Temperature Dependence of Radiation-Induced Corrosion of Stellite-6 at pH 10.6

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Abstract

The effect of γ-radiation on the corrosion of Stellite-6 has been studied by characterizing the oxide films formed at 25°C and 150°C at $pH_{25°C}$ 10.6. The effect of oxygen (aerated solution) on the film formation has also been determined at 150°C. Results show that anodic oxidation is highly promoted by irradiation at 150°C, leading to thicker oxide layers and potentially more cobalt dissolution. Surface analysis results indicate that the film formed on Stellite-6 after irradiation in a basic solution at 150°C mainly consists of $CoO/Co(OH)_2$. Dissolved oxygen (aeration) increases the ratio of CoO to $Co(OH)_2$ in the oxide film and the content of $CoCr_2O_4$ and Co_3O_4 in the film.

1. Introduction

Stellite-6 is a Co-based alloy with two distinct phases: a chromium-rich phase and a cobalt-rich phase. Due to its high mechanical strength and corrosion resistance, this alloy is used in places that require high wear-resistance, such as valve facings and ball bearings, in nuclear reactors. Although Stellite-6 is known to be highly corrosion resistant under normal water conditions, its corrosion behaviour with ionizing radiation present has not been well established [1]. Corrosion of a Co-based alloy can lead to the introduction of Co ions (dissolved in circulating cooling water) into the reactor core. In the reactor core, stable ^{59}Co can absorb a neutron to become the radioactive isotope, ^{60}Co, creating a radiological hazard for plant workers [1]. The high radiation fields present in a reactor core decompose water to a range of redox-active species (both highly oxidizing (e.g., •OH, H_2O_2) and highly reducing (e.g., $•e_{aq}^-$, $•O_2^-$)) [2]. These species can significantly influence corrosion kinetics [3]. To develop an understanding of the influence of γ-radiation and temperature on the corrosion behaviour of Stellite-6, a number of experiments have been conducted in a mildly basic solution (pH 10.6) (Table 1). The pH was chosen to match the

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coolant conditions in CANDU nuclear reactors. Corrosion potential (E_{CORR}) measurements and surface analyses were performed to characterize oxide films grown on Stellite-6 in all experiments.

	Short term (3 days)				**Long term (1 week)**	
Solution State	De-aerated				Aerated	De-aeraed
Conditions	25°C No Rad	25°C Rad	150°C No Rad	150°C Rad	150°C Rad	

Table 1: Matrix of experimental conditions.

2. Experimental

The Stellite-6 used in this study (Metal Samples Company), has the mass composition of Cr, 27.62%, Mo, 0.41%, W, 4.07%, Si, 1.07%, C, 1.42%, Ni, 2.62%, Fe, 2.92%, and Mn, 0.27% and balance Co (~59.6%). A 10-mm diameter Stellite-6 rod was cut into solid cylindrical pieces (coupons) 3-mm thick. Prior to a test a coupon was polished in sequential steps [2] followed by a sonication in a 50:50 acetone:methanol mixture for 5 min to remove polishing residues. The corrosion tests were performed with the test coupon contained in a 20 ml sealed vial (Fig. 1b). Quartz was used for the bottom of the vials thereby minimizing the incorporation of silicate into any oxide film grown on the coupon surface. The sample vial was prepared inside an Ar-purged glove box. All experiments were conducted in 0.01 M sodium borate solution ($Na_2B_4O_7$, Caledon Laboratories Ltd.) made up with water with a resistivity of 18.2 MΩ cm. The solutions were pre-purged either with Ar or air, and pH-adjusted to 10.6 by an adding appropriate amount of 1 M NaOH (Caledon Laboratories Ltd.) solution to the borate solution.

The vials were capped using aluminum crimp caps with PTFE silicone septa (Agilent Technologies) to provide an air tight seal. The sealed vials were placed inside an autoclave (250 mL Type 316 stainless steel pressure vessel (Parr Instrument, model 4760)) and the autoclave was filled with water to provide a pressure balance when heated. The autoclave was located inside an electrical heating sleeve and placed inside an MDS Nordion Gammacell 220 Excel Cobalt-60 irradiator which provided a dose rate of 5.5 kGy h^{-1}.

