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**$^{238}\text{PuO}_2/\text{Mo}$ -50 wt % Re Compatibility
at 800 and 1000 °C**

Dale R. Schaeffer and Paul E. Teaney

July 18, 1980



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Abstract

The compatibility of Mo-50 wt % Re with $^{238}\text{PuO}_2$ was investigated after heat treatments of up to 720 days at 800°C and 180 days at 1000°C. At 800°C, a 1- μm thick, continuous layer of molybdenum oxide resulted. At 1000°C, the oxide reaction product contained some plutonium and did not appear continuous. At 1000°C, a layer of intermetallic formed at the Mo-Re edge, beneath the oxide layer, creating a barrier between the Mo-50 wt % Re and the $^{238}\text{PuO}_2$. The intermetallic layer was promoted by the iron impurity in the $^{238}\text{PuO}_2$.

Introduction

The use of $^{238}\text{PuO}_2$ in radioisotopic-thermoelectric generators requires the assurance that the $^{238}\text{PuO}_2$ will remain contained during normal usage and during any possible abnormal occurrence. This compatibility study of $^{238}\text{PuO}_2$ with the Mo-50 wt % Re alloy is a part of the evaluation of possible containment materials to provide for the safe use of $^{238}\text{PuO}_2$. Previous $^{238}\text{PuO}_2$ /Mo-50 wt % Re compatibility tests [1,2] were performed at higher temperatures (1200 to 1800°C) using $^{238}\text{PuO}_2$ containing high impurity concentrations (1 to 2 wt %) in all but one 1800°C test. This study was designed to establish compatibility at a lower temperature and to separate the effects of $^{238}\text{PuO}_2$ from the effects of the $^{238}\text{PuO}_2$ impurities on the Mo-50 wt % Re by using high purity $^{238}\text{PuO}_2$ (0.25 wt % total impurities).

Experimental

Test specimens were heated at 800°C for 30 to 720 days and at 1000°C for 30 to 180 days (Table 1). The configuration of

the compatibility specimen is shown in Figure 1. The specimen consists of an inner Mo-50 wt % Re capsule that was gas-tungsten-arc welded after being loaded with $^{238}\text{PuO}_2$ and a Mo-50 wt % Re disk. The Mo-50 wt % Re capsule was subsequently electron-beam welded in a Hastelloy-X capsule. Tungsten foil, 25- μm thick, was placed between the Hastelloy-X and the Mo-50 wt % Re to reduce interdiffusion. The Hastelloy-X capsule provided oxidation resistance for the high-temperature heat treatment in air.

Analyses of the $^{238}\text{PuO}_2$ and Mo-50 wt % Re are shown in Tables 2 and 3, respectively. Approximately 0.775 g of $^{238}\text{PuO}_2$ was used in each capsule giving a $^{238}\text{PuO}_2$ weight to

Table 1 - Mo-50 wt % Re/ $^{238}\text{PuO}_2$
COMPATIBILITY TEST MATRIX^a

Temperature (°C)	Time (days)					
800	30	61	94	180	360	720
1000	30	60	91	180		

^aDuplicate specimens and a blank were tested for 60 and 180 days at each temperature and 720 days at 800°C.

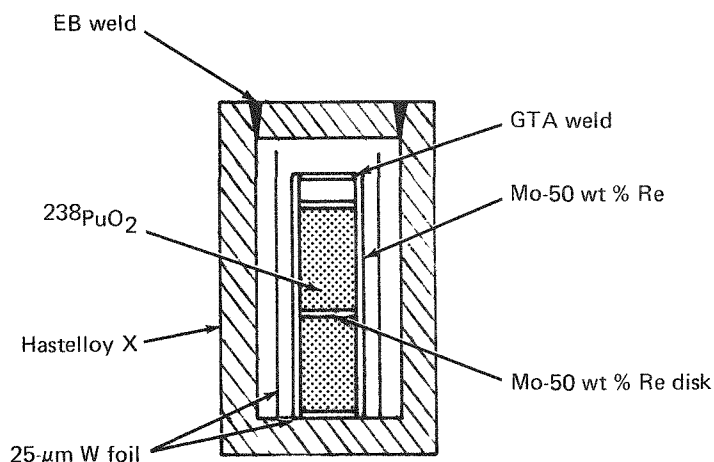


FIGURE 1 - Configuration of capsule used in plutonium-238 dioxide/Mo-50 wt % Re compatibility test.

Table 2 - IMPURITY ANALYSIS OF $^{238}\text{PuO}_2$

Element	Impurity (wt %)
Al	0.07
B	<0.01
Ca	0.03
Cr	<0.03
Cu	Trace
Fe	0.06
Mg	0.01
Na	Trace
Ni	<0.002
Si	Trace
Zn	<0.03
Total	<0.26

Table 3 - ANALYSIS OF Mo-50 wt % Re

Element	Analysis (wt %)
Al	0.003
C	0.006
Co	0.003
Fe	0.01
H	<0.001
Mg	<0.0005
Mo	52.55 (typical)
N	0.007
O	0.004
Re	Bal
Si	0.003

total Mo-50 wt % Re surface area ratio of about 0.17 g/cm^2 or roughly 0.23 g/cm^2 for direct contact.

