High-Resolution Crack Imaging Reveals Degradation Processes in Nuclear Reactor Structural Materials

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High-resolution characterization of stress-corrosion cracks illustrates the unique complementary capabilities of scanning and transmission electron microscopy and atom-probe tomography.

Corrosion and cracking represent critical failure mechanisms for structural materials in many applications. Although cracks can often be seen with the unaided eye, higher resolution imaging techniques are required to understand the nature of the crack tips and underlying degradation processes. Researchers at Pacific Northwest National Laboratory (PNNL) use a suite of microscopy techniques and site-specific material sampling to analyze corrosion and crack structures, producing images and compositional analyses with near-atomic spatial resolution. Samples are cracked components removed from commercial light-water reactor service or laboratory samples tested in simulated reactor environments.

In performing microstructural and microchemical characterizations of cracks in nickel-base alloys with high concentrations of chromium, unexpected localized corrosion in the alloy was discovered. It had long been thought that a thin, continuous film forms across the surface of the alloy and protects it from degradation in high-temperature water environments, but under certain material and water conditions, this is not the case. This localized penetrative degradation was discovered by bringing three powerful microscopy tools to truly see what happened to the materials involved.

Microscopy and material degradation
The high-temperature, high-pressure water environment in light-water reactors is extremely demanding for materials design, and requires selection of corrosion-resistant alloys for some structural components. Yet, many of these alloys are susceptible to localized corrosion and stress-corrosion cracking during long-term service. In response to cracking issues, some reactor components were replaced with a Ni alloy containing higher levels of Cr, known as alloy 690. The alloy is very resistant to corrosion and stress-corrosion cracking, and there have been no reported incidents of alloy 690 cracking after more than 20 years in reactor service. However, scientists produced cracks in the laboratory on highly cold-worked alloy 690, and research is ongoing at PNNL to understand the fundamental processes controlling material susceptibility to stress-corrosion cracking.

Even though cracking can be visible to the naked eye, appearing as an open space within an otherwise continuous, solid material (Fig. 1). However, stress-corrosion cracks formed at low stresses are often extremely narrow and difficult to see even using optical microscopy. Higher-resolution microscopy is needed to image and characterize these tiny features in detail, with different techniques bringing different benefits. For example, scanning electron microscopy (SEM) can quickly and easily provide a broad overview of the alloy microstructure and crack characteristics at dimensions from ~1 mm down to resolutions of ~5 nm. Transmission electron microscopy (TEM) often requires sophisticated site-specific sample preparation using a focused-ion beam (FIB) system, but has significantly better spatial resolution, less than 1 nm, and provides both compositional and crystallographic information. Atom-probe tomography (APT) enables near-atomic resolution measurement of three-dimensional element distributions and morphology, but again, requires elaborate sample preparation using FIB. Combining these three high-resolution analytical techniques enables obtaining a unique multiscale picture of the size, shape, and

Fig. 1 — (a) Low-magnification and (b) high-magnification SEM images of a crack in a cold-rolled alloy 690 after testing in simulated reactor primary water (360°C water). The crack weaves between several grains before terminating. High-magnification SEM image reveals localized oxidation to depths of several hundred nanometers at the sidewalls of a stress-corrosion crack. (Orange-penetrative oxidation, yellow-Ni rich Mo crack wall oxide, blue-alloy 690, green-chromium carbides).
Sample preparation is critical

Sample preparation is a critical step for microscopic examination using TEM and APT. Figure 2 shows a schematic of FIB-based sample preparation. The process begins with a polished cross section of a specimen (Fig. 2a) that contains a crack with oxide penetration, seen in the SEM as dark fingers extending from the crack wall into the metal. A thin layer of platinum is deposited on the surface to mark and protect the region of interest. Using a focused beam of gallium ions, a wedge-shaped sample (Fig. 2b) is cut out and extracted from the sample using a micromanipulator located inside the FIB chamber. The isolated piece of material (Fig. 2c) is rotated by 90° (Fig. 2d) so the crack wall is facing “up.” Finally, FIB is used to create either a ~100-nm thick foil for TEM (Fig. 2f), or a 100-nm diameter needle for APT (Fig. 2e). TEM and APT specimens containing cracks, crack walls, penetrative oxides, surface oxides, and grain boundaries are routinely produced using this approach.

Examination results

On a microscopic length scale, stress-corrosion cracks weave between several alloy 690 grains (Fig. 1a) after testing in high-temperature primary water environments simulating pressurized water reactor (PWR) service. High-magnification SEM images of the cracks reveal a more complex, unexpected localized corrosion on the nanoscale (Fig. 1b). Dark, filamentary penetrations of oxide are observed, burrowing from the crack wall into the metal below. Alloy 690 surfaces are expected to quickly form a thin layer of chromium-rich oxide that protects the metal from corrosion during exposure to high-temperature water. However, SEM images show that a continuous, protective film is not formed on the crack walls, and that nanoscopic oxide penetrations extend into the metal.

