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Effect of pre-oxidation and corrosion potential on electronic properties of passive films on Ni-Cr-Fe alloys in pure water at 288 °C

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Ni-Cr-Fe alloys such as Alloy-600 (UNS N6600) and Alloy-690 (UNS N6690) have been used extensively as tube materials in steam generators of nuclear power plants. Alloy-600, with 16% Cr and 9% Fe, is known to be susceptible to intergranular stress corrosion cracking (IGSCC) in high-temperature pure water [1]. In order to have improved corrosion and stress corrosion cracking resistance properties, Alloy-690, with 30% Cr and 9% Fe has been developed. The improved corrosion properties of Alloy-690 have been attributed to a more resistant passive film formed on the surface of the alloy owing to a higher Cr content [2]. Stress corrosion cracking (SCC) is predominantly an electrochemical process which is activated by mechanical (stress) and metallurgical (grain boundary chemistry) factors. Therefore, stability of the passive film formed on the surface of the material plays an important role in determining the SCC resistance of a material in a given environment. The oxide film formed on the surface can be considered as a semiconductor when the composition deviates from the stoichiometry. The semiconducting behavior of passive film is considered to be important in determining the corrosion resistance of the material. An essential step in achieving better passivation, according to Bocris and Reddy [3], is transformation of the surface film to a good electronic conductor. However, other researchers correlated the corrosion resistance of Ni-Cr alloys with passive films properties that showed very high electrical resistance values [4]. In any case, electronic properties of the passive film affect the corrosion properties of the material. Therefore, it is important to characterize the electronic properties of the passive film *in-situ* in order to have a better understanding of the material degradation process.

As the simulated boiling water nuclear reactor (BWR) environment is pure water, which has very low ionic conductivity, normal potentiostatic electrochemical test techniques cannot be applied to investigate the passive film properties because of the extremely high IR drop. Therefore, the contact electrical resistance (CER) technique, which measures the electrical resistance of the passive film by solid-solid contact and thus avoids the IR drop due to electrolyte resistance, has been employed for *in-situ* investigation of passive films. The experimental set-up has been described in detail elsewhere [5]. Briefly, the electrical resistance across a solid-solid contact between two specimens of similar materials exposed to the test environment is measured by passing a known value of direct current (0.75 mA and 25 mV as open circuit voltage). The surfaces of the two specimens are periodically contacted and disconnected at desired time intervals. In this study, a pair of 2 mm diameter cylindrical specimens of similar material was used. The flat surfaces of the two specimens were mechanically polished with a series of emery papers up to 4000 grit and thoroughly washed prior to immersion into the test environment. When the specimen surfaces were not in contact, they were exposed to the test environment and the surfaces were oxidized. When the specimens were brought into contact by accurate movement of a stepper motor—spring assembly, the contact electrical resistance was measured. This entire set up was introduced into an autoclave (volume 4 I) made of type 316L, stainless steel. Pure water (inlet conductivity <0.1 μS/cm) was circulated at a rate of 6 liters/h and the autoclave was pressurized to 8.5 MPa and heated up to 288 °C. After reaching the test temperature the CER measurement was started. CER measurements were carried out at different dissolved oxygen (D.O.) levels by purging pure nitrogen or a mixture of nitrogen + oxygen in the water reservoir. As dissolved oxygen acts as a chemical potentiostat [6–8], the specimens were polarized chemically by changing the dissolved oxygen content of the water. Two different cyclic polarization programs were carried out. In program I, initially the specimens were maintained at lower corrosion potentials corresponding to low dissolved oxygen levels (<0.01 ppm) for 12 h. Then the corrosion potential was increased stepwise by purging a gas mixture of nitrogen^{+} oxygen and pure oxygen to a maximum value corresponding to the dissolved oxygen content of 32 ppm in the reservoir water (cycle 1). This dissolved oxygen was maintained for 12 h after which the reverse cycle of chemical polarization was started by purging pure nitrogen until the dissolved oxygen content decreased below 0.01 ppm (cycle 2). In program 2, the order of cycles was reversed. The contact electrical resistance of the passive film formed on the specimen surfaces was measured *in-situ* while the corrosion potential was monitored (using an external Ag/AgCl reference electrode in 0.1 M KCl) simultaneously during the chemical polarization of the