The compatibility of $^{238}\text{PuO}_2$ with Mo-50 wt % Re can be estimated by comparing the partial molar free energy of oxygen ($\Delta\bar{G}_{\text{O}_2}$)

of the possible molybdenum, rhenium, and plutonium oxides. These partial molar free energies are plotted as a function of temperature (assuming unit activities) in Figure 2 [3,4,5]. Since a more negative $\Delta\bar{G}_{\text{O}_2}$ indicates an increase in stability, Figure 2 reveals that $^{238}\text{PuO}_2$ is more

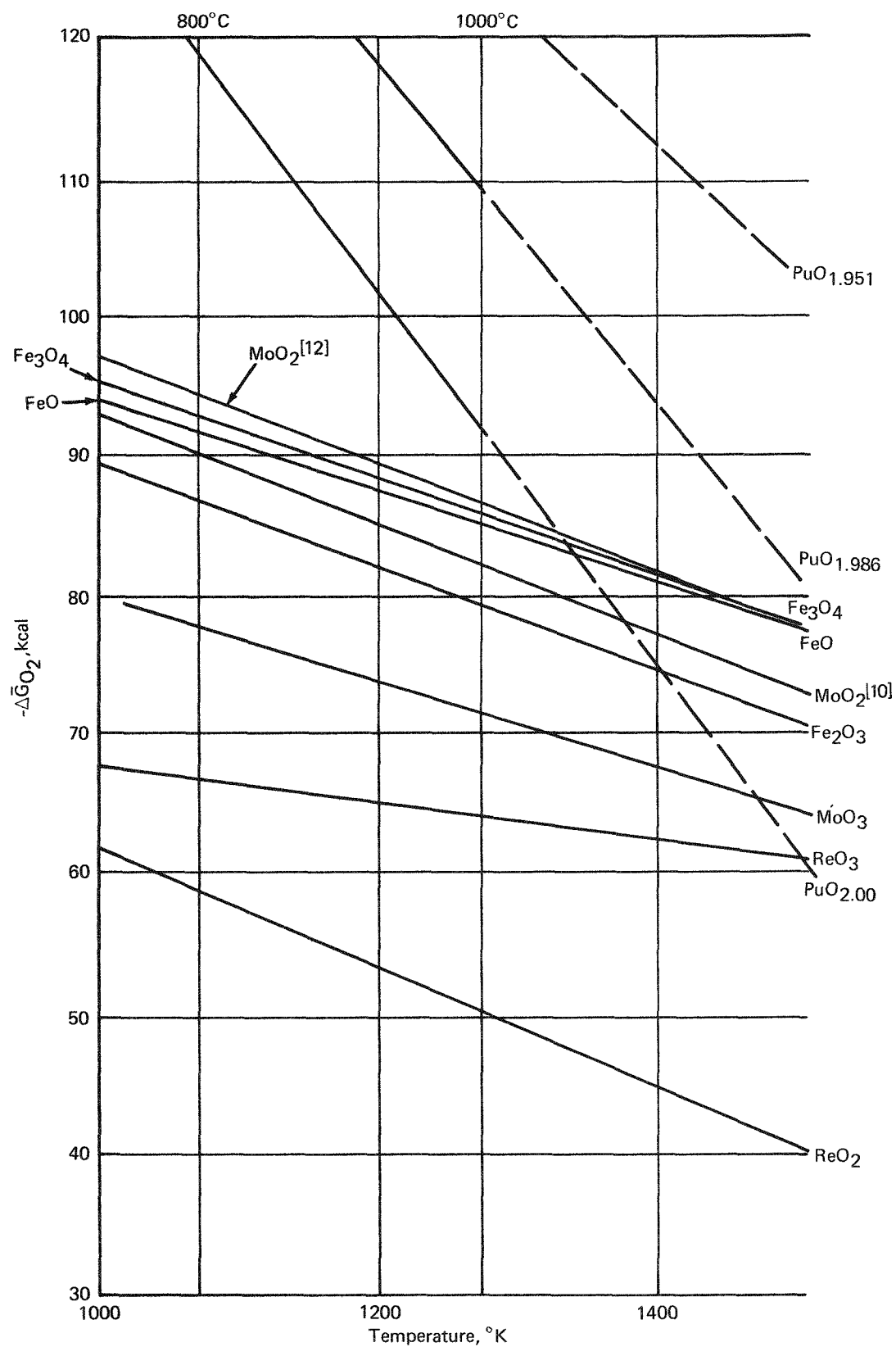


FIGURE 2 - The partial molar free energy of oxygen for Mo, Re, Fe, and ^{238}Pu oxides plotted as a function of temperature.

stable than MoO_2 or ReO_3 at temperatures lower than about 1325 K ($\sim 1050^\circ\text{C}$) and 1500 K ($\sim 1225^\circ\text{C}$), respectively. This suggests that $^{238}\text{PuO}_2$ should be compatible with Mo-50 wt % Re at both 800 and 1000°C . Above 1050°C , MoO_2 could form by reducing $^{238}\text{PuO}_2$ to a stoichiometry whose $\Delta\bar{G}_{\text{O}_2}$ matches that of MoO_2 at the appropriate temperature.

800°C results

The interaction between $^{238}\text{PuO}_2$ and Mo-50 wt % Re at 800°C is typified in Figure 3 and is characterized by the formation of a surface layer and a periodic intermetallic compound. Where intimate contact between the $^{238}\text{PuO}_2$ and the Mo-50 wt % Re container existed, a 0.5- to 1.0- μm thick, continuous layer formed on the Mo-50 wt % Re (Figure 3). The layer developed quickly (≤ 60 days) but remained at approximately the same thickness for 720 days.

Electron microprobe examination of the layer (Figure 4) determined it to be rich in molybdenum (70 to 80 wt %) with oxygen assumed to be present.* Figure 4 also reveals the presence of plutonium in the oxide layer; however, the plutonium was found infrequently and only in very small concentrations. Iron was present in the compatibility couple as an impurity in the $^{238}\text{PuO}_2$ (0.06 wt %) and was found rarely in the surface oxide. One of these iron-rich portions of the surface layer is shown in Figures 5 and 6. The high iron oxide contained 17 wt % iron, was thicker (10 μm) than the typical surface oxide, and penetrated the substrate to a maximum depth of 5 μm . No other instances of oxide penetration were observed. The scattered, high concentrations of iron

*Oxygen content of the surface layer could not be determined because of the insensitivity of the electron microprobe to oxygen.

