Preliminary Study of the Effect of Electrolyte Composition on the Electrochemical Behavior of Alloy 800NG in PWR Secondary Water Environment at 80°C and 250°C

Mônica Maria A. M. Schvartzman, Fábio A. Mansur, Célia de A. Figueiredo, Pedro Henrique B. O. Nogueira

Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN) Av. Antônio Carlos, 6627, 31270-901, Belo Horizonte, MG monicas@cdtn.br

Introduction

Incoloy[®] 800 is used in nuclear steam generators as the tubing material for pressurized water reactors (PWRs) because of its high corrosion resistance. This behaviour is due to the protective character of the oxide film formed on its surface by contact with the high temperature pressurized water. Nevertheless, corrosion has been the major cause of tube failures in nuclear steam generators. The existing experience of different nuclear power plants shows that the water chemistry has an important role in maintaining the integrity of the protective oxide films. Many of such problems have been attributed to secondary side water chemistry conditions and excursions, many of which have been resulted from condenser cooling water ingress. Alloy 800 is known to undergo passivity breakdown and pitting in the presence of chloride ions under oxidative water conditions [1, 2]. The aim of this work is to investigate the effect of chloride and sulphate ions at various concentrations on the corrosion behavior of Alloy 800 tubing at 80°C and 250°C, using electrochemical techniques.

Experimental

The material investigated in this work was a sample of the steam generator tube made of nuclear grade Alloy 800 (Alloy 800NG). Cylindrical specimens (16.2mm diameter and 14.8mm length) were cut from the as-received material and abraded with 600 grit silicon carbide paper. Experiments at 80°C were performed in a glass cell with Ag/AgCl (3M KCl) as the reference electrode and a platinum plate as the auxiliary electrode. Experiments at 250°C were carried out in a static 1.8L stainless steel autoclave. The reference electrode was an yttrium stabilized zirconia (YSZ) electrode filled with a mixture of Ni/NiO powder and the counter electrode was a platinum plate. Two tests were performed for each condition. Test solutions were prepared by adding NaCl and Na₂SO₄ (analytical grade reagents) to deionized water. A deaerated condition was achieved by sparging nitrogen gas for at least 48h prior to each experiment. The test solution pH at room temperature was 9.8. It was adjusted by bubbling ammonia gas in the deaerated solution. Six different concentrations of chloride and sulphate ions were used, namely: (i) 200ppb Cl^{-} + 200ppb SO_4^{2-} ; (ii) 500ppb Cl^{-} + 500ppb SO_4^{2-} ; (iii) 1ppm Cl^{-} + 250 ppb SO_4^{2-} ; (iv) 1ppm Cl^{-} + 1 ppm SO_4^{2-} ; 5ppm Cl^{-} + 5ppm SO_4^{2-} . Anodic potentiodynamic polarization tests were performed with a scan rate of 0.167 mV.s⁻¹ [3]. The potential was scanned from -0.2 V to 2.0 V with relation to the open circuit potential. The tests were performed using an Autolab potentiostat PGSTAT12 with software GPES (General Purpose Electrochemical System 4.9). Cyclic polarization tests were performed according to ASTM G61-86 [4]. The scan was started at the corrosion potential and continued in the anodic direction until an anodic current density of about 10⁻³Å.cm⁻² was reached. At this point, the scan direction was reversed and the potential was decreased. Corrosion morphology observations were performed using scanning electron microscopy (SEM).

Results and Discussion

The corrosion behavior of Alloy 800NG in chloride-and sulphate-containing solutions at 80°C is presented in Figure 1. The shape of the polarization curves of Alloy 800NG in the test

solutions was quite similar. At 80°C the specimens were in the passive state at the corrosion potential. For the tests performed in solutions with ion concentrations until 500ppb, with the increase in the potential, a passive region was observed followed by a slight current increase probably related to a change in the passive film. Further potential increase led to a second passive region followed by a transpassive region. For 1ppm and higher ion concentrations the polarization curves were shifted to the right indicating a small anodic film dissolution. No localized attack was observed on the metallic surface after anodic polarization in all studied conditions, indicating that the final increase of current was solely due to oxygen evolution.



Figure 1. Effect of ion concentration on the corrosion behavior of Alloy 800NG in PWR secondary water at 80°C.

Figure 2 presents typical anodic polarization curves obtained at 250°C in deionized water at pH 9.8 and in solutions containing chloride and sulphate. In all studied environments Alloy 800NG exhibits an anodic peak associated to a weak active-passive transition. The polarization curve for 200ppb Cl⁻ + 200ppb SO₄²⁻ solution was found to be similar to the obtained in deionized water. Figure 2 also shows that the length of the passive region decreases when the concentration of solution was equal to 1ppm Cl⁻ + 250ppb SO₄²⁻. In this solution the passive region was very short and unstable, indicating a film stability lower than in the other solution. It can also be observed that the critical current density is higher than in the other conditions. In experiments performed in 200ppb Cl⁻ + 200ppb SO₄²⁻ solution, the passive current densities measured at 250°C were one order of magnitude higher than that at 80°C, suggesting that the oxide films formed at higher temperature showed lower corrosion resistance.



Figure 2. Effect of ion concentration on the corrosion behavior of Alloy 800NG at 250°C.

Figure 3 shows the microscopic examination of the specimen, after the anodic polarization test in 5ppm Cl^- + 5ppm SO_4^{-2} -solution at 80 °C.

At 250°C , the morphology of the corrosion attack on Alloy 800NG after anodic polarization test was related to the ion concentration in the solution (Figure 4). No localized corrosion was found on the samples tested in 200ppb Cl^{-} + 200ppb SO_4^{-2} -solution and in deionized water, but it was observed a high density of widespread shallow pits filled with corrosion products in experiments performed in 1ppm Cl^{-} + 250ppb SO_4^{-2} -solution.



Figure 3. Optical photomicrograph of Alloy 800NG obtained after the anodic polarization test in 5ppm Cl^2 + 5ppm $\text{SO}_4^{2^2}$ solution at 80°C.



Figure 4. Morphology of the corrosion attack observed on Alloy 800NG after anodic polarization in 1ppm Cl⁻ + 250ppb SO_4^{2-} solution at 250°C.

Conclusions

The anodic behavior and passivity breakdown of Alloy 800NG in aqueous solution of sodium chloride and sodium sulphate at 80°C and 250°C were studied using electrochemical techniques. At 80°C the material passivated spontaneously and no localized or substantial generalized corrosion was observed in all studied solutions. At 250°C, an active-passive transition occurred in all studied conditions. The major changes were a displacement of the curves towards higher current densities and lower potentials with increase of temperature at all potentials suggesting less corrosion resistance of oxide films formed in this condition. At 250°C, the localized corrosion of Alloy 800NG only occurred at 1ppm chloride concentration.

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