

Novel characterization of stress corrosion cracks

Sergio Lozano-Perez

Department of Materials, University of Oxford, Parks Road, OX1 3PH Oxford, UK

sergio.lozano-perez@materials.ox.ac.uk

Abstract. A multi-scale approach to stress corrosion cracking is presented in this paper. It will be shown that the same crack and, more importantly, the crack tip region can be characterized with surface techniques such as NanoSIMS and EBSD and later prepared for TEM or Atom Probe. This will offer a unique insight into the chemistry and microstructure, proving that the right combination of techniques can provide most of the information needed to correctly understand the mechanisms of crack propagation.

1. Introduction

Predicting Stress Corrosion Cracking (SCC) is not an easy task. To date, no one has been able to put forward a theory that can satisfactorily explain all the observed cases of SCC and their characteristics. Without a single “unified” theory, the only way to be sure that any particular alloy is not susceptible to SCC in any particular environment is to obtain actual experimental data. SCC has been traditionally investigated using indirect methods, either because the available techniques did not have enough resolution or because the region of interest (crack tip) was not accessible for higher resolution techniques such as Transmission Electron Microscopy [1, 2] or 3D Atom-Probe [3]. It has not been until recently that modern sample preparation techniques have allowed the characterization of the crack tip area.

In this paper, an ambitious systematic method to examine cracked samples across length scales ranging from millimetres to Angstroms will be presented. Samples have been analyzed at all scales, using leading edge analytical techniques (electron microscopy, 3D Atom-Probe and NanoSIMS) in order to explore the interaction between SCC, chemistry and microstructure. A collection of analytical tools to ensure the reproducibility of experiments has been designed for that purpose. By writing measurement-specific scripts that control the electron microscope acquisition, reproducibility of experimental conditions can be ensured. This way, routinely complex acquisitions have been achieved. Finally, a robust method that enables the processing and interpretation of the large amount of data generated from the experiments has been designed. A great proportion of the data has come from (S)TEM microanalysis, simultaneously acquiring HAADF, EELS and EDX. Multivariate Statistical Analysis (MSA) has been found the perfect tool for this important task and has been implemented into a comprehensive software package, allowing its systematic application to large microanalysis datasets.

This holistic approach has been used to characterize a set of 304 type stainless steel samples, which were tested under simulated pressurized water reactor (PWR) primary water conditions. The results have provided new insights into the cracking mechanisms and will hopefully contribute to

make a major contribution to the fundamental understanding of this challenging and technologically important problem.

2. Material

The material employed in this study is a type 304 Japanese grade stainless steel (SUS304). Type 304 stainless steel is widely used in Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs). The composition of the alloy used is, in weight %: 0.04 C, 0.31 Si, 1.6 Mn, 0.003 P, 0.001 S, 9.2 Ni, 18.3 Cr, < 0.01 Mo and 70.54 Fe. The alloy was solution treated (at 1060 °C for 100 min) and then water-quenched. The specimen was cold-rolled to a reduction of 20% prior to testing. It will be referred as 20% cold work (20% cw).

The SCC test was performed using a 1/2T CT specimen, under constant load and a simulated PWR primary water chemistry (500 ppm B + 2 ppm Li, + 30 cm³-STP/kg-H₂O DH2) at 320 °C. The SCC test lasted 666 h and produced intergranular cracks over 100 µm in length.

3. Methodology

A region containing the cracks was extracted using a spark eroder and mounted in a 10 mm diameter and 4 mm height tube. The surface containing the cross-section was then polished, finishing with 1 µm diamond paste followed by silica suspension. Surface characterization included optical examination, EBSD orientation mapping, Scanning Auger Microscopy and NanoSIMS mapping.

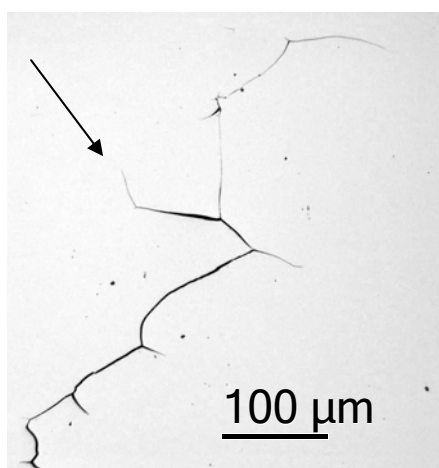


Figure1. Optical micrograph showing the stress corrosion crack and the crack tip selected for NanoSIMS and TEM analysis (arrowed)

Optical examination provided preliminary information on the crack length, crack opening and, in the case of cold work samples, it revealed if the shear bands had been oxidized. In Figure 1, an optical micrograph illustrates the extent of the cracking.

