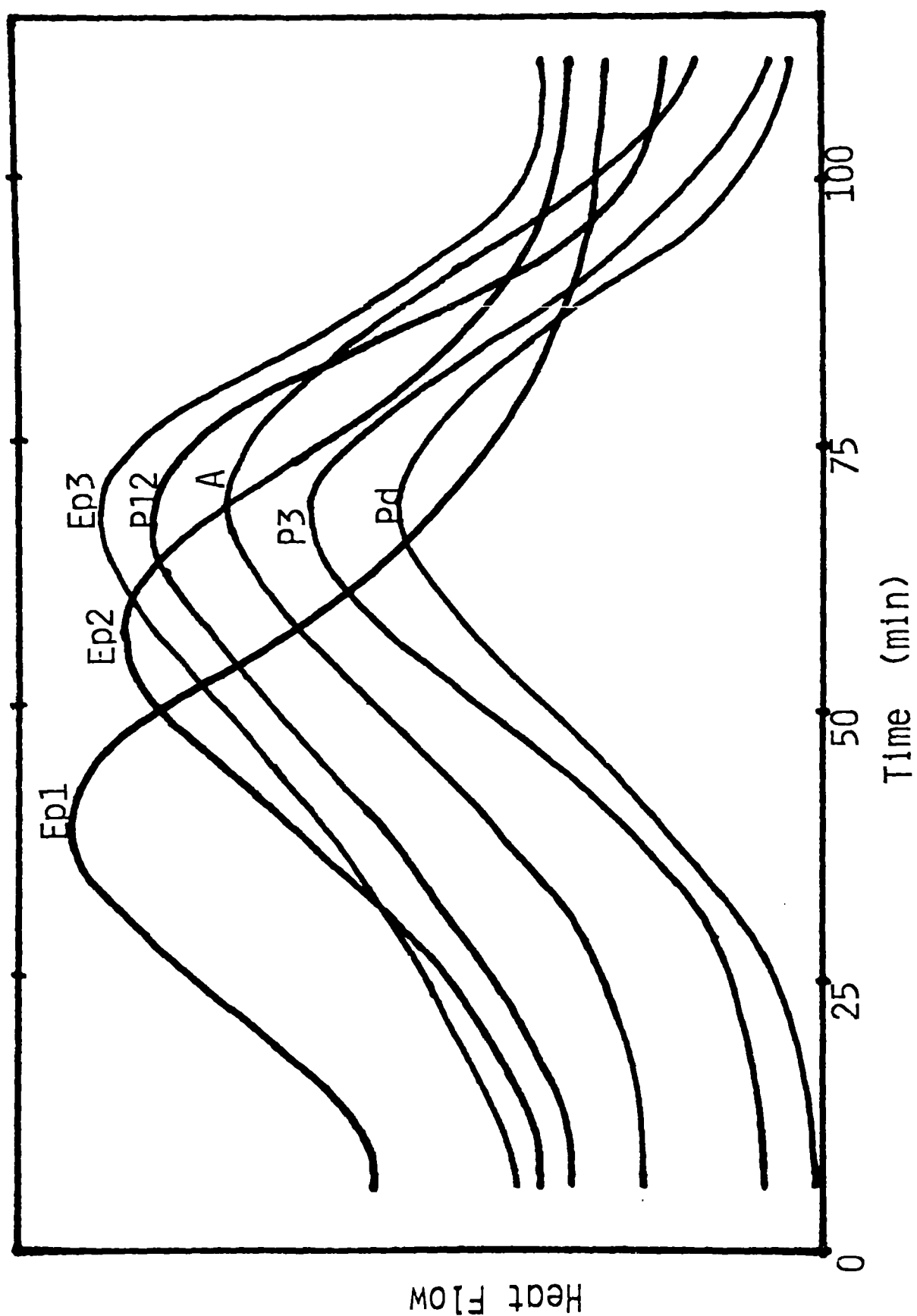


Fig.8-1 The effect of surface polishing: isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ with different surface polishing. A - amorphous Fe₄₀Ni₄₀B₂₀ as-supplied, P12 - polished with 1200 SiC, P3 - polished with 320 SiC, Pd - polished with 15μm diamond paste, Ep1 - electropolished (50% off), Ep2 - electropolished (20% off), Ep3 - electropolished (20% off) followed by 1200 SiC polishing.

crystallisation start, peak and finish times in each case of ~ 10, 70 and 120min respectively. The similarity of as-supplied and mechanically polished specimens indicated that mechanical polishing alone had little effect on the amorphous alloy crystallisation behaviour. Unlike mechanical polishing, electrolytic surface polishing accelerated the crystallisation process, with an increasing effect as heavier electropolishing was applied.

As shown in Fig.8-1, however, electropolishing followed by mechanical polishing restored the as-supplied crystallisation kinetics, implying that the acceleration was caused by a change in surface chemistry, rather than the removal of surface material.

8.3.1.2 Different surface treatments with fixed pre-annealing

Fig.8-2 shows isothermal DSC traces at 390 C for a series of amorphous Fe₄₀Ni₄₀B₂₀ specimens which were pre-annealed for 20h at 350 C and then subjected to different surface treatments. The DSC traces in Fig.8-2 correspond to amorphous alloy specimens in the following conditions: (a) as-supplied, (b) pre-annealed with no subsequent surface treatment; (c) pre-annealed followed by mechanical polishing with 320 SiC, 1200 SiC, 15um diamond, and 1200 SiC followed by 15um diamond; (d) pre-annealed followed by electropolishing to remove 20% of the amorphous ribbon thickness; and (e) mechanical polishing with 1200 SiC followed by pre-annealing.

Pre-annealing for 20h at 350 C with no subsequent surface treatment produced no significant difference in the crystallisation kinetics compared with the as-supplied samples, indicating that pre-annealing alone did not change the crystallisation process. Similarly, mechanical polishing with 1200 SiC followed by pre-annealing for 20h at 350 C also produced no significant difference in the crystallisation kinetics compared with the as-supplied samples, indicating that mechanical polishing followed by pre-annealing did not change the crystallisation process. However,

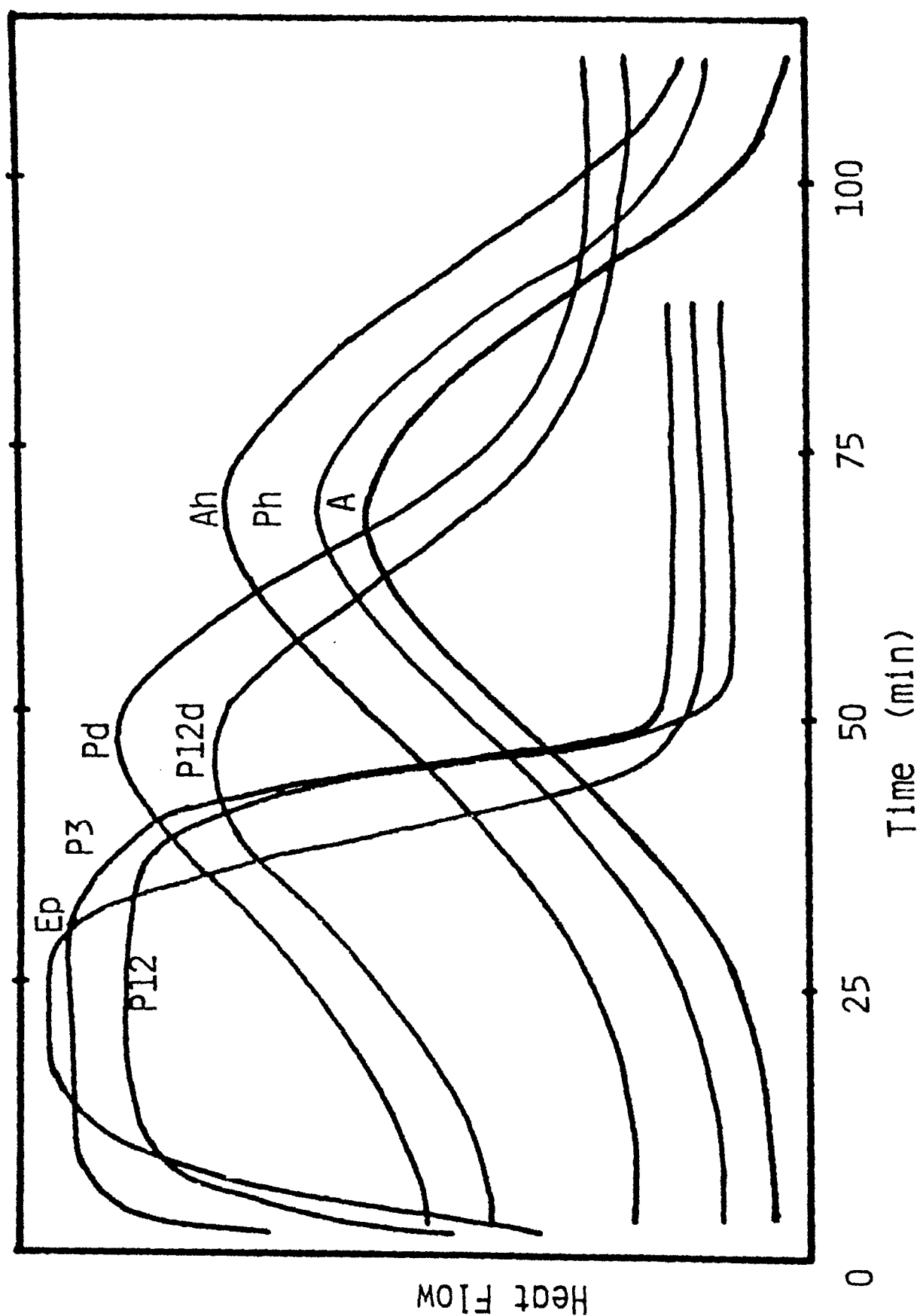


Fig.8-2 The effect of surface polishing after pre-annealing: isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C followed by different surface polishing. Ah - without polishing, P12 - polished with 1200 SiC, P3 - polished with 320 SiC, Pd - polished with 15μm diamond paste, P12d - polished with 1200 SiC, then 15μm diamond paste, Ep - electropolished (20% off), Ph - 1200 SiC polished before pre-annealing. A - amorphous Fe₄₀Ni₄₀B₂₀ as-supplied.

pre-annealing followed by mechanical polishing with 1200 or 320 SiC accelerated the crystallisation process very sharply, with crystallisation start, peak and finish times reduced to ~ 2, 20 and 55min respectively, compared with the as-supplied and unpolished values of 10, 70 and 120min. Pre-annealing followed by electropolishing to remove 20% of the ribbon thickness also accelerated the subsequent crystallisation process, to the same extent as mechanical polishing with 1200 or 320 SiC, ie a stronger effect than that achieved by electropolishing alone (Fig.8-1). Pre-annealing followed by mechanical or electropolishing did not only accelerate the crystallisation process, but also changed the exothermic peak from a broad near-Gaussian shape to a near rectangular shape with sharp start and finish, evidence of a change in crystallisation mechanism. On the other hand, polishing with 6 μ m diamond, or with 1200 SiC followed by 6 μ m diamond, caused only a slight acceleration in the crystallisation process.

8.3.2 The effect of pre-annealing

8.3.2.1 Pre-annealing at different temperatures for a fixed time

Fig.8-3 shows isothermal DSC traces at 390 C for a series of amorphous Fe₄₀Ni₄₀B₂₀ specimens which were pre-annealed for 20h at temperatures of 325, 330, 340 and 350 C, followed by the same surface mechanical polishing treatment with 1200 SiC. With increasing pre-annealing temperature, the rate of crystallisation increased progressively and the crystallisation peak changed from a broad near-Gaussian shape to a near-rectangular shape. There was little effect when the pre-annealing temperature was 325 C, indicating that a sufficiently high pre-annealing temperature was essential for achieving the accelerated crystallisation behaviour.

8.3.2.2 Pre-annealing for different times at a fixed temperature

Fig.8-4 shows isothermal DSC traces at 390 C for a series of amorphous

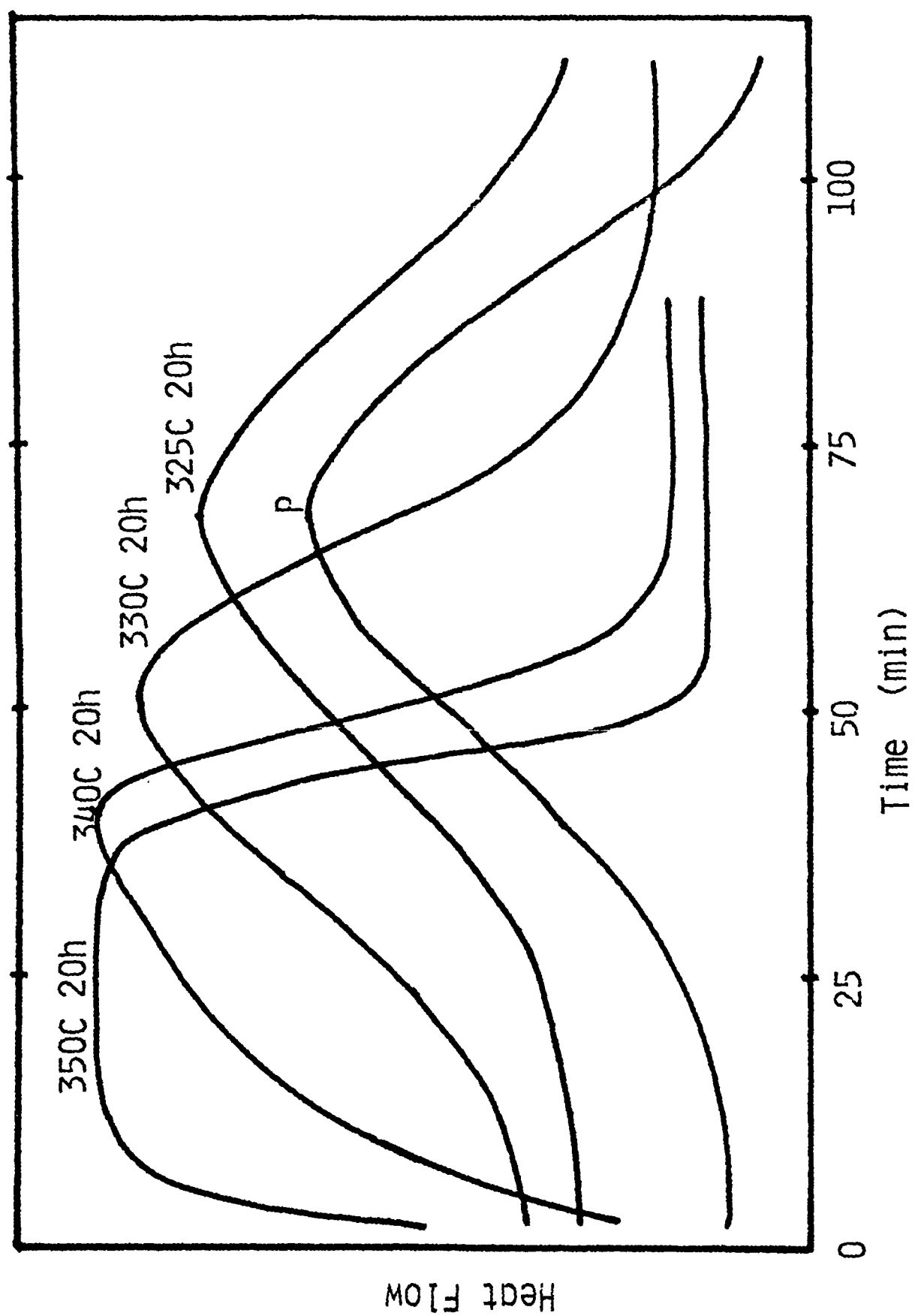


Fig.8-3 The effect of pre-annealing temperature: isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at different temperatures followed by mechanical polishing with 1200 SiC. P - polished with 1200 SiC without any pre-annealing treatment.

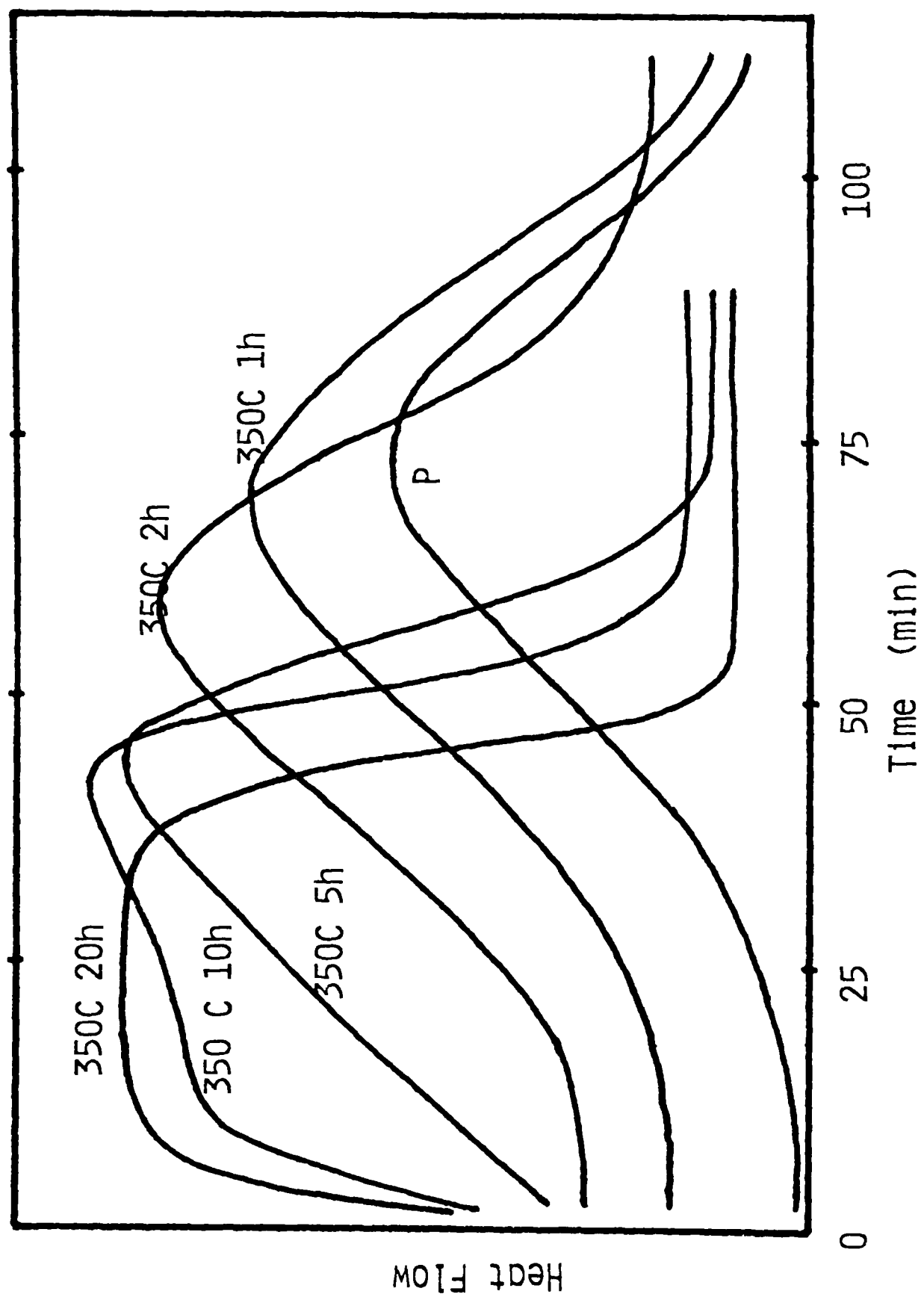


Fig.8-4 The effect of pre-annealing time: isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for different times at 350°C followed by mechanical polishing with 1200 SiC. P - polished with 1200 SiC without any pre-annealing treatment.

Fe₄₀Ni₄₀B₂₀ specimens which were pre-annealed at 350 C for times of 1, 2, 5, 10 and 20h, followed by the same surface mechanical polishing treatment with 1200 SiC. With increasing pre-annealing time, the rate of crystallisation again increased progressively, and the crystallisation peak again changed from a broad near-Gaussian shape to a near-rectangular shape. There was little effect when the pre-annealing time was 1h, indicating that a sufficiently long pre-annealing time was essential for achieving the accelerated crystallisation behaviour.

Fig.8-5 shows isothermal DSC traces for amorphous Fe₄₀Ni₄₀B₂₀ specimens pre-annealed at 300 C for 100 and 500h followed by the same surface mechanical polishing with 1200 SiC. Although pre-annealing for 100h at 300 C had little effect, 500h at 300 C accelerated the crystallisation process, similar to the effect of pre-annealing for 5h at 350 C. Fig.8-5 shows that the effect of pre-annealing can be accumulated with sufficiently long annealing time at a lower temperature.

8.3.3 The effect of Ni plating

Fig.8-6 shows isothermal DSC traces at 390 C for amorphous Fe₄₀Ni₄₀B₂₀ specimens which were treated with (a) Ni plating alone; (b) pre-annealing for 20h at 350 C followed by Ni plating; and (c) Ni plating followed by pre-annealing for 20h at 350 C. The thickness of the Ni plating was 4-5µm on each side of the ribbon specimens. Ni plating alone, and pre-annealing followed by Ni plating both had little effect on the crystallisation kinetics compared with as-supplied amorphous Fe₄₀Ni₄₀B₂₀. However, Ni plating followed by pre-annealing for 20h at 350 C accelerated the crystallisation process, although the crystallisation peak was not changed to a near-rectangular shape.

