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Surface Analysis of Pressurized Water Reactor Steam Generator Tubing Specimens

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The surface oxides of RCS components play an integral role in the corrosion, corrosion product transport, and deposition processes within the primary circuit. Little plant data exist in the public literature regarding these oxides [1,2]. This study analyzes primary side surface oxides of steam generator tubes from five U.S. PWRs. The main aim of this study is to characterize corrosion films formed on steam generator tubing from various plants in order to better understand corrosion product release and transport in PWR reactor coolant systems. It is part of a series of studies funded by EPRI Fuel Reliability Program.

Steam generator tube surfaces from archived tubes were analyzed using Scanning Electron Microscopy, and a new technique that combines focused ultrasonic descaling with analytical Transmission Electron Microscopy. The archive tube samples were from Vogtle 1 & 2, Oconee 2, Diablo Canyon 1 and Seabrook plants. The specimens were mostly Alloy 600, with a few Alloy 690 specimens from Oconee 2 after steam generator replacement.

Based on descaling of the corrosion film and analysis using TEM (Figure 1), it was determined that on average, the composition of the corrosion films was close to $NiCrFeO_4$ (or more precisely, $Ni_{0.9}Cr_{1.0}Fe_{1.1}O_4$). This indicates that the Ni released during corrosion is quite significant relative to Cr and Fe. The observation that the iron content in the corrosion film is distributed toward the coolant interface and is roughly equal to the chromium suggests that although Alloy 600 and Alloy 690 steam generator tubes release Ni while capturing Fe. Iron constitutes a major component of core crud, and in many axial offset anomaly (AOA) cycles, it was the dominant constituent. If steam generator tubing is not a source of iron release during the cycle, then stainless steel components within the RCS or components of the chemical and volume control system must be responsible for much of the core crud inventory. Establishing which components contribute significantly to iron release will be important for future crud control efforts.

Limited SEM data show that localized attack at grain boundaries and surface defects is likely a significant cause of corrosion product release. Figure 2A shows formation of hexagonal crystals at a Cr-rich grain boundary of Alloy 690, and Figure 2B shows a cross sectional view of a Vogtle 2 tube with extensive corrosion at the grain boundaries at the surface of the tubes. More detailed study using a larger and more diverse sample population is needed.

If localized corrosion at grain boundaries and surface defects controls steam generator corrosion product release, then releases from new steam generators can be controlled by optimizing heat treatments and surface finishing. Additional studies of localized corrosion on steam generator ID surfaces may help to determine what constitutes the best grain boundary conditions and surface finishes. The localized nature of corrosion should also be considered when optimizing chemistry for in-service steam generators.

References

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[3] Funding for this program was provided by Electric Powder Research Institute, Palo Alto, CA, under contract # 1018720

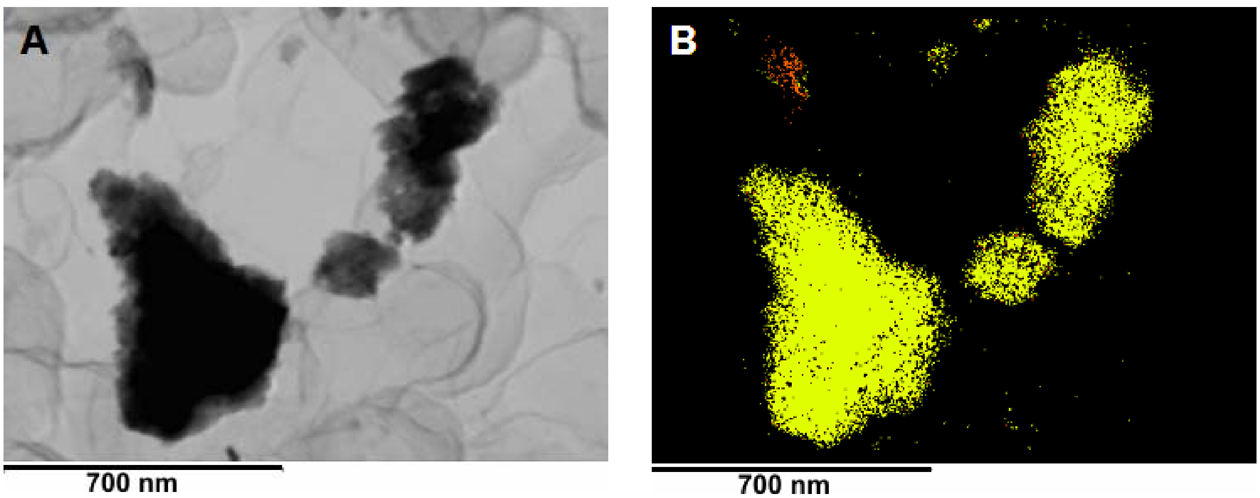

FIG. 1. (A) Bright-field TEM a sample of Diablo Canyon 1 EOC7 descaled corrosion film. (B) The XEDS phase map highlighting clusters with approximate composition of $NiCrFeO_4$ in yellow.

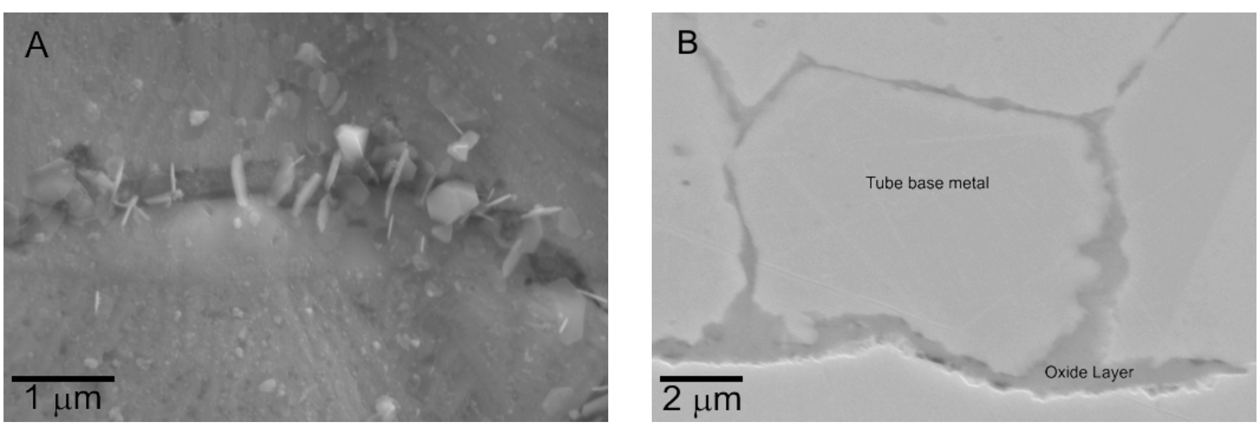

FIG. 2. (A) Top-down SEM of Oconee 2 Alloy 690 tube showing the formation of corrosion products at the grain boundaries. (B) Cross-section SEM of Vogtle 2 Alloy 600 tube showing significant corrosion at the grain boundaries near the tube surface.

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