

NanoSIMS によるステンレス鋼の応力腐食割れき裂先端分析の新評価法

Novel Characterization of Stress Corrosion Cracks in Stainless Steels by NanoSIMS

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要約 NanoSIMS による高分解能分析を、ステンレス鋼の粒界型応力腐食割れき裂先端部と接液表面部における元素マッピングに初めて適用し、この分析方法が、ホウ素や硫黄などの微量成分が層状酸化物に対してどのように振舞うかを明確にできるなど、この種の評価に理想的であることを立証した。また、試料準備作業および比較的広範囲の領域を分析するのに要する時間が短くてすむので、NanoSIMS は改善された統計精度で、系統的な腐食のキャラクタリゼーションに最適な手段であり、これにより現実的な時間内でき裂先端部の実用的分析が可能となる。

キーワード 高分解能2次イオン質量分析, ステンレス鋼, 応力腐食割れ, き裂先端, 元素マッピング

Abstract For the first time, high resolution analysis using a NanoSIMS has been used to map the oxide chemistry in intergranular cracks and on the exposed surfaces in stainless steels. The technique has proven ideal for this type of samples, as it is able to discern between the different oxide layers and clarify the role of minor segregants such as boron and sulphur. The short time required to prepare and examine multiple regions makes the NanoSIMS an optimum tool for a systematic corrosion characterization and allows a realistic analysis of all the crack tips in a record time, with improved statistics on the results.

Keywords NanoSIMS, stainless steel, stress corrosion cracking, crack tip, elemental mapping

1. Introduction

Environmentally assisted cracking is one of the least understood and most important degradation phenomena in predicting the safe lifetime of structural steels. The complex interaction of environment, microstructure and mechanical loading requires analysis by a wide range of different techniques in order to obtain a complete picture of the critical processes and mechanisms. In particular, the mechanisms controlling stress corrosion cracking (SCC) and irradiation assisted stress corrosion cracking (IASCC) of austenitic steels and Ni based alloys employed in nuclear reactor components need to be properly understood if reliable predictions of lifetime are to be achieved^[1-4].

ing the detailed morphology and internal structure of cracks in SCC specimens originating from laboratory tests and in samples extracted from operating plants [5-8]. The primary objective of these studies is to gain an improved understanding of the critical phenomena controlling SCC, and have revealed, for example, characteristic narrow oxide-filled cracks in the case of nickel alloys, details of the oxide microstructure, evidence of porosity and details of interaction of cracks with dislocations, defects and precipitates in the surrounding metallic matrix.

It is clear that the characterization of cracks in samples subjected to SCC should provide information at high spatial resolution ($\sim 1-10\text{nm}$) on:

1. Oxide composition, including levels of minor constituents such as B, P and S. These trace

Considerable effort has been placed on characteris-

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impurities are known to have a strong influence on intergranular fracture [9-13]. In particular it is important to obtain composition profiles across the crack flanks and crack tip and in the metal matrix immediately ahead of the crack tip.

2. Oxide structure both at the crack flanks and at the crack tip. Information on oxide porosity, orientation relationships with the surrounding metal matrix, and how the oxide grows with respect to the original grain boundary is also of value. Of importance is also the interaction of any oxide with crystallographic features such as dislocations, deformation bands or twins.
3. Information on the metal matrix containing the crack (s), for example grain orientation, grain boundary parameters, dislocation density in the material adjacent to the crack tip and flank.

A schematic representation of a crack is shown in Figure 1 to illustrate the features described above. It is also important to examine a sufficient number of individual cracks to identify typical behaviour. This has been a particular problem in the past in studies relying heavily on transmission electron microscope (TEM) analysis.

Characterisation of cracks successfully addressing these requirements has come predominantly from studies in modern TEM with the latest analytical capabilities [5,14,15]. Such studies necessarily involve complex and time consuming specimen preparation to obtain electron transparent samples from the crack flank and crack tip. In addition, it is only possible to examine a very restricted region of cracks within the sample. Techniques where a larger volume and more statistically significant number of cracks may be examined have been employed; for example traditional surface characterization methods including scanning electron microscopy (SEM), Scanning Auger Microscopy (SAM) and secondary ion mass spectroscopy (SIMS) [16,16-19]. To date none has been able to demonstrate the required high spatial resolution and high elemental sensitivity

necessary to provide chemical information to compare with that available from the TEM.

In this paper we will describe, for the first time, the benefits of using a Cameca NanoSIMS (secondary ion mass spectrometer) for characterizing stress corrosion cracks, and demonstrate that it has a major role to play, particularly for improved insight into the oxide composition and the influence of crystallographic features on oxide formation.

2. Material

The materials employed in this study are a Type 304 stainless steel (SUS304) and two 304-like alloys that have lower Cr levels but with the levels of other alloying elements chosen to match the original SUS304 composition (12Cr and 15Cr). Type 304 stainless steel (SUS304) is widely used in Pressurised Water Reactors (PWRs) and Boiling Water Reactors (BWRs). The compositions of the alloys used are shown in Table 1. All alloys were solution treated (SUS304 at 1060° C for 100 min and 12Cr and 15Cr alloys at 1100° C for 100min) and then water-quenched. The specimens were cold-rolled to a reduction of 20% prior to testing. They 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 (500ppm B + 2ppm Li, +30cc-STP/kg-H₂O DH₂) at 320° C. The SCC test lasted 666h and produced intergranular cracks over 100 μ m in length. Some samples were fatigued after testing in order to complete the fracture.

