Microstructural Analysis of the Preferential Intergranular Oxidation Behavior of Alloy 600 in H_2-Steam Environment

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Considerable research programs have focused on understanding the mechanism of Stress Corrosion Cracking (SCC) in nuclear power systems, particularly in the primary water environment of pressurized water reactors (PWRs). Although the "internal oxidation" model proposed by Scott and Le Calvar [1] is considered to be the most plausible SCC mechanism for Alloy 600 (Ni-~16 Cr-~9 Fe), this has been refined as a result of advanced analytical TEM (ATEM) studies [2]. Detailed TEM and STEM-EDX data have demonstrated that the initial reactions of the material with the environment involve preferential intergranular oxidation (PIO) associated with diffusion-induced grain boundary migration (DIGM) [2-4].

In this study, oxidation experiments were performed in an atmospheric pressure (low pressure) superheated H_2-steam system to accelerate the oxidation kinetics. This system had been shown to reproduce the correct electrochemical condition representative of a PWR primary water system [2-3]. The oxidizing potential in the H_2-steam environment can be described by a parameter, R, which is defined as the ratio of the oxygen partial pressure at the Ni/NiO transition over the oxygen partial pressure in the test environment. Maximum susceptibility to SCC in PWRs has been shown to occur in the vicinity of the Ni/NiO transition. In this study, solution-annealed and water-quenched Alloy 600 coupon samples polished with SiO_2 suspension (OPS) were exposed to the H_2-steam environment at 480 °C for 210 h for a range of conditions (range of R values) in order to further assess the grain boundary migration and the extent of localised oxidation in the more reducing and more oxidizing environments than the Ni/NiO transition.

Field emission gun (FEG) scanning electron microscopy (SEM), focused ion beam (FIB) sectioning, and analytical transmission electron microscopy (ATEM) were used to characterize the samples after environmental exposure. Cross-sections of selected grain boundaries were prepared using an FEI Helios 660 Dual Beam FIB equipped with an OI X-Max 150 SDD and EBSD system. The PIO trend for the different R values was analyzed for a minimum of 20 grain boundaries for the exposure conditions. The morphology of the grain boundaries (Figure 1) after exposure was strongly influenced by the environmental conditions; DIGM was detected at grain boundaries in the R=1/6 sample whereas PIO associated with DIGM was observed for R=6 specimen. More detailed STEM-EDX analyses performed using an FEI Talos F200A equipped with a Super X EDX (4 SDDs) detector configuration showed the presence of an external oxide layer highly enriched in Cr, Fe and Ni with localized Al- and Ti- enrichments at the grain boundary oxide (Figure 2f-g). Grain boundary migration was also observed in the sample exposed in the oxidizing environment, similar to the observations for specimens exposed in a reducing environment [2-3]. Therefore, whilst the role of the Al- and Ti- enrichments may play an important role for the development of intergranular oxide [3] and SCC, the oxidation of these minor alloying elements does not appear to be a rate-controlling step, at least under oxidizing conditions.

[1] P. Scott, M. Le Calvar, 6th Int. Symp. Environ. Degrad. Mater. Nucl. Power Syst. - Water React., (TMS, 1993) 29-36.

[2] G. Bertali *et al.*, Corrosion Science, 2015, doi:10.1016/j.corsci.2015.08.010.

[3] G. Bertali *et al.*, Corrosion Science, 2017, doi:10.1016/j.corsci.2016.11.004.

[4] G. Bertali et al., Met. Mat. Trans. A, 2018, doi: /10.1007/s11661-018-4491-9.

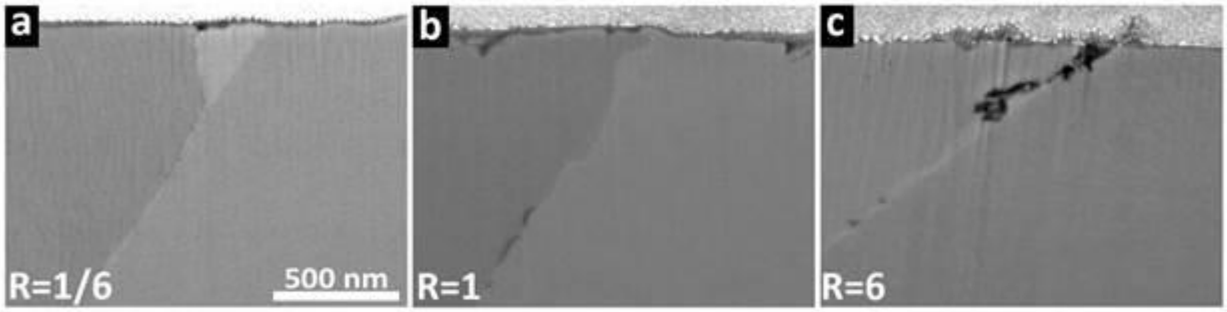

Figure 1: (a)-(c) SE images of FIB cross-section specimens prepared from samples exposed to H_2-steam environments at 480 °C for 210 h for the different R values. For R<1, the environment is more oxidizing than the Ni/NiO transition whereas for R>1 the environment is more reducing.