8.3.4 The effect of pre-annealing atmosphere

Amorphous Fe₄₀Ni₄₀B₂₀ specimens pre-annealed in different atmospheres

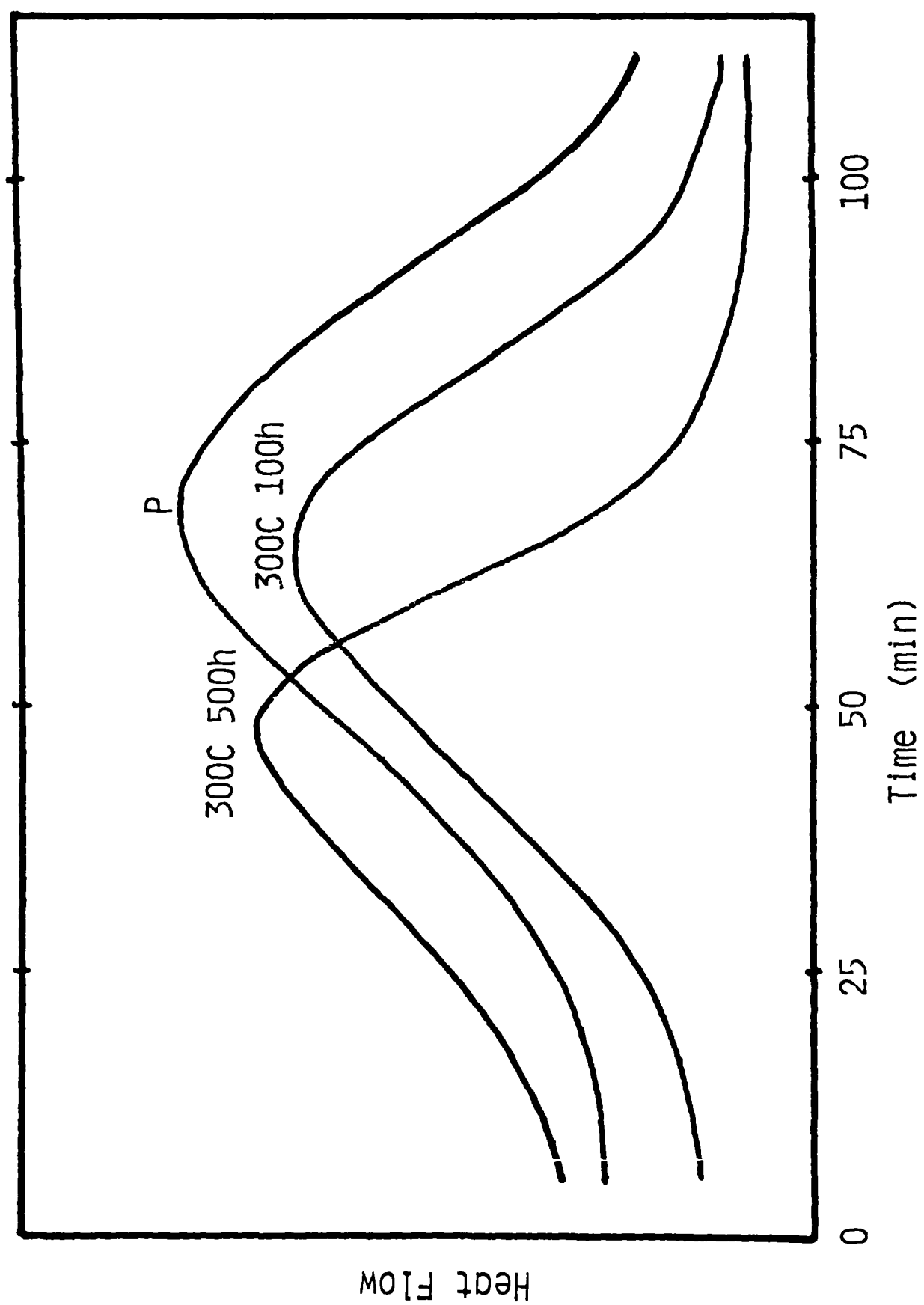


Fig.8-5 The effect of pre-annealing time: isothermal DSC traces at 390°C for amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ pre-annealed for 100h and 500h at 300°C followed by mechanical polishing with 1200 SiC. P - polished with 1200 SiC without any pre-annealing treatment.

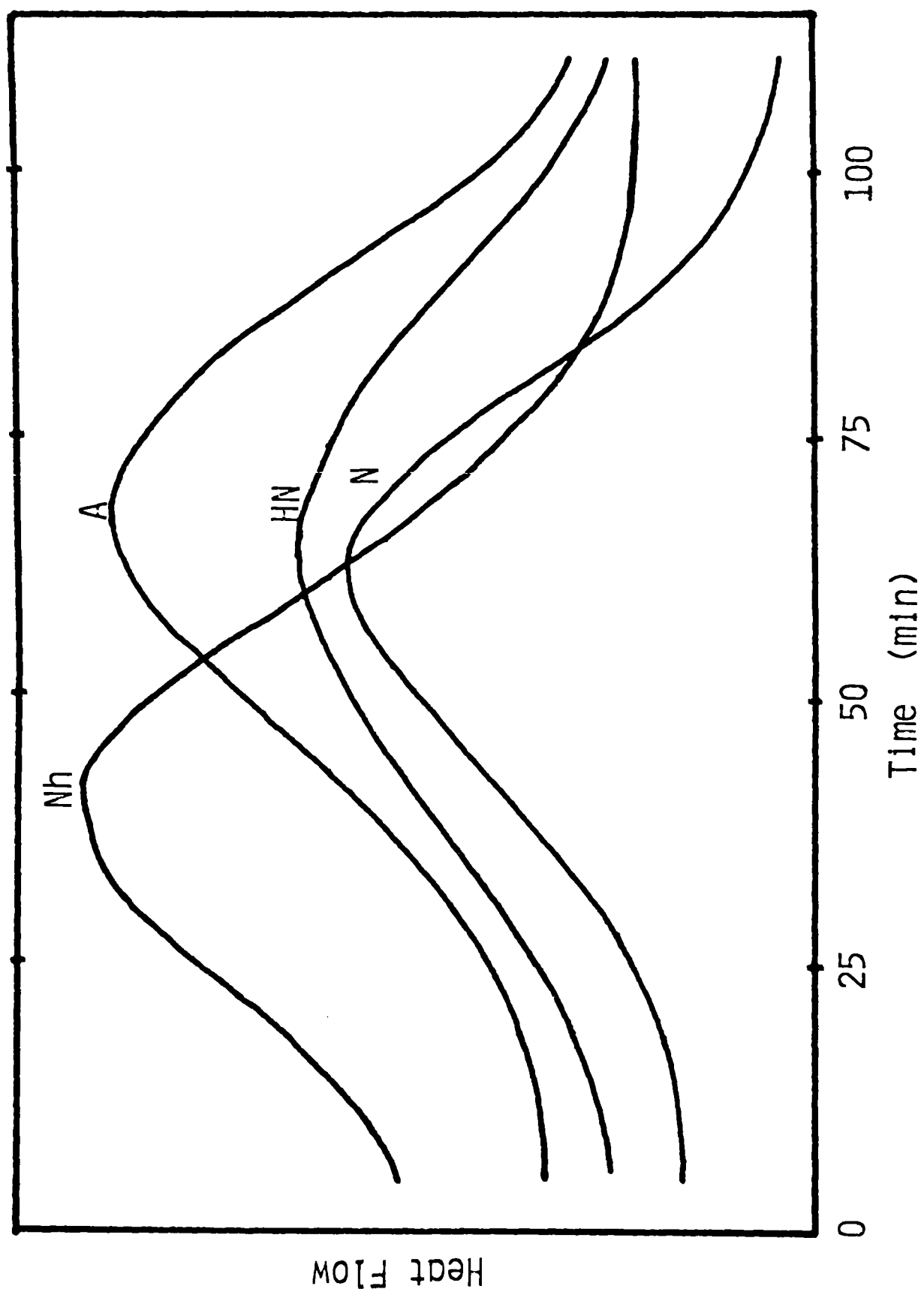


Fig.8-6 The effect of Ni plating: isothermal DSC traces at 390°C for amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ with and without Ni plating. A - amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ as-supplied, N - Ni plated without pre-annealing, Nh - Ni plated followed by pre-annealing for 20h at 350°C , HN - pre-annealed for 20h at 350°C followed by Ni plating.

had different surface appearances, indicating different extents of oxidation. Samples pre-annealed in air showed a light yellow colour on both sides, with some darker yellow stripes on the unchilled ribbon surface; samples pre-annealed in argon showed a lighter yellow colour on both sides, without any darker stripes; and samples pre-annealed in vacuum remained shiny and bright without any detectable colour change. Fig.8-7(a) shows isothermal DSC traces for amorphous Fe₄₀Ni₄₀B₂₀ samples pre-annealed for 20h at 350 C in air, argon and vacuum without any subsequent surface mechanical polishing treatment; Fig.8-7(b) shows isothermal DSC traces for the same pre-annealed samples with a subsequent surface mechanical polishing with 1200 SiC. Different annealing atmospheres had no significant effect on the crystallisation kinetics of either the polished or unpolished samples.

8.3.5 The effect of crystallisation temperature

In order to establish the detailed kinetics of crystallisation, two series of amorphous Fe₄₀Ni₄₀B₂₀ specimens were subjected to identical pre-annealing and surface polishing treatments, followed by isothermal crystallisation in the DSC over a range of temperatures between 381 and 396 C. The first series of amorphous Fe₄₀Ni₄₀B₂₀ specimens were all pre-annealed for 20h at 350 C in air with no subsequent surface polishing. The resulting DSC traces are shown in Fig.8-8(a). These specimens all exhibited the slower crystallisation kinetics characteristic of the as-supplied amorphous alloy, with a broad, near-Gaussian exothermic peak. There was virtually no incubation time for the onset of crystallisation at any of the isothermal annealing temperatures, and the rate of crystallisation decreased as expected with decreasing isothermal annealing temperature.

The second series of amorphous Fe₄₀Ni₄₀B₂₀ specimens were also all

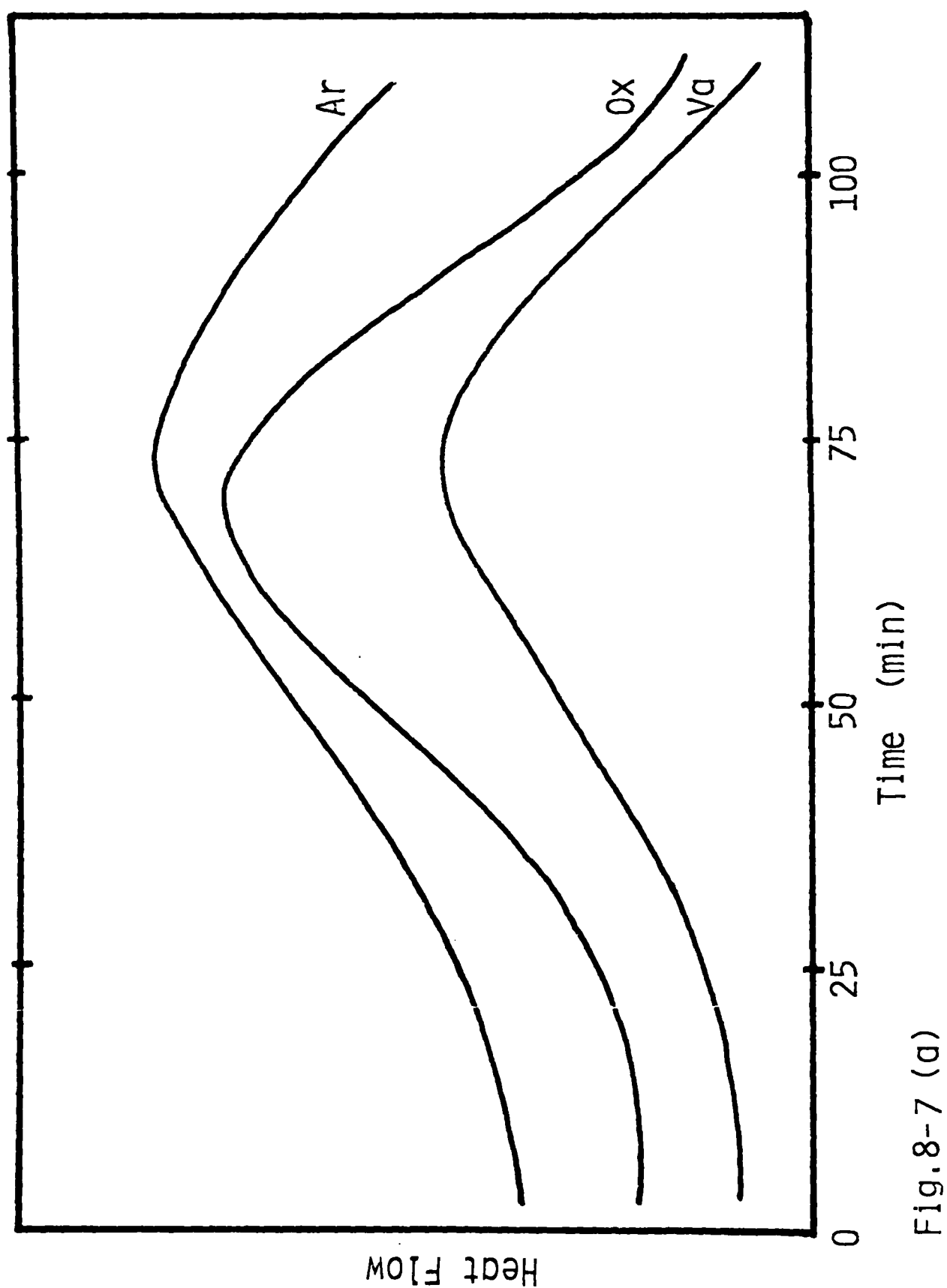


Fig.8-7 The effect of pre-annealing atmosphere: (a) isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C in different atmospheres; (b) isothermal DSC traces at 390°C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C in different atmospheres followed by polishing with 1200 SiC. Ox, Va and Ar represent pre-annealed in air, vacuum and argon respectively.

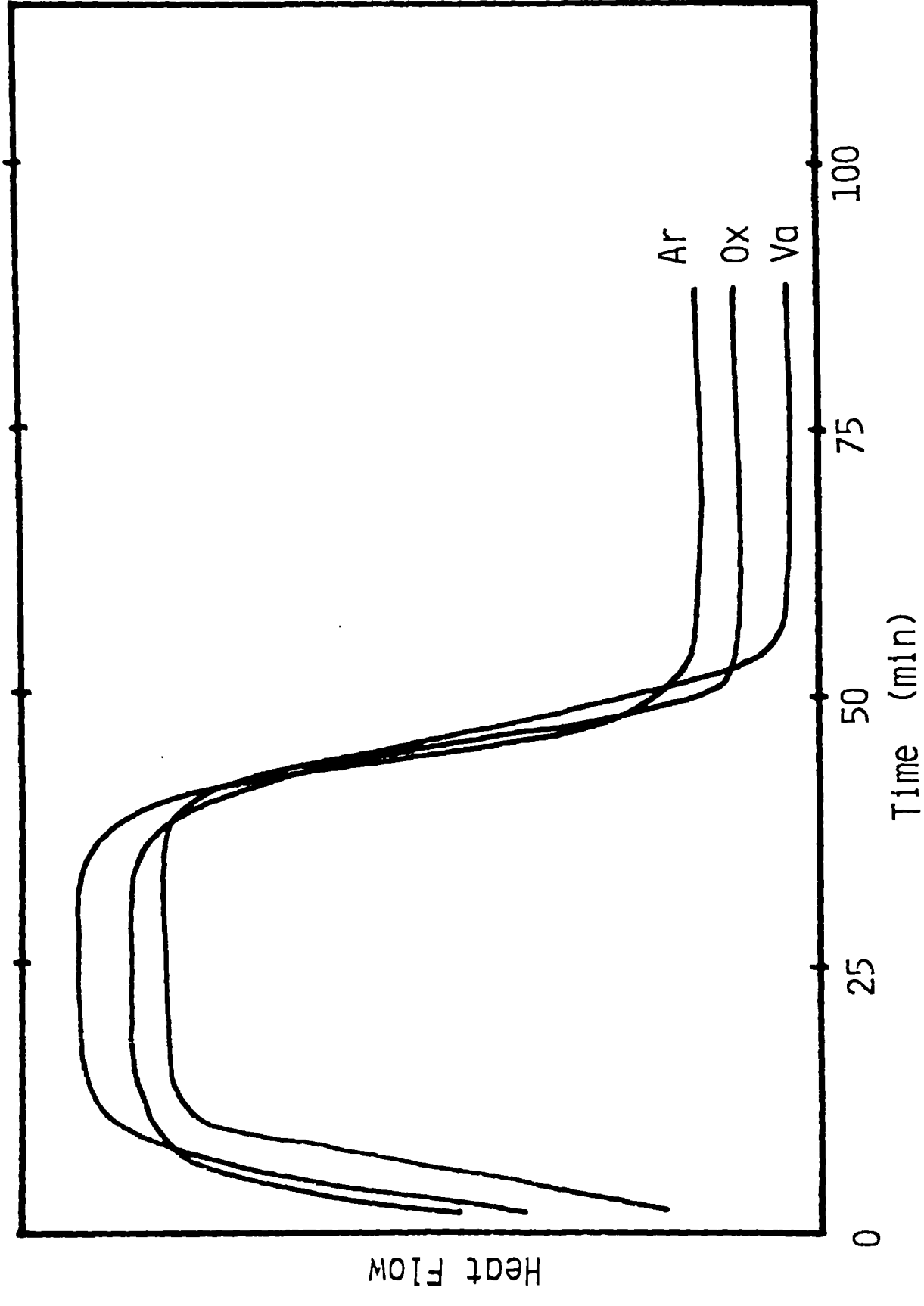


Fig.8-7 (b)

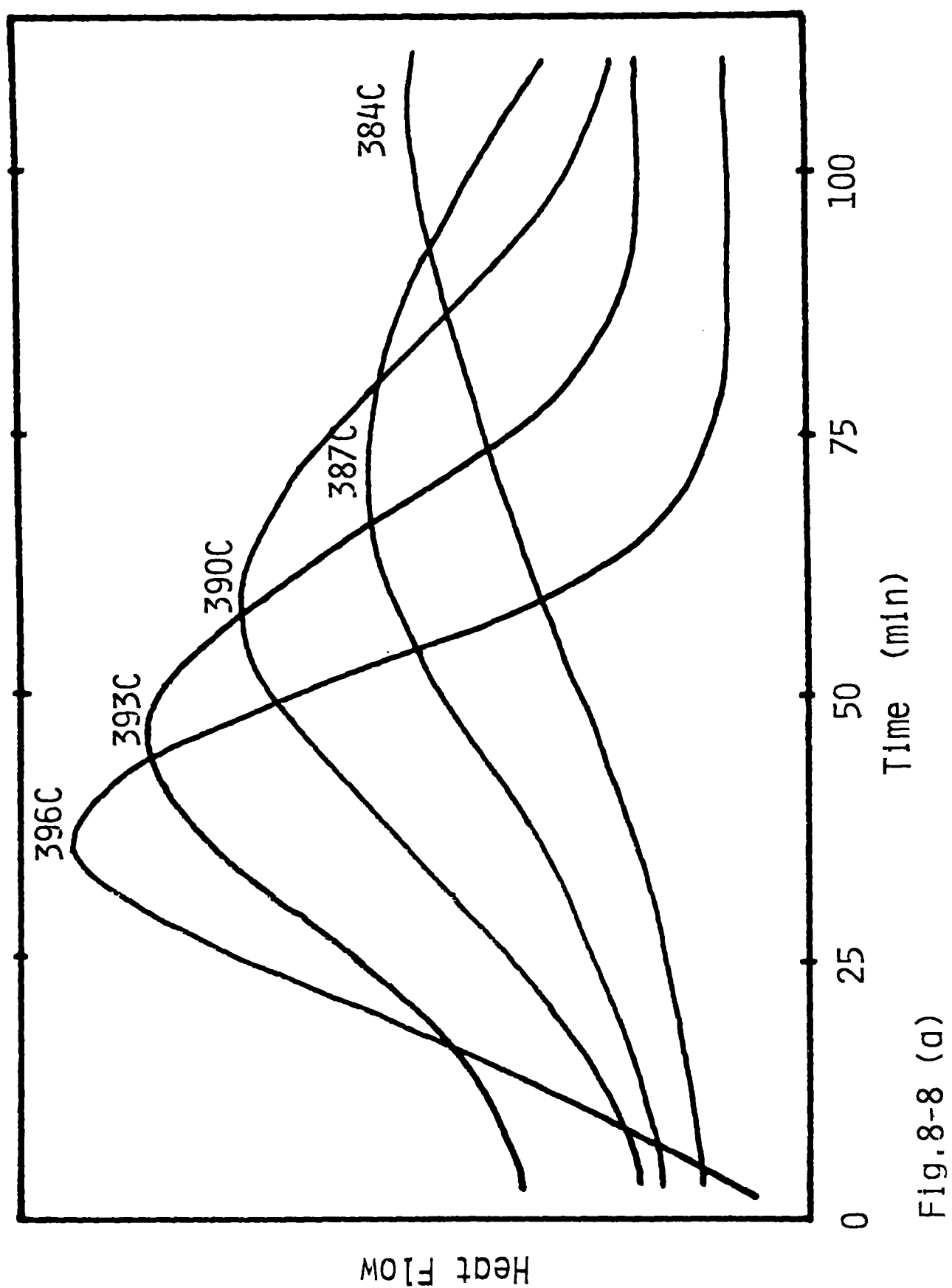


Fig.8-8 (a) Isothermal DSC traces at 384-396 C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C without subsequent polishing.

