High Temperature Oxidation Studies of Ni-base Alloys: Understanding the Role of the “Precursor Events” during the Early Stages of Stress Corrosion Cracking

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Ni-base alloys, such as Alloy 600 and Alloy 690, are widely used in nuclear power plants (NPPs) thanks their excellent mechanical and anti-corrosion properties. However, both alloys are susceptible to primary water stress corrosion cracking (PWSCC). Despite several models have been developed to explain the occurrence of the PWSCC in Ni-base alloys, the very early stages of PWSCC are still unclear and further studies are needed to assess the role of the so-called “precursor events” on the PWSCC initiation stages. The term “precursor events” indicate the stages associated with one or several phenomena that lead to crack initiation; for the specific case of Ni-base alloys these events are associated with the preferential intergranular oxide (PIO) penetrated along a high angle grain boundaries (HAGBs) that exhibits local diffusion-induced grain boundary migration (DIGM). Therefore, the aim of this study was to clarify the effect of PIO and DIGM during the PWSCC early stages and initiation of Alloy 600 and Alloy 690.

In this PhD study, oxidation experiments were performed in a low pressure superheated H₂-steam system that can accelerate the oxidation kinetics of Ni-base Alloys without changing the mechanism. The capability of the H₂-steam system to reproduce the correct electrochemical corrosion conditions present in nuclear power plants were evaluated in-situ by using advanced electrochemical measurements that employ a purposely built using a Y₂O₃-ZrO₂ solid state reference electrode. The environmental conditions typical of primary water conditions in a nuclear power plant were monitored as a function of the Ni/NiO phase transition, which depend on temperature as well as hydrogen fugacity. These electrochemical conditions were reproduced over a temperature range between 372 °C and 480 °C thus enabling superheated H₂-steam to be used as surrogate system for performing oxidation experiments in environmental conditions that are thermodynamically relevant to a PWR primary water reactor.

Solution annealed (SA) Alloy 600 samples were exposed to H₂-steam at 480 °C to clarify the role of PIO/DIGM and local microchemical segregation during the early stages of PWSCC as a function of electrochemical conditions. Advanced electron microscopy techniques showed that the PIO was more susceptible to occur under reducing conditions, whereas DIGM occurred independently from the environment. These results suggest that DIGM is a not sufficient condition for the occurrence of PIO and subsequent SCC initiation.
However, it was found that SCC initiation occurred in correspondence of the intergranular oxide that developed along a migrated grain boundary and displayed a local Al/Ti rich oxide. It was thus suggested that the local Al and Ti enrichment can create incoherent surfaces along the migrated grain boundary, and they can provide a further accelerating factor for the inward oxygen diffusion.

Evidence of the occurrence of local grain boundary migration and minor chemical segregation was also found in Alloy 690 TT and SA after exposure to H₂-steam at 480 °C under reducing conditions. However, despite the alloy showed evidence of DIGM, it did not undergo to PIO. It is probable that the higher Cr content (compared to the Alloy 600) induced the formation of a much denser and more protective external Cr-rich oxide that inhibited the inward oxygen diffusion and provided the driving force for the occurrence of DIGM. Therefore, these results show that DIGM can be considered as a secondary (e.g., accelerating) also for the Alloy 690, although this is not a sufficient phenomenon for the occurrence of PIO and cracking.

In summary, it was found that the early stages of SCC of Ni base Alloys cannot be explained only as the result of one single dominant phenomenon but due to the synergistic interactions between Al/Ti oxide and DIGM which are accelerating factors for the development of PIO which fracture upon the effect of applied stress, if chemical and environmental conditions can lead to the instability of the external oxide.