

Study of Oxide Formation on Alloy 800 by Potentiostatic Polarization

Chong Hun Jung^{a*}, M. Momeni^b, C. J. Wren^b

^aKorea Atomic Energy Research Institute,

Decontamination & Decommissioning Research Dept.

^bUniversity of Western Ontario, Chemistry Dept.

*Corresponding author: nchjung@kaeri.re.kr

1. Introduction

INCOLOY alloy 800 is a widely used material for construction of equipment requiring corrosion resistance, heat resistance up to 1500°F, and mechanical strength. In chemical and petrochemical processing, the alloy is used for heat exchangers and piping systems in nitric acid media. In nuclear power plants, it is used for steam generator tubing in pressurized water reactors (PWRs), including Canadian Deuterium Uranium (CANDU®) reactors. However, failures resulting from localized corrosion such as pitting, crevice and stress corrosion cracking (SCC) have been observed in the service environments. There exists still considerable controversy over the type of oxide that can be formed and the mechanism of oxide formation on Alloy 800.

The objectives of study are to investigate the effect of potential on oxide formation and conversion on alloy 800 under potentiostatic conditions. For this study we have focused primarily on corrosion at pH_{25°C} 8.4

2. Methods and Results

2.1 Experimental Methods

The studied material in this work was Alloy 800 containing 43 wt% Fe, 33 wt% Ni and 22 wt% Cr. Electrodes prepared from the metals had a flat, circular face, with a surface area of 0.7 cm². Prior to each experiment the sample surface was abraded manually with 400, 600, and then 1200 grit SiC papers, polished with 1 μm MetaDi Supreme diamond paste suspension (Buehler) on Texmet microcloth (Buehler), and then finally sonicated in an acetone/methanol mixture for 5 min to remove surface residues. All experiments were conducted at room temperature in Ar-sparged 0.01 M sodium borate solutions. The de-aerated solutions were prepared using reagent grade Na₂B₄O₇. A pH of 8.4 was obtained by adding appropriate amounts of 1 M boric acid solution to the borate solution.

A Solartron model 1480 multistat was used in all electrochemical measurements. Before each experiment the electrolyte solution was Ar-purged for at least 60 min. The freshly prepared working electrode was then cathodically cleaned at -1.1 V_{SCE} for 5 min.

2.2 Potentiostatic polarization on Alloy 800

Figure 1 shows potentiostatic polarization results for the Alloy 800 at room temperature and pH_{25°C}=8.4. At

high potentials, the current stays at high value for couple of seconds ($t < 3$ s) and then drops. This behavior can be attributed to the cations speciation in the defective air-formed oxide and consequent IR-drop. The rapid change to a state where the current is almost independent of E_{APP} indicates that the concentration gradient of the 'free' metal cations inside the initial oxide layer reaches a (pseudo-) steady state that is independent of E_{APP} and potential-gradient-induced ion migration through the Cr₂O₃ layer is no longer the rate determining step for metal oxidation. At longer times, the oxidized metal cations can react with oxygen anions, either converting the existing Cr₂O₃ oxide to a more defect-free oxide (such as FeCr₂O₄) and/or growing an oxide/hydroxide layer of a single metal element such as Ni(OH)₂/NiO. As these oxides grow the transport of the metal cations or oxygen anions across the oxide layer takes longer. As well, if a more defect-free oxide is formed, transport will become more difficult and both of these factors will reduce the net metal oxidation rate. Consequently, the current decreases with time as the oxide grows, and the rate of change in current with time depends on the type of oxide that grows and the oxide growth mechanism. For more accurate discussion about the difference in the behavior of this alloy at various potentials, accumulated charge density is used as shown in Figure 1.

Prior to discussion on the changes in the time-dependent behavior of current or total charge Q , it should be noted that at potentials below $\square 0.3V_{SCE}$, the net current is initially positive but then switches to cathodic but the time for this switch to occur depends on E_{APP} and temperature. It shows that the oxides formed on the surface may be passive in terms of ionic conductivity at these potentials but they clearly do not suppress electron conductivity and hence, the electrode can support cathodic reduction. Due to this reduction process the rate of any metal oxidation that may also continue to occur on the working electrode at long times cannot be directly extracted from the measured current at these low potentials.

At a given E_{APP} , the $\log |i|$ vs. $\log t$ plot over the duration when the net current is positive (i.e., when the cathodic current is significantly smaller than the metal oxidation current) shows a number of stages (periods) having distinctly different slopes. We count these stages after the initial Stage 0 for $t < 3$ s. The number of different stages present during 5-h polarization and the duration of each stage depend on E_{APP} . The number of stages observed in $\log |i|$ vs. $\log t$ data strongly

correlates with the number of different oxides that form over the polarization period.