(b) Isothermal DSC traces at 381-396 C for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C followed by polishing with 1200 SiC.

pre-annealed for 20h at 350 C in air, followed in each case by mechanical polishing with 1200 SiC before isothermal crystallisation in the DSC. The resulting DSC traces are shown in Fig.8-8(b). These specimens all exhibited accelerated crystallisation kinetics with a near-rectangular exothermic peak. Once again there was virtually no incubation time for the onset of crystallisation at any of the isothermal annealing temperatures, and the rate of crystallisation again decreased with decreasing isothermal annealing temperature.

8.3.6 Continuous heating DSC traces

Fig.8-9 shows continuous heating DSC traces at 10K/min for a series of amorphous Fe₄₀Ni₄₀B₂₀ specimens after various combinations of pre-annealing and surface mechanical polishing treatments. As shown in Fig.8-9(a), as-supplied Fe₄₀Ni₄₀B₂₀ crystallised during continuous heating at 10K/min with a relatively sharp exothermic peak with crystallisation onset and peak temperatures of ~ 425 and 443 C respectively. As with the isothermal DSC experiments, no significant change in crystallisation behaviour was detected after surface mechanical polishing with 1200 SiC alone, pre-annealing for 20h at 350 C alone, or surface mechanical polishing with 1200 SiC followed by pre-annealing for 20h at 350 C. However, samples pre-annealed for 20h at 350 C followed by surface polishing with 1200 SiC again exhibited accelerated crystallisation, with a broader exothermic peak and lower onset and peak temperatures of ~ 408 and 438 C respectively. These results were consistent with the isothermal DSC results shown in Figs 1 and 2. Fig.8-9(b) shows continuous heating DSC traces for amorphous Fe₄₀Ni₄₀B₂₀ specimens which were all pre-annealed for 20h at 350 C, followed by identical mechanical polishing with 1200 SiC on either the chilled ribbon surface alone, the unchilled ribbon surface alone, or on both surfaces. Polishing a single surface had approximately half the

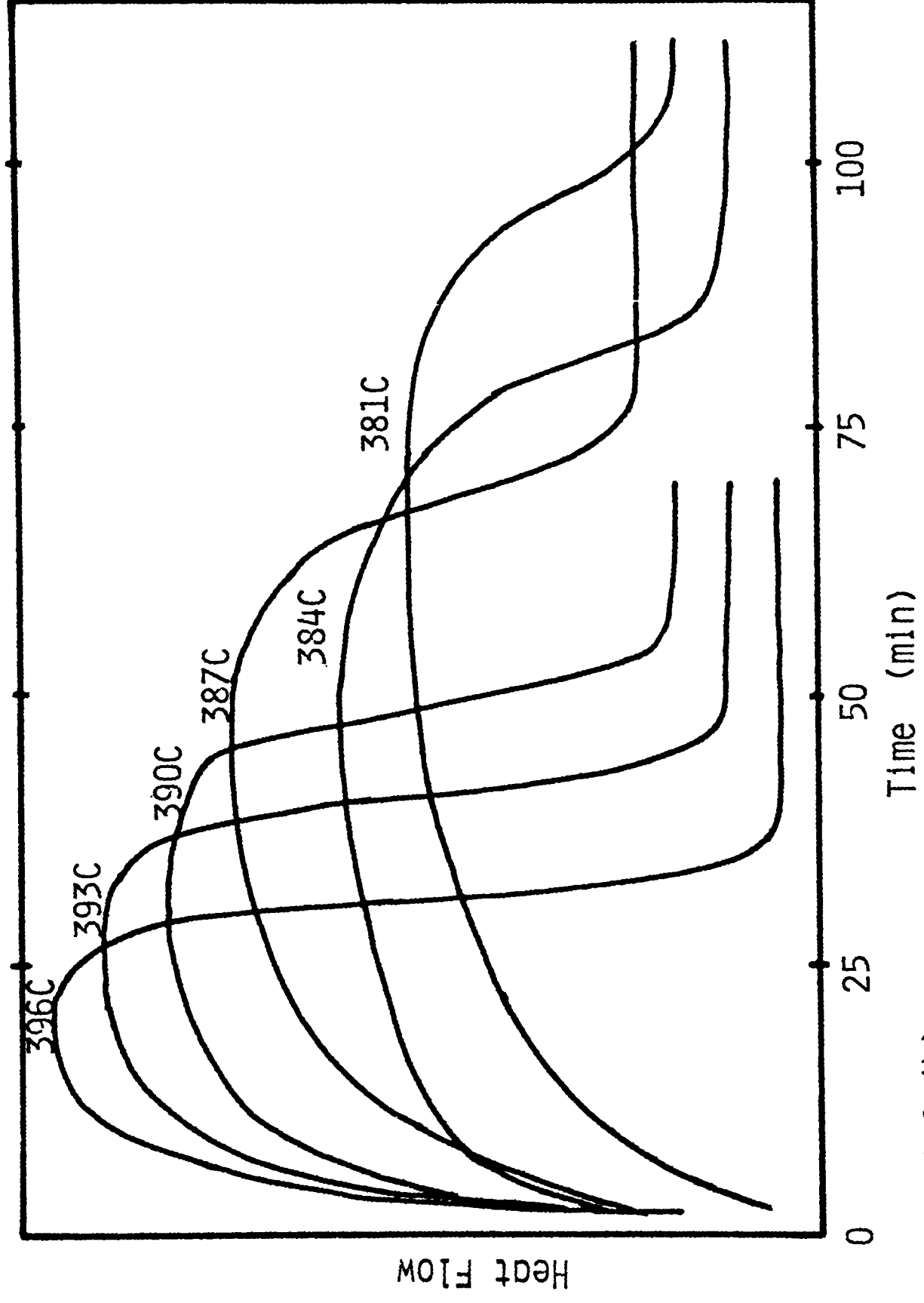


Fig.8-8 (b)

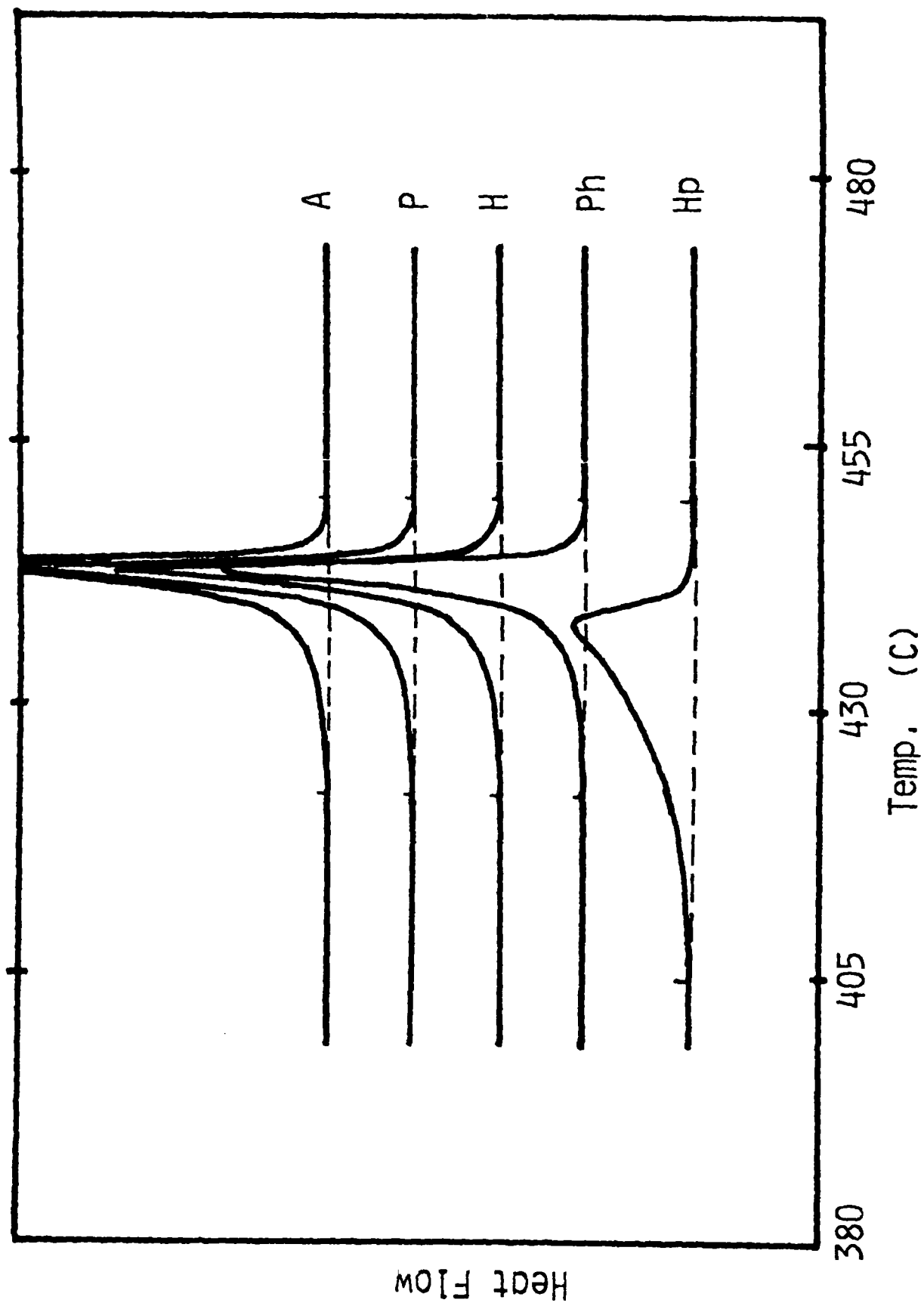
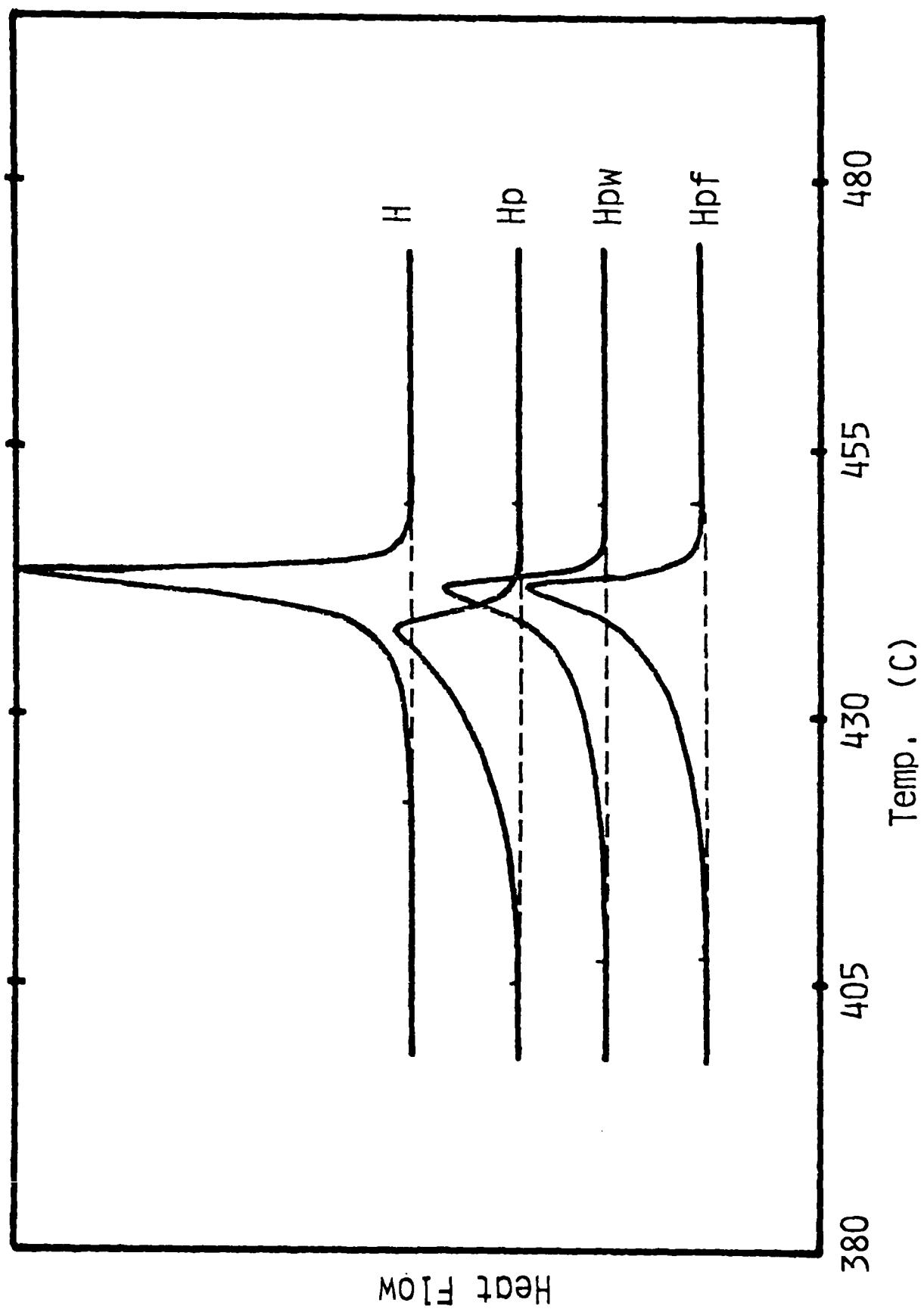


Fig.8-9 Continuous heating DSC traces at a heating rate of 10K/min for amorphous Fe₄₀Ni₄₀B₂₀ after various combinations of pre-annealing and polishing:
(a) A - amorphous Fe₄₀Ni₄₀B₂₀ as-supplied, P - polished with 1200 SiC without pre-annealing, H - pre-annealed for 20h at 350°C without polishing, Ph - polished with 1200 SiC followed by pre-annealing for 20h at 350°C, Hp - pre-annealed for 20h at 350°C followed by polishing with 1200 SiC.



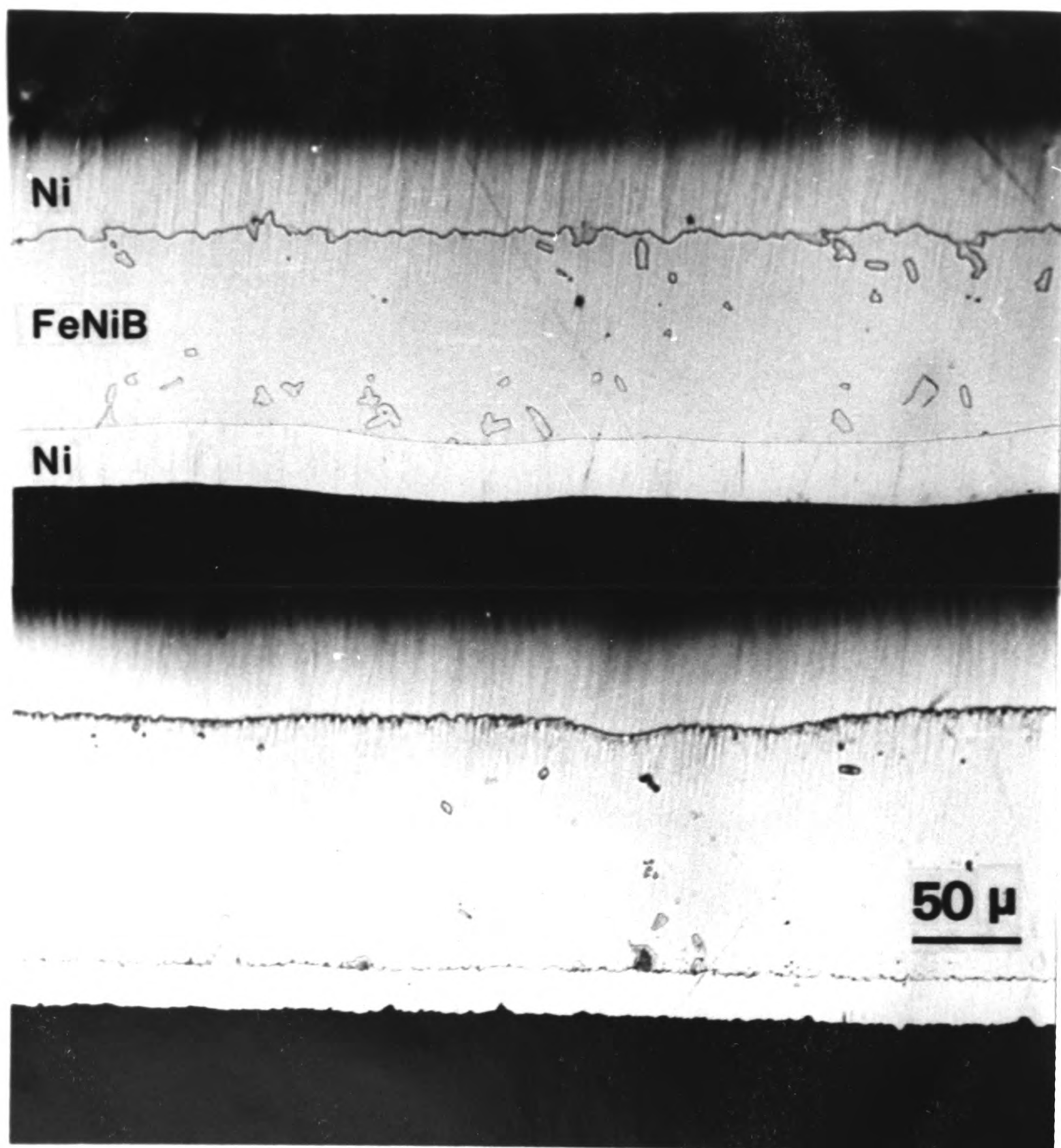
(b) H - pre-annealed for 20h at 350°C without polishing, Hp - pre-annealed for 20h at 350°C followed by polishing with 1200 SiC on both sides, Pw - pre-annealed for 20h at 350°C followed by polishing with 1200 SiC only on the chilled side, Pf - pre-annealed for 20h at 350°C followed by polishing with 1200 SiC only on the unchilled side.

effect of polishing both surfaces, and was independent of which surface was polished.

8.3.7 Optical microscopy

Fig.8-10 shows a series of cross section optical micrographs from amorphous Fe₄₀Ni₄₀B₂₀ specimens with different pre-annealing and surface polishing treatments, all followed by partial crystallisation in the DSC by isothermal annealing at 390 C for 15min. Fig.8-11 shows a similar series of optical micrographs from amorphous Fe₄₀Ni₄₀B₂₀ specimens, with the same range of pre-annealing and surface polishing treatments, but followed by a longer isothermal annealing time in the DSC of 40min at 390 C to induce a greater degree of partial crystallinity. The different sample pre-treatments were as follows: (a) pre-annealed for 20h at 350 C in air with no surface polishing; (b) surface polished with 1200 SiC followed by pre-annealing for 20h at 350 C; (c) pre-annealed for 20h at 350 C followed by surface polishing with 1200 SiC; and (d) Ni plated followed by pre-annealing for 20h at 350 C.

Samples (a) and (b), pre-annealed alone and surface polished followed by pre-annealing, exhibited the slower crystallisation kinetics characteristic of the as-supplied amorphous alloy, with a broad near-Gaussian exothermic DSC peak. The cross section optical micrographs from samples (a) and (b) were similar after each annealing time. Crystallisation took place by bulk nucleation, and the overall crystallisation rate was slow, with ~ 5 and 10% of near-randomly distributed crystals after 15 and 40 minutes at 390 C respectively. Samples of type (c), pre-annealed followed by surface polishing, exhibited accelerated crystallisation kinetics with a near-rectangular exothermic DSC peak. Unlike samples (a) and (b), the cross section optical micrographs from samples of type (c) showed that crystallisation took place by surface



(a)/(b)

Fig.8-10 Cross section optical micrographs of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ samples partially crystallised by isothermal heating for 15min at 390°C , after various combinations of pre-annealing for 20h at 350°C and surface mechanical polishing with 1200 SiC: (a) pre-annealed alone; (b) polished followed by pre-annealing; (c) pre-annealed followed by polishing, (d) Ni plated followed by pre-annealing.