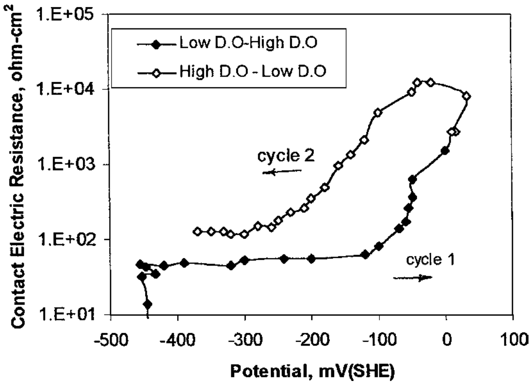

Figure 1 Contact electrical resistance of the passive film of Alloy 600 exposed to pure water at 288 °C. The specimens were cyclic-polarized chemically by varying the dissolved oxygen (D.O.) from 0.01 to 32 ppm (cycle 1) and back to 0.01 ppm (cycle 2).

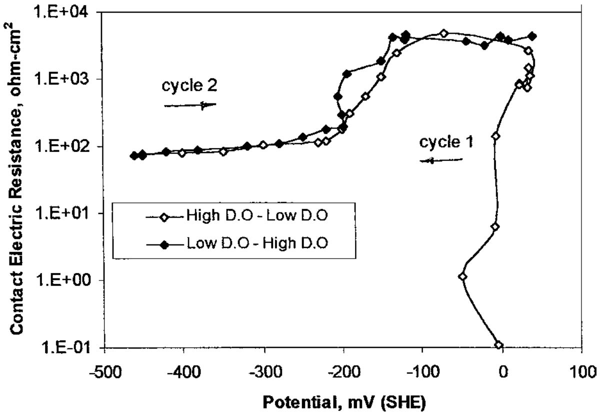

Figure 2 Contact electrical resistance of the passive film of Alloy 600 exposed to pure water at 288 °C. The specimens were cyclic-polarized chemically by varying the dissolved oxygen (D.O.) from 32 to 0.01 ppm (cycle 1) and back to 32 ppm (cycle 2).

specimens. The measured corrosion potential was converted to the standard hydrogen electrode (SHE) scale after temperature corrections. All the tests were carried out at 288 °C following the above procedure. The materials investigated were nickel base alloys, Alloy 600 (15.5% Cr, 8.4% Fe, 0.02% C), and Alloy 690 (30.23% Cr, 9.17% Fe, 0.02% C). After *in-situ* CER measurements, the specimens were removed from the autoclave and analyzed by Raman spectroscopy to identify the oxides.

Fig. 1 shows the variation of electrical resistance of the passive film of Alloy 600 during cyclic chemical polarization of the specimens from a low corrosion potential (0.01 ppm of D.O.). Initially the electrical resistance was very low and reached a steady state value of about 45 ohm-cm^2 during continued exposure to low D.O. water. When the corrosion potential was raised, the electrical resistance of the passive film did not increase until reaching a potential of −120 mV, after which it increased steadily to a value of 1500 ohm-cm^2 at the end of 12 h exposure to water containing 32 ppm of D.O. The increase in electrical resistance with increase in corrosion potential denotes *n*-type semiconductivity of the passive film [6]. During reverse chemical polarization (cycle 2), the corrosion potential was decreased by decreasing the oxygen content. The electrical resistance increased with decreasing potential, showing *p*-type semiconducting behavior until the corrosion potential was −40 mV, below which the resistance started to decrease restoring the *n*-type semiconductivity of the passive film. The observed *p*-type behavior during oxygen removal could be attributed to non-equilibrium concentration of oxygen ions present in the oxide making it a *p*-type semiconductor. With continuous nitrogen purging, oxygen vacancies were created and reached equilibrium with the corresponding partial pressure of oxygen resulting in the *n*-type behavior. The forward and reverse chemical polarization resulted in hysteresis of electrical resistance values of the passive film of Alloy 600. Similar results have been observed for austenitic stainless steels [6–8]. The electrical resistance at lower potentials after cyclic polarization was observed to be two times larger than the values observed initially.

