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Atom probe tomography of stress corrosion crack tips in SUS316 stainless steels

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ABSTRACT

Novel atom probe tomography (APT) data of an intergranular stress corrosion crack tip has been acquired. Using APT for stress corrosion cracking research, very small, localized features and their distribution around the crack tip can be studied in 3D. This work details the development of a technique for the preparation of atom probe needles. Initial characterization via analytical transmission electron microscopy provides with a complementary analysis and accurately locates features that can be correlated with the reconstructed APT data. Ni enrichment and intergranular oxidation ahead of the crack tip have been studied with APT in 3D and with near-atomic resolution.

1. Introduction

Stress corrosion cracking (SCC) has been studied extensively over the past two decades as it is considered to be an important problem regarding the safety of nuclear power systems [1–3]. A number of models have been proposed in an attempt to explain the underlying mechanisms of SCC, however, no universal model has been discovered yet [4–9]. Nevertheless, there is a general agreement amongst researchers that the propagation of SCC depends on the crack tip chemistry, its surrounding matrix as well as the mechanical behavior of the region around the crack tip.

Little high-resolution data in this particular region exists due to the limitations in resolution or detectability of beam-based analysis techniques such as transmission electron microscopy (TEM). These limitations can be overcome by atom probe tomography (APT), which has been previously applied in studies of grain boundary oxidation and segregation and allows the generation of 3D maps of atomic structures with near-atomic resolution [10–13].

APT is a 3D atomic scale microscopy technique. In APT the specimen, shaped as a thin needle with ~50–100 nm tip radius, is subjected to an intense standing electric field, on to which is superimposed either a very sharp pulsed electric field or pulsed laser to trigger the highly controlled field evaporation of individual ions from the surface of the needle. Hence the technique is destructive to the specimen. Using time-of-flight, the mass-to-charge ratio and thus chemical identity of each ion can be determined. Furthermore, the incident position at which each ion strikes the detector, together with a simple back-projection algorithm enables the original location of the ion within the specimen to be reconstructed in 3D [14].

In APT, a typical analyzed sample volume is very small (~80 nm × 80 nm × 200 nm), depending on the type of sample and analysis. Before the advent of the focused ion beam (FIB), electropolishing was used for preparing atom probe needles [15,16]. Site-specific analysis was very challenging and unreliable due to the small volume that is usually analyzed. With the development of the FIB, an abundance of new applications became accessible to APT [17,18]. A number of other publications describe techniques using the dual-beam FIB for the re-sharpening of blunt electropolished needles, for in situ lift-out from the bulk as well as for the construction of atom probe needles from thin sheets, ribbons or powder particles [13,18–28].

For the characterization of SCC via APT, site-specific specimen preparation is crucial in order to study surface oxides, crack tips, matrix composition and the relevant grain boundaries. Earlier work from the authors reported for the first time of the use of single-beam FIBs for the preparation of APT needles containing crack tips, although the success rate and reproducibility proved insufficient [29]. Since then, site-specific preparation of SCC-related features for atom probe characterization has been reported, but actual data

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Table 1
Chemical content of the alloy used in this study (wt.%).

Alloy	Fe	Cr	Ni	C	Si	Mo	Mn	P	S
316INSS	Bal.	16.54	10.00	0.047	0.045	2.07	1.42	0.024	0.001

from regions close to (and at known distance from) the crack tip is limited [12,30–36]. A possible explanation for this lack of reported results is the difficulty of the task (placing the entire crack tip centrally and at the right distance from the apex into the small APT needle volume), which could suggest that the sample preparation methodology could be improved.

This paper describes a new experimental approach concerning the preparation of atom probe needles containing a SCC crack tip. The procedure involves a sequence of tasks commencing with sample preparation via FIB, initial observation via TEM and finally APT. First atom probe data of the grain boundary chemistry ahead of a SCC crack tip, at known distance, and substantial Ni enrichment will be demonstrated.

2. Material

The material used for this study was type SUS316 (reactor grade) stainless steel tested under pressurized water reactor (PWR) primary water conditions, provided by INSS (Japan). Its composition is listed in Table 1.

