

SIMS STUDY OF COMPOSITIONAL CHANGES OBSERVED IN A PuO<sub>2</sub> HEAT SOURCE CLADDING ALLOYW. H. Christie,<sup>1</sup>, D. H. Taylor,<sup>2</sup>, R. E. Eby,<sup>3</sup> and D. Pavone<sup>4</sup><sup>1,3</sup>Analytical Chemistry Division, ORNL, Oak Ridge, TN 37831<sup>2</sup>Savannah River Laboratory, Aiken, SC 29801<sup>4</sup>Los Alamos National Laboratory, Los Alamos, NM 87545

## ABSTRACT

Secondary ion mass spectrometry (SIMS) has been used to investigate changes that occur in an advanced Ir-0.3W alloy during high temperature aging. This alloy is used to clad <sup>238</sup>PuO<sub>2</sub> heat sources used in thermoelectric generators for deep space reconnaissance satellites. Long-term direct contact with PuO<sub>2</sub> at 1400°C leads to physical and chemical changes within the cladding alloy that affect its metallurgical properties. SIMS was used to show that Cr, Fe, Ni, and in some cases O, diffuse from the PuO<sub>2</sub> into the alloy. Thorium and aluminum diffuse out of the alloy in these same regions. This SIMS study suggests that inward O diffusion and subsequent formation of ThO<sub>2</sub> on grain boundaries may stabilize the alloy against enhanced grain growth.

## INTRODUCTION

Pu-238 oxide is used as a general purpose heat source to power radioisotopic thermoelectric generators for NASA deep space probes, such as the upcoming Galileo mission to Jupiter (launch 1985). After being fabricated into ceramic pellets approximately 2.5 cm long by 2.5 cm in diameter, the PuO<sub>2</sub> is encapsulated in a 700 μm thick iridium shell which is vented on one end to permit escape of the decay helium. The major purpose of the iridium shell, or clad vent set (CVS), is to provide containment of the PuO<sub>2</sub> in the event of a mission failure involving a high velocity impact of the GPHS capsules with the ground. An iridium alloy (DOP 26) consisting of 0.3% tungsten, and nominally 50 wt ppm aluminum and 60 wt ppm thorium was chosen as the cladding material because of its high temperature strength and ductility and chemical inertness, especially to PuO<sub>2</sub>. The alloying elements enhance the impact strength and ductility by increasing the coherent strength of the grain boundaries (ref. 1). Perhaps even more importantly these elements, in particular thorium, help maintain ductility during high temperature aging of the iridium by preventing grain

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growth (ref. 1). Thorium is effective as a grain growth inhibitor because it exists primarily as discrete particles on the grain boundaries.

Although the microstructure and grain boundary chemistry of the iridium have been well characterized (ref. 2) for the case where the iridium has been heat treated alone, the effects of high temperature aging in the presence of  $\text{PuO}_2$  are unknown. This paper describes the results of using SIMS to investigate some of the effects on iridium DOP 26 alloy of high temperature aging under service conditions in the presence of  $\text{PuO}_2$ . Optical microscopy of polished specimens, prepared from aged sections of this cladding alloy (Fig. 1), showed a significant increase in average grain size in the near-surface regions exposed to  $\text{PuO}_2$ . One sample exhibited less grain growth in this region and SIMS was used in an attempt to determine what chemical differences exist between samples exhibiting large grain growth and those exhibiting lesser growth.



Fig. 1. Aged specimen of Ir-0.3W showing enhanced grain growth at inside surface (top of micrograph).

Sections were cut from three CVS's (A, B, and C) that had been aged for 6 months in vacuum at  $1441^\circ\text{C}$  (fuel temperature). These specimens were mechanically abraded and then chemically etched ( $\text{HF}/\text{HNO}_3$ ) to remove adhering  $\text{PuO}_2$ .

Transverse cross sections of these decontaminated specimens were then mounted in epoxy and metallurgically polished until a smooth mirror-like finish was obtained. The mounted specimens, which showed no smear removable alpha activity, were then overcoated with 20-30 nm of spectrographic grade carbon, prior to SIMS analysis, so as to render the entire surface conducting.

