

## Characterization of Corrosion Films on Austenitic Stainless Steels Exposed to High-Temperature Deaerated Water

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Austenitic stainless steels are well known for their passivity and corrosion resistance in high-temperature water, and these characteristics made them a material of choice for the first water-cooled nuclear reactors [1]. A significant number of studies have since been performed on the corrosion films that form on 304 stainless steel in high-temperature water [1-3], but less information is available on Mo-bearing austenitic stainless steels. This paper therefore provides a characterization and a comparison of the corrosion films on 304, 317L, 904L, and AL-6XN® stainless steels. Oxide films were grown on these materials in the same 3200 hour autoclave exposure in 260°C deaerated water. Total-corrosion measurements were found to vary by approximately a factor of two as determined from the difference between initial-coupon and final-descale masses. The 304 and 317L exhibited higher corrosion values of 24 and 27 mg/dm<sup>2</sup> respectively, and the 904L and AL-6XN® exhibited lower corrosion values of 12 and 11 mg/dm<sup>2</sup> respectively.

The corrosion films on all four stainless steels were characterized by Transmission Electron Microscopy (TEM) in an FEI Tecnai F20 microscope. Energy Dispersive X-ray (EDX) spectra were acquired from features of interest in scanning-transmission mode using an Oxford Instruments X-Max<sup>N</sup> 100TLE silicon drift detector, and selected-area electron diffraction patterns were recorded in transmission mode to identify the crystal structure of the corrosion films and underlying base metals. TEM foils of the corrosion films were prepared using a focused ion beam liftout method in an FEI Nova NanoLab dual-beam system. The oxide films on all materials were found to have a dual-layer structure consisting of an outer oxide layer composed of faceted crystallites and an underlying inner oxide layer (Figure 1). The inner oxide layer in each material is more uniform in thickness than the outer oxide layer, but the thicknesses of both oxide layers vary among the four stainless steels. The total thickness of the combined dual layers is greater in 304 and 317L (1600 and 830 nm respectively) and is lower in 904L and AL-6XN® (400 and 410 nm respectively). In addition, the inner and outer oxide layers each make up approximately half of the total oxide thickness on each material.

The inner oxide layers have a crystal structure and composition consistent with (Fe,Ni)(Fe,Cr)<sub>2</sub>O<sub>4</sub> spinel. Cr and Fe are the primary cations in this structure, but lower levels of Ni, Mn, and Mo are also present. This oxide layer has an ultrafine grain size and is enriched in Cr and depleted in Fe relative to the underlying base metals. EDX line scans show that Cr and Fe levels vary within the films by approximately 13-14 wt.% from region to region. In addition, there is a notable gradient in Cr and Fe levels across the inner oxide in 317L, 904L, and AL-6XN® that is not present in 304. Cr levels decrease and Fe levels increase within this gradient from the base metal to the outer oxide. Mo is also incorporated into the inner oxide in 317L, 904L, and AL-6XN®; it is present at concentrations between 8-12 wt.% in the oxide adjacent to the base metal, and it transitions down to negligible levels part way through the inner oxide layer. Mo is not detected in the inner oxide in 304 which is also not present in this base metal.

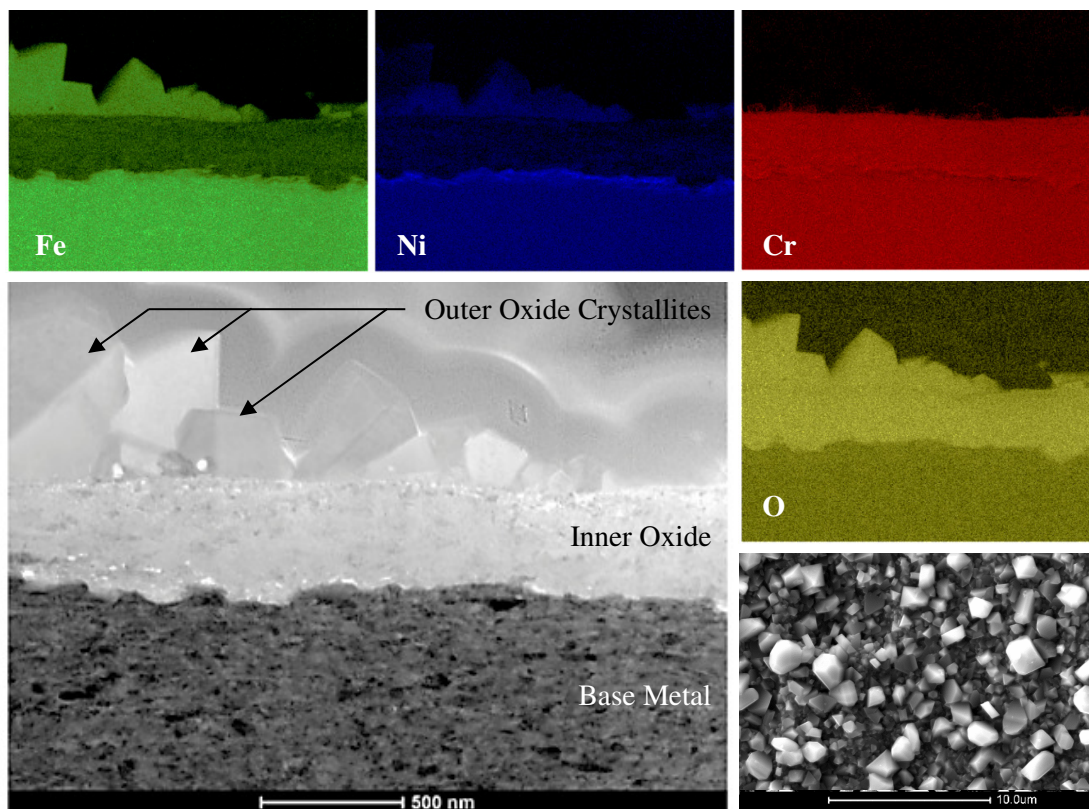
The outer oxide crystallites on all materials have a crystal structure and composition consistent with a (Fe,Ni)Fe<sub>2</sub>O<sub>4</sub> spinel. Ni levels vary from 4-21 wt.% among samples and increase with the Ni content of

the underlying base metal. Similarly, Fe/Ni ratios in the outer oxide crystallites also track those in the base metals which suggests that the outer oxide layer is formed at least in part by diffusion of Fe and Ni ions out of the base metals to form oxide crystallites. This hypothesis is also supported by the observation that the outer oxide layers for each alloy are approximately the same thickness as the inner oxide layers, the depletion of Fe and Ni from the inner oxide layer, and the corresponding enrichment of Fe and Ni in the outer oxide layer.

The base metals adjacent to the oxidized surface in all materials have a sub-grain structure much finer than that present in the bulk. This sub-grain structure is consistent with highly-deformed material associated with the machined coupon surfaces, and the base metal grains have the fcc austenite structure. A layer enriched in Ni is also present at the interface with the inner oxide layer. This is attributed to a selective oxidation process in which Ni, being a more noble metal than Fe or Cr, is not incorporated into the oxide layer and is subsequently concentrated in the metal near the oxide/metal interface [4].

#### References:

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 [2] K Wang *et al*, *Materials and Design* **82** (2015) 155.  
 [3] Y Asakure *et al*, *Corrosion* **45:2** (1989) 119.  
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**Figure 1.** Scanning-transmission image and EDX elemental maps of base metal, inner oxide, and outer oxide crystallites in 317L stainless steel. Also shown is an SEM image of the crystallites on the corrosion surface.