Fig. 2 shows the variation of electrical resistance of the passive film with corrosion potential when the cyclic chemical-polarization was carried out from a higher potential to a lower potential (cycle 1) and back to higher potential (cycle 2). The resistance was initially low because of the "film-free" surface and it increased with increase in exposure time at higher potential as the film thickened and reached almost a steady state value at the end of the 12 h exposure. This electrical resistance value was observed to be smaller than that observed at the same potential but polarized initially from a lower potential (Fig. 1). Decreasing the corrosion potential below −120 mV decreased the electrical resistance values of the passive film (Fig. 2). The same potential value (−120 mV) was associated with increase in electrical resistance value when the specimen was polarized from lower to higher potential (Fig. 1). Interestingly, the hysteresis observed in Fig. 1 is absent in Fig. 2.

Fig. 3 shows the electrical resistance of the passive film of Alloy 690 as a function of corrosion potential when the specimens were cyclically polarized from a lower corrosion potential. No threshold potential was

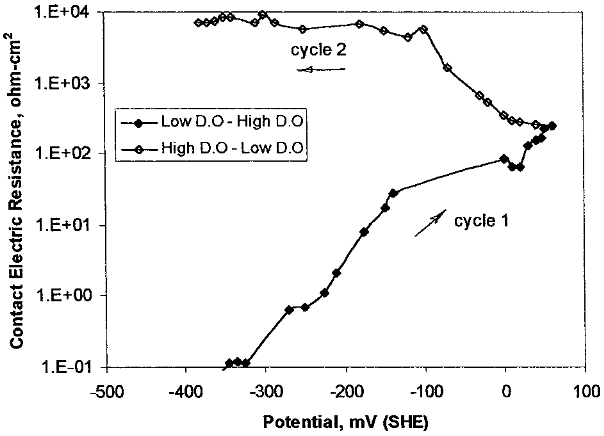

Figure 3 Contact electrical resistance of the passive film of Alloy 690 exposed to pure water at 288 °C. The specimens were cyclic-polarized chemically by varying the dissolved oxygen (D.O.) from 0.01 to 32 ppm (cycle 1) and back to 0.01 ppm (cycle 2).

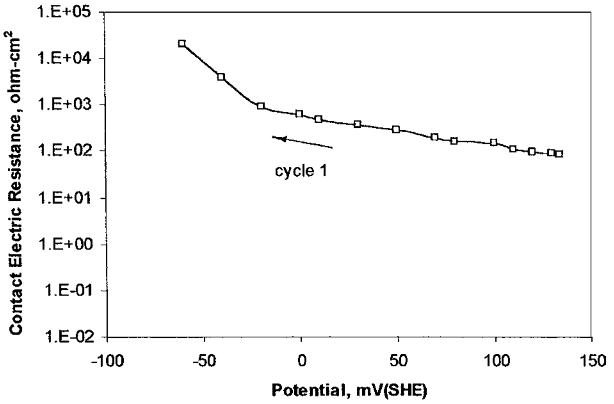

Figure 4 Contact electrical resistance of the passive film of Alloy 690 exposed to pure water at 288 °C. The specimens were chemically polarized by varying the dissolved oxygen (D.O.) from 32 to 0.01 ppm (cycle 1). The resistance values remained very high during reverse cycle (back to higher D.O. content), which is not shown in the figure.