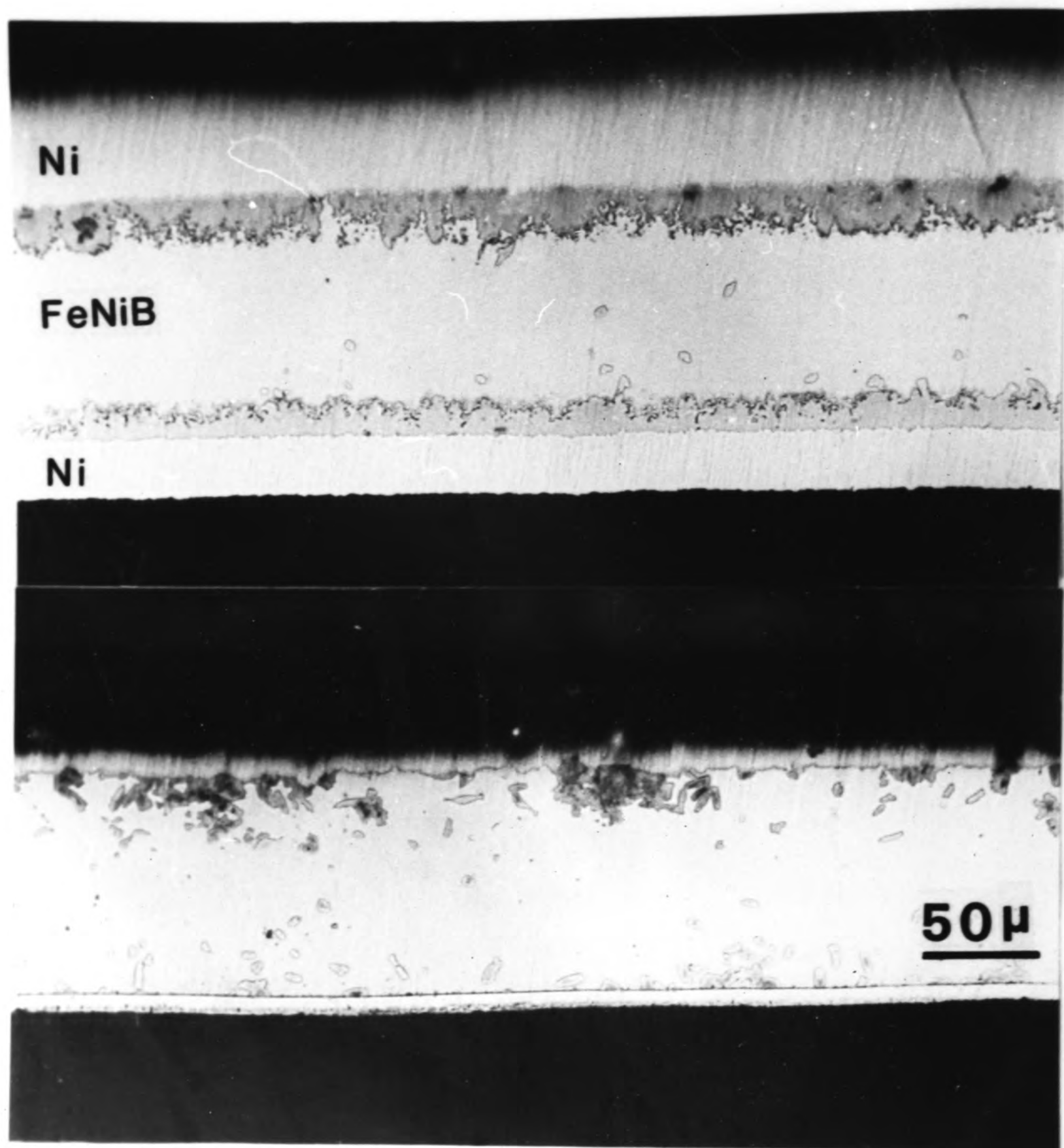
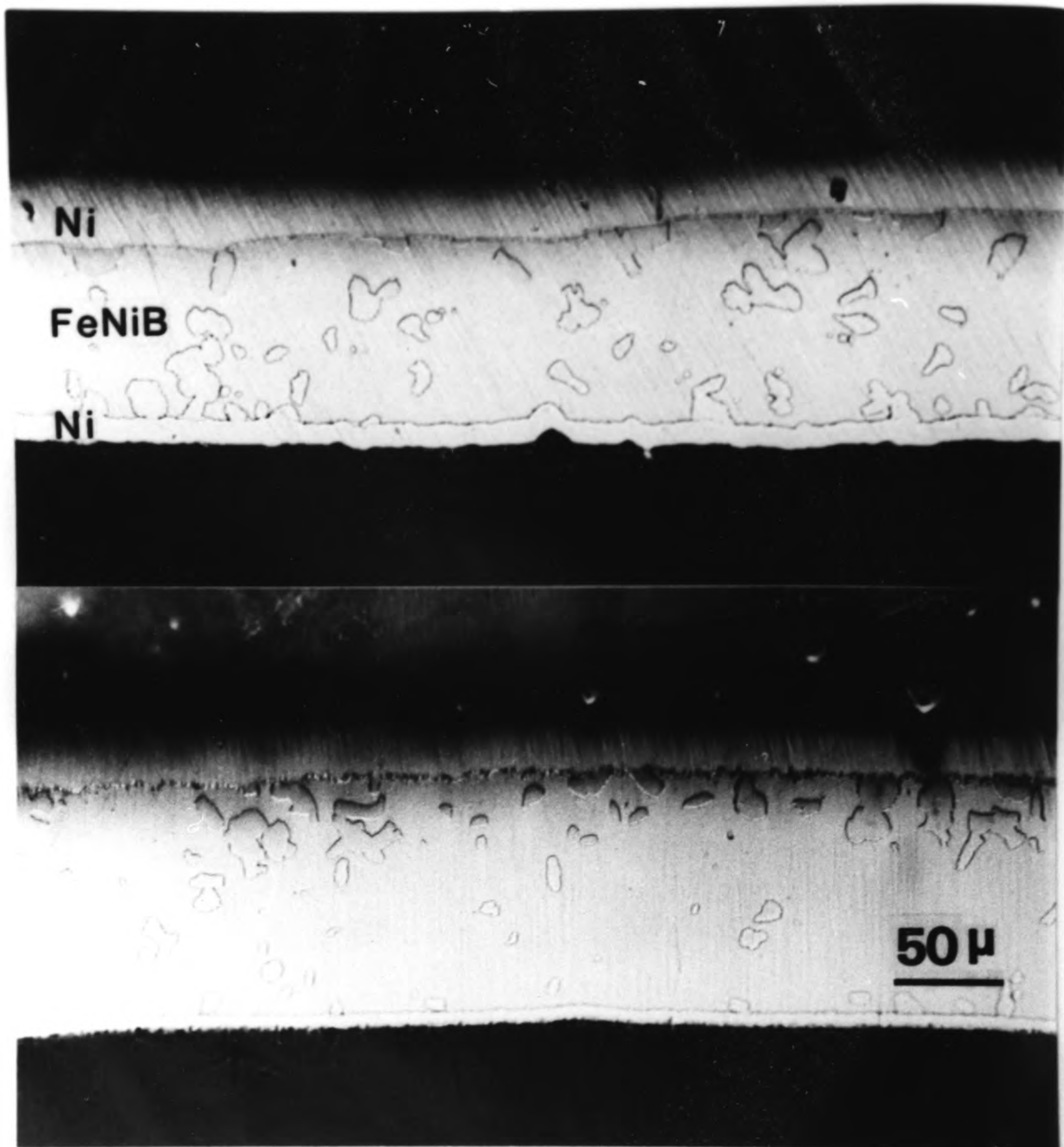


Fig.8-10

(c)/(d)



(a)/(b)

Fig.8-11 Cross section optical micrographs of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ samples partially crystallised by isothermal heating for 40min at 390°C , after various combinations of pre-annealing for 20h at 350°C and surface mechanical polishing with 1200 SiC: (a) pre-annealed alone; (b) polished followed by pre-annealing; (c) pre-annealed followed by polishing; (d) Ni plated followed by pre-annealing; (e) schematic isothermal DSC curves for the different amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ specimens indicating the degree of partial crystallisation corresponding to the optical micrographs in Figs.8-10 and 8-11.

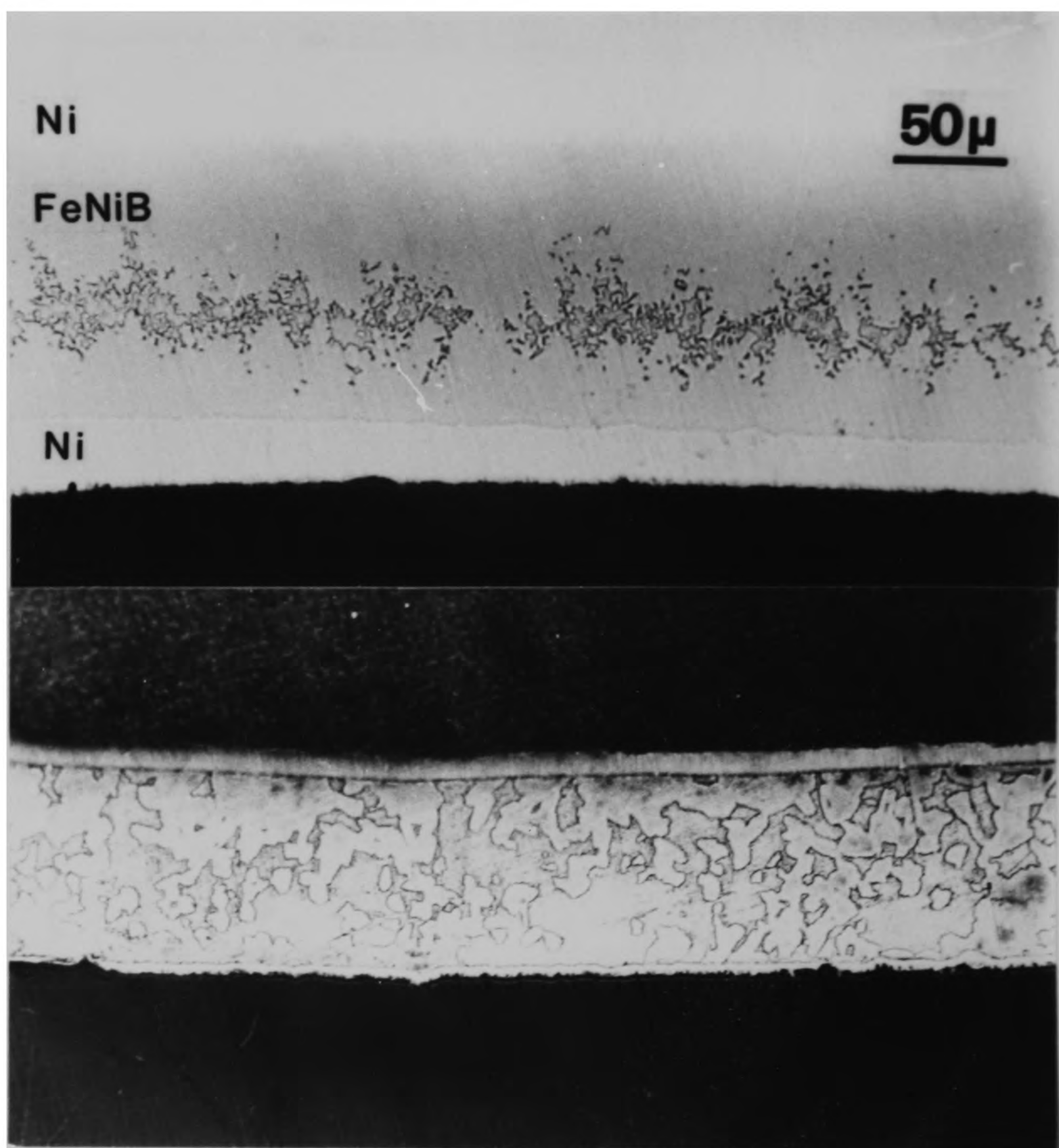


Fig.8-11 (c)/(d)

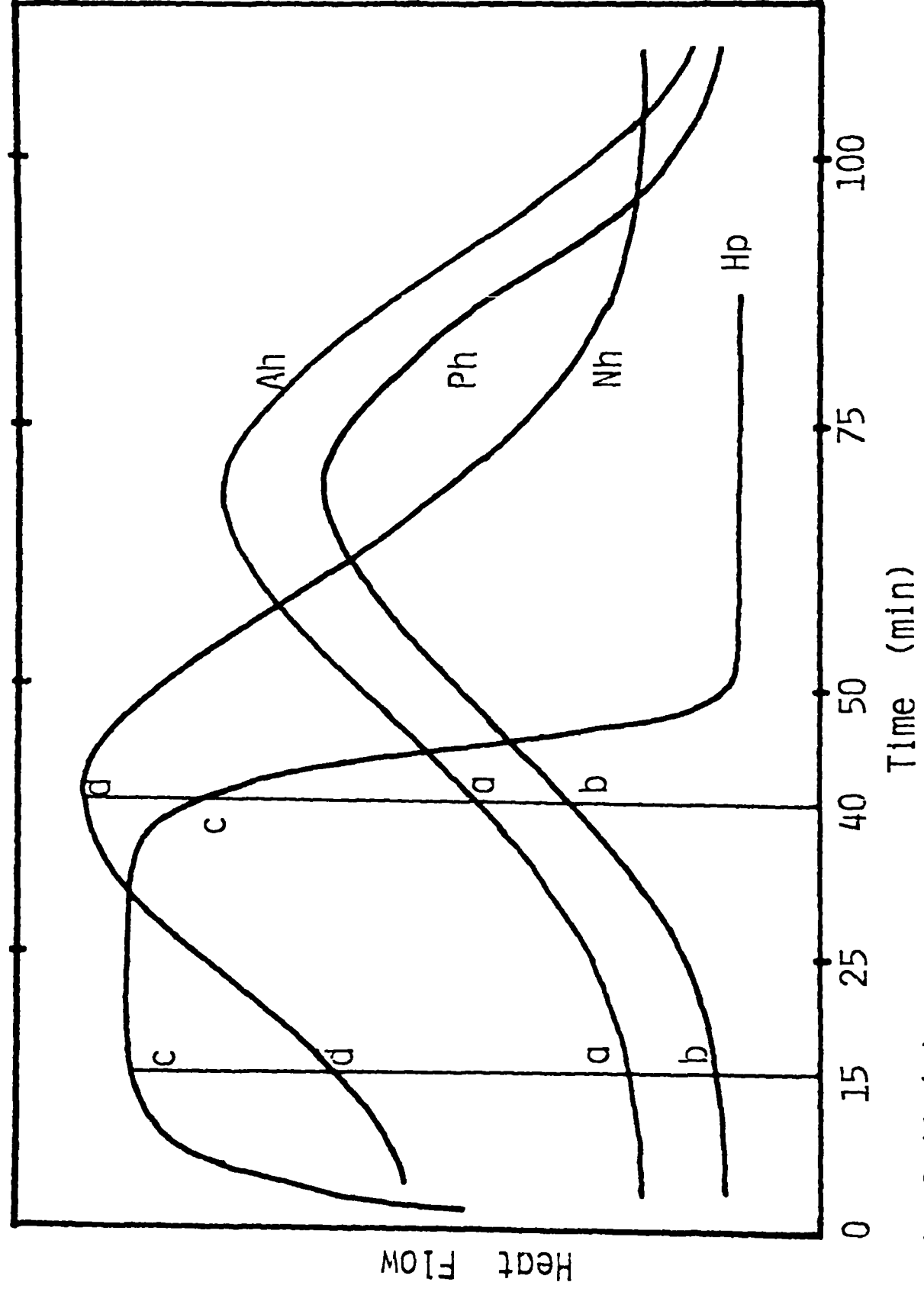


Fig.8-11 (e)

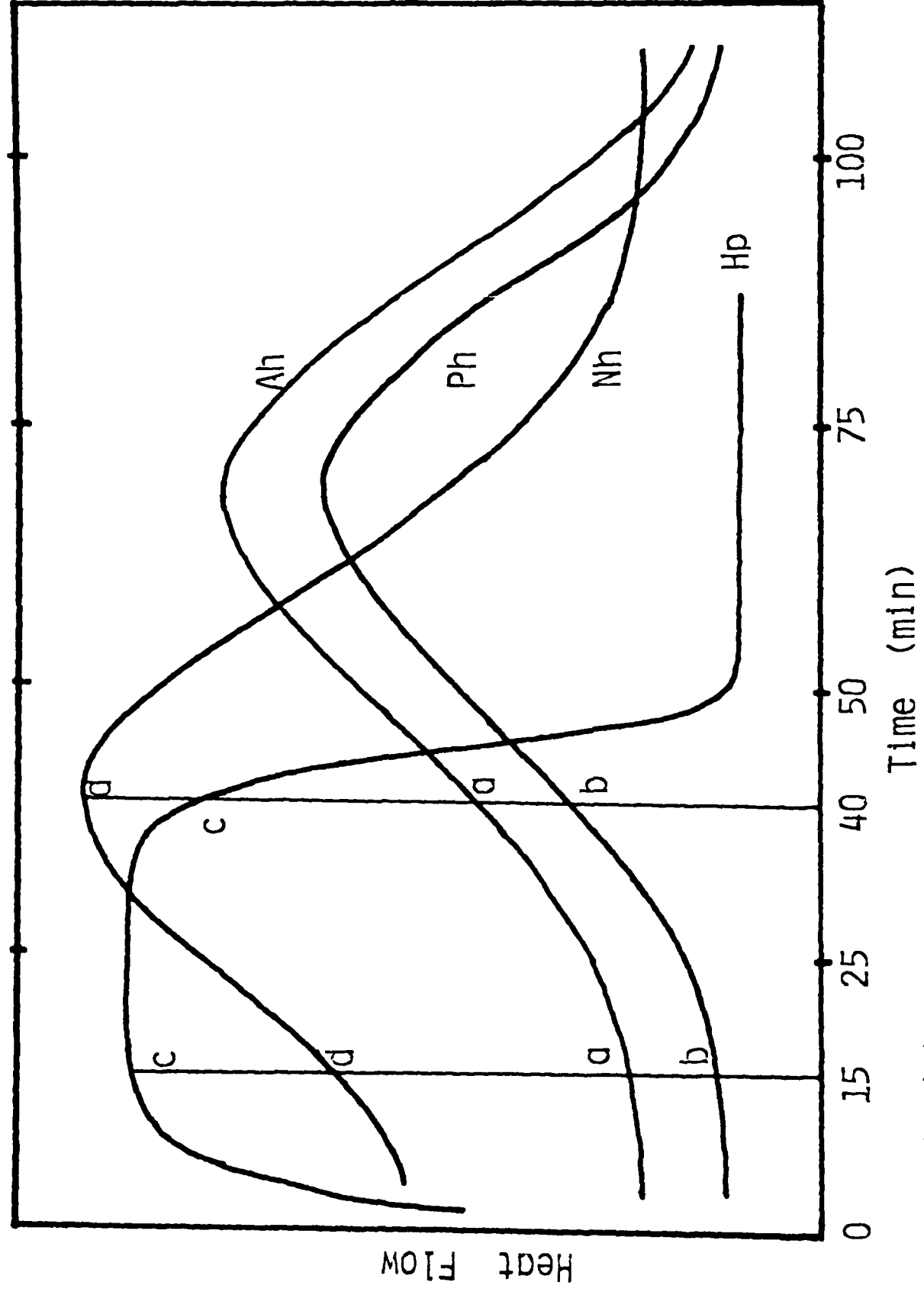


Fig.8-11 (e)

nucleation, followed by growth of an approximately planar crystallisation front inwards from each surface towards the middle of the ribbon. Because of the faster overall crystallisation rate, the crystalline regions occupied ~ 20 and 90% of the amorphous alloy ribbon after 15 and 40 min at 390 C respectively.

Samples of type (d), Ni plated followed by pre-annealing, exhibited a partial acceleration of the crystallisation process, as shown in the DSC curves of Fig.8-6. The cross section optical micrographs from the Ni plated samples showed some preference for surface crystallisation but not as strongly as in the pre-annealed/surface polished samples of type (c). Moreover, the Ni plated samples exhibited a different growth mechanism, with individual crystals growing from surface as well as bulk nuclei, and no clearly defined crystallisation front. The overall crystallisation rate was also intermediate between the (a) and (c) samples, with ~ 10 and 50% crystallinity after 15 and 40 min at 390 C respectively. Fig.8-11(e) shows the extent of crystallisation in each the cross section optical micrographs of Figs.8-10 and 8-11, by indicating the relevant positions on schematic isothermal DSC curves.

8.3.8 X-ray diffractometry

Fig.8-12(a) shows an X-ray diffractometer trace for amorphous Fe₄₀Ni₄₀B₂₀, pre-annealed for 20h at 350 C with no surface treatment, and then partially crystallised in the DSC by isothermal annealing for 110min at 390 C. This X-ray traces represents the crystalline structure formed by bulk nucleation and equiaxed growth. Fig.8-12(b) shows a comparison X-ray diffractometer trace for amorphous Fe₄₀Ni₄₀B₂₀, pre-annealed for 20h at 350 C followed by mechanical surface polishing with 1200 SiC, and then partially crystallised in the DSC by isothermal annealing for 40 min at 390 C. This X-ray trace represents the crystalline structure formed by surface

Fig.8-12 X-ray diffractometer traces from crystallised Fe₄₀Ni₄₀B₂₀: (a) pre-annealed for 20h at 350°C with no subsequent polishing, crystallised at 390°C for 110min; (b) pre-annealed for 20h at 350°C followed by polishing with 1200 SiC, crystallised at 390°C for 40min. Both show the eutectic structure of orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni).

