

Some physico-chemical and radiation properties of plutonium-238 metal prepared by electrochemical amalgamation

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Abstract

Pu-238 metal was prepared by electrolytic amalgamation from Pu(III) acetate aqueous solution and by followed by the thermal decomposition of the Pu amalgam. The density, specific heat power, γ -spectra, neutron flux, and corrosion kinetics in dry air at ambient temperature of the prepared ^{238}Pu metal were measured. The neutron flux and γ -spectra from ^{238}Pu metal have been attributed to spontaneous and induced fission and to $(\alpha, \alpha'\gamma)$, $(\alpha, p\gamma)$, and $(\alpha, n\gamma)$ nuclear reactions on light nuclei. The electrochemically prepared ^{238}Pu metal was shown to generate fewer neutrons, produce less gamma radiation, and contains lower ^{10}B , ^{19}F , and ^{28}Si impurities in comparison with biomedical $^{238}\text{PuO}_2$. The increase of neutron flux from the sample due to the reaction $^{18}\text{O}(\alpha, n\gamma)^{21}\text{Ne}$ was shown to be proportional to the increase of the mass of the ^{238}Pu metal with time due to corrosion in dry air. ^{238}Pu metal corrosion rate maximum and average values (1.1×10^{-2} and $4.7 \times 10^{-3} \text{ mg cm}^{-2} \text{ h}^{-1}$, respectively) obtained in dry air were an order of magnitude higher than the rates published for ^{239}Pu under similar experiment conditions. The difference between the ^{239}Pu and ^{238}Pu metal corrosion rate and mechanism is proposed to be due to the greater radiation effects and temperature on the ^{238}Pu surface.

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1. Introduction

^{238}Pu is widely applied as a power source in cardiac pacemakers (each using $\sim 160 \text{ mg } ^{238}\text{Pu}$) and in remote power generation (e.g., the Apollo spaceships contained $14 \text{ kg } ^{238}\text{Pu}$ for its power generators [1]). The ^{238}Pu generally is present as $^{238}\text{PuO}_2$ with natural oxygen or with oxygen depleted in ^{17}O and ^{18}O to reduce neutron yields from (α, n) reactions [2]. The properties of ^{238}Pu metal are studied in less details than those of ^{239}Pu metal. The goal of this work is to study some properties of ^{238}Pu metal prepared by the non-conventional method of electrochemical amalgamation from Pu(III) aqueous solution and subsequent thermal decomposition of the plutonium amalgam [3]. The primary research focus is on ^{238}Pu metal pellet corrosion in air and to the increase of neutron flux and γ -radiation from the pellet arising due to the formation of $^{238}\text{PuO}_2$ and the nuclear reactions

$^{18}\text{O}(\alpha, n\gamma)^{21}\text{Ne}$ and $^{18}\text{O}(\alpha, \alpha'\gamma)^{18}\text{O}$. Despite data from numerous studies of ^{239}Pu metal corrosion [3–5], analogous data for ^{238}Pu are, for us, inaccessible or absent. The corrosion rates of ^{238}Pu and ^{239}Pu metals are expected to differ because of the higher specific α -activity of ^{238}Pu metal.

2. Experimental

The plutonium used in this testing, purified of its daughter uranium, had the isotope composition, determined by mass-spectrometry, as given in Table 1. The reduction of Pu(III) to the intermetallic compounds $\text{Pu}(\text{Hg})_n$, where $0 \leq n \leq 4$ (up to $0.5\text{--}0.6 \text{ kg Pu per liter Hg}$), was made by electrolytic amalgamation of 0.08 M Pu(III) in $1 \text{ M acetate buffer solution}$ ($\text{pH } 3.5\text{--}4.5$) at $(0.90\text{--}1.2) \cdot 10^3 \text{ A/m}^2$ current density at a Hg cathode at $10\text{--}15^\circ\text{C}$. The plutonium was isolated from the amalgam by its thermal decomposition. The mercury was swept from the plutonium by an argon stream at 600°C ; removal of residual Hg and trace sodium occurred at vacuum melting at 1100°C . A more detailed description of ^{238}Pu metal preparation by electrolytic amalgamation is given in [3]. The obtained plutonium ingots were pressed at $4.5\text{--}7.5 \text{ kbar}$ under an air atmosphere to prepare cylindrical pellets of 5 mm diameter and $2\text{--}4 \text{ mm height}$. The plutonium metal pellet corrosion experiments were carried out in boxes with $25 \pm 3^\circ\text{C}$ air atmosphere at 30% relative humidity. The photon flux from the prepared Pu pellets and from biomedical-quality $^{238}\text{PuO}_2$ were measured in the energy region