3. Methodology

Samples with a suitable geometry for NanoSIMS analysis (9mm diameter and 1mm thick disks) were extracted from the bulk samples using a spark eroder machine. Once mounted in suitable holders, they were polished with 1200 SiC paper, 3 micron diamond paste and finished with silica suspension (with 0.04 μ m average grain size). This was the

Table 1. Chemical content of examined alloys (wt%)

Alloy	Fe	C	Si	Mn	P	S	Ni	Cr	Mo
20% CW SUS304	Bal.	0.04	0.31	1.6	0.003	0.001	9.2	18.3	< 0.01
20% CW 15Cr	Bal.	0.06	0.5	1.5	0.002	0.001	10	15.0	< 0.01
20% CW 12Cr	Bal.	0.06	0.5	1.6	0.002	0.001	9.6	12.0	< 0.01

only sample preparation required for effective analysis of crack and surface chemistry.

In this work, both primary and secondary cracks were examined. A primary or dominant crack is defined as a crack which is growing throughout the test as a result of the applied stress and the corrosive environment. A secondary crack might have been dominant at some point during propagation but it was overrun by another crack, being left behind and exposed to the environment for a longer period of time, mostly under a lower stress than that experienced by the primary crack. These secondary cracks are normally located near triple points and are found filled by magnetite.

Analyses were performed using the Cameca NanoSIMS 50 in the Department of Materials, University of Oxford. A Cs⁺ primary beam, focussed 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. The mass spectrometer was calibrated using pure metallic Ni, Cr, and Fe standards, and tuned to high mass resolution to eliminate any isobaric interference.

The areas containing the features of interest were cleaned prior to examination by scanning a defocused primary beam over the surface for up to 1 hour, depending on the initial surface condition. Images were acquired by scanning a 0.5pA primary beam over areas ranging from 5 to 35 mm square. Image resolutions of 512x512 or 256x256 pixels, with count times of up to 40ms per pixel, were obtained.

Ion induced secondary electron images were acquired concurrently. The octopoles controlling the symmetry of the probe were tuned before each acquisition to ensure a stigmatism-free image. In 8 days of operation, with morning and afternoon sessions, more than 100 regions were analyzed.

In order to assess the value of these observations in the NanoSIMS, a comparison has been made to TEM examination of specimens obtained from the same samples, and also with TEM specimens of equivalent materials examined in previous studies.

4. Results

For each of the alloys shown in Table 1, several cracks and their associated features were analyzed using the NanoSIMS. Both primary and secondary cracks have been analysed. A cross-sectional view of the 20% CW SUS304 sample after testing, cutting and polishing can be seen in Fig. 2. The fatigue pre-crack is at the bottom of the image, oriented vertically. The strain direction was applied perpendicular to this crack, and it is indicated by the arrow. Once the crack region is located using the in-situ CCD camera in the NanoSIMS, the positions of the relevant features (crack tips, triple points, etc) are stored and a series of analysis performed. Up to 15 regions were analyzed per day, enabling the characterization of the most interesting cracks as well as the surface oxides.

4.1 Information from composition mapping

A typical example of the information obtainable in the NanoSIMS is shown in Fig. 3. In this figure, major

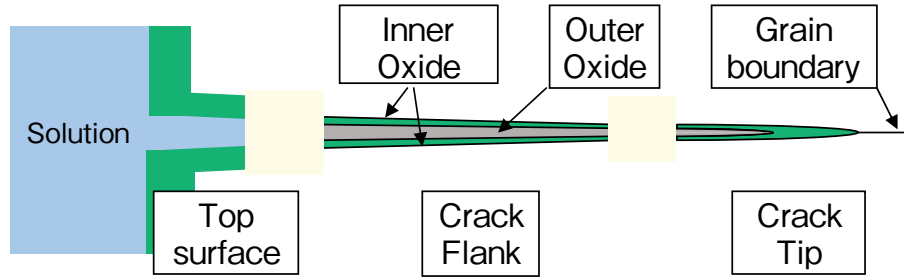


Fig. 1: Schematic representation of a Stress Corrosion crack and its representative features.