More detailed analytical analyses are obtained using TEM. Under-focus brightfield imaging indicates the morphology of the oxide filaments (Fig. 3a), and local variations in composition are illustrated by energy-dispersive spectroscopy mapping of the same region (Fig. 3b) with chromium (Cr), oxygen (O), and nickel (Ni) colorized as green, red, and blue, respectively. A large Cr-carbide particle (bright green) surrounded by a thin layer of Cr-oxide (red) is visible in the upper-left corner of the colorized elemental image. Filamentary oxide penetrations previously
observed by SEM are also Cr-rich (red), surrounded by a Ni-rich matrix (blue). Because each oxide phase has a unique crystallographic aspect, using TEM makes it possible to identify the crystal structure of the oxides using electron diffraction. One can “light up” individual oxide phases selectively by darkfield imaging. Two different oxide phases are apparent within the oxide penetrations: chromium oxide (Cr$_2$O$_3$) platelets, which are 5 to 20 nm in diameter (Fig. 3c), surrounded by a very fine-grained Ni-Cr-Fe oxide with the cubic MO (rocksalt type) structure. Cr$_2$O$_3$ platelets are discrete particles, while the MO oxides form the continuous networks observed by both SEM (Fig. 1b) and brightfield TEM (Fig. 3a) imaging.

APT is used to generate a three-dimensional elemental map of the oxide penetrations within a small cylindrical volume of material approximately 100 nm diameter by 300 nm deep. To illustrate APT results, atom maps for Fe, Cr, and Ni are presented in Fig. 4 together with a map for oxidized Cr as CrO molecules. Representative 10-nm slices of an APT reconstruction are depicted, with each dot specifying the location of an individual atom that was chemically identified and positioned in three dimensions. The CrO signal defines the filamentary nature of the Cr-rich oxide penetrations, while the metallic signals indicate localized enrichment or depletion.

Many other elements and compounds are identified by

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**Fig. 4** — Elemental maps of Ni, Cr, Fe, and CrO from an APT reconstruction as 10-nm slices for a region of penetrative oxidation off a crack wall.
APT in this region of penetrative oxidation\(^4\), but only major constituents are shown to highlight comparisons among techniques. One example of compound identification is shown in Fig. 5, where solid surfaces are drawn at concentrations of Cr + O greater than 95 at.\% (red). The red surface defines the locations of Cr\(_2\)O\(_3\) precipitates, which have very high Cr + O concentrations within the nanocrystalline MO oxide penetrations (CrO signal - blue). There is good agreement for the size, shape, and distribution of Cr\(_2\)O\(_3\) platelets in APT reconstructions and TEM darkfield observations. Clear distinction of isolated Cr\(_2\)O\(_3\) particles (red) surrounded by MO-type oxide (blue) also demonstrates the unique ability of APT to measure compositions in nano-scale particles. Platelets are nearly pure Cr\(_2\)O\(_3\), while the MO contains Ni, Cr, and Fe.

**Conclusions**

Environment-induced materials degradation represents a dominant issue impacting light-water reactor reliability, availability, and potentially safe operation. Such degradation may become even more important as plants continue to extend their operations past 40 years. Extended service and continued materials aging in extreme reactor environments where materials are subjected to high temperatures, chemically aggressive coolants, cyclic and static stresses, and a high radiation flux in the core may increase degradation susceptibility for components and introduce new degradation modes. Therefore, proactive research is required to better understand corrosion and cracking mechanisms in reactor materials. One aspect of this research is the application of complementary high-resolution characterization methods to analyze stress-corrosion cracks at millimeter to near-atomical dimensions.

The high-resolution microscopic examinations described here reveal that a continuous protective oxide film is not formed on alloy 690 in PWR primary water. Instead, a network of Cr-rich oxide penetrations is produced below the surface. Combining the analytical powers of TEM and APT, we determined that these penetrations consist of a mixture of discrete Cr\(_2\)O\(_3\) platelets and filaments of Ni-Cr-Fe oxide. Many aspects of this localized penetrative oxidation remain unclear, but our detailed nano-scale microscopic character-
izations provide new insights into alloy 690 corrosion. Research is continuing on cracks, crack tips, and surfaces, focusing on oxidation and corrosion processes. Modifications that enable high-resolution TEM and APT examinations on the same samples enable analyses of specific degradation structures in detail. Integration of these powerful analytical techniques will extend the fundamental understanding of corrosion and cracking processes in light-water reactor environments.

Summary

High-resolution characterization of stress-corrosion cracks illustrates the unique, complementary capabilities of SEM, TEM, and APT. It has long been thought that a thin, continuous oxide forms and protects high-Cr, Ni-base alloy 690 from degradation in high-temperature water environments. Research at PNNL shows this is not the case under certain material and water conditions; the metal becomes internally corroded. These results raise fundamental questions about the mechanisms of corrosion and cracking resistance for this important light-water reactor structural alloy. Understanding the sequence of events that result in penetrative oxidation will help researchers tailor alloys to be more resistant to degradation in service.

References


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