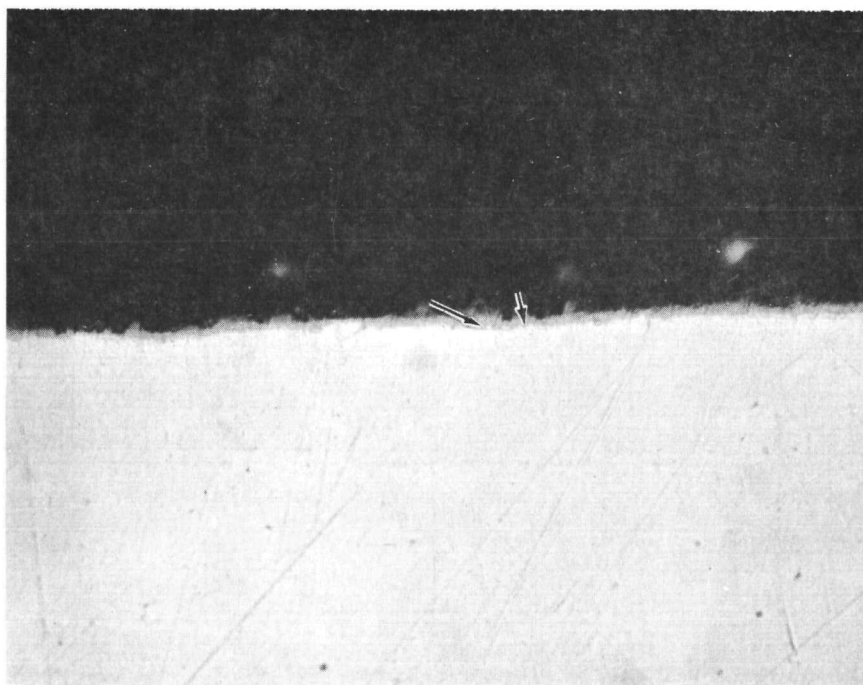


FIGURE 3 - At 800°C , the edge of the Mo-50 wt % Re typically formed a thin oxide layer with small formations of an intermetallic just under the oxide. The arrows indicate the position of the intermetallic phase (360 days at 800°C ; 1210X, unetched).

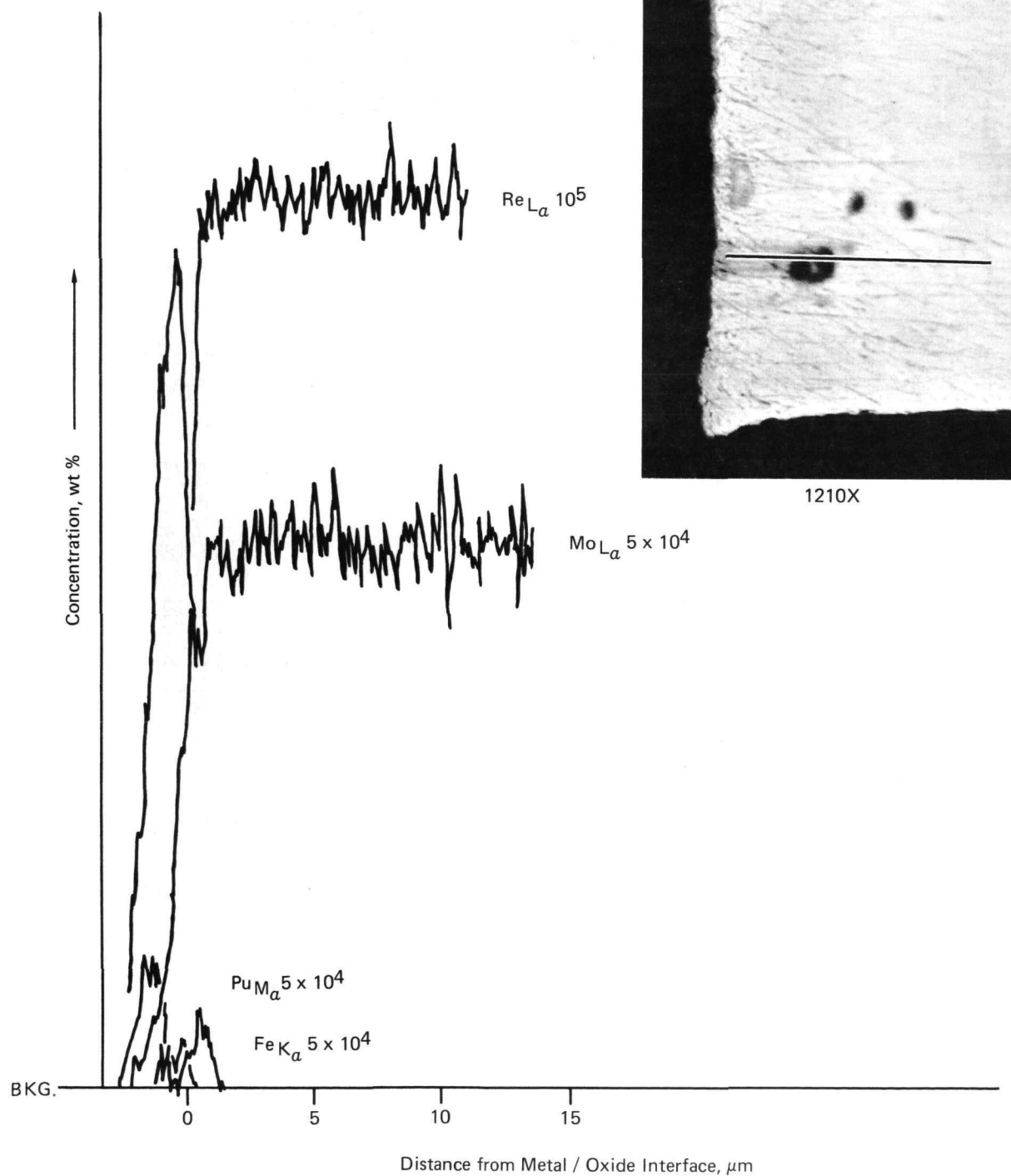


FIGURE 4 - This electron microprobe trace analysis indicates the formation of a molybdenum surface oxide. The presence of plutonium and iron was observed only occasionally. The line on the photomicrograph (1210X, unetched) gives the position of the trace analysis (360 days at 800°C).