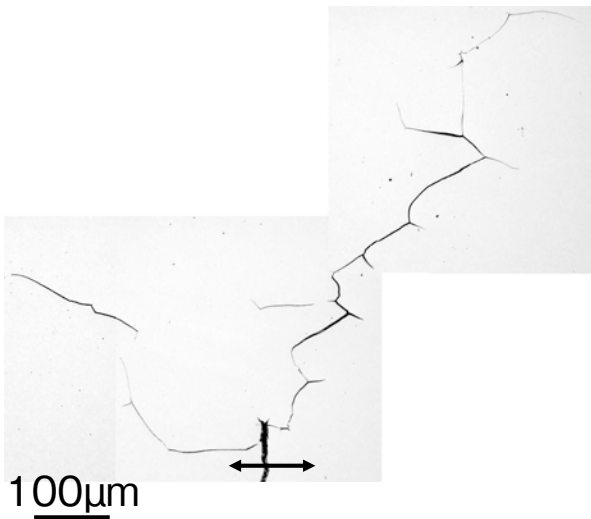


Fig. 2. Optical micrograph showing a bifurcated stress corrosion crack in a 20% CW SUS304 sample after the test. The wider crack at the bottom of the image is the fatigue pre-crack lying perpendicular to the strain direction (indicated by the arrow).

element distribution in the oxide formed on the flanks of a secondary crack in the 20% CW 12Cr alloy are shown. The oxides found always consist of an inner Cr-rich layer and an outer Fe rich oxide which tends to fill the crack as it opens (see Fig 1 for definition of inner and outer). This observation is in agreement with previous work, showing a double oxide layer in similarly tested 304 alloys^[15,20]. In Fig. 4, results from a STEM observations of a similar sample are shown. The Dark-Field (DF) STEM image shows a portion of a secondary crack, which was found to be filled by oxides. Interpretation of the structure is easier with the aid of EDX elemental maps, which are also shown in Fig. 4. It can be seen that the inner oxide layer is Cr-rich (depleted in Fe but not in Cr), and the outer is formed by Fe-rich

oxide crystals. From electron diffraction data it has been established that the inner layer is Cr rich spinel and that the outer oxide is magnetite. The Ni levels in the oxides have also been shown to be lower than the original metallic bulk level. The linear features intersecting the crack are discussed below.

Fig. 5 shows the NanoSIMS mapping of major elements in the oxide formed at crack tip region in a primary crack in the 20% CW 12Cr sample. In this case a Cr-rich oxide can be seen on the right hand side of the crack tip and an Fe-rich oxide is seen on the left hand side of the crack. Regions depleted in Ni can be observed where the Cr-rich oxide has formed and rejected nickel accumulates around it. Again linear features intersecting the crack flank are visible.

The NanoSIMS can also be a powerful tool for the study of trace element distributions around cracks because of the very high sensitivity of SIMS analysis for many impurities in steel samples. A NanoSIMS line profile across the Cr-rich oxide layer of the flank of the fatigue pre-crack in the 20% CW SUS304alloy is presented in Fig. 6 to illustrate the detection of minor constituents of the oxide. Line profiles were measured directly from the ion images, which were acquired using 10ms/pixel and a current of 7.9nA. All profiles have been normalized in order to account for the different yields. Boron is enriched at the original sample interface, while S seems to stay at the outside, probably as an impurity from the sample preparation process. No traces of B could be found by EDX or EELS analysis in the TEM samples extracted from the crack tip region of a secondary