After using EBSD to characterize the grain misorientation in the affected boundaries, all or most of the crack tips were analysed by NanoSIMS [4]. Analyses were performed using a Cameca NanoSIMS 50. A Cs⁺ primary beam, focused to less than 50 nm, was used to sputter negative secondary ions from the sample surface. Secondary ions were mapped on five detectors simultaneously. The ion species analysed were ¹²C⁻, ¹⁶O⁻, ¹¹B¹⁶O₂⁻, ³²S⁻, ⁵⁸Ni⁻, ⁵²Cr¹⁶O⁻, and ⁵⁶Fe¹⁶O⁻, on masses 12, 16, 32, 43, 58, 68 and 72, respectively. NanoSIMS maps from a crack tip are shown in Figure 2. The resolution is enough to separate the iron oxide (magnetite) (in Figure 2a) from the chromium oxide (in Figure 2b). Boron enrichment at the interface between the oxide and the fresh boundary is clearly visible (Figure 2c). If the intensity scale is changed, it can be revealed boron also segregated to the grain boundary (Figure 2d).

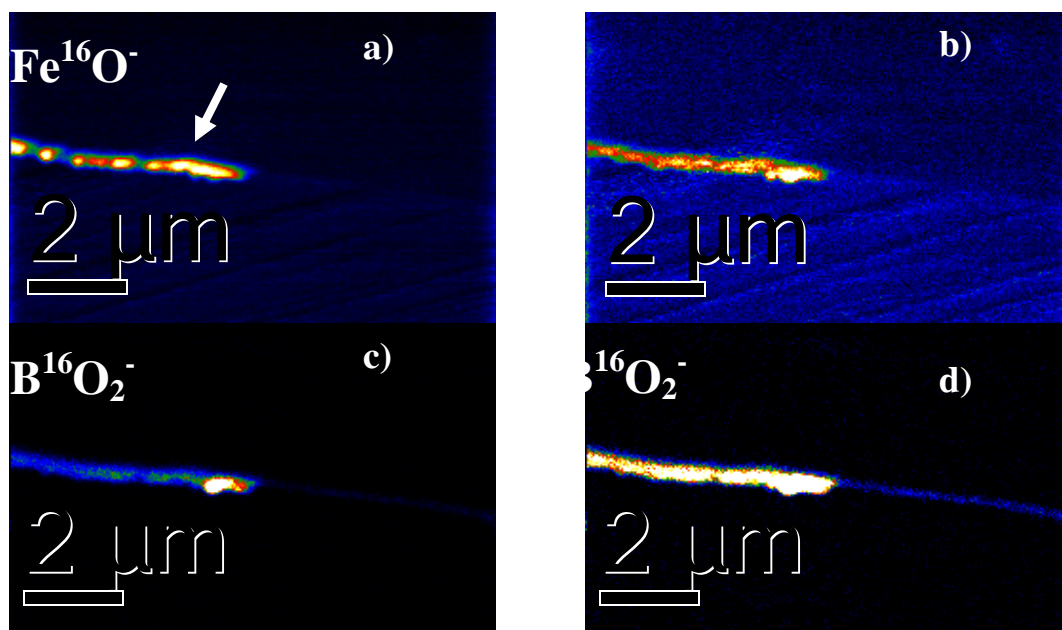


Figure 2. NanoSIMS maps from the region arrowed in Figure 1. The same boron map is shown twice at different intensity scales to reveal the enrichment at crack tip (c) and grain boundary segregation (d)

TEM samples were prepared by FIB, using an FEI 200 equipped with a “home-made” in-situ micromanipulator. In Figure 3a it can be seen how the volume containing the crack tip is lifted from the bulk sample attached to the micromanipulator. After lifting, the samples are welded to the inner rim of a Cu or Mo slot, previously cut into two (see Figure 3b). This method allows as much thinning as required to obtain the desired electron transparency. A thickness of ≈ 50 nm is easily achieved and found optimum for EDX and EELS mapping. The final TEM sample can be seen in Figure 3c.