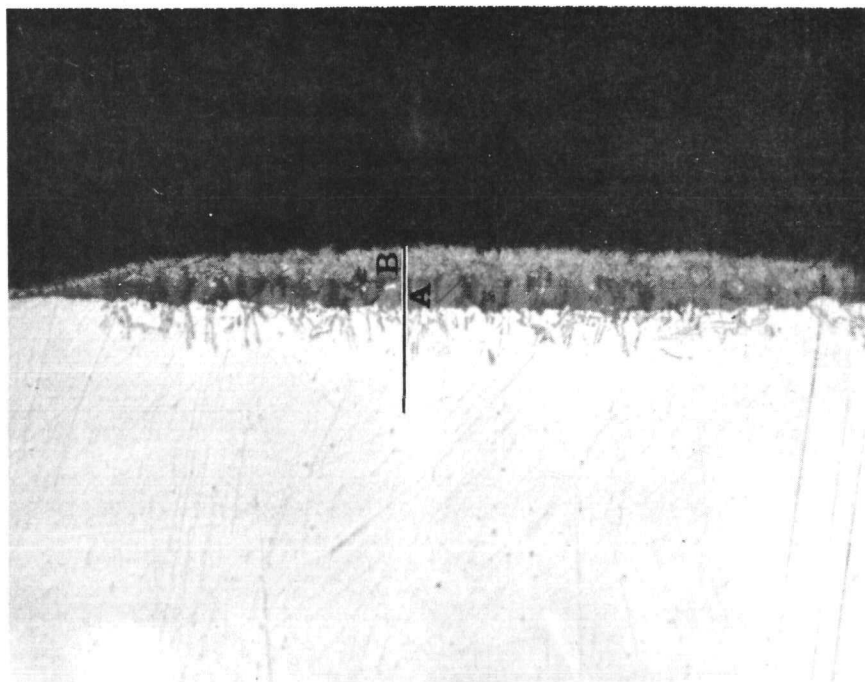


FIGURE 5 - Photomicrograph of a rare occurrence of the high (~17 wt %) iron, molybdenum oxide (360 days at 800°C; 1210X, unetched).

are perhaps indicative of the distribution of the iron impurity in the $^{238}\text{PuO}_2$.

The typical surface layer is thought to be MoO_2 because MoO_2 is stable at lower oxygen pressures than MoO_3 (Figure 2); the vapor pressure of MoO_3 at 800°C is high enough so that MoO_3 would volatilize as fast as it would form [6]; and the molybdenum content of the oxide appears slightly closer to MoO_2 , than to MoO_3 . Support for identification of the layer as MoO_2 comes from Gullbransen [7] (who determined that a layer of MoO_2 formed on molybdenum at 500 to 1000°C when under a vacuum). The Mo/Fe/O phase remains unidentified; however, FeMoO_4 , which contains 26 wt % iron, is one possibility.

The intermetallic phase is seen in Figure 3 and formed as small particles ($\leq 1 \mu\text{m}$)

just under the oxide surface layer. Electron microprobe analysis determined that the intermetallic is enriched in rhenium and depleted in molybdenum with respect to the Mo-50 wt % Re base metal and that it also contained a small amount of iron. Similar intermetallics (without iron) were found throughout the Mo-50 wt % Re substrate but were usually larger and not as numerous. The propensity for the intermetallic to form at the edge is probably the result of the presence of iron and/or the depletion of molybdenum caused by the formation of the molybdenum-rich surface oxide.

Examination of the Mo-50 wt % Re not in immediate contact with the $^{238}\text{PuO}_2$ revealed no evidence of degradation other than a slight depletion of molybdenum (about 6 wt %), which resulted in a corresponding