Prior to autoclave testing, the specimen underwent solution treatment followed by water quenching and uni-directional cold-rolling to a thickness reduction of 20%. The SCC test was performed at the INSS (Japan) laboratories using a pre-cracked ½ CT specimen in the T-S direction in an autoclave under constant load (30 MPa $m^{1/2}$). The sample was exposed to a testing environment of simulated PWR water chemistry (hydrogenated water: 500 ppm B + 2 ppm Li, + 30 cm^3-STP/kg-H_2O DH_2) for 700 h at 360 °C. The sample exhibited SCC by the time the test was concluded.

The cross-sectioned surface of the sample was ground with SiC paper and polished with 1-μm diamond suspension. Mirror-finish was achieved by final treatment (15 min) with colloidal silica.

3. Instrumentation

A FEI FIB200 (single-beam) fitted with a static in situ micromanipulator and a Pt gas injection system (GIS) was used for the lift-out. A Zeiss NVision 40 (dual-column) FIB was subsequently used for the atom probe needle sharpening process. Initial TEM imaging was performed with a JEOL 2100 LaB_6 TEM operated at 200 kV and EELS and EDX was carried out with a JEOL ARM200F (cold-FEG) TEM at 200 kV equipped with a Gatan GIF spectrometer and a JEOL Centurio 100 mm^2 EDX detector. APT was performed using a LEAP 3000 HR local electrode atom probe instrument using laser-pulsing mode (0.5 nJ laser energy, 55 K, 160 kHz pulse frequency, 0.15%, evaporation rate).

4. Methodology

In 2008, Lozano-Perez et al. published a guide on FIB preparation of samples containing stress corrosion crack tips for TEM and atom-probe analysis, which describes initial attempts to prepare an atom probe needle containing a stress corrosion crack tip [29]. Only single-beam FIB instruments were utilized in that study and it was often found that the welding to the supporting tip was insufficient, the location of the grain boundary while milling was uncertain and no control existed on the location of the crack tip with respect to the apex of the sample. However, with increased access to dual-beam FIB instruments, this method has since been adapted and improved in recent years. As will be shown, a new procedure has been developed and produced novel atom probe results of a stress corrosion crack including open crack, crack tip and the oxidized grain boundary directly ahead of the crack tip.

Fig. 1 illustrates a FIB SE image of an intergranular stress corrosion crack in the SUS316 stainless steel specimen, highlighting the 25 μm × 5 μm region of interest to be extracted from this bulk specimen. Within the highlighted region of interest, the crack tip was located vertically central and horizontally ~5–7 μm from the right end of the lift-out region.

After an in situ protective Pt deposition on top of this region (for protection of the crack region from the milling or re-deposition of matrix material in the open crack), trenches were milled below, on top and on the right-hand side. Under-cuts separated the volume from the bulk specimen, which was lifted out via in situ micromanipulator; for details see Fig. 2a or [29]. In the next step, the lift-out was welded onto a blunt (~30 μm diameter), needle-shaped Cu tomography holder (Fig. 2b) both applicable for TEM and APT. This step is key for an initial analysis via TEM after the final tip sharpening in order to determine the location of the crack tip within the needle and to locate distinguishing features for later correlation with the atom probe data.

For the most part, the described lift-out methodology is not novel. However, an important difference to other reported techniques is the final orientation of the stress corrosion crack within the atom probe needle. Viskari et al. for instance, prepare an atom probe specimen encapsulating a section of the grain boundary from a region within 0.5 μm ahead of the crack tip [36]. Other authors report of preparing a number of atom probe specimen by cutting pieces off the previously lifted out wedge and welding

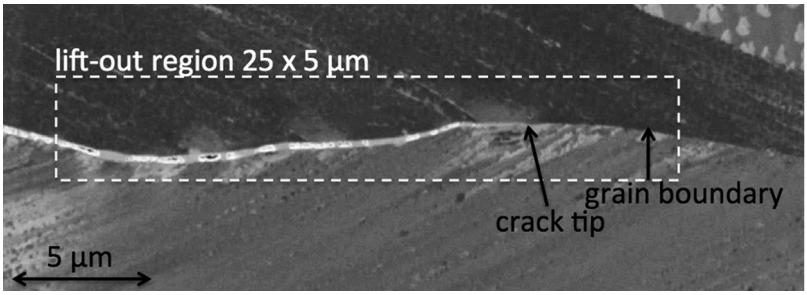

Fig. 1. FIB image (FEI FIB200) of intergranular stress corrosion crack in stainless steel specimen: a region of 25 μm × 5 μm has been selected for lift-out; both crack tip and grain boundary are indicated.