required to increase the electrical resistance from a steady state value as the resistance increased steadily with increase in corrosion potential, showing a typical *n*-type semiconducting behavior. The "steady state" electrical resistance at higher potentials was much less than that observed for Alloy 600. However, the interesting observation to be noted is the continuous increase in electrical resistance value with decreasing corrosion potential for Alloy 690, indicating a *p*-type semiconducting behavior. For Alloy 600 also, a change from *n* to *p*-type semiconductivity could be observed within a small potential range. However, *n*-type behavior was found to be restored below a certain potential in Alloy 600. Whereas, the passive film of Alloy 690 showed *p*-type semiconductivity after exposure to higher corrosion potential. Fig. 4 also confirmed this behavior when the Alloy 690 specimens were cyclically polarized from higher corrosion potential. Decreasing the corrosion potential increased the electrical resistance of the passive film. The observed resistance values were much higher and above the measurement range of the instrument. Therefore, the resistance values at lower potentials could not be determined. When the polarization was reversed back to higher potential, no noticeable change in resistance could be observed as the values were out of range of the instrument. The observed transformation from *n*-type to *p*-type semiconductivity could be attributed to the transpassive dissolution of chromium in the oxide layer. Such dissolution of metal could generate cation vacancies and result in *p*-type semiconducting behavior.

Ex situ Raman spectroscopy studies carried out on the specimens after CER measurements indicated the presence of only $NiFe_2O_4$ type oxide film. Other investigators have reported a two layered passive film on Ni-Cr alloys; an inner layer of Cr_2O_3 type and the outer layer of NiO type [9]. Both NiO and Cr_2O_3 are considered as *p*-type semiconductors. Therefore, the passive film should reveal *p*-type behavior at all potentials. Montemor *et al.* [10] observed that the composition of the film varied with pH of the solution and the temperature. Also, they observed a *p*-type inner layer and *n*-type outer layer on both Alloy 600 and 690 by *ex-situ* analyses. Thermodynamic considerations of corrosion of Alloy 690 [4] and Alloy 600 [11] indicated the presence of $NiFe_2O_4$ surface layers. Therefore, the top layer of the passive film of both alloys could be considered as spinel of $NiFe_2O_4$. However, the type of inner layer could not be detected by Raman spectroscopy.

The corrosion resistance of a material could be influenced by both the magnitude of conductivity and the type of semiconductivity of the passive film. Baek *et al.* [12] observed that the semiconductivity of the passive film of Alloy 600 changed from *p*-type to *n*-type at a particular potential (0.2 V vs. pure nickel in that test environment) above which the SCC growth rate retarded in 10% NaOH solution at 310 °C. The decreased susceptibility of the material at potentials higher than 0.2 V was attributed to the formation of better corrosion-resistant *n*-type film. The *p*-type film was considered as less corrosion resistant as it contained predominant metal cation vacancies, which promoted easy transportation of metal ions to the film/electrolyte interface [12]. However, following the same line of reasoning using a point defect model [13], one can argue that an *n*-type film may be more susceptible to SCC in chloride environments, as oxygen vacancies in the *n*-type film are preferential sites for chloride incorporation and subsequent film breakdown by condensation of vacancies at the metal/oxide interface. In this present study, the reported higher corrosion resistance of Alloy 690 could not be attributed to a particular type of semiconductivity as the electrical resistance of the passive film was found to be influenced by prior oxidation conditions. Exposure to a higher oxygen content was found to alter the film properties and subsequent lowering of the corrosion potential resulted in a very high electrical resistance. This could be attributed to a change in conduction mode from electronic (at initial lower potentials) to mixed mode viz, both ionic (at the outer layer of the film) and electronic (at the inner oxide layer). The two layered oxide layer was not directly revealed by CER measurements as the polarization of potentials was not sufficient enough to result in degeneration by band bending. However, the observed higher electrical resistance of passive film of Alloy 690 could be attributed to the higher corrosion resistant properties of the alloy.

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