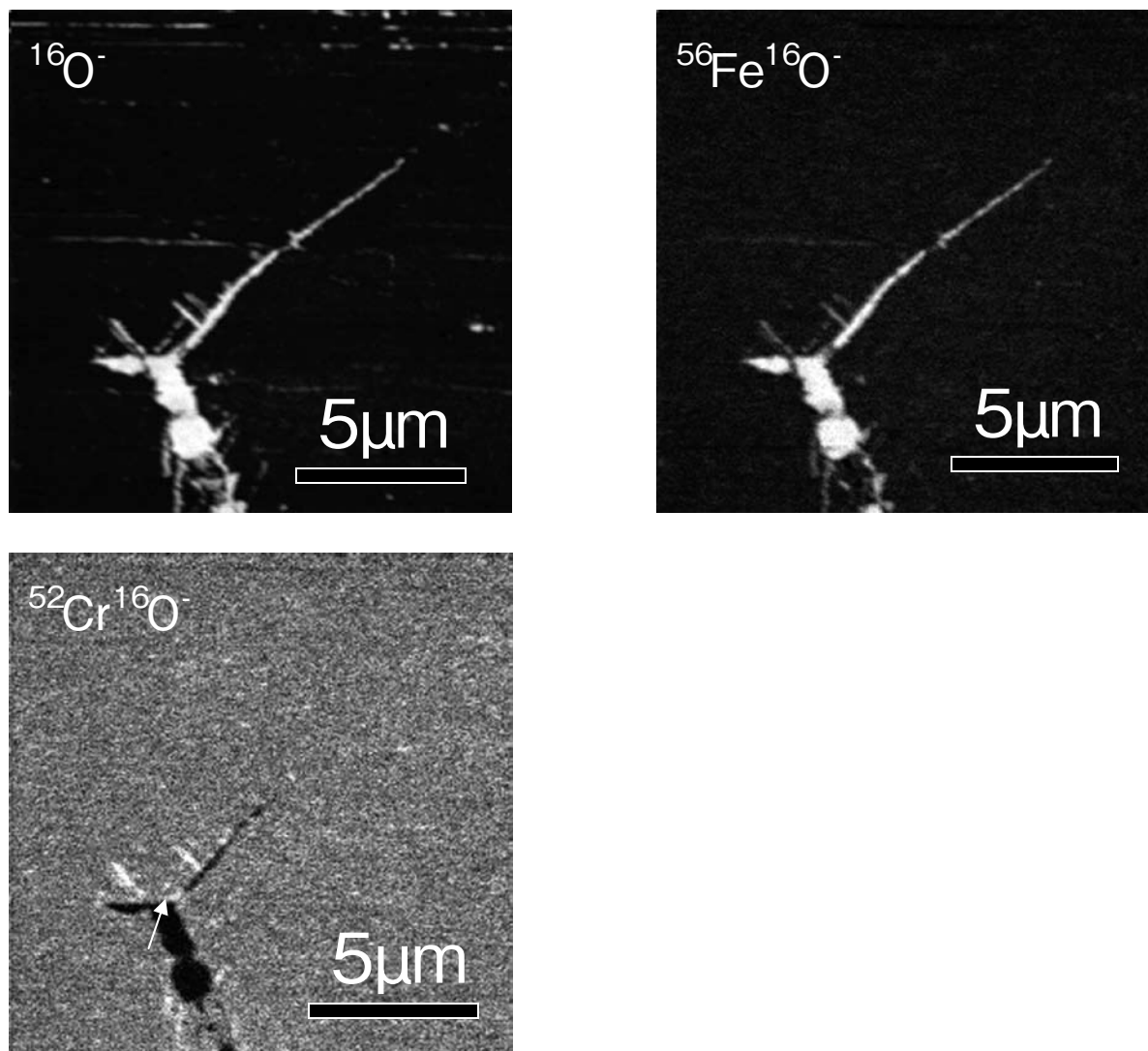


Fig. 3. NanoSIMS maps from a secondary crack in the 20% CW 12Cr sample.

crack in the 20% CW 15Cr alloy. In addition, in regions of the crack flank, where B was observed in the NanoSIMS (with a SNR of ~ 25), no B was detected in the Scanning Auger Microscope.

4.2 Oxide interaction with the crystallographic features in the matrix.

The NanoSIMS cannot provide data (other than composition) that allows the structure of the oxides to be identified, although this can be provided by conventional TEM techniques. However, it has been found in this study that the ability to characterise extensive regions of crack flanks and a number of crack tips in several samples enables information to

be obtained in a systematic manner on the influence of pre-existing crystallographic features in the metal matrix on subsequent oxide formation.

In Fig. 7 deformation along slip bands in the grain interiors can be seen as a result of the slight etching caused by the silica polishing in the 20% CW 15 Cr alloy. NanoSIMS images of similar regions in the 20% CW 12Cr alloy are shown in Fig. 8. It is clear that the enhanced contrast next to the crack flank is actually due to formation of a Cr-rich oxide along these deformation bands. It can also be seen that there the oxide contains Fe but that, as expected, Ni levels are reduced (since it is rejected by the formation of Cr-rich oxide). It is also obvious that

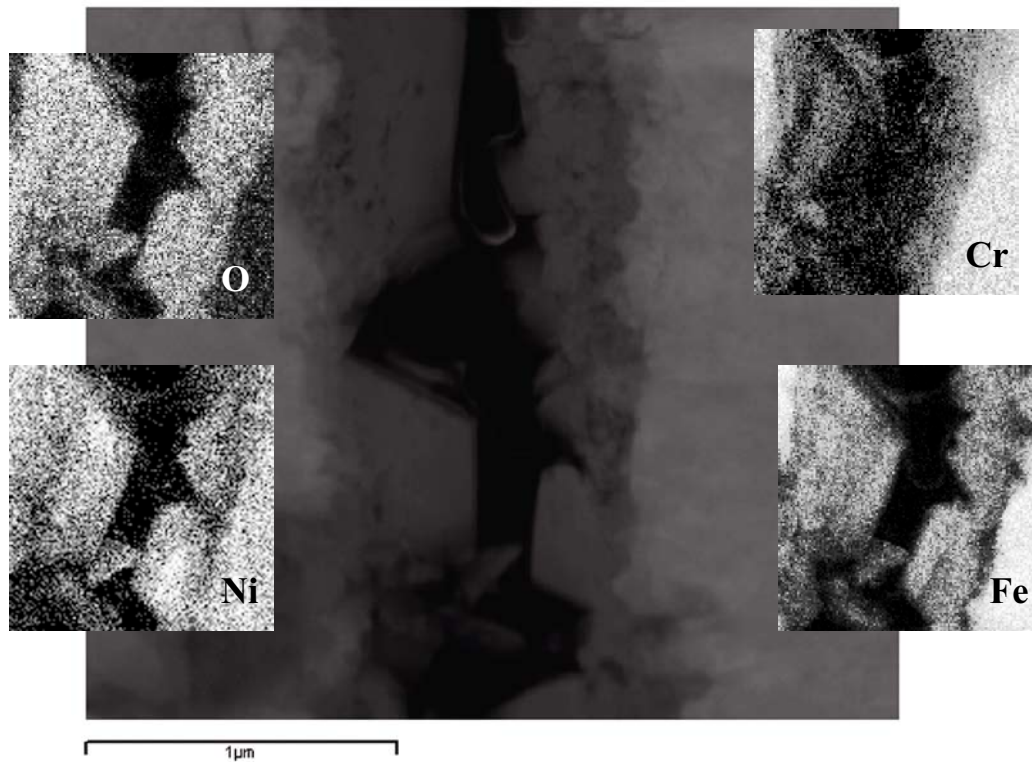


Fig. 4. DF STEM image showing a secondary crack flank in a SUS304 sample (without CW). On the sides, STEM EDX elemental maps are shown for O, Cr, Ni and Fe.

each grain oxidises differently.