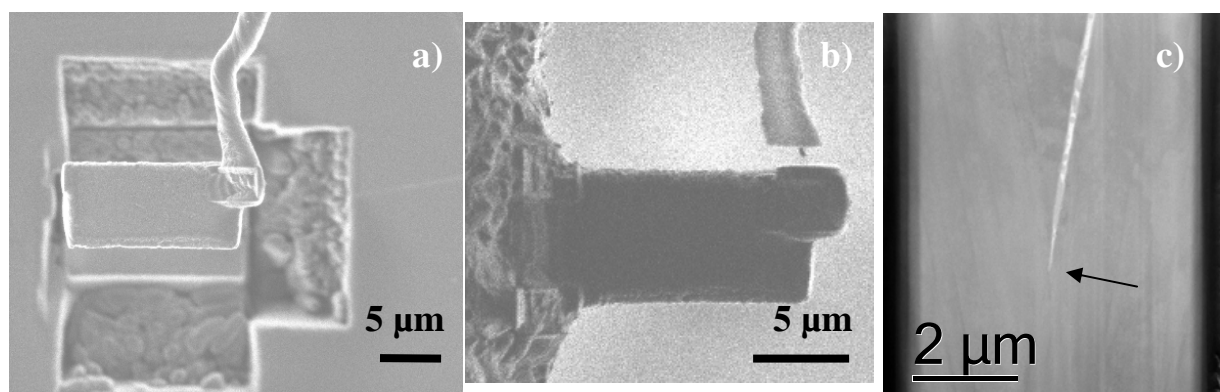


Figure 3. (a) Lifting the volume containing the crack tip with the micromanipulator; (b) Welding it to the support; (c) STEM BF image showing the TEM sample after thinning

(S)TEM examination was performed using a Jeol 3000F operated at 300 kV and a VG HB501 operated at 100 kV. In Figure 3c a STEM HAADF image acquired with the Jeol 3000F is shown to illustrate how the crack tip has been successfully preserved during the sample preparation. The crack was found to be filled by magnetite. The crack tip region was analyzed in more detail using EFTEM, EDX and EELS mapping. In Figure 4, the maps obtained from an EFTEM acquisition (400-800 eV, in steps of 10 eV, using a 10 eV energy slit and a 12.2 mrad half-angle objective aperture) are shown,

together with a Ni map from EDX mapping in the VG HB501. Although some drift occurred in the horizontal direction during the acquisition, the Ni enriched region ahead of the crack tip is clearly visible. In order to minimise the noise all datacubes were processed by multivariate statistical analysis [5] prior to map extractions.

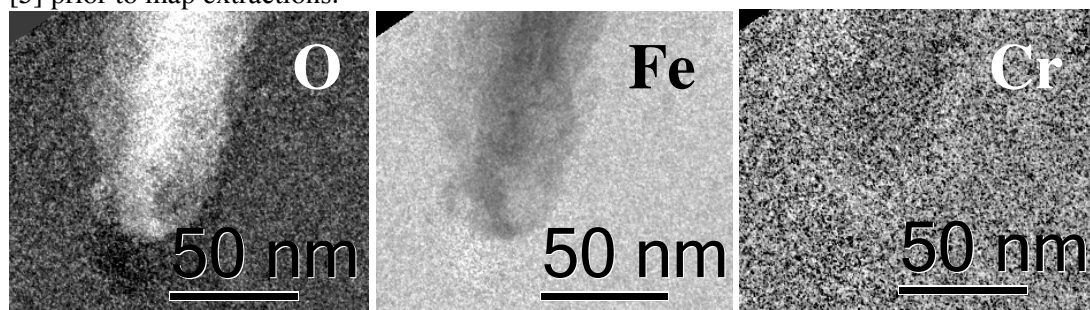


Figure 4. EFTEM maps from the crack tip arrowed in Figures 1 and 2c

4. Discussion and conclusions

The right combination of techniques can provide the right information needed to understand crack propagation in nuclear reactor materials. NanoSIMS has the advantage over TEM that can provide a quick analysis at the resolution needed to understand the oxide structure at the crack tip. Changes are observed when changing sample composition, water chemistry or test temperature. Besides, it allows mapping of minor segregants such as B and S which would be impossible with other techniques.

TEM sample preparation of crack tips is greatly simplified when using an in-situ micromanipulator in an FIB. With a very high yield, it allows the preservation of all key features during the whole thinning process. TEM observation provides information on the exact morphology of the crack tip, and with the aide of high-resolution microanalysis techniques such as EFTEM or EDX SI, it can reveals changes in the local chemistry at a sub-nanometre scale.

With the approach shown in this paper, it is possible to characterize the same crack tip with a comprehensive range of techniques, providing information at an unprecedented level.

References

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