Secondary ion mass spectrometry was used to study the movement of impurity elements from the  $\text{PuO}_2$  fuel into the cladding alloy as well as changes in the cladding dopant elements Al and Th. Several modes of data acquisition were used. Mass spectra were taken from regions representing the inside edge (close to the  $\text{PuO}_2$  fuel), the center and outside edge of each specimen. These spectra were evaluated to determine which elements needed further study. Line scans were made by traversing a finely focused (2-5  $\mu\text{m}$ )  $\text{O}_2^+$  or  $\text{N}_2^+$  ion beam across the 700  $\mu\text{m}$  width of the alloy. Elements identified as being of interest in the mass spectra were monitored in this fashion. Elements found via the line scans to have undergone diffusion or precipitation were then examined in detail via ion imaging and depth profiling techniques.

## RESULTS AND DISCUSSION

Prior to fabrication of the clad heat sources, certain dopants were added to the  $\text{PuO}_2$  fuel. Major dopants, determined by spark source mass spectrometry (SSMS), are listed, along with sample pretreatment steps in Table 1.

TABLE 1  
SSMS Analysis of  $\text{PuO}_2$  Fuel (Wt. ppm)

Element	Sample			Reference Specification	
	A <sup>2</sup>	B <sup>1</sup>	C <sup>2</sup>		
Al	30	60	900	<150	1. $\text{PuO}_2$ heat treated for 6 hours at 1525°C in oxygen.
Ca	2	3	600	<300	
Cr	-	-	2000	<250	2. $\text{PuO}_2$ heat treated as in 1, followed by vacuum outgassing for 1 hour at 1500°C.
Fe	900	2000	10000	<800	
Ni	-	-	2000	<150	
Si	40	100	1000	<200	
P	4	4	40	<15	

Dopant levels above the reference specification levels in Table 1 were added to determine their effect on the cladding alloy during the aging studies.

Mass spectra showed all three samples of the aged cladding alloy (A, B, and C) to have significant Cr, Fe, and to a lesser extent Ni contamination in the inside surface region. The deepest penetration (up to 150  $\mu\text{m}$ ) and highest levels were generally observed in sample C. Line scans across the 700  $\mu\text{m}$  thickness also showed little Ca and Si and no detectable Pu to have diffused into any of the cladding samples. It was also observed that Al, added as a dopant in the cladding alloy, underwent some depletion from the alloy in regions where Cr and Fe had diffused in. Thorium, also a cladding dopant, was less abundant in the inside surface region as compared to the center of the sample. Other workers have reported Th loss associated with grain growth in thermally aged samples (ref. 2). Line scans across the specimens demonstrated some variability in amount and depth of penetration of Cr and Fe into the alloy. Ion images were then made to further understand these observed variations. These studies showed that Cr and Fe diffused into the alloy primarily along grain boundaries. The amount of Cr or Fe observed in any particular line scan and the depth of penetration depended to some extent on how that line scan intersected grain boundaries; but in general it was shown that for sample C the concentration maxima at the inside surface was approximately 0.5 to 1.0 atom % and decreased to background (5-10 ppm atomic) at a depth of about 150  $\mu\text{m}$ . For sample A the maximum concentration of Cr and Fe was about the same as sample C at the surface, but the depth of penetration was significantly less being only 30-50  $\mu\text{m}$ . The concentration of Cr and Fe at the surface of sample B was also approximately the same as for C and the depth of penetration was midway between A and C.