Observations from the NanoSIMS have also enabled preliminary interpretations on how the oxide at a crack tip forms in relation to the grain boundary chemistry. In Fig. 9, a dominant crack tip has been analyzed in the 20% CW SUS304 alloy and some line profiles have been measured from the crack tip region along the continuing grain boundary. Both $^{56}\text{Fe}^{16}\text{O}^-$ and $^{11}\text{B}^{16}\text{O}_2^-$ maps are shown to aid the interpretation. The $^{11}\text{B}^{16}\text{O}_2^-$ map is very useful as it shows B segregation to the grain boundary, thus enabling its location in the matrix to be determined at the same time as studying the crack and grain boundary chemistry. It can also be seen that oxidation occurs preferentially on the bottom grain, possibly due to its more favourable crystallographic orientation.

5. Discussion and conclusions

The high lateral resolution of the NanoSIMS together with the high chemical sensitivity to certain elements means that it can be an important new tool in establishing a multi-scale approach to the study of stress corrosion cracks in steels. The benefits of applying the NanoSIMS are:

1. Ease of sample preparation. It has to be emphasised that the elaborate preparation techniques necessary for TEM or Atom Probe analysis are not required for NanoSIMS, making the analysis quick and easy to perform
2. A lateral spatial resolution of less than 50nm for the major elements found in the oxides associated with cracks
3. Ability to detect both major elements (Cr, Fe and Ni) and also minor elements such as S, P and B. It is to be noted that S and B segregation in these samples could not be detected using TEM