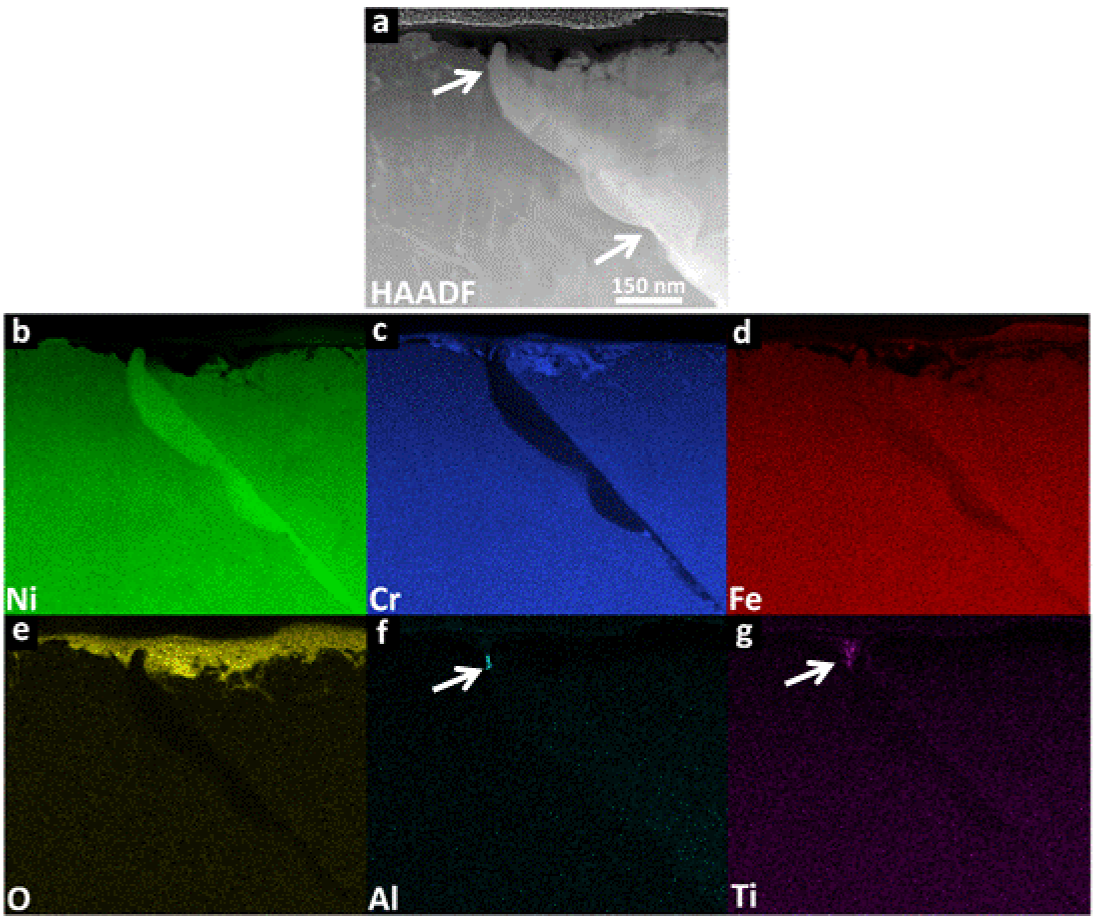

Figure 2: Detailed ATEM characterization of the R=1/24 (more oxidizing environmental exposure) sample. (a) STEM-HAADF image showing ~500 nm length (arrowed) of grain boundary which has migrated ~50 to ~100 nm in extent. (b)-(g) Elemental maps for (b) Ni, (c) Cr, (d) Fe, (e) O, (f) Al, and (g) Ti extracted from the STEM-EDX dataset showing the new migrated GB with the highly Cr-depleted region and the Al- and Ti- enrichment (arrowed).