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Table 1
Isotope composition of studied plutonium

Isotope	Content (mass%)
^{238}Pu	80.7
^{239}Pu	16.0
^{240}Pu	2.7
^{241}Pu	0.6

0.1–1.5 MeV without filter and in 1.1–3.0 MeV with a 20 mm lead and 3 mm iron filter. The fast neutron fluxes of the prepared ^{238}Pu metal pellets were measured using the Russian model UNS neutron coincidence counter. Standard sources of biomedical $^{238}\text{PuO}_2$ were used for counter calibration. Summary inaccuracy of neutron flux measurements was lower 5%.

3. Results and discussion

3.1. Some physical properties of prepared ^{238}Pu metal

The densities of the pellets samples prepared by pressing of plutonium ingots were calculated after the measuring of their masses and the geometrical sizes. The densities were found to depend weakly on the preparation pressure in the studied 4.5–7.5 kbar interval, and their values varied from 16.1 to 17.0 g cm⁻³. Prepared ^{238}Pu metal was supposed to crystallize in alpha-phase at ambient temperature and obtained densities were about 81–85% of the density of α - ^{239}Pu measured by Xray diffraction technique at the same conditions. The thermal power was found by calorimetry to be 0.45 W/g for the studied Pu samples. The results of γ -spectra measurements from prepared ^{238}Pu metal and from biomedical $^{238}\text{PuO}_2$ are given in Table 2. The identification of the nuclear reactions and light nuclei impurities were done by their photon energy using published data [6,7]. The data of Table 2 show that no radioactive impurities were present in either the biomedical $^{238}\text{PuO}_2$ or in the ^{238}Pu metal. Stable light-element impurities of F, B, and Si were detected by gamma analysis in $^{238}\text{PuO}_2$ samples but no impurities were found by gamma analysis of the ^{238}Pu metal samples. This indicates that proposed electrochemical method of Pu metal preparation provides high purification of plutonium from light impurities and hence provides a lower level of photon and neutron irradiation from Pu metal in comparison with biomedical $^{238}\text{PuO}_2$.

Table 2
Gamma-spectrometric determination of light nuclei impurities in biomedical $^{238}\text{PuO}_2$ and in ^{238}Pu metal prepared by electrochemical amalgamation

Sample	Detected photon energy (keV)	Measured photon intensity, photon/s g ^{238}Pu	Detection limit for photon of this energy, photon/s g ^{238}Pu	Nuclear reaction ^a
Biomedical $^{238}\text{PuO}_2$	1236	$(4.2 \pm 0.6)1 \times 0^3$	170	$^{19}\text{F}(\alpha, \alpha'\gamma)^{19}\text{F}$
	1275	$(1.1 \pm 0.2) \times 10^4$	170	$^{19}\text{F}(\alpha, p\gamma)^{22}\text{Ne}$
	1395	$(2.0 \pm 0.6) \times 10^3$	250	$^{18}\text{O}(\alpha, n\gamma)^{21}\text{Ne}$
	1528	$(1.1 \pm 0.6) \times 10^3$	190	$^{19}\text{F}(\alpha, n\gamma)^{22}\text{Na}$
	1632	$(2.5 \pm 0.6) \times 10^3$	240	$^{10}\text{B}(\alpha, \alpha'\gamma)^{10}\text{B}$
	1779	$(1.3 \pm 0.6) \times 10^3$	300	$^{28}\text{Si}(\alpha, \alpha'\gamma)^{28}\text{Si}$
	1982	$(1.6 \pm 0.6) \times 10^3$	340	$^{18}\text{O}(\alpha, \alpha'\gamma)^{18}\text{O}$
	2081	$(4.4 \pm 0.6) \times 10^3$	470	$^{19}\text{F}(\alpha, p\gamma)^{22}\text{Ne}$
	2234	$(2.7 \pm 0.6) \times 10^3$	600	$^{28}\text{Si}(\alpha, p\gamma)^{31}\text{P}$
^{238}Pu metal	None found	–	–	–