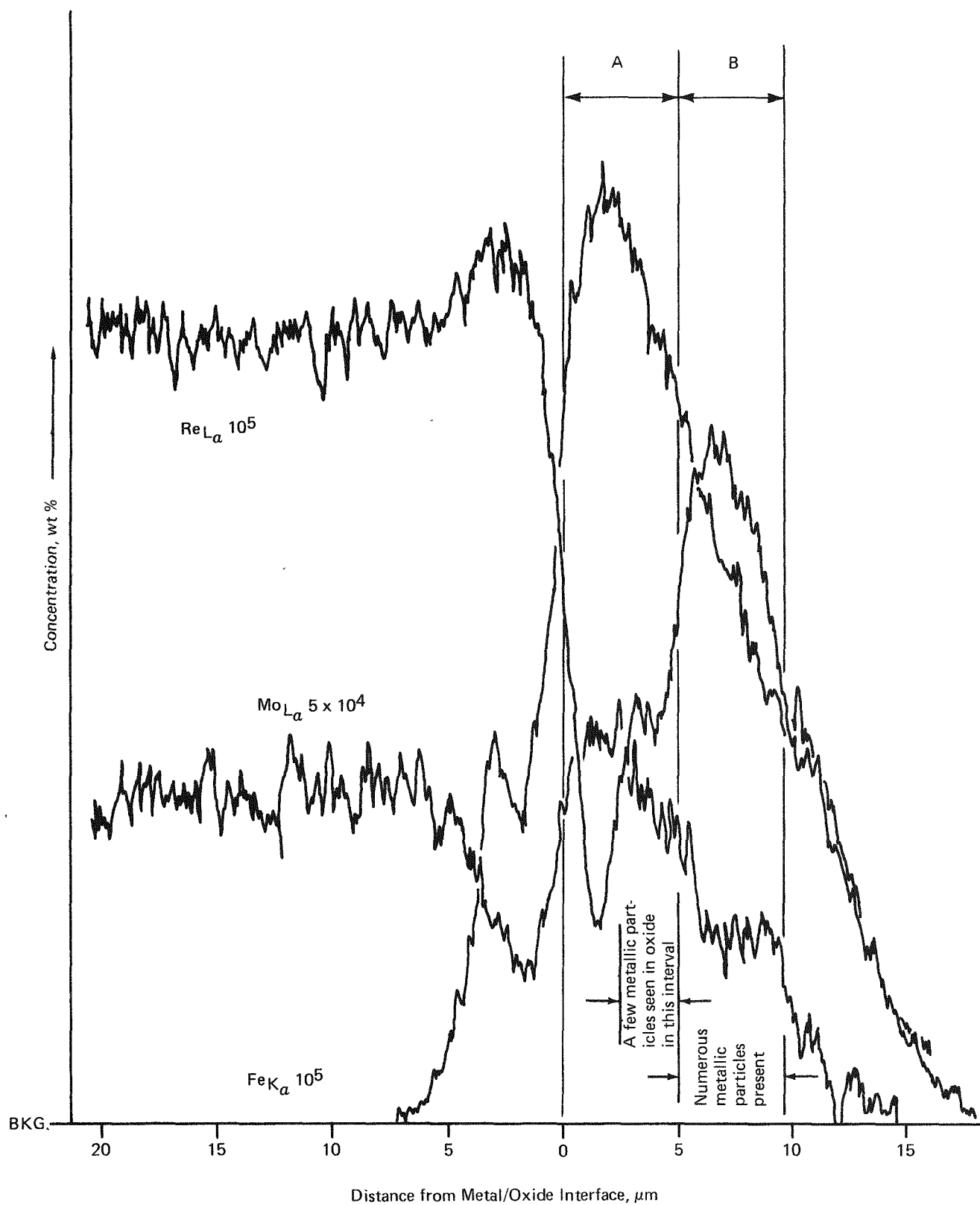


FIGURE 6 - An electron microprobe trace analysis of the high iron, molybdenum oxide seen in Figure 5.

renium enrichment. The depletion, which disappeared about 4 μm into the substrate, is probably the result of mass transport via volatile oxides.

Microhardness determinations found no gradient in the Mo-50 wt % Re nor any difference between the Mo-50 wt % Re capsules which contained $^{238}\text{PuO}_2$ and similarly heat treated, empty capsules. The average hardness determined with a 100-g weight was 340 DPH.

1000°C results

The 1000°C interaction is characterized by the formation of a surface oxide, a continuous intermetallic layer, and diffusion of iron into the base metal. Photomicrographs that typify the resultant Mo-50 wt % Re/ $^{238}\text{PuO}_2$ compatibility couple are shown in Figures 7 and 8. The thick-

ness of the surface oxide varied from 1 to 10 μm on all samples irrespective of the time at 1000°C. The oxide did not appear continuous, but the continuity and the quantity of the oxide could not be established; possibly some loss occurred during metallographic preparation. Electron microprobe analysis of the surface oxide is displayed in Figure 9. The surface oxide is identified by "A" in Figure 9 and contains 60 to 80 wt % molybdenum, a minor amount of plutonium, with oxygen assumed to be present. Possible identification of this oxide is MoO_2 with some plutonium solubility. Support for MoO_2 was discussed previously. The smaller phases in this oxide were too small to resolve with the electron microprobe, but the dark phase appears higher in plutonium and lower in molybdenum than the surrounding oxide matrix (see zone "B" in Figure 9).

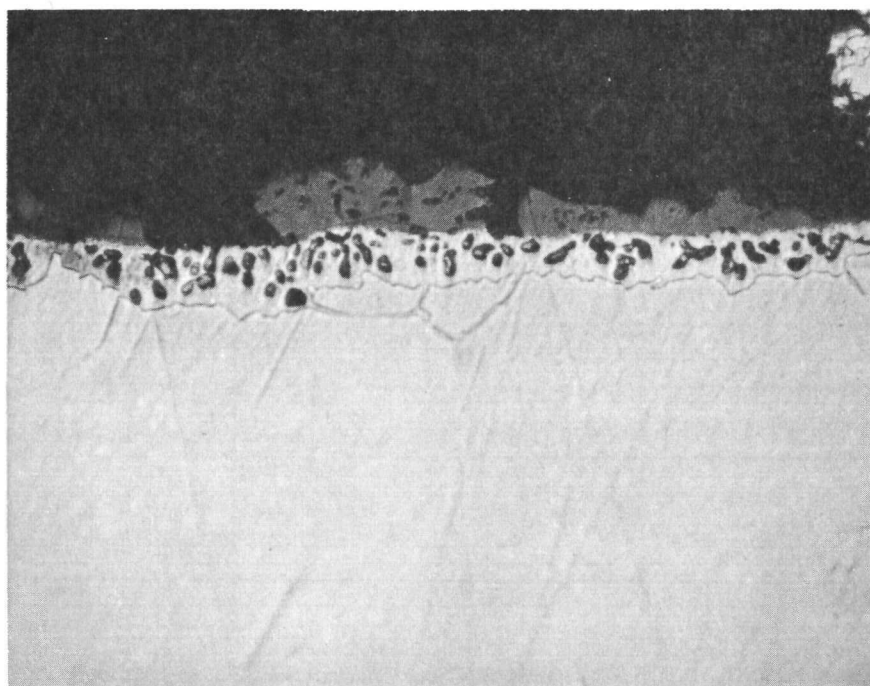


FIGURE 7 - At 1000°C, isolated particles of Mo/Pu/O reaction product form. A layer of intermetallic forms on the Mo-50 wt % Re edge, which appears lighter in color than the substrate in this photomicrograph. The lines also indicate the position of the intermetallic (180 days at 1000°C; 1210X, unetched).

