

Effect of Gamma-Irradiation on Stellite-6 Corrosion: Dependence on pH and Temperature

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Stellite-6 is a Co-based alloy that is used in many applications that require high corrosion and wear resistance at elevated temperatures, such as valve facings and in nuclear reactors. However, even limited corrosion and failure of the protective oxide film on Stellite-6 can lead to release of Co. This is a challenge because, in the reactor core, stable ^{59}Co can absorb a neutron to become radioactive, ^{60}Co , thereby creating a radiological hazard to nuclear plant workers [1].

Ionizing radiation generates water radiolysis products that change aqueous redox conditions and influence corrosion processes. 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 three pHs 6.0, 8.4 and 10.6 (measured at 25 °C). The results show that the texture and thickness of the oxide film depend on the water conditions and that the effect of radiation on corrosion kinetics also depends on temperature and pH.

The driving force for aqueous corrosion is the difference in the electrochemical potentials of the two interacting phases, the metal/metal oxide and water. This potential difference is related to the corrosion potential, E_{CORR} , at the metal/water interface. Due to the production of redox active species, γ -radiation increases E_{CORR} on Stellite-6, Figure 1.

Comparison of the E_{CORR} values with the equilibrium potentials of possible redox reactions of the constituent elements in Stellite-6, Figure 2, shows that γ -irradiation increases E_{CORR} from a point on the border between oxidation regions Ox I and Ox II, where the metal oxidation is limited to the formation of Co^{II} oxides ($\text{CoO}/\text{Co}(\text{OH})_2$) to a point on the border between Ox II and Ox III, where the Co^{II} can oxidize further to form a mixed $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ oxide and/or Co^{III} oxides or hydroxides.

Changing pH shifts the values of all of the redox equilibrium potentials of the metal oxidation and water reduction equally by 59 mV per unit pH change. Hence, changing pH has no significant effect on the composition of the oxide that forms on Stellite-6. Consequently, the oxide films formed at all three pHs studies are mainly composed of CoCr_2O_4 and $\text{CoO}/\text{Co}(\text{OH})_2$. Changing temperature also had no significant effect on the characteristic oxidation potential regions and the oxide formation mechanisms.

Although solution pH and temperature do not influence the oxide composition, they do significantly affect the morphology and thickness of the oxide that is formed and the rate of metal dissolution. These effects arise from the control by those parameters of non-faradaic processes such as surface hydration, dissolution, condensation. For example, the solubility of Co^{II} is pH dependent and has a minimum near pH 11 at 25 °C. Therefore, a higher rate of cobalt dissolution during corrosion is expected at pH 6 than at pH 8.4 or 10.6. Both Auger and XPS results show that the thinnest film is formed at pH 6, independent of

heating and radiation conditions. Similarly, we observed the formation of a thicker spinel oxide film (CoCr_2O_4) at 150 °C than at room temperature, due to an increase in the rates of oxide-crystal condensation and metal cation diffusion.

The effect of ionizing radiation depends on the solution conditions. The pH-dependent effect of irradiation on the morphology and the thickness of the oxide films formed at 150 °C is shown in Figure 3. The XPS and SEM analyses of the films show that the oxide layer formed at pH 10.6 is uniform and thick whereas at pH 6, where the rate of cobalt dissolution is high, the film is very thin and the surface shows Co_3O_4 crystallite deposits.

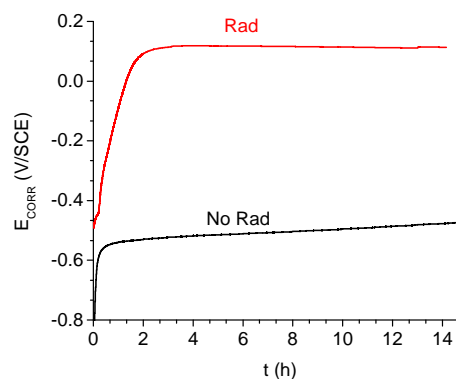


Figure 1: E_{CORR} as a function of time on a Stellite-6 electrode with and without γ -radiation present (at pH 10.6 and at 25 °C).

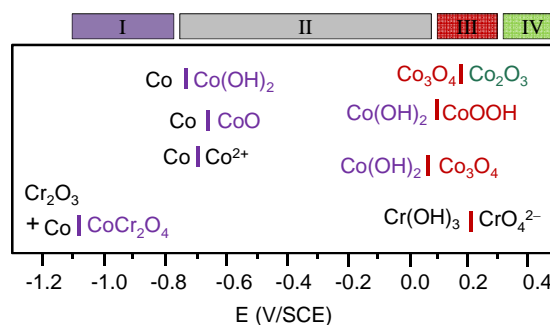


Figure 2: Calculated equilibrium potentials for various redox reactions are indicated by vertical lines. The horizontal bars delineate different oxidation regions.

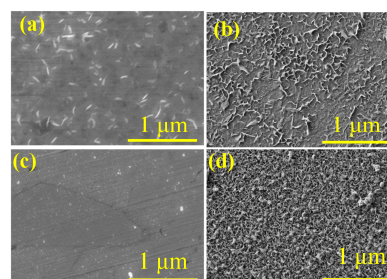


Figure 3: SEM images of Stellite-6 surfaces corroded at 150 °C: (a) and (b) in absence of radiation at pH 6 and 10.6, and (c) and (d) in presence of radiation at pH 6 and 10.6, respectively.

References

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- [2] M. Behazin, M.C. Biesinger, J.J. Noël, J.C. Wren, *Corros. Sci.* 63 (2012) 40-50.