The existence of distinctly different stages during polarization suggests that there are changes in metal oxidation mechanism as polarization proceeds and different oxides grow. That the number of stages depends on E_{APP} further indicates that the extent of metal oxidation and hence the type of oxide that can be formed depend on the potential applied to the alloy/oxide interface.

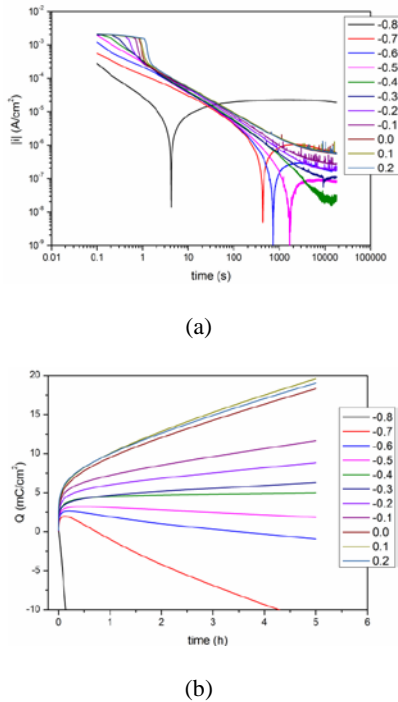


Fig. 1. Potentiostatic results on the Alloy 800 in the form of (a) $\log|i|$ vs. $\log t$, (b) accumulated charge vs. t at room temperature.

3. Summary

The results presented in Figures 1 show that in the range from $-0.8 V_{SCE}$ to $+0.2 V_{SCE}$ there are four potential regions having distinctly different short- and long-term characteristics in the $\log|i|$ vs. $\log t$ and Q vs. t plots. At a potential below $-0.8 V_{SCE}$, the current becomes cathodic immediately (< 10 s) upon polarization, indicating negligible metal oxidation and hence is not of interest.

Region I ($-0.8 V_{SCE} \leq E_{APP} < -0.6 V_{SCE}$): In this region the time-dependent behavior of $\log|i|$ vs. $\log t$ at short times (when the net current is anodic) depends strongly on E_{APP} (Figure 1). The net current switches to cathodic within 20 min of applying a potential. As seen in Figure 1, this region is characterized by a very rapid increase in Q to a maximum value before it decreases at

a constant rate with time. The magnitude of the cathodic current (the negative slope of Q vs. t) decreases with increasing E_{APP} .

Region II ($-0.6 V_{SCE} \leq E_{APP} < -0.4 V_{SCE}$): This region has a very narrow potential range but it exhibits characteristics that are distinctly different from those observed in Region I or Region III. The difference can be seen from charge slope in Figure 1. Unlike in Region I, the current in Region II decreases nearly linearly with time before it switches to cathodic and its time-dependent behavior is nearly independent of E_{APP} . Accordingly the Q at short times (< 15 min) is independent of E_{APP} . The steady-state current at long times becomes more positive with E_{APP} , continuing the trend that was observed in Region I. However, the trends in Q as a function of t and the slope of Q vs. t as a function of E_{APP} change as the potential moves into Region III; the Q at short times is larger at a higher E_{APP} while the net current at long times becomes zero. At $80^\circ C$, the differences between the regions are better seen in the dependences of the maximum value for Q and the slope of Q vs. t on E_{APP} . The steady-state cathodic current (the negative slope of Q vs. t) also shows a different dependence on E_{APP} , a negligible change with E_{APP} within Region II whereas it decreases with E_{APP} in Region I. These trends change again when the potential moves into Region III.

Region III ($-0.4 V_{SCE} \leq E_{APP} \leq -0.2 V_{SCE}$): In this region, the slope of charge vs. time changes again. The Q vs. t plots show a small dependence on E_{APP} but most of this dependence is due to the dependence of current on E_{APP} at very short times (in Stage 0).

Region IV ($-0.2 V_{SCE} < E_{APP} \leq 0.2 V_{SCE}$): In this region the current decreases with time and the behavior of $\log|i|$ vs. $\log t$ at times < 15 min (900 s) is nearly independent of E_{APP} . The $\log|i|$ vs. $\log t$ plots have a slope of -1 up to ~ 15 min after which the current starts deviate more progressively from the linear decrease with time (Stage IV). Eventually the current reaches a constant positive value after 3 h of polarization (Stage V). The constant current in Stage V indicates that the oxide is no longer growing and any oxidized metal (formed at a very slow rate) dissolves into solution. In Region IV, the effect of E_{APP} on Q is relatively small at short times (Stages I/II/III) but is significant at long times (Stages VI and V).

REFERENCES

- [1] W. Xu, K. Daub, X. Zhang, J.J. Noel, D.W. Shoesmith, J.C. Wren, *Electrochimica Acta* 54 (2009) 5727.
- [2] Q.W. Knapp, J.C. Wren, *Electrochimica Acta* 80 (2012) 90.