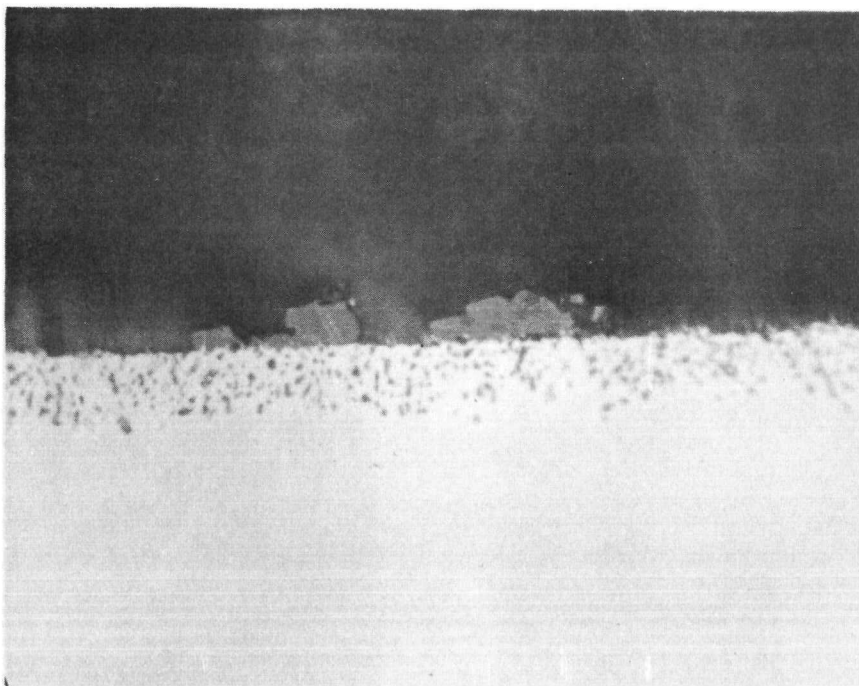


FIGURE 8 - Typical portion of the 1000°C interface showing oxide reaction product and intermetallic layer (180 days at 1000°C; 1210X, unetched).

The inner phase of the reaction zone (identified by "C", "D", and "E" in Figure 9) forms a 2- to 7- μ m thick layer on the metallic substrate. The thickness of the layer did not appear to change with time at 1000°C. This phase protrudes into the base metal to a maximum depth of 20 to 25 μ m, appears metallic, and contains: 50 to 70 wt % rhenium, 30 to 45 wt % molybdenum, and 5 to 7 wt % iron. The iron content decreases with increasing distance into the base metal. Bulk diffusion of iron is also seen in Figure 9, reaching about 25 μ m into the substrate after 180 days. The iron content of the intermetallic layer (assuming a 4- μ m thickness with 6-wt % iron) could account for all iron present as an impurity in the $^{238}\text{PuO}_2$ with little or no iron in the lattice of the Mo-50 wt % Re. Since the thickness of the layer appears inde-

pendent of the time at 1000°C, the iron impurity apparently reacts quickly (≤ 30 days) with the molybdenum.

Within the intermetallic layer are voids and possibly some internal oxides. Voids could be the result of the faster outward diffusion of molybdenum relative to the inward diffusion or iron. Internal oxidation was observed at 800°C in the area of high iron concentrations and, hence, if there are oxides in the intermetallic, they might be promoted by iron.

Figure 10 is a photomicrograph of a portion of the 1000°C, Mo-50 wt % Re capsule that was not in intimate contact with the $^{238}\text{PuO}_2$ (Note the absence of the Mo/Pu oxide and the substantial decrease in the amount of the Re/Mo/Fe intermetallic phase).

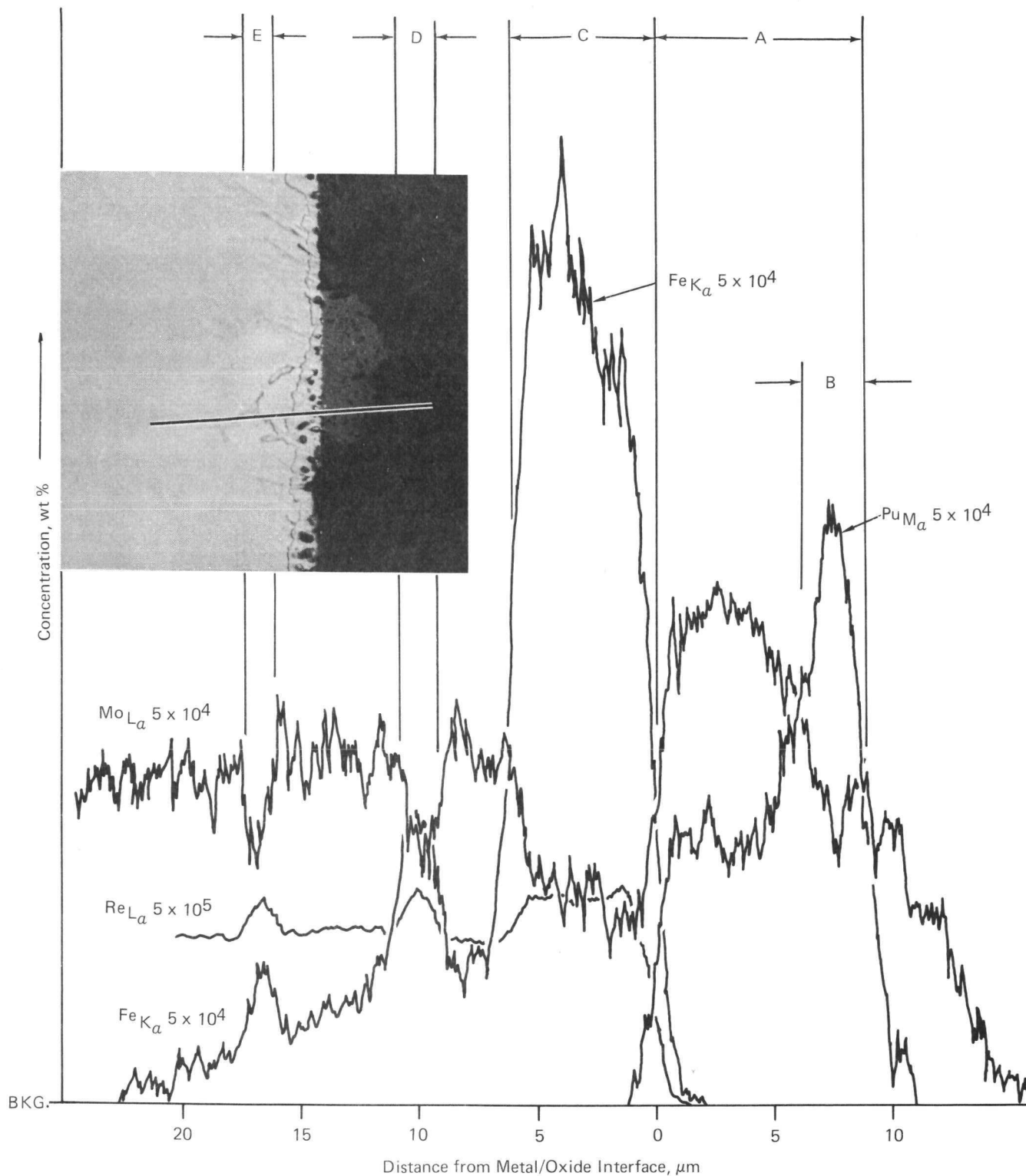


FIGURE 9 - The electron microprobe trace analysis of the 1000°C reaction interface determines the oxide to be rich in molybdenum with a small amount of plutonium. The intermetallic is enriched in rhenium and iron, and depleted in molybdenum relative to the base metal. The line on the photomicrograph (1210X, unetched) gives the location of the trace analysis. (180 days at 1000°C).