Following a test the sample vial was removed from the autoclave and samples were extracted from the cover gas in the vial using a gas-tight syringe. Then the vials were opened and the coupons were removed, dried in flowing argon gas, and stored in the glove box, and the residual solution in the vial was analyzed only for pH. SEM was used to examine the morphology of corroded coupon surfaces. To determine the chemical composition and phase of the oxides present in the surface film, x-ray photoelectron spectroscopy of the coupons was performed. Under normal analysis conditions the analysis spot size was approximately 400 µm × 700 µm. Broad-spectrum survey scans were recorded at a pass energy of 160 eV to verify surface composition and cleanliness. High-resolution spectra (20 eV pass energy) were used to examine the peaks for Co 2p (binding energy at ~780 eV), Cr 2p (~574 eV), O 1s (~530 eV), and C 1s (calibration set point 284.8 eV) (from adventitious carbon) [4].

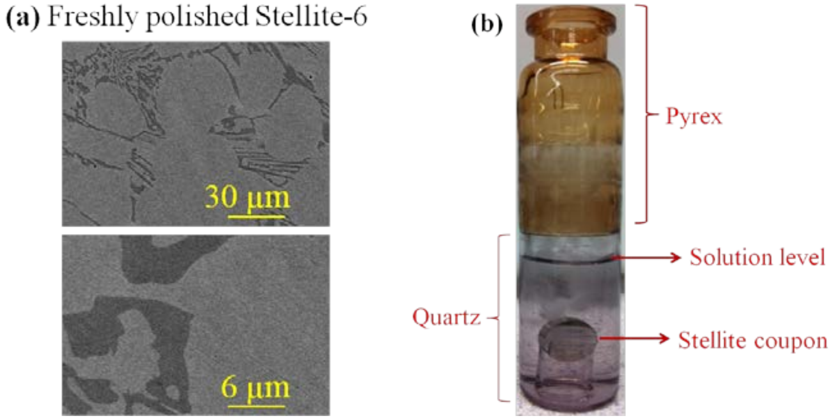

Figure 1: a) SEM image of pre-oxidized Stellite-6 surface, and b) photograph of the vial and coupon.

3. Result and discussion

Figure 1a shows images of a freshly polished Stellite-6 coupon with two distinct phases visible on the surface (a cobalt-rich phase and a chromium-rich phase). Figures 2a and b show SEM images of samples after 3 d at 150° without and with radiation present, respectively. X-ray photoelectron spectroscopy (XPS) analysis of the coupon surfaces (results not shown) indicates that the oxide film consists of an inner cobaltous chromite ($CoCr_2O_4$) layer and an outer $CoO/Co(OH)_2$ layer, and that, on both irradiated and non-irradiated surfaces, the films are very thin (~7 nm). The SEM images show that the film formed in presence of radiation is more compact and uniform (Fig. 2b). There is no preferential oxidation or dissolution seen on either the cobalt-rich phase or the chromium-rich phase of the alloy, or along the phase boundaries.

The presence of oxygen initially in the solution further promotes anodic oxidation, leading to a thicker film and more uniform film coverage of the surface, Fig. 3. The XPS analysis shows that the oxide film formed in an aerated solution contains more CoO than $Co(OH)_2$ while the relative contributions of these species is reversed in the oxide film formed in a de-aerated solution. This is consistent with the formation of a thicker outer layer of Co^{II}

oxide/hydroxide since the hydration of Co^{II} species ($CoO(H_2O) \leftrightarrows Co(OH)_2$) occurs at or near the oxide/water interface and hence, its fraction will be smaller for a thicker oxide.

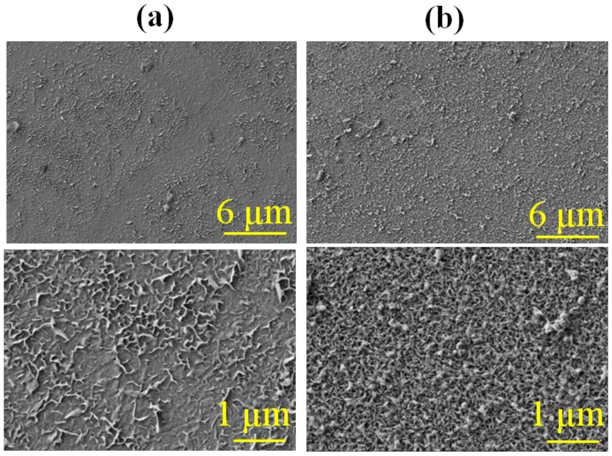

Figure 2: SEM images of a Stellite-6 coupon a) after 3 d at 150°C with no radiation and b) after 3 d at 150°C in presence of γ-radiation.