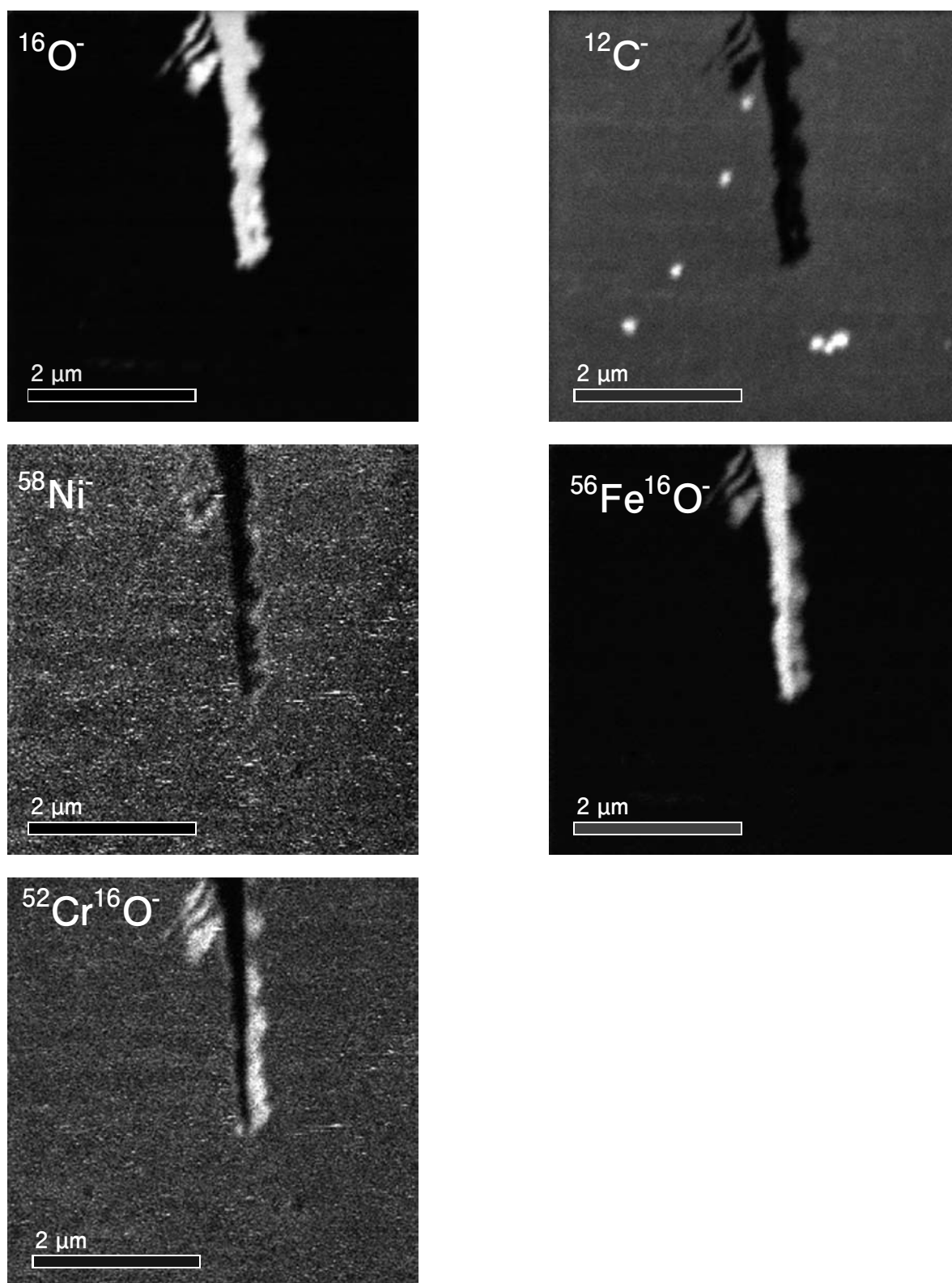


Fig. 5. NanoSIMS maps showing the crack tip region in the 20% CW 12Cr sample.

or SAM.

The major disadvantage is that the necessary calibrations for the yield of the elements of interest in

a steel matrix have not been performed in the NanoSIMS, preventing the acquisition of truly quantitative data at this stage. All the data shown in this work is thus qualitative. Several random grain

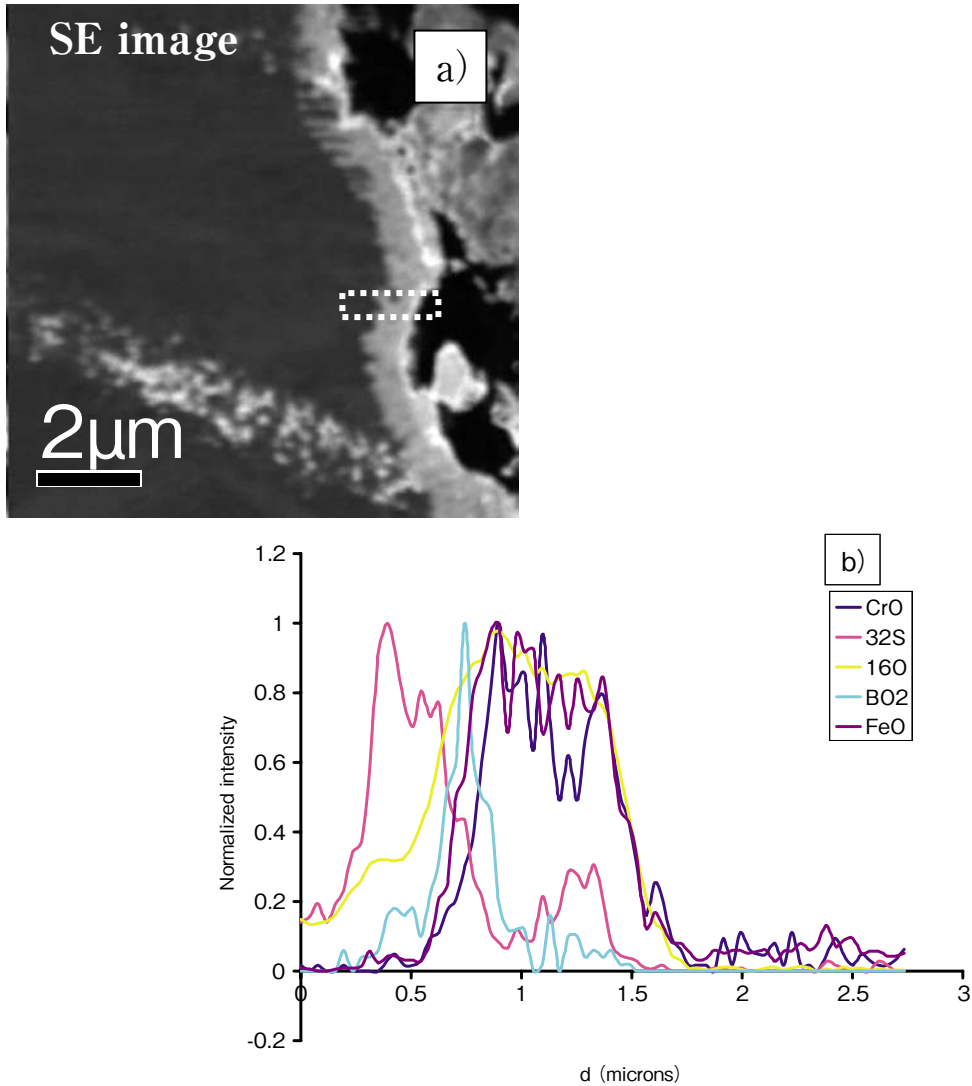


Fig. 6 Detail of surface oxidation in the 20% CW SUS304 sample. (a) SE image showing position of line profile (b) NanoSIMS line profile results (normalized to unity).