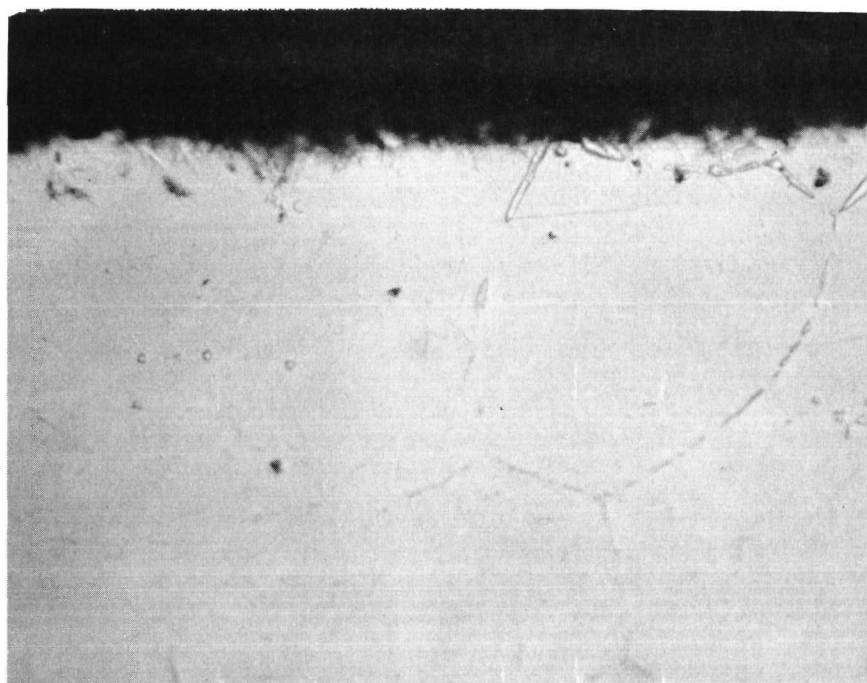


FIGURE 10 - A photomicrograph of the edge of the Mo-50 wt % Re capsule not in direct contact with the $^{238}\text{PuO}_2$. This edge is visually unaffected (1210X, unetched).

Microhardness measurements determined that the edge of the Mo-50 wt % Re was hardened as a result of direct contact with the $^{238}\text{PuO}_2$. After 90 days at 1000°C , the hardening effect was found to be ≥ 75 μm and ≤ 125 μm into the Mo-50 wt % Re substrate. The lattice diffusion of iron would add to the hardening; however, the hardness increase extends deeper into the base metal than the iron. The hardening is probably a result of oxygen diffusion, which is a major factor in Mo-50 wt % Re/ $^{238}\text{PuO}_2$ compatibility at higher temperatures [1].

Discussion

At temperatures below $\sim 1050^\circ\text{C}$, the oxidation of molybdenum in a Mo-50 wt % Re capsule containing $^{238}\text{PuO}_2$ is not expected from thermodynamic considerations (Fig-

ure 2). One possible explanation involves the presence of impurities in the $^{238}\text{PuO}_2$. These impurities are present as oxides and can serve as an oxygen source if the oxides are less noble than MoO_2 . The iron is probably present as Fe_2O_3 , which, if completely reduced, could provide sufficient oxygen to form the observed quantity of MoO_2 at 800°C ; however, the complete reduction of Fe_2O_3 by molybdenum appears questionable, depending on the value of the $\Delta\bar{G}_{\text{O}_2}$ for MoO_2 that is accepted (Figure 2). Further reduction of Fe_2O_3 could be encouraged by the formation of the iron-bearing intermetallic.

Another source of oxygen could be water adsorption on the $^{238}\text{PuO}_2$ surface, which could be partially reduced by molybdenum. Thermogravimetric analysis of the $^{238}\text{PuO}_2$ detected a weight loss at about 100 to

150°C [8] supporting the possibility of water adsorption.

In previous Mo-50 wt % Re/ $^{238}\text{PuO}_2$ compatibility tests, there was no evidence of any form of molybdenum oxidation at either 1200 or 1800°C [1,2]. It was reported that the absence of oxidation at 1800°C was a result of rapid reduction of the oxygen partial pressure by diffusion through the Mo-50 wt % Re [1]. The diffusion rate decreases rapidly with temperature (see Table 4), and the diffusion rates empirically appear low enough to permit formation of a solid oxide at both 800 and 1000°C.

Molybdenum oxidation was observed in TZM (titanium, zirconium, molybdenum alloy) and pure molybdenum/ $^{238}\text{PuO}_2$ compatibility tests at 1200°C [2]; however, the molybdenum oxide was volatile, causing mass transport of molybdenum, rather than present as a solid as reported in this study. The formation of a solid molybdenum oxide at 800 and 1000°C and a volatile oxide at 1200°C when oxidized at low oxygen partial pressures is possibly the result of the increasing vapor pressure of the oxide with increasing temperature (Table 4). This conclusion is supported by Vahldiek [9] who reported that complete vaporization in vacuum occurs at 1155°C.

The formation of an intermetallic at the Mo-50 wt % Re/ $^{238}\text{PuO}_2$ interface was also observed previously at 1200°C [2]. The 1200°C intermetallic layer was thicker (~30 μm for thermal exposures from 32 to 180 days as compared to about 4 μm at 1000°C), lower in rhenium content, and had a higher concentration of iron, cobalt, chromium, and nickel. These differences are the result of higher concentrations

of these metals as impurities in the $^{238}\text{PuO}_2$. The intermetallic layer did not form on the 1800°C samples [1]. The authors proposed that its absence was the result of a smaller ratio of plutonia volume to container volume* and rapid diffusion rates of the impurities through the Mo-50 wt % Re.