^a The identification of the light nuclei was done using data [6,7].

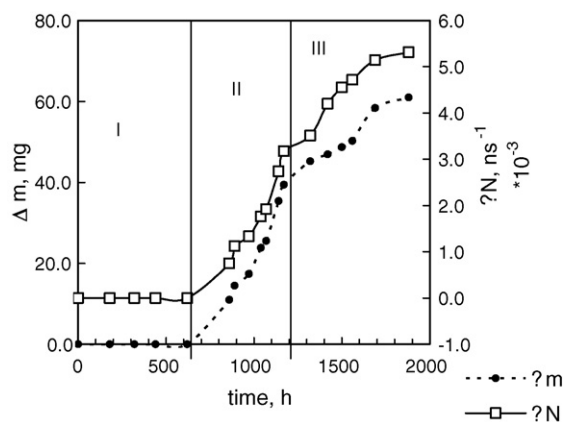


Fig. 1. Mass sample and neutron flux increase during ^{238}Pu metal corrosion in air at 25 °C. Mass sample 1.1 g, $S = 0.82 \text{ cm}^2$, air humidity 30%. I, II and III—the stages of the corrosion process.

Table 3
 ^{238}Pu metal corrosion rate at different stage in dry air

Interval (h)	Corrosion rate (mg Pu/cm ² min)
(I) 0–700	Non detected
(II) 700–1350	1.1×10^{-2}
(III) 1350–1820	3.3×10^{-3}
Average corrosion rate, 0–1820	4.8×10^{-3}

3.2. ^{238}Pu metal corrosion in air and the increase of neutron flux from the sample

The corrosion rate of ^{238}Pu metal was determined by measuring the sample mass increase and the neutron flux increase as function of time. The parameters were found to be proportional and changed in the same manner during the experiment time. The mass sample increase in dry air due to combination with oxygen and the reaction $^{18}\text{O}(\alpha, n\gamma)^{21}\text{Ne}$ (Fig. 1) demonstrate the kinetics of ^{238}Pu metal corrosion. Three separate corrosion stages (steps) could be marked. The corrosion rates, calculated from the Fig. 1 data for each stage, are given in Table 3. Comparison of rate values from Table 3 with published data shows that ^{238}Pu metal corrodes in 25 °C air about 10-times more rapidly than does

Table 4
Kinetic parameters of ^{238}Pu metal oxidation in air^a at 25 °C

Determination method	Measured parameters	Stage 2	Stage 3
Measurement of mass increase	k_{eff} (mg Pu cm ⁻² h ⁻¹)	$(3.1 \pm 1.8) \times 10^{-3}$	$(2.7 \pm 0.99) \times 10^{-4}$
	n	4.10 ± 0.15	1.00 ± 0.04
Neutron flux measurement	k_{eff} (mg Pu cm ⁻² h ⁻¹)	$(2.7 \pm 1.9) \times 10^{-3}$	$(2.4 \pm 0.8) \times 10^{-4}$
	n	4.15 ± 0.12	0.96 ± 0.05

^a Air humidity was 30%, mass sample 1.1 g.