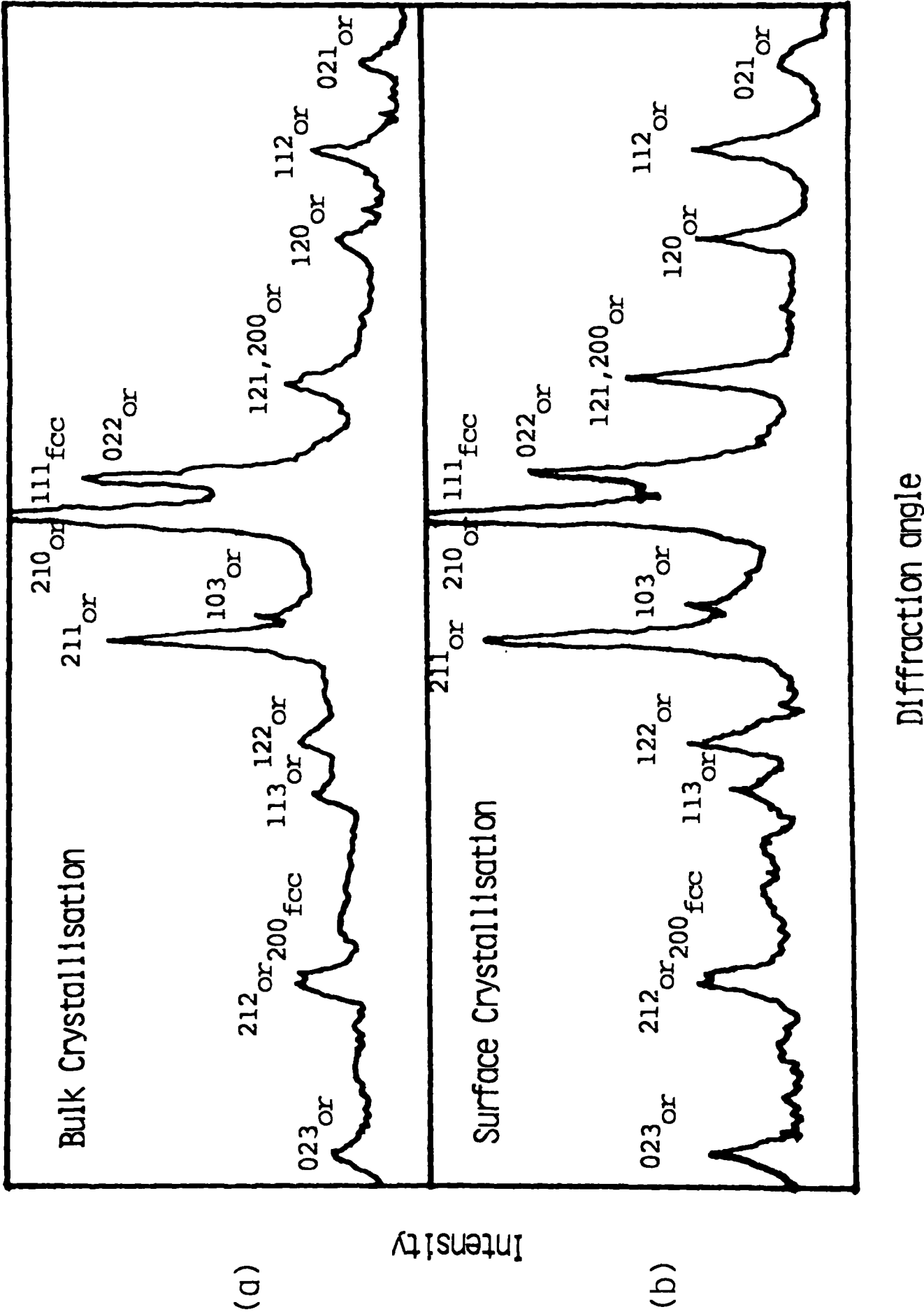


Table 8-1 Calculated d spacings and relative intensities from X-ray diffractometer traces of crystallised Fe₄₀Ni₄₀B₂₀, together with the d spacings of orthorhombic (Fe,Ni)₃B and fcc Ni

Sample (a)		Sample (c)		or-(Fe,Ni) ₃ B		fcc-Ni	
d (nm)	int.(%)	d (nm)	int.(%)	d (nm)	(hkl)	d (nm)	(hkl)
2.48	15	2.48	15	2.46	021		
2.38	20	2.37	25	2.37	112		
2.29	15	2.28	25	2.27	120		
2.17	20	2.18	40	2.21, 2.15	121, 200		
2.08	65	2.07	70	2.07	022		
2.05	100	2.05	100	2.04	210	2.034	111
1.985	20	1.980	30	1.977	103		
1.957	70	1.955	80	1.950	211		
1.884	15	1.880	35	1.875	122		
1.859	15	1.855	30	1.852	113		
1.753	20	1.760	30			1.762	200
1.743	25	1.740	40	1.737	212		
1.656	20	1.670	40	1.697	023		
1.245	20					1.246	220
1.108	25					1.063	311

Sample (a) Pre-annealed for 20h at 350 C, and then crystallised by isothermal annealing in the DSC for 110min at 390 C.

Sample (c) Pre-annealed for 20h at 350 C followed by surface polishing with 1200 SiC, and then crystallised by isothermal annealing in the DSC for 40min at 390 C.

nucleation and planar growth. For both types of pre-treatment, the crystalline structure was found to be a mixture of orthorhombic $(\text{Fe,Ni})_3\text{B}$ and fcc (Fe,Ni) . Measured d spacings and relative intensities from the X-ray traces of both types of partially crystallised amorphous alloy specimen are listed in Table 8-1, together with d spacings calculated from orthorhombic $(\text{Fe,Ni})_3\text{B}$ and fcc- (Ni) (3).

8.3.9 Transmission electron microscopy

Fig.8-13 shows typical TEM micrographs from an amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ specimen which was pre-annealed for 20h at 350 C with no surface treatment, and then partially crystallised in the DSC by isothermal annealing for 40min at 390 C. This specimen exhibited the slower crystallisation kinetics characteristic of the as-supplied amorphous alloy, and was prepared by thinning from both sides, so as to examine the structure of crystals formed by bulk nucleation and equiaxed growth in the middle of the amorphous alloy ribbon. Figs.8-13(a) and (b) show bright field images of the partially crystallised structure; and Figs.8-13(c) and (d) show a selected area diffraction pattern from the crystal in (a) and its indexing.

After 40min at 390 C, most of the $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ specimen remained amorphous but some relatively large equiaxed crystals had formed, as shown in Fig.8-13(a). These equiaxed crystals were found to consist of a fine scale lamellar eutectic mixture of orthorhombic $(\text{Fe,Ni})_3\text{B}$ and fcc (Fe,Ni) , as shown in Figs.8-13(a), (c) and (d). The lamellar eutectic spacing was $\sim 20\text{nm}$, and the crystal structures had lattice parameters of $a = 0.36\text{nm}$ for fcc (Fe,Ni) and $a = 0.44$, $b = 0.53$, and $c = 0.66\text{nm}$ for orthorhombic $(\text{Fe,Ni})_3\text{B}$, in good agreement with the eutectic crystal structure previously reported in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ by Muller and Heimendahl (3). The orientation relationship between the two eutectic phases corresponded to $\{200\}_{\text{fcc}} // \{122\}_{\text{or}}$, and $\langle 013 \rangle_{\text{fcc}} // \langle 011 \rangle_{\text{or}}$ in Figs.8-13 (c) and (d). Small crystals

Fig.8-13 TEM micrographs from an Fe₄₀Ni₄₀B₂₀ specimen pre-annealed for 20h at 350°C, then partially crystallised by isothermal annealing at 390°C for 40min. The pre-treatment is the same as in Fig.8-11(a), and the specimen was thinned from both sides: (a) bright field image showing the eutectic structure; (b) bright field image showing small crystals and the amorphous matrix; (c) SAED pattern from the eutectic crystal in (a); (d) indexing of the SAED pattern showing the eutectic structure of orthorhombic (Fe,Ni)₃B + fcc(Fe,Ni).

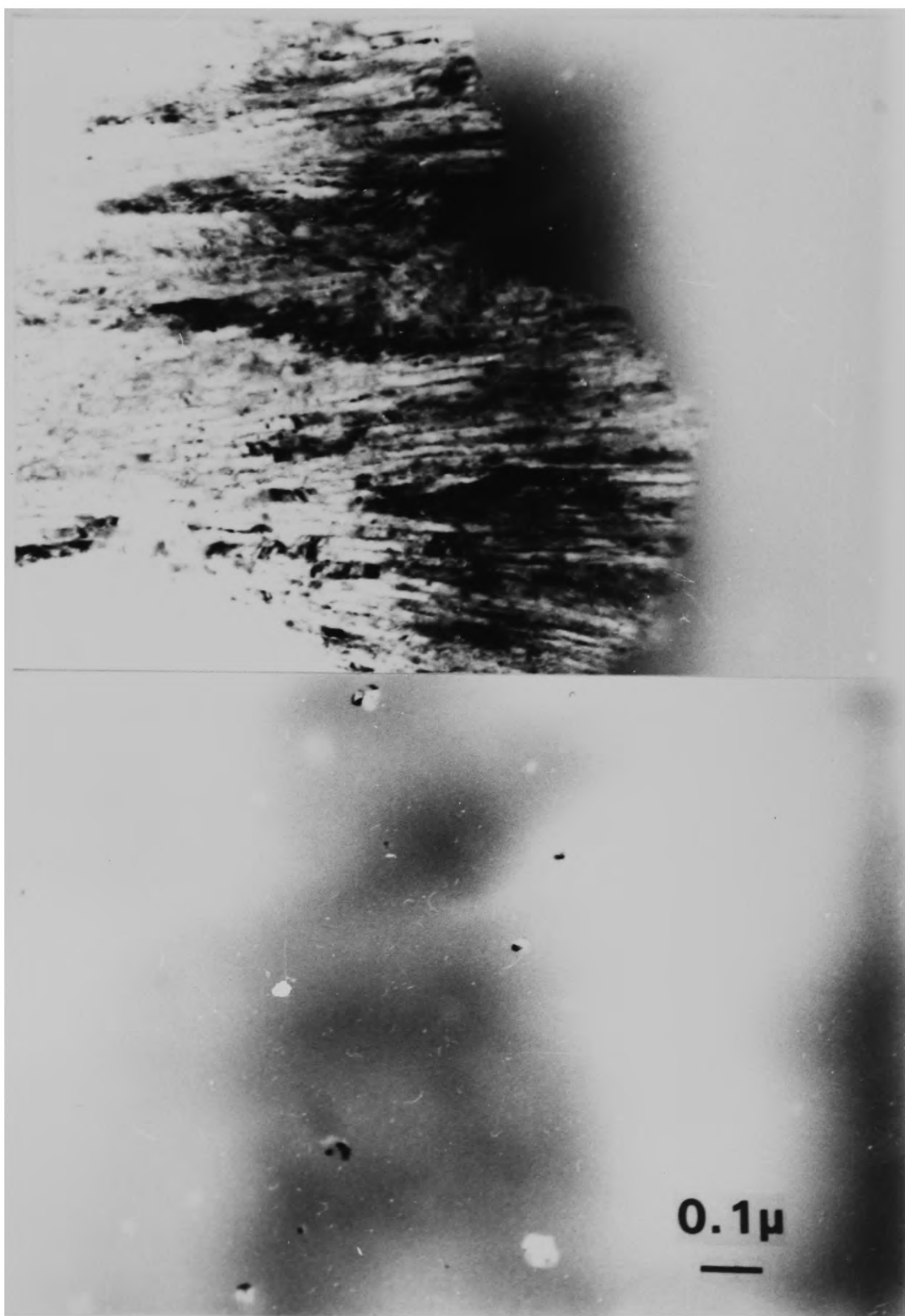
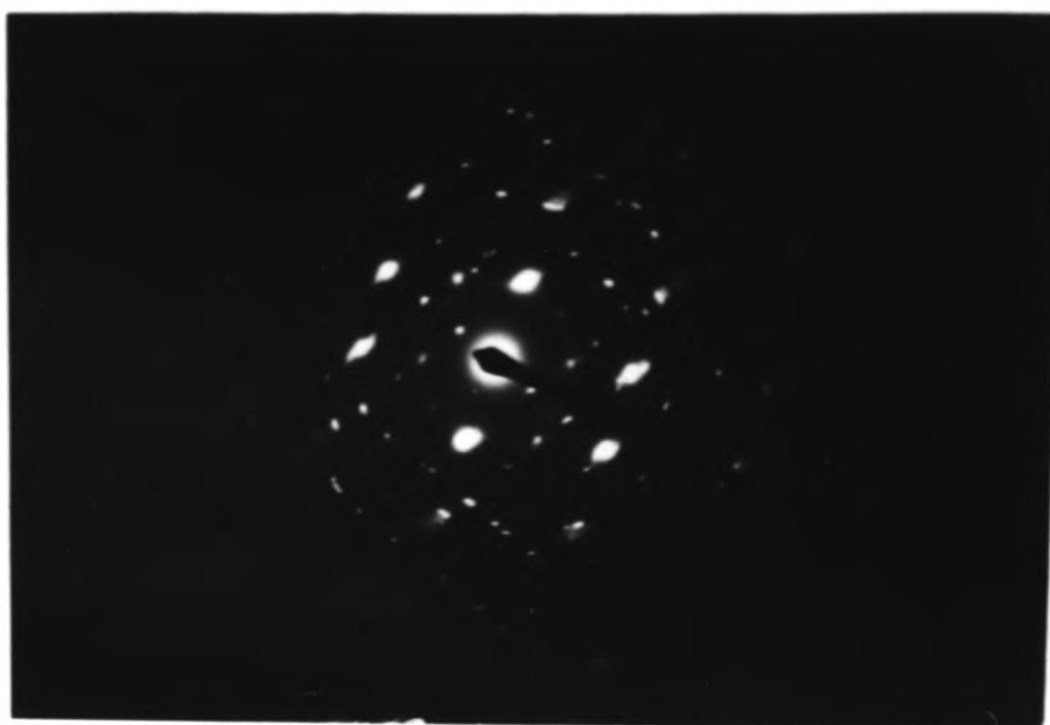
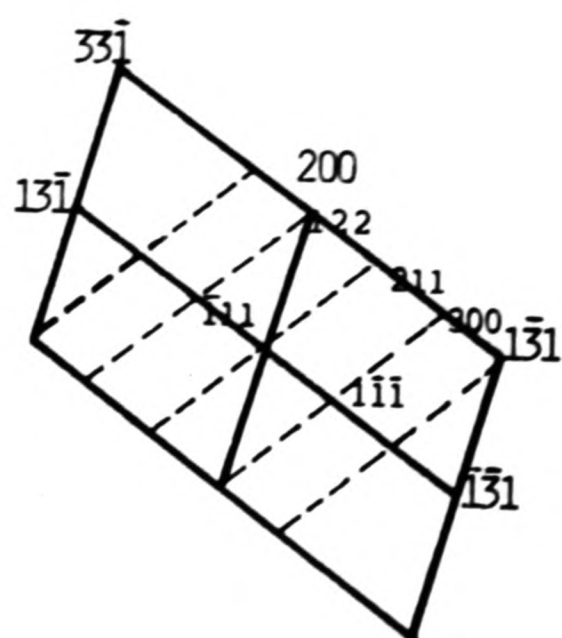


Fig.8-13

(c)



(d)

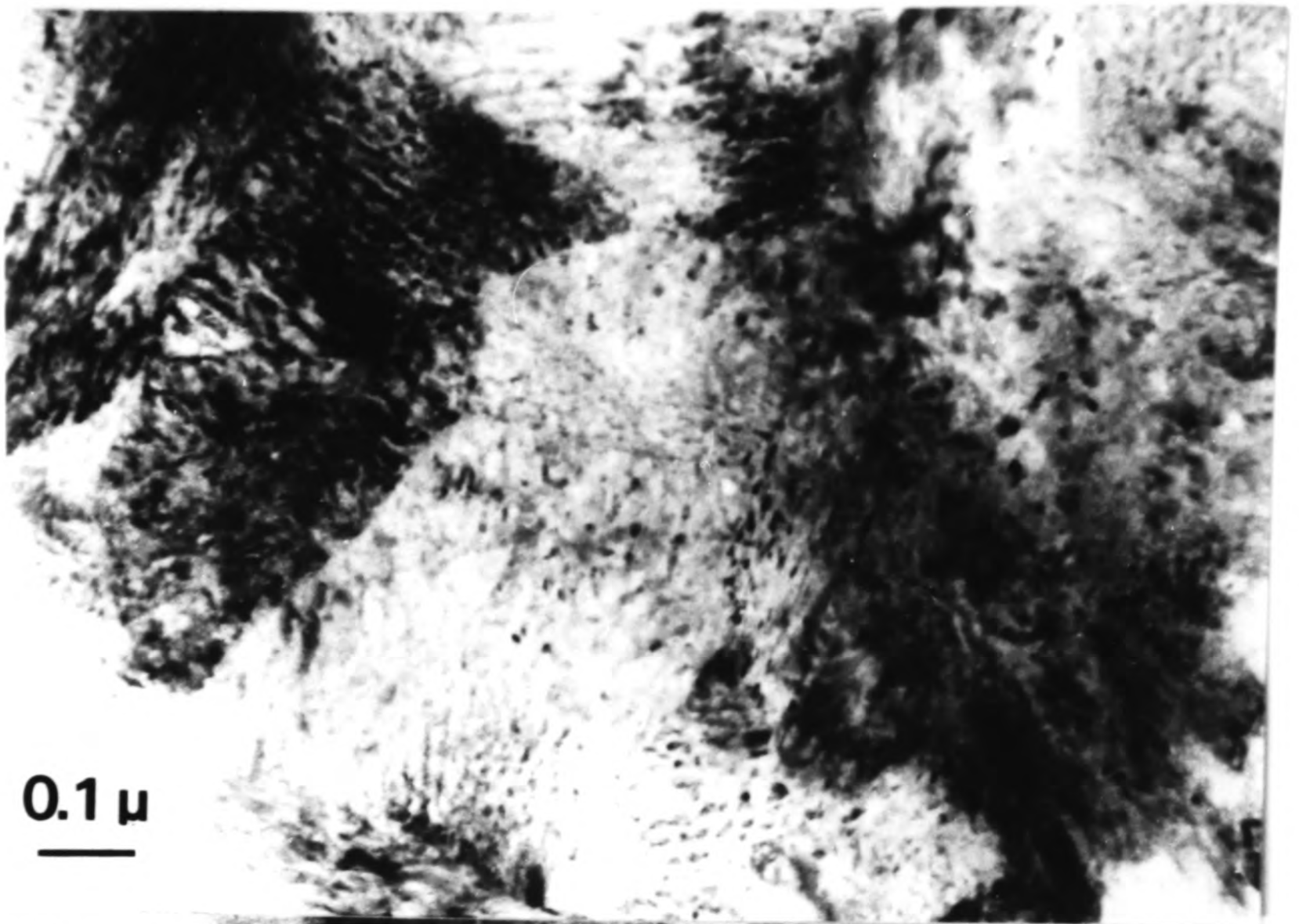


$[013]_{\text{fcc}}$, $(011)_{\text{orth}}$

of a different type were also found in the partially crystallised amorphous Fe₄₀Ni₄₀B₂₀ alloy, as shown in Fig.8-13(b), but these small crystals were insufficient in quantity to influence the overall crystallisation kinetics significantly.

Fig.8-14 shows typical TEM micrographs from an amorphous Fe₄₀Ni₄₀B₂₀ specimen which was pre-annealed for 20h at 350 C followed by surface mechanical polishing with 1200 SiC, and then partially crystallised in the DSC by isothermal annealing for 40 min at 390 C. This specimen exhibited accelerated crystallisation kinetics, and was prepared by grinding and thinning from the unchilled surface, so as to examine the structure of crystals formed by surface nucleation on the chilled surface. Figs.8-14(a) and (b) show bright field images of the partially crystallised structure; Figs.8-14(c) and (d) show dark field images corresponding to (b) obtained by using orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni) reflections; and Figs.8-14(e) and (f) show a selected area diffraction pattern from the crystal in (b) and its indexing. After 40min annealing at 390 C, the surface region of the Fe₄₀Ni₄₀B₂₀ specimen had crystallised completely, and the surface nucleated crystals were again found to consist of a fine scale lamellar eutectic mixture of orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni), as shown in Figs.8-14(a) to (f). The lamellar eutectic spacing was ~ 15nm, and the crystal structures had lattice parameters similar to those formed by bulk nucleation, as shown in Fig.8-13. The orientation relationship between the two eutectic phases corresponded to be {111}fcc // {013}or, and <011>fcc // <100>or in Figs.8-14 (d) and (e). Because the eutectic crystals grew perpendicular to the plane of the amorphous alloy ribbon, ie approximately parallel to the electron beam and direction of observation in Fig.8-14, the eutectic growth direction was approximately parallel to <011>fcc and <100>or.

Fig.8-14 TEM micrographs from an Fe₄₀Ni₄₀B₂₀ specimen pre-annealed for 20h at 350°C followed by mechanical polishing with 1200 SiC, then partially crystallised by isothermal annealing at 390°C for 15min. The pre-treatment is the same as in Fig.8-10(c), and the specimen was thinned from the unchilled surface only: (a) and (b) bright field images showing the eutectic structure; (c) dark field image of orthorhombic (Fe,Ni)₃B; (d) dark field image of fcc (Fe,Ni); (e) SAED pattern from the eutectic structure in (b); (f) indexing of the SAED pattern, showing the eutectic structure of orthorhombic (FeNi)₃B + fcc (Fe,Ni).