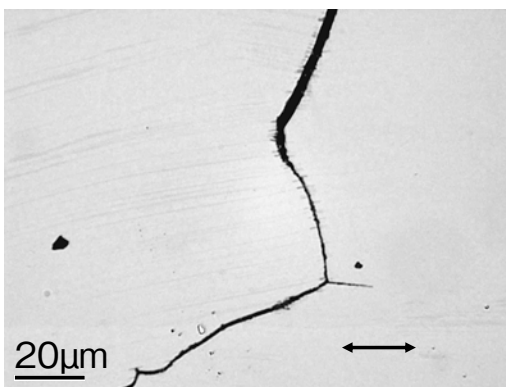


Fig. 7. Optical micrograph showing a portion of a SC crack in the 20% CW 15Cr alloy. Deformation bands along slip directions can be seen as a result of the slight etching caused by the silica polishing. The arrow represents the strain direction.

boundaries were analyzed in the bulk (a few mm far from the cracked region) in order to confirm the observed B segregation to grain boundaries. A similar B enrichment was observed. Due to the high yield of B, NanoSIMS is able concentrations of the order of ppm. As mentioned before, no B was observed at boundaries with any of the other techniques, so its enrichment is expected to be well below 1 at% .

Critically, in a typical experimental campaign on the NanoSIMS a significant number of cracks can be examined. This has two benefits; firstly the oxide structures in different cracks can be compared and 'typical behaviour' established, and secondly, re-

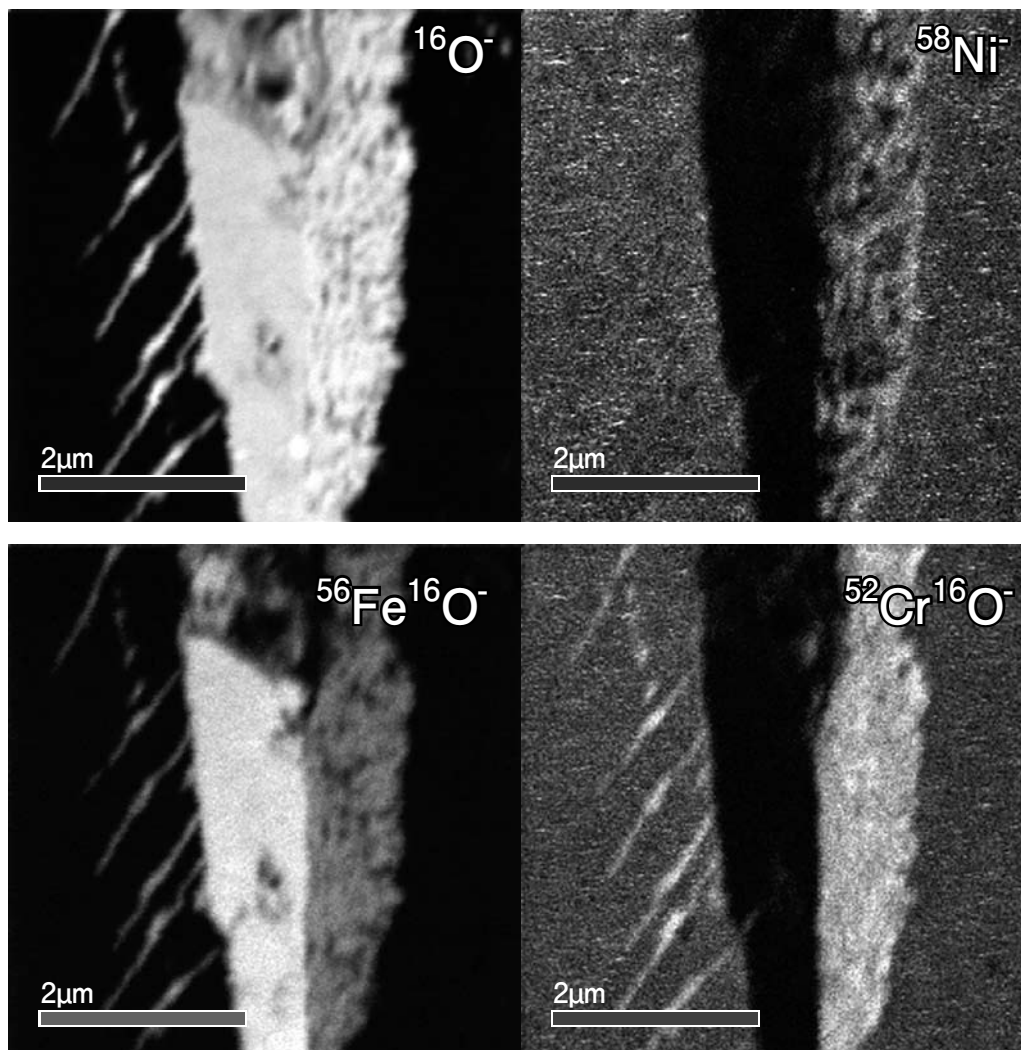


Fig 8. NanoSIMS maps showing the dominant crack in the 20% CW 12Cr sample.

gions for subsequent examination in the TEM or 3DAP can be identified. The latter enables these higher resolution techniques, which involve time-consuming specimen preparation, to be focussed on the critical regions.