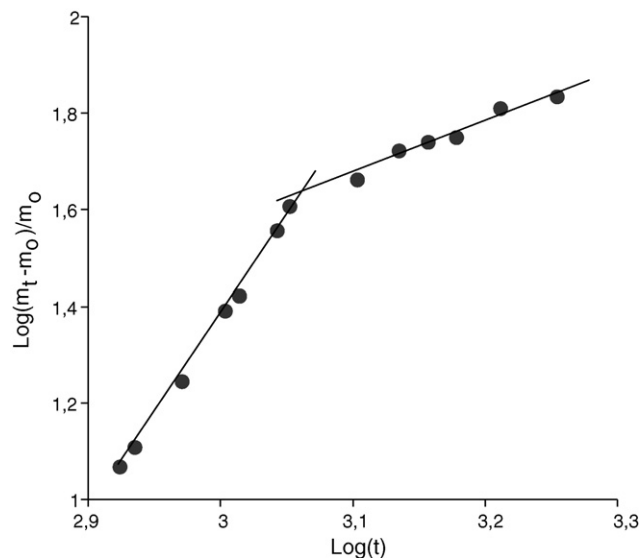


Fig. 2. ^{238}Pu metal corrosion kinetics in air at 25 °C in logarithmic coordinates. Sample mass 1.1 g, 30% relative humidity air.

^{239}Pu (10^{-4} to 10^{-3} mg cm⁻² h⁻¹ [4,5]) under similar closed conditions. The difference in corrosion rates between ^{238}Pu and ^{239}Pu is likely caused by the higher specific activity of ^{238}Pu , which is 275-times greater than that of ^{239}Pu [6], to produce higher surface temperature and greater radiolytic decomposition of adsorbed water vapor film on the ^{238}Pu metal surface. It is important to note that the ~ 1 g ^{238}Pu metal sample in an open glass tube did not show visible corrosion, weight gain, or increased neutron radiation during the first 30 days in 25 °C air at 30% humidity. Alloying with Ga, Zr, or other metals with $Z > 20$ is necessary to obtain better corrosion stability of ^{238}Pu .

The corrosion mechanism developed for ^{239}Pu [4,5] includes the formation of intermediate products Pu_2O_3 and PuH_3 before the final product PuO_2 . This mechanism can be accepted for ^{238}Pu with some additions. The first step (≈ 30 days) is latent slow corrosion during which no increase of sample mass or neutron flux is detected. Water vapor adsorption on the metal surface and the formation of initial corrosion centers (embryo), containing Pu_2O_3 and PuH_3 , occurs during the first latent stage. The corrosion rate increases quickly at the second stage, which continues ≈ 30 days and gives $^{238}\text{PuO}_2$ as the main product. The third stage is characterized by some corrosion rate diminution due to the formation of a thick passive $^{238}\text{PuO}_2$ film, which hinders diffusion of oxygen and water vapor to the plutonium metal surface. The logarithmic analysis of corrosion kinetic curves on

the stages 2 and 3 shows (Fig. 2) that the process can be described by the following equation:

$$k_{\text{eff}} t^n = \frac{d(m_t m_0 / m_0)}{dt} \quad (1)$$

where k_{eff} is the effective constant of ^{238}Pu metal corrosion rate, n in an empirical exponent dependent on surface changes and the active reagent diffusion rate through the surface. The values k_{eff} and n obtained by measuring mass increase and by neutron flux increase are given in Table 4. Plutonium nitride formation, which is negligible during ^{239}Pu corrosion in air, becomes more probable as a ^{238}Pu metal intermediate corrosion product because the Pu atoms and N_2 molecules receive more excitation energy due to alpha-radiolysis and recoil phenomenon on the ^{238}Pu surface than in the case of ^{239}Pu .

4. Conclusions

1. The ^{238}Pu metal prepared from aqueous solution by the electrochemical amalgamation method contains lower concentrations of light nuclei B, F, and Si impurities than standard biomedical $^{238}\text{PuO}_2$ to produce significantly less photon and neutron radiation due to ($\alpha, n\gamma$) reactions.
2. The ^{238}Pu metal corrosion rate, measured in air by the increase of ^{238}Pu metal mass sample and by the increase of neutron flux from the sample, was found to be order of magnitude higher than that of ^{239}Pu metal at similar conditions.

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