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TEM Studies of Oxides Formed on Nickel-Based Alloys in Secondary Side Water

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Alloy 600 and Alloy 690 have been extensively used as steam generator tubing in pressurized water reactors (PWR). Several studies have been carried out to understand the mechanism of stress corrosion cracking, which is one of the important degradation phenomena in PWR [1-4]. In the present work we have investigated the effect of pre-oxidation on the evolution of oxide layer during exposure to secondary side water chemistry using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and focus ion beam (FIB).

Alloy 690 (60% Ni, 30% Cr, 10% Fe) was studied before and after pre-oxidation at 482 C and 50mbar for 100 hours and then subjected to 6000 hours of autoclave exposure at 282 C in simulated secondary side environment. TEM samples were prepared by in-situ FIB and lift-out from the top surface layer. Electron microscopy was performed with a JEOL 2010F TEM operated at 200 kV equipped with a Gatan Imaging Filter and Hitachi S-4500 Field Emission SEM operated at 5kV.

A cross-sectional FIB image from the sample subjected only to 6000 hours of autoclave exposure is shown in Fig 1a. This image shows no intergranular attack at the grain boundaries based on the technique described in reference [5]. Near the topmost surface the samples show grains 1-2 μm in size due to the surface finishing process, while bigger particles around 15 μm in size were observed below the surface. After the oxidation process, the SEM micrographs showed the existence of a fine layer at the top surface and large particles (Fig 2). Scanning transmission electron microscopy dark-field imaging (Fig. 3) and point-measurements with electron energy loss spectroscopy (EELS) (Fig. 4) reveal the presence of Cr oxide in the fine nanocrystalline layer near the sample surface (region 1), while Fe oxide is detected in larger particles protruding from the fine surface layer (region 2). STEM energy dispersive X-ray spectroscopy (EDS) maps (Fig. 5) show a thin layer of Cr oxide and Fe uniformly distributed into the finer particle. Oxygen appears to be penetrating around 200 nm below the surface, along a grain boundary, as it is indicated by the arrow in the O map. Further work will demonstrate the capability of the combination of analytical electron microscopy and focused ion beam microscopy in the study of oxidation in alloys.

References

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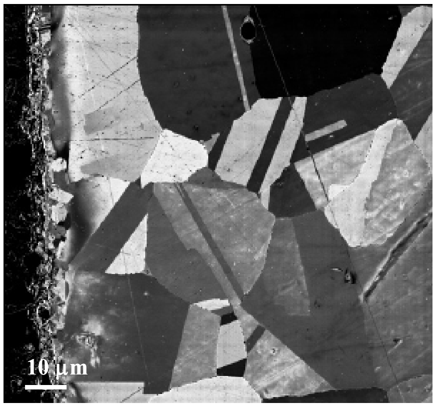

Fig 1. Cross sectional FIB image of the sample before the pre-oxidation process and 6000 hours of autoclave exposure

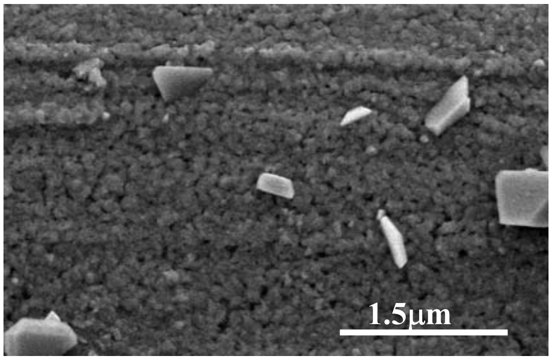

Fig 2. SEM image of the top surface

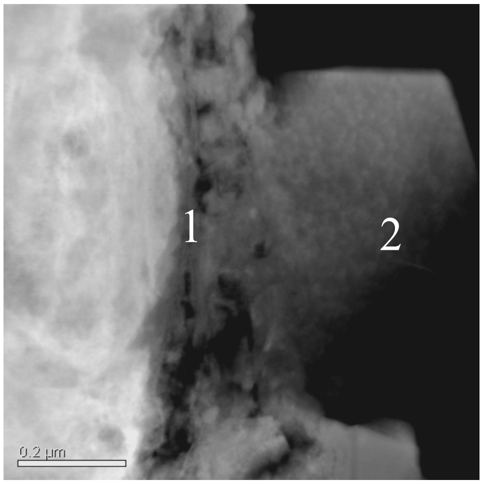

Fig 3. DF STEM image of the top surface layer

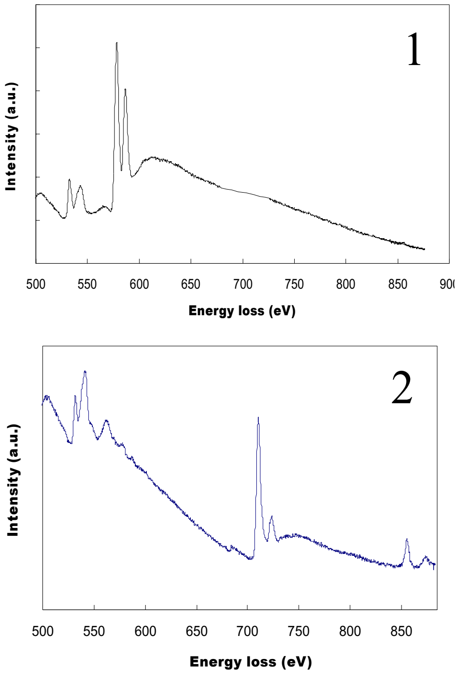

Fig. 4. EELS spectra extracted from the positions indicated in Fig. 3

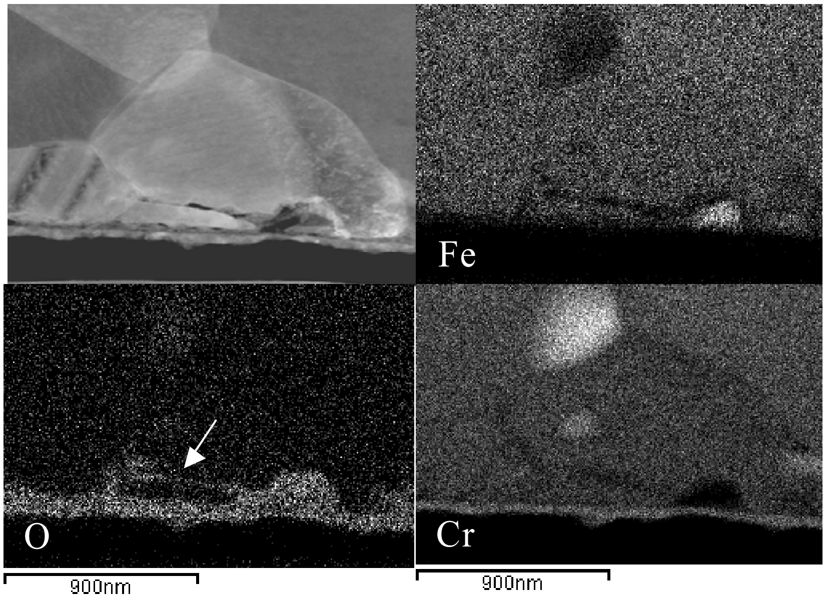

Fig. 5. STEM EDS maps of the surface layer. The arrow indicates penetration of the O along one grain boundary .

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