A detailed analysis of the crack flank and crack tip region has provided very important information. Firstly, the results agree with previously reported observations of a dual oxide layer consisting of an inner Cr-rich oxide layer and an outer Fe-rich oxide layer (see Fig. 4) [15,16,20]. Second, it has been possible to observe oxide penetrating along crystallographic deformation bands into the adjacent grain. This observation has not been found in the literature and more detailed analysis of the relation between oxide formation along deformation bands and surrounding

grains microstructure is being performed. These observations might have important implications on the mechanisms of crack propagation and are currently being investigated into more detail.

In conclusion, the high lateral and mass resolution together with the high sensitivity of the NanoSIMS provide a unique tool for the extensive investigation of stress corrosion cracks in stainless steels. Information with fine detail complementing that obtained by TEM, but with better chemical sensitivity, was easily obtained on polished bulk samples. No special sample preparation was necessary. It has been shown that the NanoSIMS can provide information on the oxide composition with a resolution good enough to separate the different oxide layers. It also provides detailed compositional profiles across/along features

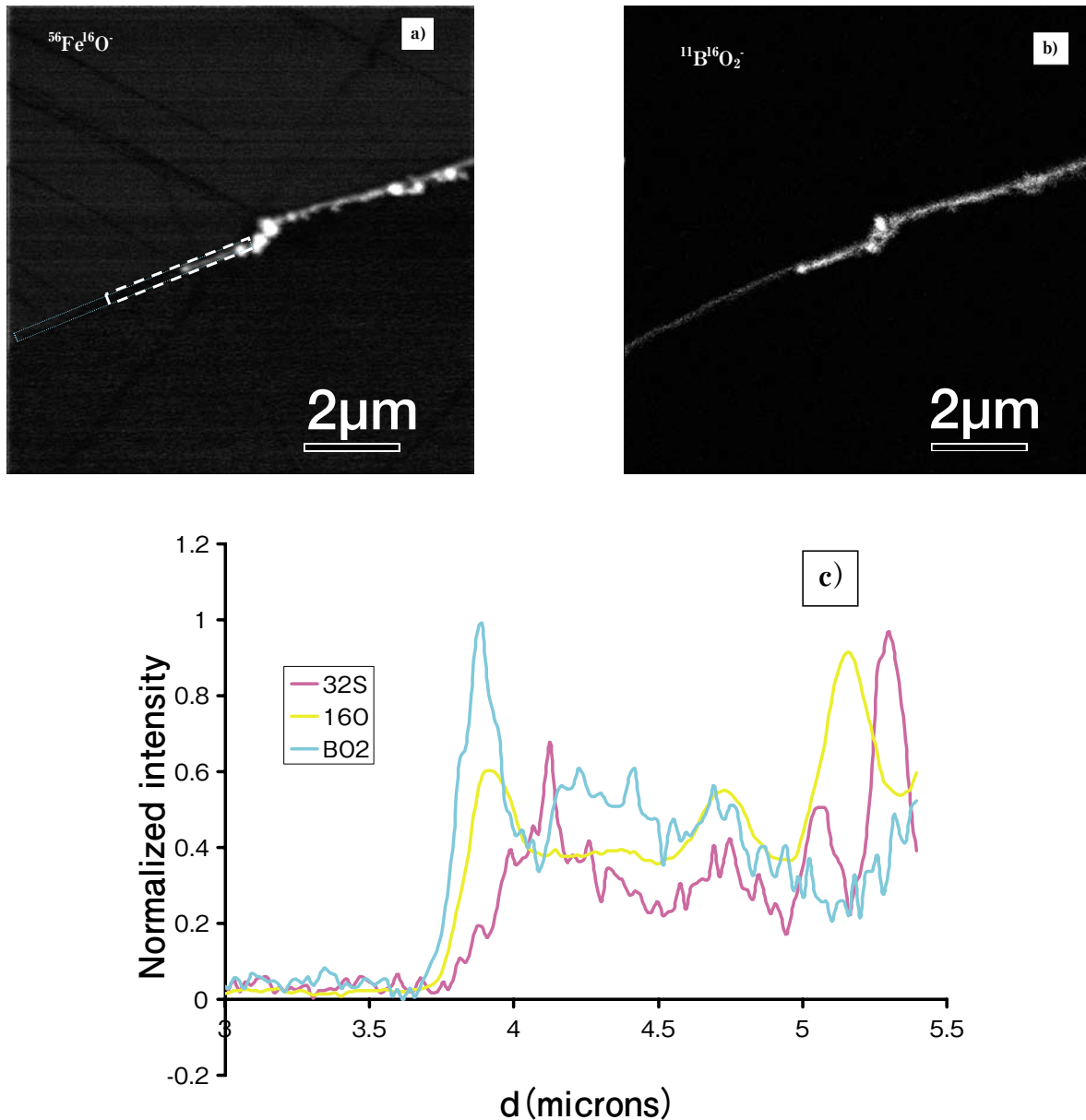


Fig 9. Dominant crack tip region in the 20% CW SUS304 sample (a) NanoSIMS $^{56}\text{Fe}^{16}\text{O}$ map showing position of line profile (b) NanoSIMS $^{11}\text{B}^{16}\text{O}_2$ map from same region and (c) NanoSIMS line profiles (normalized to unity).

of interest and very valuable information on the distribution of minor segregants (S, B).

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