The effect of the oxidation of molybdenum and formation of the intermetallic on the containment properties of Mo-50 wt % Re appears to be limited to a thin hardened case on the inside edge. This would promote the formation of small cracks that might degrade the impact properties of the capsule; however, evidence that the oxidation alone does not affect the mechanical properties of Mo-50 wt % Re was given by Donnelly [10]; who performed tensile tests on Mo-50 wt % Re after 2000 hr of exposure to oxygen at 1×10^{-5} torr at 825°C and found no change in the mechanical properties.

One of the objectives of this test was to eliminate or at least separate the effects of the $^{238}\text{PuO}_2$ from the effects of the impurities. Unfortunately, the level of impurities in the "pure" $^{238}\text{PuO}_2$ used in this test was still sufficient to affect the results. The impurities promoted an intermetallic layer in the 1000°C test; and the impurities increased the amount of oxygen in the closed system, which promoted the formation of the oxide reaction product. These phases could inhibit

*The ratio of plutonia volume to container volume and the ratio of the weight of the $^{238}\text{PuO}_2$ to total surface area for the 1800°C test were smaller than the corresponding ratios in the present test; however, the ratio of the weight of $^{238}\text{PuO}_2$ to the surface area which is in direct contact with the $^{238}\text{PuO}_2$ was larger (0.39 g/cm²) in the 1800°C test than the same ratio in the 800 and 1000°C capsules used in this study (0.17 g/cm²).

Table 4 - Mo-50 wt % Re, TZM, AND PURE MOLYBDENUM COMPATIBILITY DATA

Containment Material	Test Temperature (°C)	Observations	Relative Diffusion Rate ^a of O in Mo (DT/D ^{1800 K})	Approximate Vapor Pressure of MoO ₂ ^b	Reference
Mo-50 wt % Re	800	Solid Molybdenum Oxide	2.3×10^{-2}	1×10^{-17}	This effort
Mo-50 wt % Re	1000	Solid Molybdenum Oxide	3.6×10^{-3}	1×10^{-13}	This effort
Mo-50 wt % Re	1200	No Molybdenum Oxidation	8.6×10^{-2}	1×10^{-10}	9
Mo-50 wt % Re	1800	No Molybdenum Oxidation	1	3×10^{-5}	8
TZM	1200	Mass Transport of Mo by Volatile Oxide	8.6×10^{-2}	1×10^{-10}	9
Molybdenum	1200	Mass Transport of Mo by Volatile Oxide	8.6×10^{-2}	1×10^{-10}	9
Molybdenum	1800	No Molybdenum Oxidation	1	3×10^{-5}	8

^aThe diffusion rates were estimated by assuming an activation energy of 25 kcal (typical for interstitial diffusion) for both the pure molybdenum and the alloys. The diffusion rate for Mo-50 wt % Re is reportedly lower than for pure molybdenum [1] and, thus, these rates are admittedly rough estimates.

^bReference 12.

interaction by reducing diffusion and thus interaction, if they are continuous. If the layers are not protective, the impurities increase the interaction.

Summary and conclusions

The Mo-50 wt % Re/ $^{238}\text{PuO}_2$ * interaction at 800 and 1000°C is basically the minor oxidization of molybdenum at the Mo-50 wt % Re edge. At 800°C, the oxidation results in the formation of a continuous, 1- μm thick layer. Thermodynamic considerations and compositional analyses suggest that the oxide layer is MoO_2 . Occasionally, the oxide takes on a different morphology. In these instances, the oxide is about 10- μm thick, contains metallic particles, has high iron content (~17 wt %), and penetrates the substrate a maximum of 5 μm . At 1000°C, the oxidation results in a thicker oxide reaction product that does not appear continuous. Except for the presence of a minor amount of plutonium, compositionally it appeared similar to the 800°C oxide.

As a result of the inward diffusion of iron and the depletion of molybdenum, an intermetallic compound forms just below the oxide reaction product. The intermetallic occurs as very small particles at 800°C and as a 2- to 7- μm continuous layer with 25- μm protrusions at 1000°C. Relative to the Mo-50 wt % Re base metal, the intermetallic is enriched in rhenium and depleted in molybdenum and contains about 6 wt % iron.

Since mass transport of molybdenum appeared almost negligible, there was only minor

depletion of molybdenum in the Mo-50 wt % Re edge not in direct contact with the $^{238}\text{PuO}_2$.

No increase in hardness was observed in the Mo-50 wt % Re tested at 800°C; however, an increase was observed 75- to 124- μm deep into the edge after 90 days at 1000°C. The hardening was probably the result of oxygen diffusion.

Rhenium did not appear to interact directly with the $^{238}\text{PuO}_2$. Higher concentrations of rhenium caused by molybdenum depletions could encourage the formation of an intermetallic compound. Good rhenium compatibility is substantiated by 2000°C tests in which only mass transport via volatile oxide was found [1].

Compatibility of $^{238}\text{PuO}_2$ and Mo-50 wt % Re is dependent on the purity of the fuel. Oxide impurities with a lower (smaller negative) $\Delta\bar{G}_{\text{O}_2}$ than MoO_2 will be reduced providing oxygen for the oxidation of molybdenum and cations for the formation of an intermetallic at the Mo-50 wt % Re edge.

The effect of $^{238}\text{PuO}_2$ on Mo-50 wt % Re at 800°C extends only a few micrometers into the substrate after 720 days and appears too small to have any deleterious effect on the containment properties of the Mo-50 wt % Re.

The effect of $^{238}\text{PuO}_2$ on Mo-50 wt % Re at 1000°C extends about 100 μm into the substrate after 90 days. The effect is to slightly harden the base metal possibly making the edge more susceptible to cracking.

*Since the interaction is dependent on the impurity content, this description applies specifically to the $^{238}\text{PuO}_2$ with the impurity content used in this test.

Acknowledgement

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