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Oxide Formation on Alloy 800 at $pH_{25°C}$ 8.4

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1. Introduction

INCOLOY alloy 800 is a widely used material for construction of equipment requiring corrosion resistance , heat resistance up 1500F, 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 potentiodynamic 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 cm^2. 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 $Na_2B_4O_7$. 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. For tests performed under each set of temperature conditions, A series of electrochemical tests on cyclic voltammetry at different vertex potentials with the scan rate of 0.17 mV/s was performed.

2.2 Cyclic Voltammetry on Alloy 800

Figure 1 shows the CV results at room temperature at three different vertex potentials i.e -0.2, 0.0 and 0.4 V_{SCE}. In the CV results, there are some peaks labeled as A1, A2 and A3 for anodic peaks and C1 for the cathodic peak. These peaks show the transformation of one type of oxide to the other one.

<u>Peak A1</u>

In the range of potential of peak A1, anodic oxidation of Fe to Fe^{2+} oxide like FeO, $Fe(OH)_2$ or $FeCr_2O_4$ and Fe to $Fe^{2+}/^{3+}$ oxide i.e. Fe_3O_4 is all possible from thermodynamic point of view. For all three vertex potentials, the intensity of peak increase by cycles and the potential shifts to more negative values. It shows that number of reactive sites increases by number of cycles and the shift to more negative potentials might be an indication of more feasible formation of iron chromate. It can be said that surface is covered by a two types of oxide after peak A1, an inner layer of iron chromate and outer layer of magnetite. Both of these oxides are known to have a spinal structure, highly insoluble and hard to reduce. This is why there is no corresponding cathodic peak for peak A1. The cathodic at very negative potentials is due to water reduction.

Oxidation of Cr to Cr^{3+} and hydrated Fe^{2+} hydroxide to α-FeOOH is also thermodynamically possible in the potential range of peak A1, however, both of these reactions are kinetically slow. Oxidation of Cr to Cr^{3+} requires the movement of chromium cations and oxygen anions through the pre-existed air-formed oxide and also chromate and magnetite layer on the surface which produces a very large energy barrier for this reaction. Conversion of hydrated Fe^{2+} hydroxide to α-FeOOH is likely impossible because it needs significant change in oxide structure. In addition to all of above reasons, the paths for formation of magnetite and chromite are facile and their formation is more likely from kinetic point of view.

<u>Peak A2and peak C1</u>

Another peaks appear at potential range of -0.45 V_{SCE} and in backward scan a cathodic peak at the same potential. Although the intensity of the peak does not change significantly, due to other peaks current intensity and background current density, this peak is more obvious when the upper limit of scan is below 0.0 V_{SCE}.

In addition, the intensity of this peak is diminished by increase in number of cycles which shows lower reactive sites for this reaction is possible at higher cycles. Previous studies showed that this peak for both carbon steel and SS316 is due to conversion of Fe_3O_4 to γ-Fe_2O_3 [1-2] and here the same reaction is considered. Magnetite and Maghemite have nearly close crystalline structure and this makes their conversion to occur easily.

Considering high amount of nickel in this alloy (~33 wt%), it can be seen that in addition to the iron oxides conversion, oxidation of Ni to Ni^{2+} in the form of $NiO/Ni(OH)_2$ and $NiFe_2O_4$ is also possible. As a result, this peak can be also attributed to the oxidation of nickel.

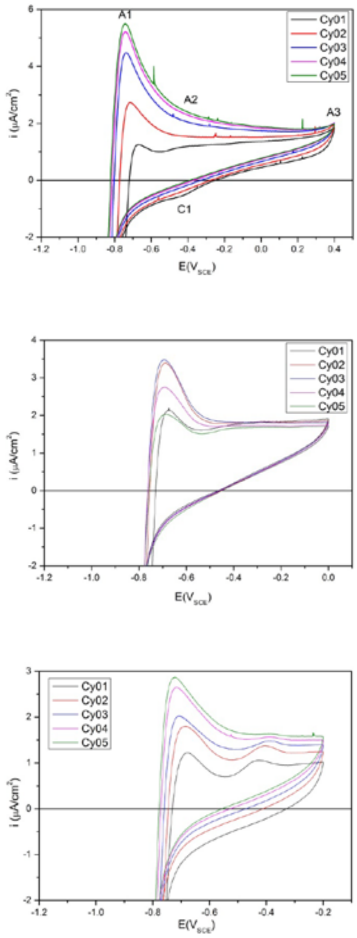

Fig. 1. Cyclic Voltammetry (CV) results on the Alloy 800 at room temperature and $pH_{25°C}$=8.4 and three different vertexpotentials a) 0.4 V_{SCE}, b) 0.0 V_{SCE}, c) -0.2 V_{SCE}

Peak A3

When the scan limit is beyond 0.2 V_{SCE}, at potentials just below 0.4 V_{SCE} the current density starts to increase. By looking to the thermodynamic potentials this increase in current is due to the oxidation of Cr^{3+} to Cr^{6+}.

Mechanism for this oxidation is presented previously [2], here in short, since oxidation of magnetite to γ-FeOOH is also possible from thermodynamic point of view and the fact that it is known that this oxidation causes fracture in oxide, it exposes the inner Cr^{3+} oxide to the solution and its oxidation to highly Cr^{6+} oxide occurs and leads to an increase in current density.

3. Conclusions

Based on this discussion, potential regions in CV results can be summarized as follow:

Region I ($E<-0.5V_{SCE}$): in this potential range, oxidation of Fe is limited to formation of $Fe^{2+}/^{3+}$ oxides. The initial air-formed chromium oxide which is defective is converted to chromite as an inner oxide layer and there will be a magnetite oxide as an outer oxide layer.

Region II ($-0.5V_{SCE}< E<0.0V_{SCE}$): in this potential range, oxidation of $Fe^{2+}/^{3+}$ to Fe^{3+} is possible and also the conversion of the initial pre-existed oxide to chromite is completed.

Region III ($0.0V_{SCE}<E<0.3V_{SCE}$): At potential above 0.0 V_{SCE}, oxidation of Fe_3O_4 to γ-FeOOH is possible and causes some fractures in the oxide. These fractures in the presence of aggressive halides can lead to the localized corrosion like pitting and crevice corrosion.

Region IV ($E > 0.3V_{SCE}$): In this region, oxidation of Cr^{3+} oxide to Cr^{6+} occurs and since Cr^{6+} is highly soluble, current density increases.

By looking to the CV and corrosion potential measurement results, corrosion potential in this pH and room temperature locates at the region one, i.e. the surface is covered by an inner iron chromate oxide and an outer magnetite.

REFERENCES

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