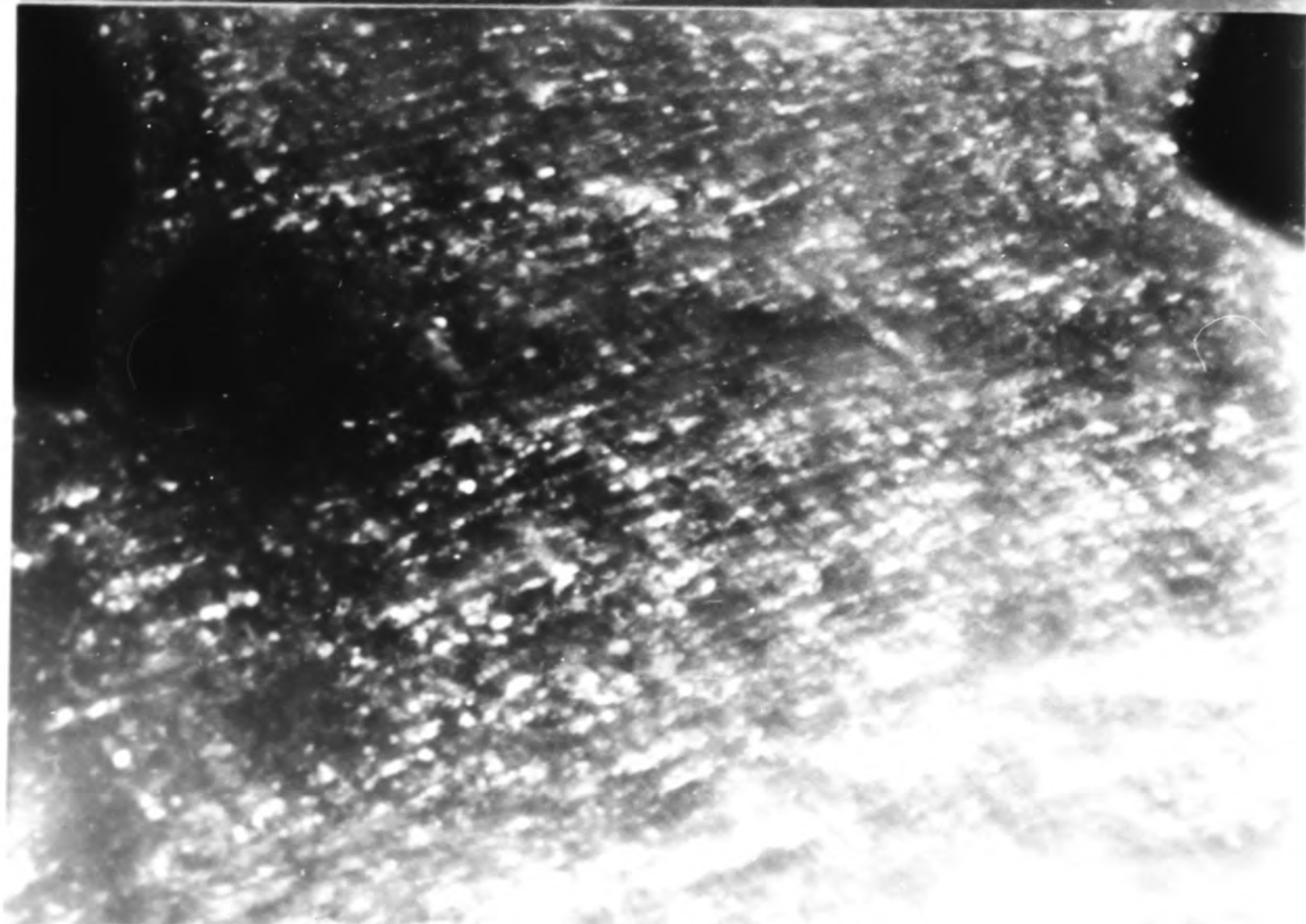
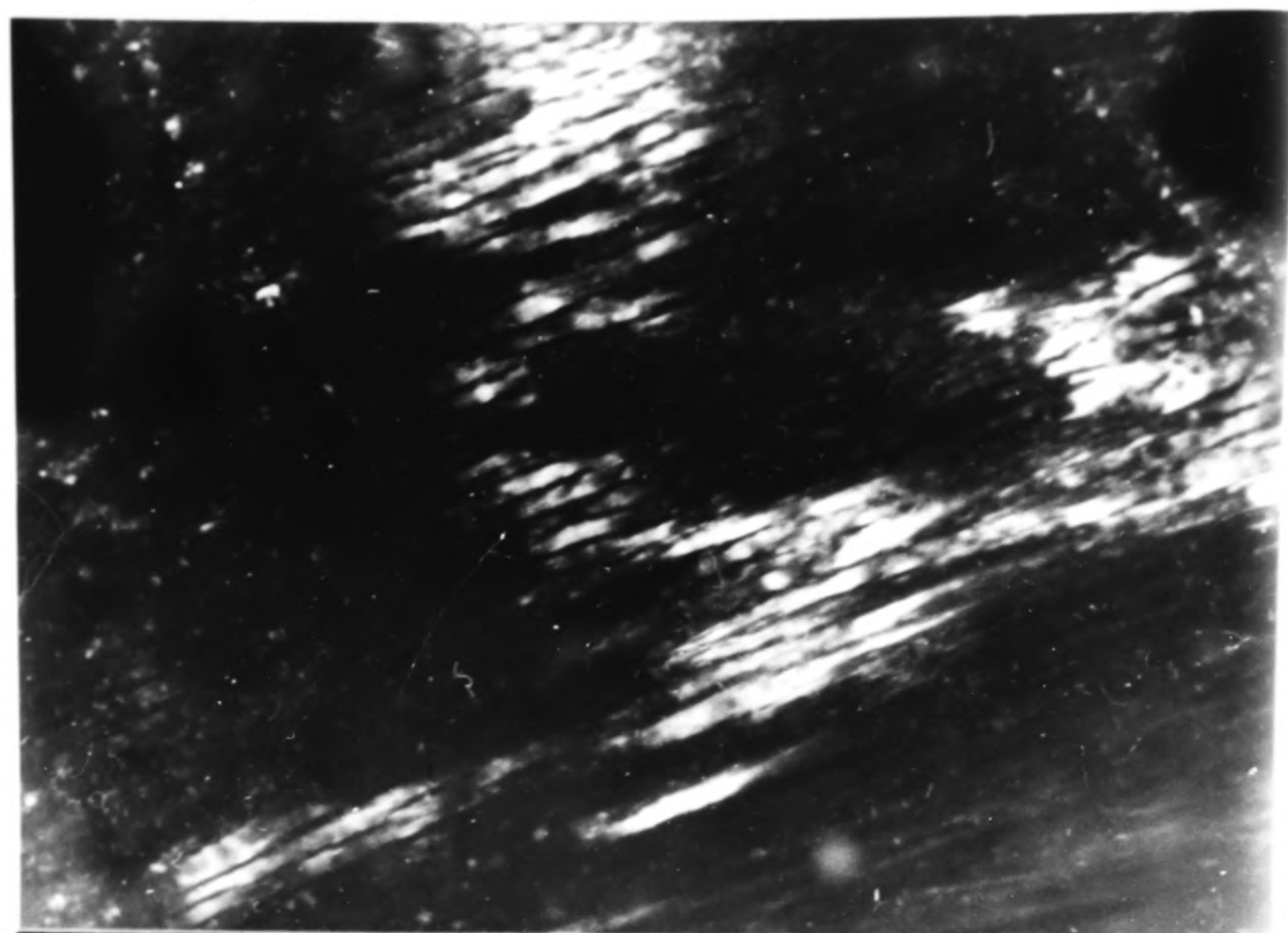
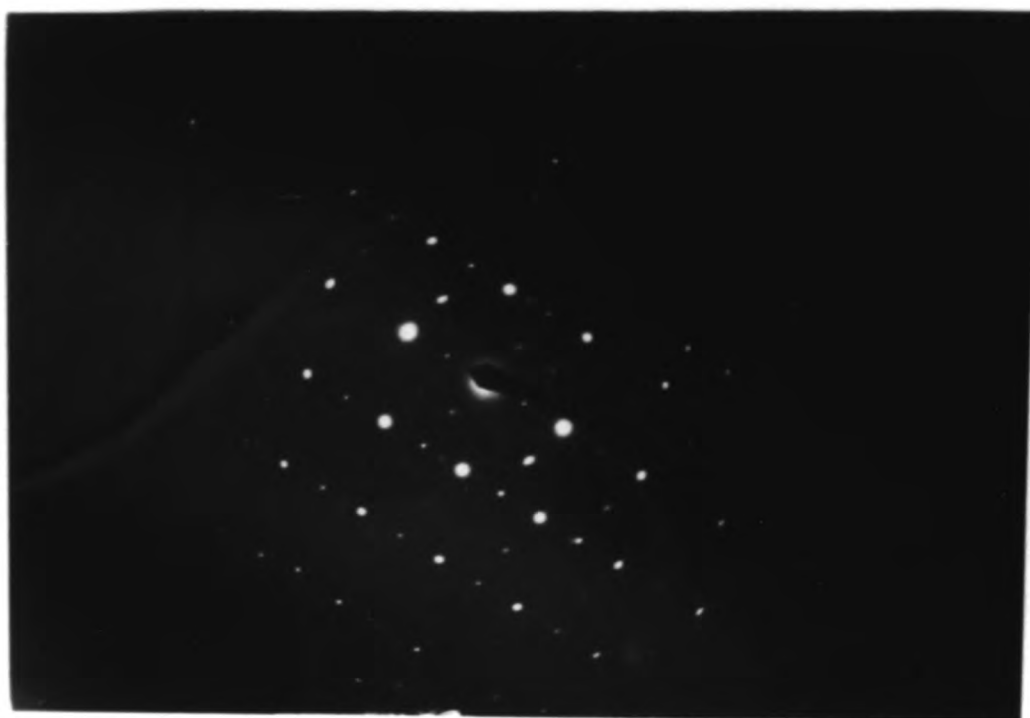
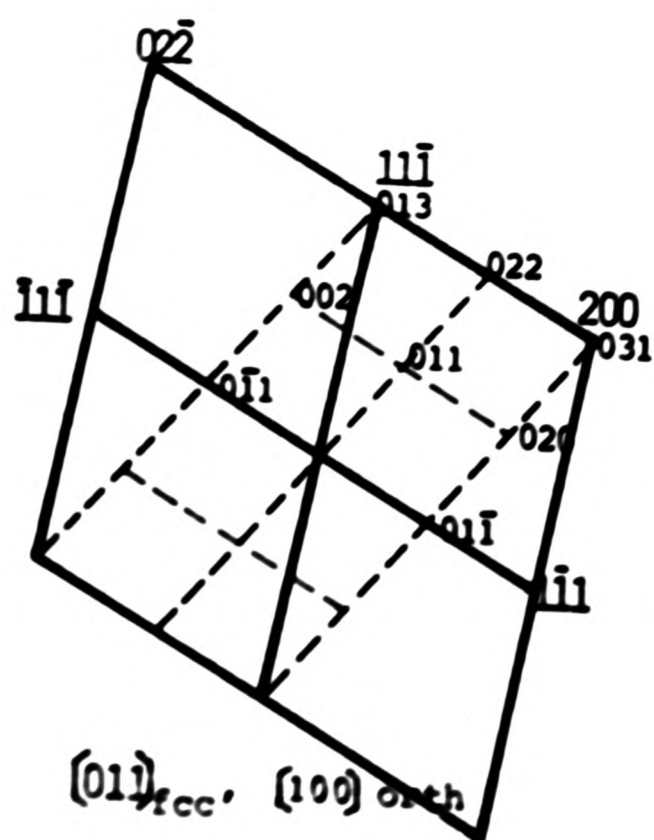


Fig.8-14

(e)



(f)



8.4. Discussion

8.4.1 Crystallisation kinetics

It can clearly be seen from the isothermal DSC thermograms in Figs.8-1 to 8-8 and the optical micrographs in Figs.8-10 and 8-11 that the crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ can take place by two different mechanisms: either by fast surface nucleation and inward, near-planar growth, or by slow bulk nucleation and equiaxed growth.

8.4.1.1 Surface nucleation and inward, near-planar growth

After pre-annealing for 20h at 350 C followed by mechanical polishing with 1200 SiC, amorphous Fe₄₀Ni₄₀B₂₀ exhibits the characteristic accelerated crystallisation behaviour which is typified by the isothermal DSC traces in Fig.8-8(a), optical micrographs in Figs.8-10(c) and 8-11(c), and TEM micrographs in Fig.8-14. On heating to a temperature in the range 381-396 C, crystallisation begins immediately, with dense surface nucleation of eutectic crystals of orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni), which rapidly form a continuous crystalline surface layer. Crystallisation then proceeds by steady state inward growth at an approximately planar crystallisation front, with a constant growth rate and therefore constant rate of heat evolution and near-rectangular exothermic DSC peak. Finally, crystallisation is terminated sharply when the growing eutectic crystals from both amorphous ribbon surfaces meet in the centre of the ribbon.

This type of accelerated crystallisation behaviour can only be induced by a suitable combination of pre-annealing and surface treatment. A sufficiently extended pre-annealing treatment is required, typically at least 5h above 350 C, 20h above 330 C, or 500h above 300 C, as shown in Figs.8-3 to 8-5; and the pre-annealing treatment must be followed by a sufficiently heavy surface treatment, typically mechanical polishing with 1200 SiC or electropolishing, as shown in Fig.8-2. Accelerated

crystallisation is not produced by pre-annealing alone, surface polishing alone, or surface polishing followed by pre-annealing, as shown in Figs.8-1,8-2,8-10 and 8-11.

The overall kinetics of this type of accelerated crystallisation can be expressed approximately as:

$$Y = 2GAt \quad (8-1)$$

where Y is the crystalline volume fraction, G is the crystal growth rate, A is the ribbon surface area, and t is the time. The linear transformation kinetics of equation (8-1) are clearly seen by integrating the near-rectangular isothermal DSC peaks, as shown in Fig.8-15(a), except for short periods of non-linearity at the beginning and end of crystallisation.

The eutectic crystal growth rate G is temperature dependent, so that the crystallisation finish times increase with lower isothermal annealing temperatures, as shown in Fig.8-8(a). The growth rate G can be calculated directly at each temperature from:

$$G = d/2t_c \quad (8-2)$$

where d is the specimen thickness of 32µm for the amorphous Fe₄₀Ni₄₀B₂₀ ribbon, and t_c is the average crystallisation time measured from each DSC curves in Fig.8-8(a) as the average width of the near-rectangular exothermic peak. Over the range of isothermal annealing temperatures 381-396 C, the crystallisation times and eutectic crystal growth rates range from 1650-5240s and 3-10nm/s respectively, and are listed in detail in Table 8-2.

For a thermally activated eutectic crystal growth process, the growth rate can be fitted to an Arrhenius equation:

$$G = G_o \exp(-Q/RT) \quad (8-3)$$

where Q is the activation energy for the rate controlling process, T is the absolute temperature, R is the gas constant and G_o is a constant. Fig.8-16

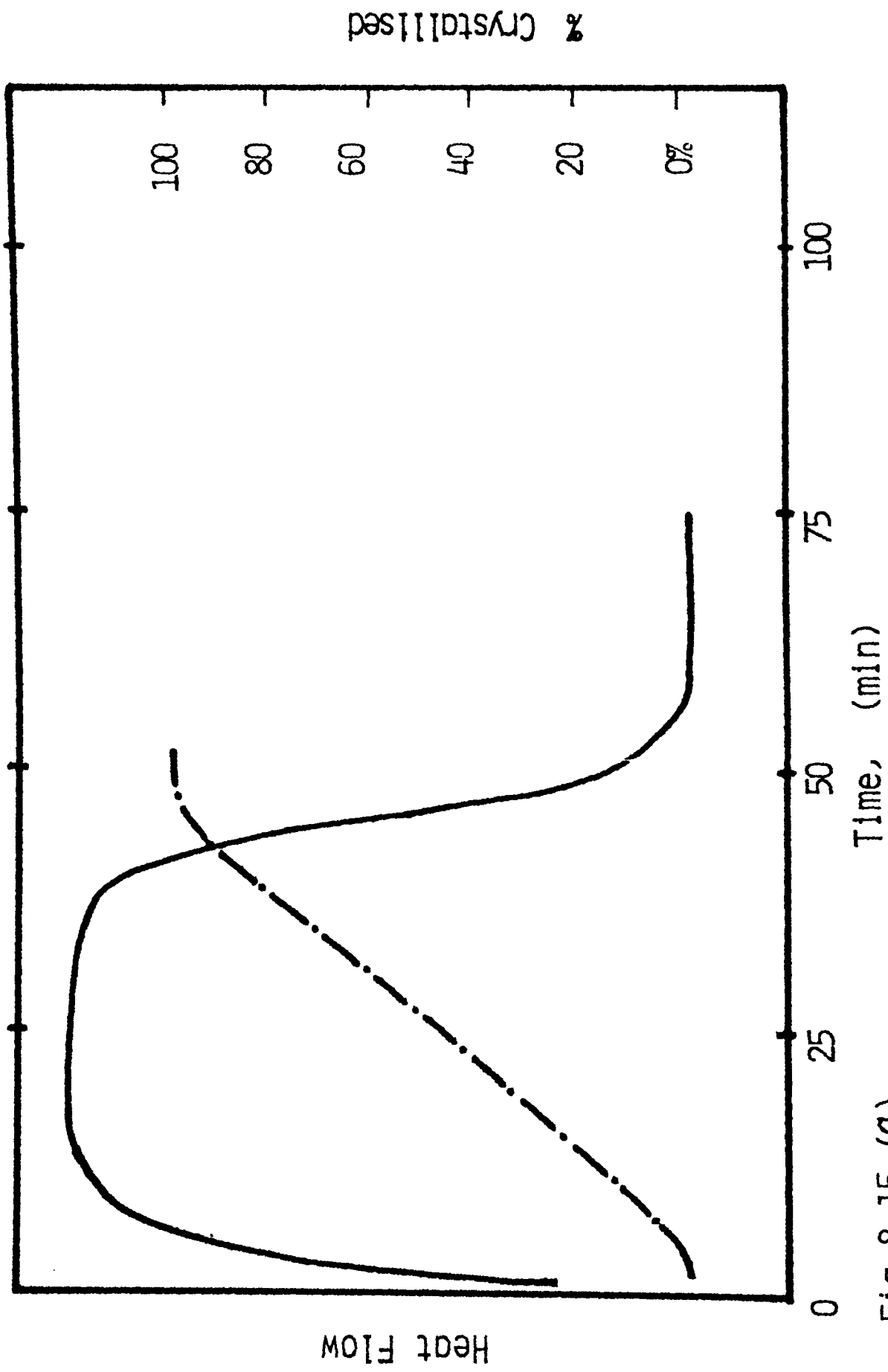


Fig.8-15 (a)

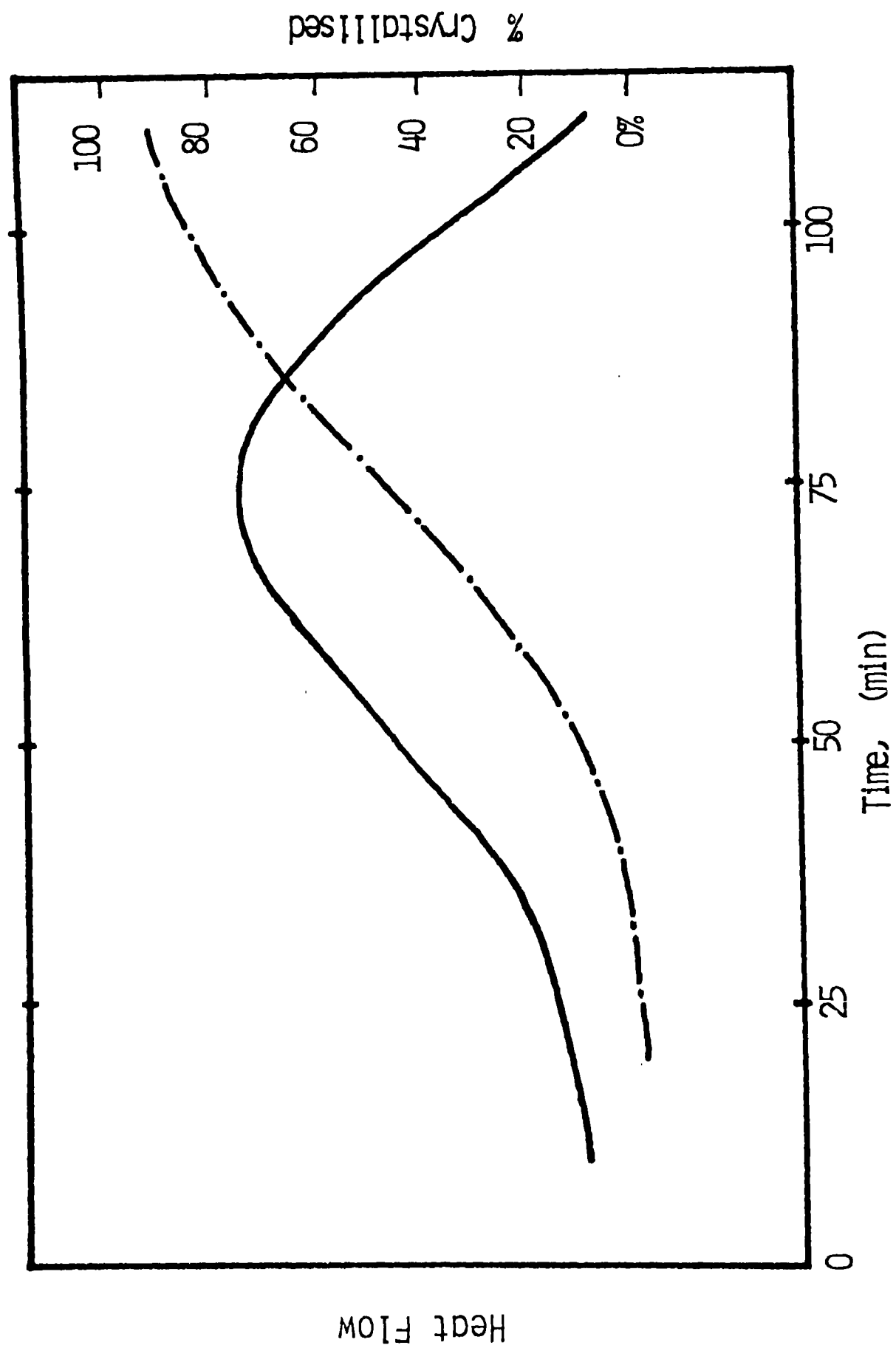


Fig.8-15 (b)

Fig.8-15 Typical isothermal DSC curves at 390°C for the two types of crystallisation mechanism, together with integrated curves which show the transformed volume fraction: (a) pre-annealed for 20h at 350°C without polishing; (b) pre-annealed for 20h at 350°C followed by polishing with 1200 SiC.