Our previous study on the electrochemistry of Stellite-6 [5] has shown that irradiation increases the corrosion potential from ~ -0.5 V_{SCE}, where the formation of $CoO/Co(OH)_2$ on $CoCr_2O_4$ can occur, to ~ 0.15 V_{SCE}, where the $Co(OH)_2$ can further oxidize to CoOOH (Fig. 4). This explains the greater degree of oxidation seen with radiation present.

Temperature has little influence on the equilibrium potentials of the different oxides (since heating is less effective at increasing chemical potential than radiolysis or photolysis) [3]. Thus, an increase in temperature should not significantly affect the type of oxide that can be formed. However, temperature can affect the rates of metal dissolution and oxide phase conversion. Our results show that the contribution of $CoCr_2O_4$ in the oxide film increases at 150°C compared to the film made at room temperature. This could be due to faster oxidative conversion of the pre-existing, defective Cr_2O_3 oxide to a chromite layer, or the faster hydration of Co^{II} species at the oxide/water interface.

Under irradiation the corrosion potential increases, which increases the rate of Co oxidation to form the outer Co^{II} oxide/hydroxide layer and the further oxidation of Co^{II} to CoOOH. The Co^{III} oxyhydroxide is insoluble and insulating, and hence, it will not form a thick layer, but its presence can suppress cobalt dissolution. The net cobalt dissolution under irradiation will thus depend on the rates of two competing reactions: Co to Co^{II} oxidation and the subsequent oxidation of Co^{II} to Co^{III}. Hence, detailed studies on the effects of pH and temperature to elucidate these rates under irradiation conditions are currently being carried out.

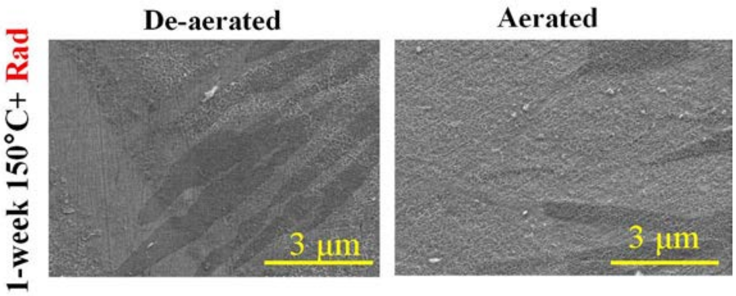

Figure 3 SEM images of a Stellite-6 coupon surface after 7 d exposure to a pH 10.6 solution at 150°C in the presence of radiation.

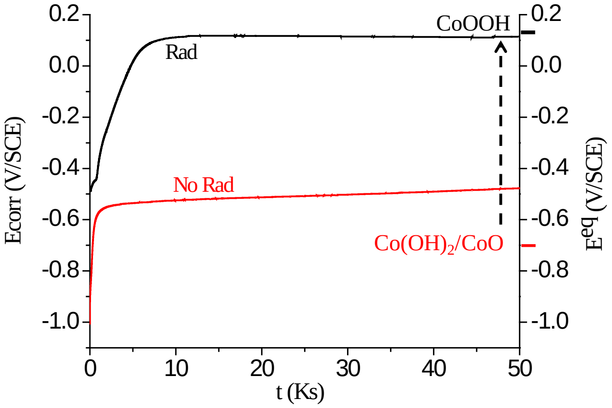

Figure 4: E_{CORR} as a function of time recorded on the Stellite-6 electrodes with and without γ-irradiation at pH 10.6 and at room temperature.

Acknowledgements

This research was funded under the Natural Science and Engineering Council of Canada (NSERC) and Atomic Energy of Canada Limited (AECL) Industrial Research Chair Agreement. Dr. Mark Biesinger at Surface Science Western is gratefully acknowledged for assistance in performing the surface analyses.

4. References

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