

Aqueous Corrosion Behavior Of Plutonium Metal

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Plutonium, an element known to man for less than 60 years, exists in only limited quantities. However, unlike other "man-made" elements, plutonium is of significant technological importance. Plutonium is used in applications that utilize its fissionable nature. Plutonium metal is primarily used in nuclear weapons. Plutonium oxide is commonly used for mixed-oxide fuel in civilian reactors and is present as a fission product in spent uranium fuel.

Because of its radiological and chemical toxicity, plutonium is kept from contacting the environment. The lack of environmental exposure of plutonium, in combination with its scarcity and handling difficulties, have resulted in limited study of plutonium metal corrosion. Recently, interest in the corrosion of plutonium has increased. For instance, it has been reported that accidents have resulted in the release of plutonium into the ocean.¹ Additionally, plutonium metal stored in vaults or housed in gloveboxes oxidizes when exposed to air or water vapor. Both the loss of metal and the production of potentially respirable oxide have become more urgent concerns. Therefore, the corrosion of plutonium metal requires study.

The majority of plutonium corrosion studies to date have focused on gaseous corrosion. The earliest reports on plutonium oxidation were issued in the 1940s² and 1950s³. Additional studies have been released since that time. Almost all have examined weight gain as a function of time, temperature, and environment. There are a variety of inconsistencies between the literature data.⁴ Inconsistencies may be explained by the fact that plutonium has five allotropes between room temperature and its melting point (640°C), and because plutonium experiences self-heating due to radioactive decay. For instance, studies have revealed logarithmic⁵, linear⁶, and parabolic⁷ oxidation, respectively, with time. Many observers note distinct mechanistic changes with time and temperature which contributes to the variable behavior.⁸

The effects of pressure, moisture, temperature, and alloy composition on the oxidation rate of plutonium have been examined. The corrosion rate of delta-phase stabilized Pu – 1 wt% Ga has been shown to be independent of oxygen pressure below 100 Torr.⁸ Above this threshold, increasing oxygen concentration increases the corrosion rate.^{6,8} In the presence of moisture, plutonium corrosion was found to be greater in Ar than in air.⁹ The addition of moisture to air or inert gas has been shown to dramatically accelerate corrosion.^{5,7,10,11} Increasing temperature increases the corrosion rate of plutonium. Arrhenius behavior is observed over ranges of temperature but changes in reaction mechanism (slope on Arrhenius plot) are commonly observed.^{4,5,6,8} Alloying plutonium with other elements usually increases the corrosion resistance of metal.^{5,6,12,13}

The oxide scale on plutonium metal is primarily composed of PuO₂. An innermost region of composed of Pu₂O₃ has been observed and there is some suggestion that Pu⁺⁶ may be present in the oxide.¹⁴ An ellipsometric study of the oxide thickness on Pu – 1 wt% Ga indicated that films were tens to hundreds of nanometers thick one hour after sputter cleaning.⁴

In aqueous solution, plutonium can exist in the trivalent (Pu⁺³), tetravalent (Pu⁺⁴), pentavalent (PuO₂⁺), and hexavalent (PuO₂²⁺) states depending on solution composition. Many oxidation states can coexist simultaneously.¹⁵ Although the aqueous solution chemistry has been well studied, the aqueous corrosion behavior of plutonium metal has hardly been characterized. Immersion tests indicate that plutonium is attacked by tap water¹⁶, halides^{17,18}, perchloric acid¹⁶, and phosphoric acid¹⁶. No attack is observed upon exposure to nitric and acetic acids.¹⁶

Modern electrochemical testing of plutonium metal is necessary. This work will examine the polarization and electrochemical impedance response of plutonium metal as function of solution chemistry and pH. Passivity and the nature of the oxide film will be discussed. In addition, a history of plutonium metal corrosion will be reviewed.

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