Table 8-2 Average isothermal crystallisation times and eutectic crystal growth rates for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350 C followed by polishing with 1200 SiC, during subsequent isothermal crystallisation at temperatures in the range 381 to 396 C

Crystallisation Temperature	Average Crystal- lisation time t _c	Crystal growth rate G
(C)	(s)	(nm/s)
381	5240	3.0
384	4410	3.6
387	3600	4.4
390	2730	5.9
393	2250	7.1
396	1650	9.7

shows the eutectic crystal growth rates in Table 8-2 on an Arrhenius plot of $\ln$ growth rate versus inverse temperature, with good linear behaviour as predicted by equation (8-3). The best fit linear slope to the data in Fig.8-16 gives an activation energy of 3.0 eV/atom, with a correlation coefficient of 0.997, in good agreement with previous measurements of 3.0eV/atom for the activation energy for crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ (12,13). Eutectic crystal growth kinetics are controlled by lateral diffusion ahead of the growing eutectic crystal interface. B diffuses away from growing lamellae of B-deficient fcc (Fe,Ni), to head the growth of adjacent lamellae of B-rich orthorhombic (Fe,Ni)₃B; at the same time, Fe and Ni diffuse in the reverse direction, away from growing lamellae of Fe- and Ni-deficient orthorhombic (Fe,Ni)₃B, to head the growth of adjacent lamellae of Fe- and Ni-rich fcc (Fe,Ni). As expected from this model of eutectic crystal growth, the value of 3.0eV/atom measured from Fig.8-16 for the activation energy for eutectic crystal growth in amorphous Fe₄₀Ni₄₀B₂₀ is intermediate between previous activation energy measurements of 3.0 - 3.6eV/atom for diffusion of B and 2.0 - 2.4eV/atom for diffusion of Fe in Fe₄₀Ni₄₀B₂₀ (14-20). Experimental and theoretical aspects of the eutectic crystal growth mechanism in amorphous Fe₄₀Ni₄₀B₂₀ are discussed in detail elsewhere (21).

No incubation time is detected for the onset of accelerated crystallisation over the temperature range 381-396 C, indicating that a given number of surface crystal nuclei are in existence at time $t = 0$. The density of nuclei per unit area of surface was measured from TEM micrographs such as Fig.8-14, giving a value of $\sim 10^{13}/\text{m}^2$.

8.4.1.2 Bulk nucleation and equiaxed growth

After pre-annealing for 20h at 350 C with no surface polishing, amorphous Fe₄₀Ni₄₀B₂₀ exhibits the slower crystallisation behaviour, which

is typified by the DSC traces in Fig.8-8(b), optical micrographs in Figs.8-10(a) and 8-11(a), and TEM micrographs in Fig.8-13. On heating to a temperature in the range 381-396 C, crystallisation begins immediately with randomly distributed bulk nucleation of eutectic crystals of orthorhombic $(\text{Fe,Ni})_3\text{B}$ and fcc (Fe,Ni) . The eutectic crystals grow with a near-spherical, equiaxed morphology, and the crystallisation process is characterised by a conventional near-Gaussian exothermic DSC peak.

This type of crystallisation behaviour is found in as-supplied amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, and after pre-annealing alone, surface polishing alone, or surface polishing followed by pre-annealing. Fig.8-15(b) shows a typical integrated crystallisation curve from one of the isothermal DSC traces in Fig.8-8(b), with a characteristic sigmoidal shape instead of the linear kinetics shown in Fig.8-15(a). The crystalline volume fraction increases slowly at first, then more rapidly, then slowly again.

The overall kinetics of this type of crystallisation can be expressed by the Johnson-Mehl-Avrami equation (22):

$$Y = 1 - \exp(-Kt^n) \quad (8-4)$$

where K is a thermally-activated rate constant which depends on the crystal nucleation and growth rates, and n is the Avrami exponent which depends on the crystallisation mechanism. The Johnson-Mehl-Avrami equation (8-4) can be rewritten as:

$$\ln\{-\ln(1-Y)\} = \ln K + n \ln t \quad (8-5)$$

so that the rate constant and Avrami exponent can be calculated by plotting $\ln\{-\ln(1-Y)\}$ versus $\ln t$. As shown in Fig.8-17, the isothermal DSC crystallisation curves in Fig.8-8 are in good agreement with the Johnson-Mehl-Avrami kinetics of equations (8-4) and (8-5), exhibiting linear behaviour when re-plotted as $\ln\{-\ln(1-Y)\}$ versus $\ln t$. Over the temperature range 387 to 396 C, the resulting rate constants and Avrami

exponents are in the range $1.3 \times 10^{-11} \text{ s}^{-3}$ - $10 \times 10^{-11} \text{ s}^{-3}$ and 2.97 to 3.13 respectively, as shown in Table 8-3. Values of Avrami exponent near to 3 indicate that a given number of bulk nuclei are in existence at time $t = 0$, and that crystallisation takes place by near-spherical three dimensional growth of these nuclei at a constant rate (22,23). This agrees well with the isothermal DSC curves in Fig.8-8(b), which show no detectable incubation times for the onset of crystallisation over the temperature range 381 - 396 C. From optical micrographs such as Fig.8-10(a), the average separation of nuclei was $\sim 25\mu\text{m}$, corresponding to a volume density of bulk crystal nuclei of $7 \times 10^{13}/\text{m}^3$. Johnson-Mehl-Avrami kinetics with a fixed number of nuclei, constant three-dimensioned growth rate, and Avrami exponent of ~ 3 have also been reported for other Fe-based amorphous alloys such as Fe80B20 (24).

With near-spherical eutectic crystals as shown in the optical and electron micrographs in Figs.8-10, 8-11 and 8-14, the rate constant in the Johnson-Mehl-Avrami equation can be rewritten as

$$K = (4\pi/3)G^3 N \quad (8-6)$$

where N is the volume density of the bulk crystal nuclei. Eutectic crystal growth rates calculated from equation (8-6), using the measured rate constants in Table 3 and taking $N = 7 \times 10^{13}/\text{m}^3$, are in the range 3-7 nm/s over the temperature range 387-396 C, as shown in Table 8-3. Allowing for the experimental errors in measuring bulk nucleation density, the measured growth rates in Table 8-3 for bulk nucleated eutectic crystals are in good agreement with the measured growth rates in Table 8-2 for surface nucleated eutectic crystals during accelerated crystallisation. The Arrhenius variation of $\ln$ growth rate versus inverse temperature for bulk nucleated eutectic crystals is also plotted in Fig.8-16, yielding an activation energy of 3.0 eV/atom with a correlation coefficient of 0.998, in good

Table 8-3 Crystallisation rate constants, Avrami exponents and eutectic crystal growth rates for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350 C, during subsequent isothermal crystallisation at temperatures in the range 387 to 396 C

Crystallisation temperature (C)	Rate constant K (10 ^{-11 s⁻³})	Avrami exponent n	Crystal growth rate G (nm/s)
387	1.3	2.97	3.5
390	2.5	3.03	4.4
393	5.7	3.05	5.8
396	10	3.13	7.0

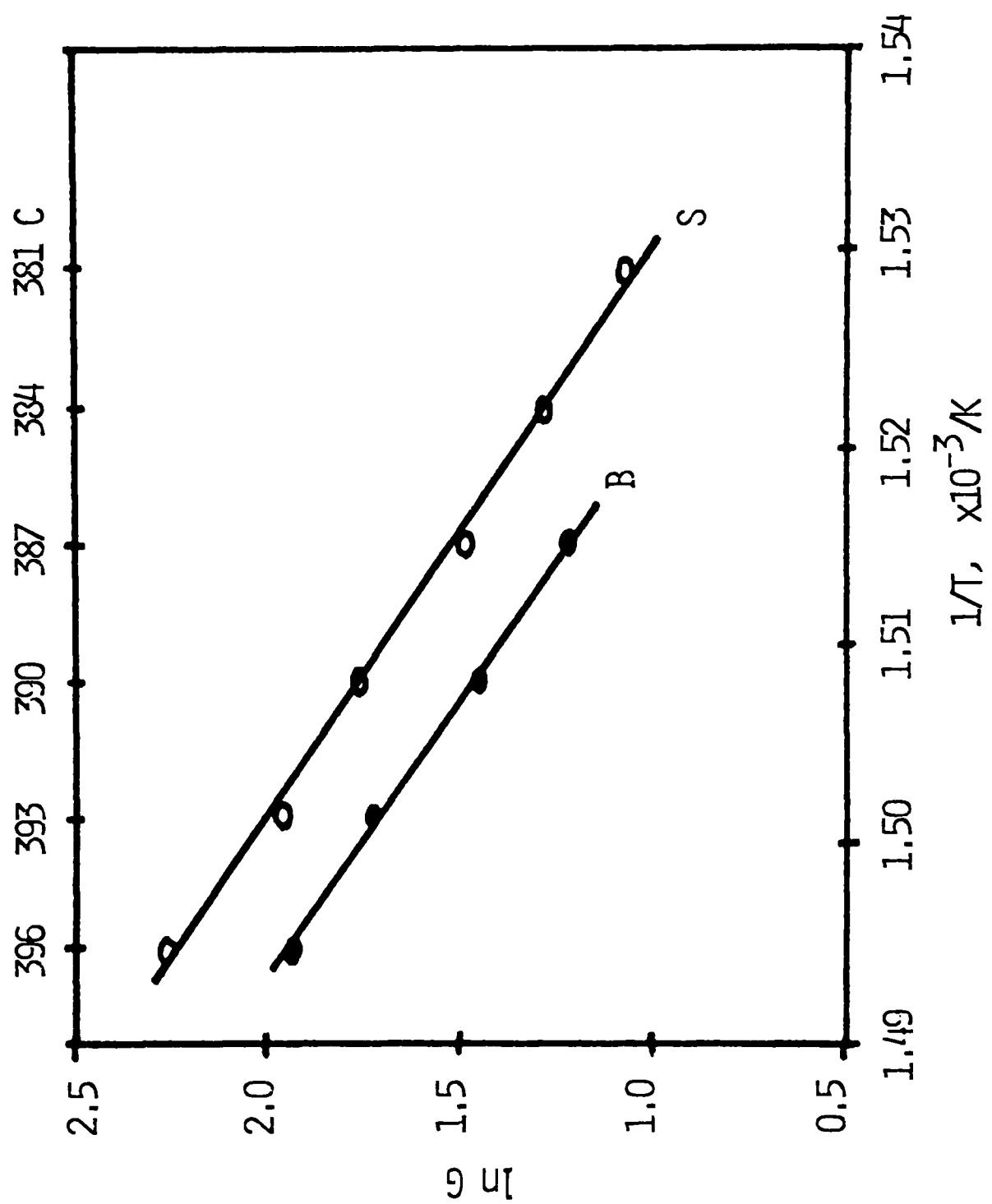


Fig.8-16 Arrhenius variation of $\ln G$ versus $1/T$ for crystallisation of amorphous $Fe_{40}Ni_{40}B_{20}$: B - samples pre-annealed for 20h at $350^{\circ}C$, corresponding to bulk crystallisation; S - samples pre-annealed for 20h at $350^{\circ}C$ followed by mechanical polishing with 1200 SiC, corresponding to surface crystallisation.

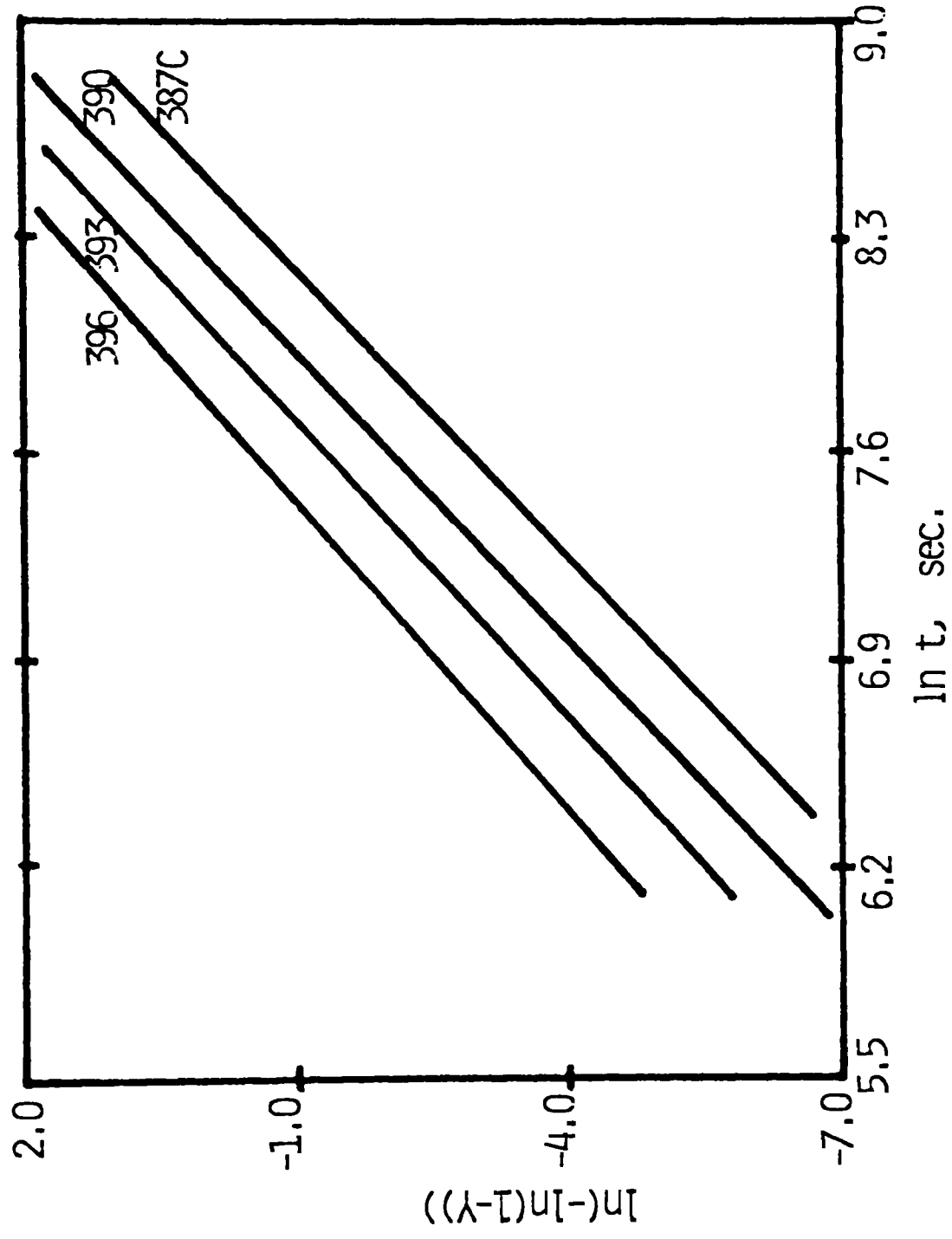


Fig.8-17 Avrami plots of $\ln\{-\ln(1-Y)\}$ versus $\ln t$ for amorphous Fe₄₀Ni₄₀B₂₀ pre-annealed for 20h at 350°C without polishing, over the range of crystallisation temperatures 387 - 396°C.

agreement with the measured activation energy for surface nucleated eutectic crystal growth, and with previous measurements of the activation energy for crystallisation of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (12,13). These results indicate that, although the nucleation mechanisms and overall crystallisation kinetics are different, the individual eutectic crystal growth rates are similar for both types of crystallisation process.

8.4.2 Surface nucleation mechanism

The present experimental results for the crystallisation behaviour of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ after various combinations of pre-annealing and surface treatments indicate that some factors which have previously been suggested as causes of surface crystallisation can be ruled out:

- (a) Mechanical surface deformation alone does not induce or suppress surface crystallisation, as shown in Fig.8-1.
- (b) Structural relaxation caused by pre-annealing alone does not induce or suppress surface crystallisation, as shown in Fig.8-2.
- (c) Surface oxidation does not induce or suppress surface crystallisation, because different annealing atmospheres do not affect the crystallisation behaviour, as shown in Fig.8-7.
- (d) Surface segregation, caused either by selective oxidation or during ribbon manufacture or specimen preparation, does not induce or suppress surface crystallisation, since there is no effect of pre-annealing in air, or mechanical polishing followed by pre-annealing, as shown in Fig.8-1. In addition, the change of crystallisation behaviour caused by mechanical polishing after pre-annealing is independent of which ribbon surface is polished, as shown in Fig.8-9.

The transition from bulk to surface nucleation of the crystallisation process in amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ is clearly caused by a more complex mechanism than either structural relaxation, surface deformation, surface

oxidation, or surface segregation alone. In fact, surface crystallisation can only be induced by certain combination of pre-heat treatment and surface polishing, typically by annealing for 20h at 350 C followed by rough mechanical polishing. In other words, mechanical surface deformation or scratching is only effective in stimulating surface nucleation of crystallisation when the amorphous alloy structure is in a fully relaxed state induced by prior heat treatment. Structural relaxation in amorphous alloys caused by heat treatment below the crystallisation temperature has been studied in some detail in amorphous Fe₄₀Ni₄₀B₂₀ (25-41). Atom probe field ion microscope observation show that the structural relaxation process in heat treated amorphous Fe₄₀Ni₄₀B₂₀ consists of separation into two amorphous phases, leading to a microstructure of B-rich amorphous particles embedded in a B-depleted amorphous matrix (25). The mean diameter of B-rich amorphous particles increases progressively with increasing annealing time, from 1.5 to 4 nm for annealing times from 0.3 to 5h at 350 C. The transition from bulk to surface nucleation of crystallisation in amorphous Fe₄₀Ni₄₀B₂₀, and the associated acceleration of crystallisation rate, take place only in amorphous alloy samples which are pre-annealed and then mechanically polished before crystallisation. As shown in Fig.8-3, the crystallisation rate increases progressively with increasing pre-annealing time from 1 to 5h at 350 C, suggesting that well-developed phase-separated B-rich amorphous particles are a necessary precursor to induce the transition in crystallisation behaviour after surface polishing. Mechanical deformation of structurally relaxed amorphous Fe₄₀Ni₄₀B₂₀ seems to activate the B-rich amorphous particles, producing a high density of embryos for surface nucleation of the subsequent crystallisation process.

8.4.3 The effect of Ni plating and electropolishing

Ni plating and electropolishing have been reported to induce surface crystallisation by enriching the Ni content near the surface of amorphous Fe₃₉Ni₃₉B₂₂ (8,10). The present experimental results indicate that Ni plating alone and Ni plating after pre-annealing for 20h at 350 C both have little effect on the subsequent crystallisation behaviour. However, Ni plating followed by 20h pre-annealing at 350 C accelerates the subsequent crystallisation process, as shown in Fig.8-6. These results suggest that the effect of Ni plating on crystallisation is caused by enrichment of Ni near the amorphous alloy surface, with Ni diffusing into the amorphous alloy from the plated Ni layer during pre-annealing. Electropolishing may have a similar effect on the crystallisation process, with Ni enrichment caused by preferential dissolution of the more electrochemically active element Fe.

8.5. Conclusions

1. The crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀ is not affected significantly by structural relaxation, surface deformation, surface oxidation, or surface segregation alone.

2. Particular combinations of pre-annealing and surface polishing, typically pre-annealing for 20h at 350 C followed by mechanical polishing with 1200 SiC, change the crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀ from bulk nucleation and near-spherical growth to surface nucleation and near-planar inward growth. The overall crystallisation rate is accelerated by the transition to surface nucleation, but the resulting eutectic crystal structure and crystal growth mechanism remain unchanged.

3. Crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ by bulk nucleation and near-spherical growth follows Johnson-Mehl-Avrami kinetics of

$Y = 1 - \exp(-Kt^3)$, indicating that the transformation takes place by the growth of pre-existing bulk nuclei at a constant growth rate. The density of the pre-existing nuclei is $\sim 7 \times 10^{13} \text{ m}^{-3}$. Crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ by surface nucleation and near-planar inward growth follows linear kinetics of $Y = K't$, with a pre-existing surface nucleation density of $\sim 10^{13}/\text{m}^2$.

4. Bulk nucleation and near-spherical growth leads to a equiaxed eutectic crystal structure, consisting of orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni). Surface nucleation and near-planar growth leads to a columnar eutectic crystal structure, again consisting of orthorhombic (Fe,Ni)₃B and fcc (Fe,Ni). Eutectic crystal growth rates are similar for both types of crystallisation mechanism, and show an Arrhenius temperature dependence with an activation energy of $\sim 3.0 \text{ eV/atom}$.

5. Surface nucleation of the crystallisation process in amorphous Fe₄₀Ni₄₀B₂₀ is only induced by mechanical surface deformation when the amorphous alloy structure is in a fully relaxed state caused by prior annealing. Surface nuclei are probably created by deformation of phase-separated B-rich particles in the relaxed amorphous alloy structure.

6. Crystallisation of amorphous Fe₄₀Ni₄₀B₂₀ is also accelerated either by Ni plating followed by pre-annealing, or by heavy electropolishing, probably as a consequence of Ni enrichment at the amorphous alloy surface.

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Chapter 9 Summary and Further Work in Oxidation of Amorphous Alloys

This Chapter first summarises the oxidation behaviours of all the amorphous and crystalline alloys studied in the present work, then discusses the further research which is worth to be conducted in this subject.

9.1 Summary of the oxidation study of amorphous alloys

Eight commercially available amorphous alloys have been studied in the present research programme, including amorphous Fe₇₈Si₉B₁₃, Fe₄₀Ni₄₀B₂₀, Fe₄₀Ni₄₀P₁₄B₆, Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Co₆₆Ni₁Fe₄Si₁₅B₁₄, Co₇₆Fe₂Mn₄Si₆B₁₂, Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ and Ni₇₈Si₈B₁₄. A combination of thermogravimetry, optical microscopy, SEM, ATEM, EPMA, X-ray diffractometry and DSC has been used to investigate the oxidation kinetics, oxide structure and oxide composition. ATEM has been used extensively to study the microstructure and microcomposition of the thin oxide scales and oxidised metal foils. Pre-crystallised alloys with compositions identical to the amorphous alloys have been investigated to study the effect of alloy structure on the oxidation behaviour. A conventional industrial crystalline silicon steel Fe₉₄Si₆ has also been tested for comparison. Special attention has been paid to understanding the oxide nucleation and growth mechanisms during oxidation of amorphous and crystalline alloys.

Although the oxidation behaviours of the tested amorphous and crystalline alloys are quite different, some general conclusions can be drawn from the present research:

1. General oxidation kinetics for amorphous alloys

All the amorphous alloys obey a parabolic oxidation rate law in certain temperature range before crystallisation takes place.

2. Oxidation resistance - the effect of chemical composition and amorphous structure

The oxidation mass gains versus oxidation time at the temperatures of (a) 300, (b) 350 and (c) 400 C for all the amorphous alloys tested in the present work are shown in Fig.9-1, 9-2 and 9-3. The oxidation reaction rates were found to be quite different for these alloys, exhibiting the effects of chemical compositions and amorphous structures on the oxidation resistance. At 300 C, all the alloys remain amorphous during oxidation, and the difference of mass gains^{is} mainly caused by the chemical composition of the alloys. The oxidation resistance at 300 C in air follows the order: Fe₄₀Ni₄₀P₁₄B₆ < Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ < Fe₄₀Ni₄₀B₂₀ < Fe₇₈Si₉B₁₃ < Ni₉₂Si₅B₃ < Fe₃₂Ni₃₆Cr₁₄P₁₂B₆, with mass gains of 68ug/cm² for amorphous Fe₄₀Ni₄₀P₁₄B₆ after oxidation for 500h at 300 C (Fig.9-1). At 350 C, the oxidation resistance order is:

Fe₄₀Ni₄₀P₁₄B₆ < Fe₉₄Si₆ < Co₆₆Fe₄Ni₁Si₁₅B₁₄ < Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ < Co₇₆MnFe₂Si₆B₁₂ < Fe₄₀Ni₄₀B₂₀ < Fe₇₈Si₉B₁₃ < Ni₉₂Si₅B₃ < Fe₃₂Ni₃₆Cr₁₄P₁₂B₆, with mass gains of 80 and ~1.5ug/cm² for amorphous Fe₄₀Ni₄₀P₁₄B₆ and amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ respectively after oxidation for 500h at 350 C (Fig.9-2). At 400 C, the oxidation resistance order is:

Fe₉₄Si₆ < Co₆₆Fe₄Ni₁Si₁₅B₁₄ < Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ < Co₇₆MnFe₂Si₆B₁₂ < Fe₄₀Ni₄₀B₂₀ < Fe₄₀Ni₄₀P₁₄B₆ < Fe₇₈Si₉B₁₃ < Ni₉₂Si₅B₃ < Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ (Fig.9-3). Because crystallisation takes place in some of the amorphous alloys during oxidation annealing, the oxidation resistance was affected by a combination of chemical composition and structure. Like in the ordinary crystalline alloys, Cr is the most effective element to improve oxidation resistance and this is why amorphous Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ has the best oxidation resistance among all the tested amorphous alloys. Si is another beneficial element for oxidation resistance. It forms a SiO₂ layer and

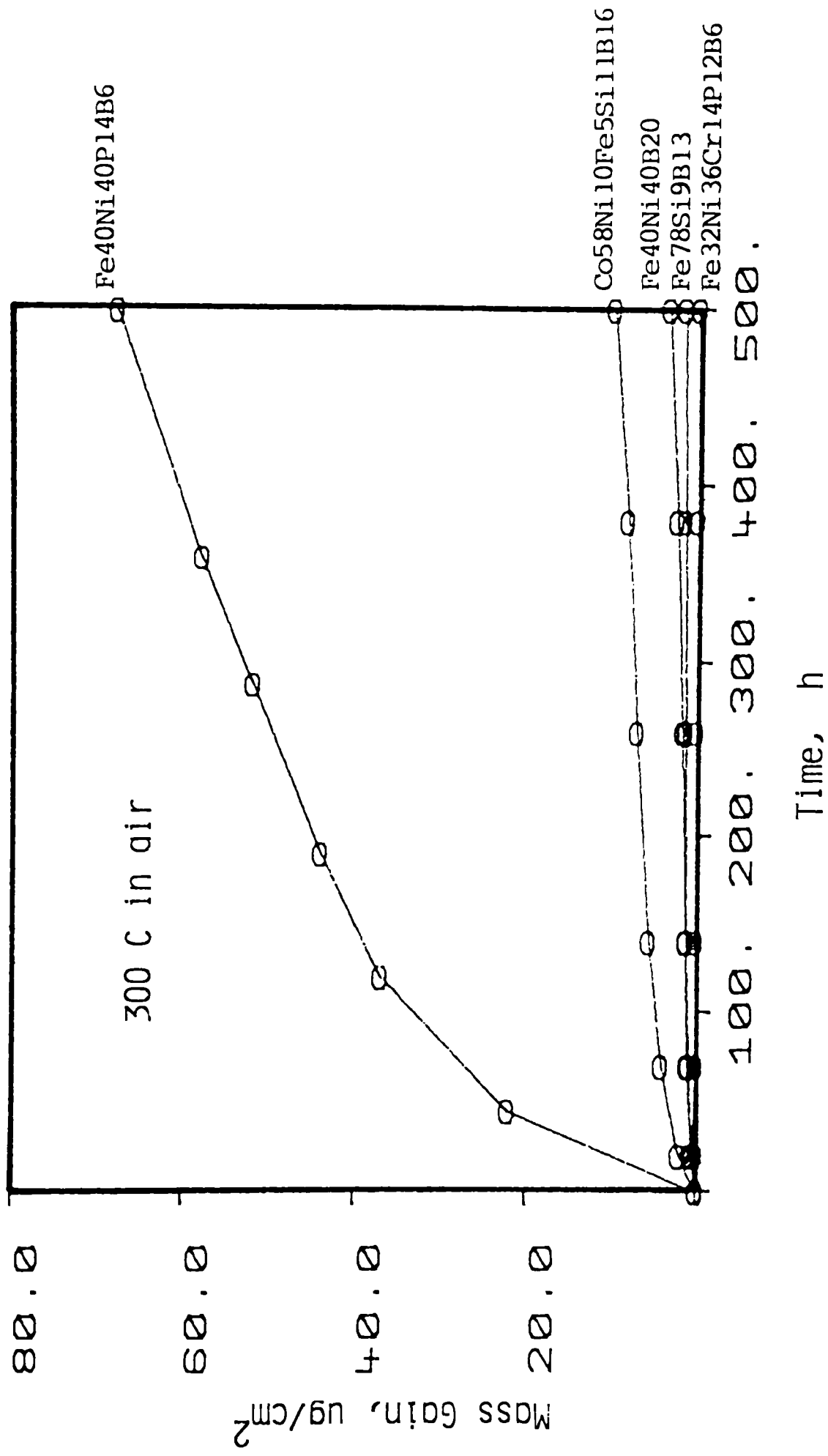


Fig.9-1 Mass gain Y versus oxidation time t at 300°C in air for all the amorphous alloys studied in the present work.

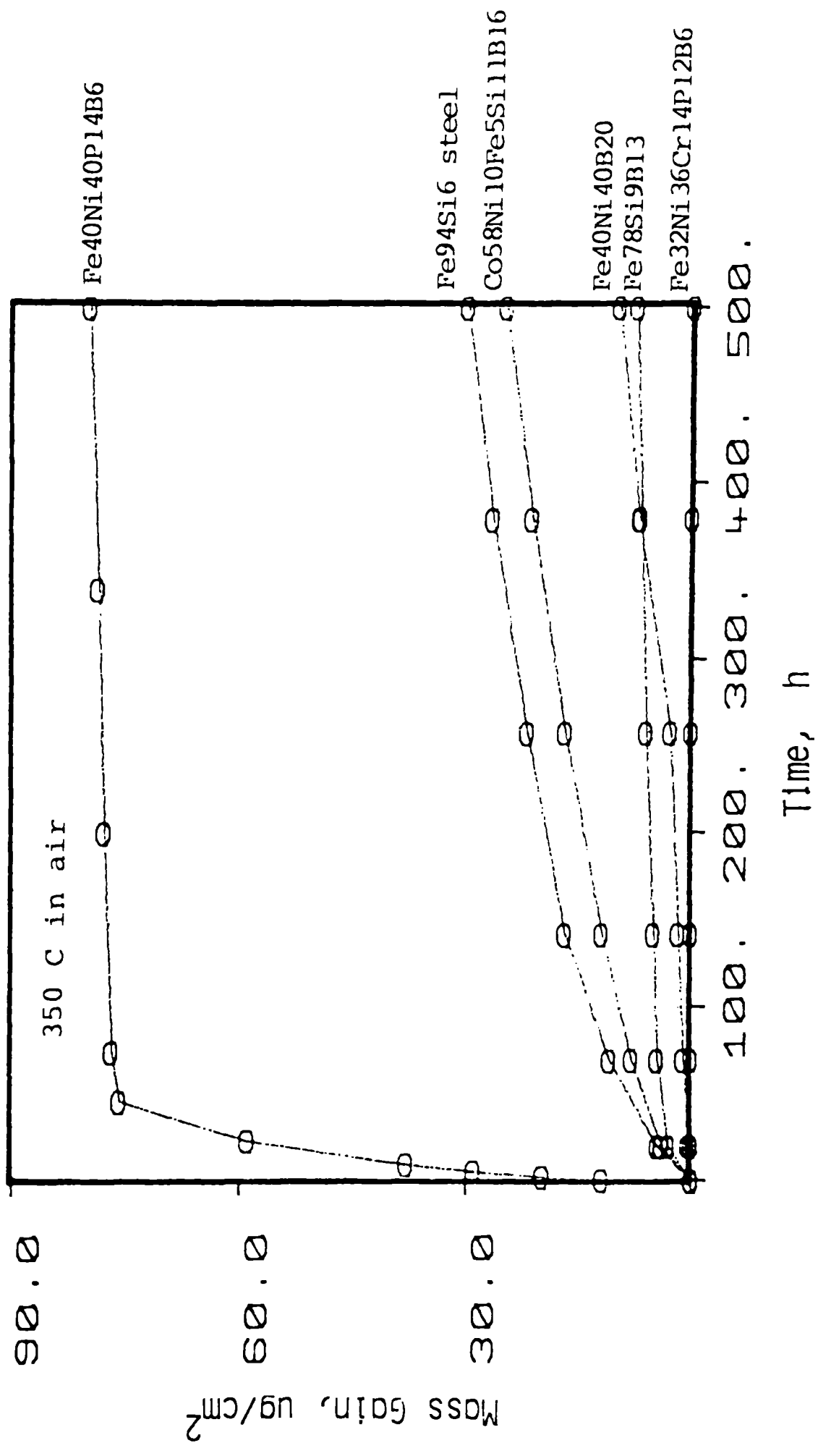


Fig.9-2 Mass gain Y versus oxidation time t at 350°C in air for all the amorphous alloys studied in the present work.

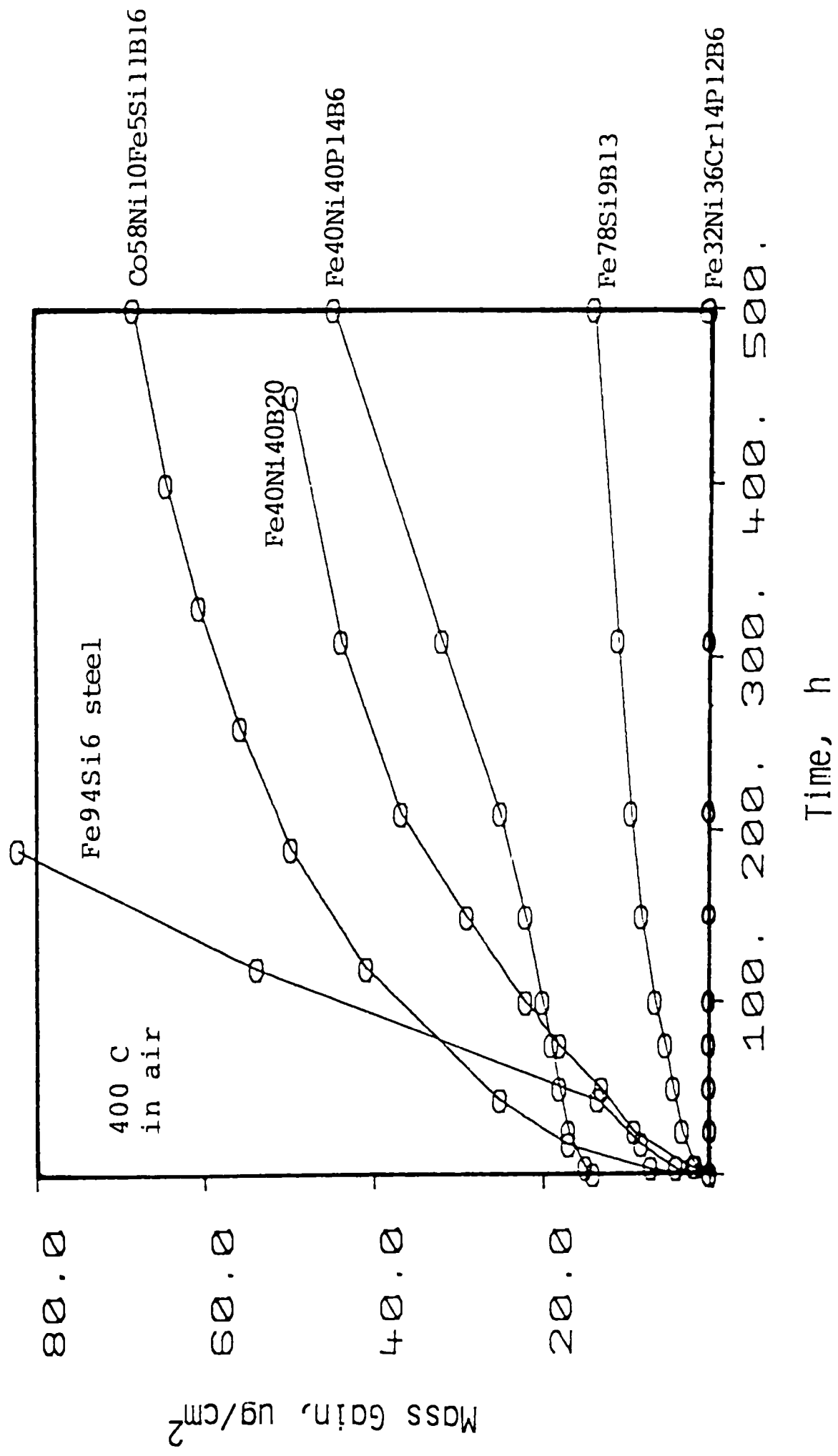


Fig.9-3 Mass gain Y versus oxidation time t at 400°C in air for all the amorphous alloys studied in the present work.

reduces the oxidation rate. This is why amorphous Fe₇₈Si₉B₁₃ has a good oxidation resistance. As for the conventional alloys, Ni based amorphous alloy Ni₉₂Si₅B₃ has a better oxidation resistance than Fe based amorphous alloys.

3. Technical applications

Most of the tested amorphous alloys, except for amorphous Fe₄₀Ni₄₀P₁₄B₆, have a better oxidation resistance than the standard core material oriented silicon steel Fe₉₄Si₆. For instance, amorphous Fe₇₈Si₉B₁₃, which has already found application as a core material for distribution and other transformers, has an oxidation rate 5-10 times smaller than the oriented silicon steel Fe₉₄Si₆ at the temperature range 350-400 C in air, implying that the oxidation degradation is unlikely to be a problem for application of amorphous Fe₇₈Si₉B₁₃ as a core material for transformers.

4. Effect of crystallisation on the oxidation behaviour of amorphous alloys

The oxidation kinetics, oxide growth mechanism and resulting oxide structure change sharply when crystallisation takes place in the amorphous alloy matrix during oxidation annealing. This is proved by comparison oxidation tests of amorphous alloys with the pre-crystallised alloys with identical chemical compositions.

5. Oxidation kinetics of crystallised alloys

Most of the crystallised alloys also obey a parabolic oxidation rate law, with the exceptions of the three crystallised Co based alloys Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Co₆₆Fe₄Ni₁Si₁₅B₁₄ and Co₇₆MnFe₂Si₆B₁₂, which obey a logarithmic rate law in the temperature range 300-400 C. Crystallised Fe₄₀Ni₄₀B₂₀ also obeys a logarithmic rate law at 350 C.

6. Oxidation resistance of amorphous and crystallised alloys with identical chemical composition

Amorphous Fe₇₈Si₉B₁₃ and Fe₄₀Ni₄₀B₂₀ have a better oxidation resistance than the corresponding crystalline alloys, while amorphous Fe₄₀Ni₄₀P₁₄B₆, Co₅₈Ni₁₀Fe₅Si₁₁B₁₆, Co₆₆Fe₄Ni₁Si₁₅B₁₄ and Co₇₆MnFe₂Si₆B₁₂ have a poorer oxidation resistance than the crystalline counterparts. In other words, crystallisation sometimes improves, sometimes degrades the oxidation resistance of amorphous alloys, it seems ^{that there is} no simple rule for the effect of crystallisation on the oxidation behaviour of amorphous alloys.

7. Structure of oxides formed on the amorphous and crystallised alloys:

In general, amorphous and crystallised alloys oxidise to form a complex fine-scale multiphase oxide scale, with an exception of amorphous Fe₄₀Ni₄₀P₁₄B₆, which oxidises to form a fast-growing, whisker-like and thick layer of Fe₂O₃. However, the detailed structures and compositions of the oxide scales formed on the amorphous and crystalline alloys are different. The different structures in the oxide scales formed on amorphous and crystalline alloys are caused by the different oxide growth mechanisms.

8. Oxide growth mechanism

Different oxidation kinetics and oxide growth mechanisms in amorphous and crystallised alloys with identical composition are caused by different microstructures and microchemistry in the alloys. Microsegregation of some elements (eg Si and Fe) in the alloy matrix influences the mechanism of oxide formation, and eventually affects the oxide structure and oxidation kinetics.

9. Ion transportation mechanism in the oxide scales:

Kinetic analysis shows that in most cases ion diffusion through fast transport paths such as grain boundaries and dislocations in the oxide

scale is the rate controlling process for oxide growth on amorphous and crystallised alloys, instead of the diffusion through the bulk crystal lattice. Because of the complexity of the oxide structures, however, it is difficult to describe the mass transportation mechanisms quantitatively in detail.

9.2 Further work in this subject

1. The effect of surface oxidation on the crystallisation behaviour of amorphous alloys.

In the present work, attention has been paid to the effect of crystallisation on the oxidation behaviour of amorphous alloys. The effect of surface oxidation on the crystallisation behaviour is another important issue relating to the thermal stability of amorphous alloys. There is a general belief based on several reports that surface oxidation itself or surface segregation caused by selective surface oxidation affects the surface crystallisation of amorphous alloys strongly (1-7). However, the experimental results are rather inadequate and confusing. It is not clear that whether the surface oxidation accelerates or depresses surface crystallisation and to what extent the effect is. Our preliminary research showed that surface oxidation had no significant effect on the overall crystallisation kinetics of amorphous Fe₇₈Si₉B₁₃, Fe₄₀Ni₄₀P₁₄B₆, Fe₄₀Ni₄₀B₂₀ and Co₅₈Ni₁₀Fe₅Si₁₁B₁₆ (8). Another important factor is that certain combination of surface deformation and pre-annealing has remarkable effects on the crystallisation behaviour of amorphous Fe₄₀Ni₄₀B₂₀, as described in Chapter 8. Is this true for other amorphous alloys? More research is needed for better understanding these effects.

of

2. The effect of surface oxidation and surface crystallisation on the magnetic properties of amorphous alloys.

Because the most important application of amorphous alloys is for ferromagnetic materials, the effects of surface oxidation and surface crystallisation on the magnetic properties are essential. Our preliminary study showed that surface oxidation affected the coercivity of amorphous Fe₇₈Si₉B₁₃, but not for amorphous Co₅₈Ni₁₀Fe₅Si₁₁B₁₆. Amorphous Fe₄₀Ni₄₀B₂₀ with partial surface crystallisation and partial bulk crystallisation had different shaped hysteresis loops and coercivities (9).

Further investigations in these topics are interesting and of technological importance.

3. Detailed studies of the growth mechanism of oxide whiskers.

There are conflict ideas for the growth mechanism of oxide whiskers (see section 2.2.3). Previous research suggested that the whiskers are "hollow tubes" and the matter is transported through the hollow tubes from the whisker bottom to tip, where the oxidation reaction takes place (10). This seems not true in the present case of amorphous Fe₄₀Ni₄₀P₁₄B₆, where the whiskers have a dimension of 5 x 100 x 2000nm and no evidence of any hollow whiskers. How the matter can be fast transported within such a thin oxide whisker blades remains unclear.

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