Figure 2 presents data obtained by scanning a 1 nA,  $\text{O}_2^+$  primary beam across sample C in a direction perpendicular to the inside surface. The scan region chosen was such that no grain boundaries were within 50  $\mu\text{m}$  of the point where the scan started on the inside edge of the sample (see grain boundary map in Fig. 2). Presumably, the Cr, Fe, and Ni that penetrated to a depth of 20-30  $\mu\text{m}$  arrived via bulk diffusion. The peaks seen at 70-80  $\mu\text{m}$  depth clearly represent diffusion along grain boundaries. SIMS showed that the concentration of Fe and Cr was maximum at the iridium grain boundaries and fell off with depth into the grains perpendicular to the grain boundaries. Near the surface of the iridium the concentration fell off very little from the maximum at the grain boundary. However, the fall off became sharper with depth into the

iridium until at the maximum depth of penetration, the Fe and Cr were located only at the grain boundaries. Iron was also shown to diffuse more rapidly along the grain boundaries and into the bulk iridium. The SIMS data graphically demonstrate that Fe and Cr diffuse rapidly into Ir along grain boundaries and from the grain boundaries into the bulk iridium.

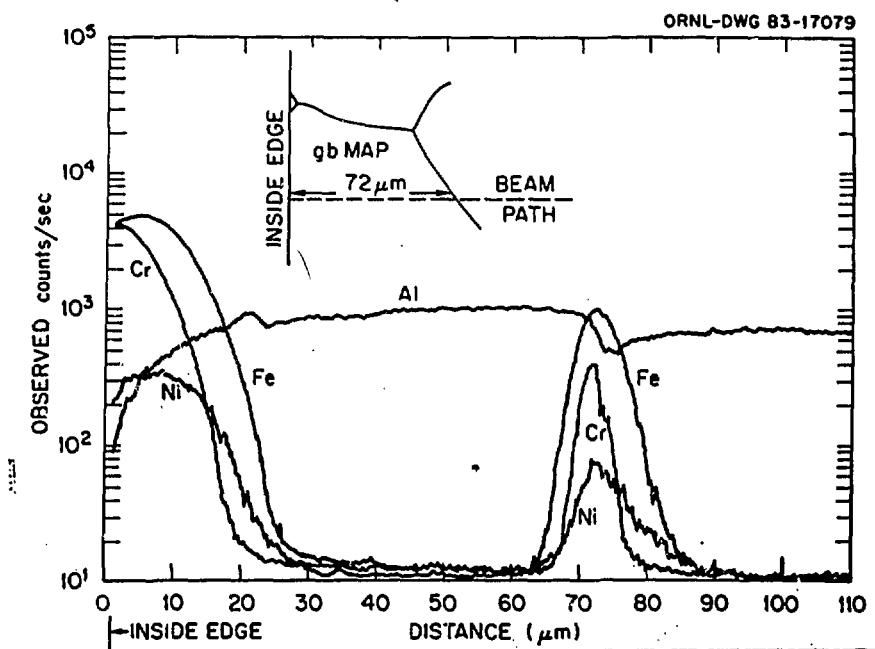


Fig. 2. SIMS line scans (1 nA,  $2 \mu\text{m O}_2^+$  primary beam) showing diffusion of Cr, Fe, and Ni into sample C. Grain boundary diffusion accounts for peaks at 70-80  $\mu\text{m}$  depth from inside edge. Aluminum loss is also noted in regions where Cr and Fe have intruded.

Ion imaging was used to show that in the interior of all samples Th was segregated to grain boundaries and also existed as discrete precipitates in the interior of grains and on grain boundaries. Thorium is lost from the alloy by diffusion along grain boundaries until it reaches the outer surface where it is presumably oxidized to  $\text{ThO}_2$ . SIMS revealed a striking correlation between reduced grain growth and the oxidation of Th on grain boundaries by the inward diffusion of oxygen in sample C. Two separate regions on the interior edge were studied, both showed  $\text{ThO}_2$  precipitates to extend along grain boundaries over 100  $\mu\text{m}$  in depth from the surface exposed to  $\text{PuO}_2$ . Earlier studies (ref. 2) showed that near surface grain growth is facilitated by loss of Th from the

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alloy along grain boundaries. The SIMS study suggests that if the oxygen partial pressure is high enough (as it must have been in capsule C), oxygen can diffuse inward along grain boundaries and oxidize Th in situ. In the locations where Th was seen to exist as ThO<sub>2</sub>, minimum grain growth was observed. This suggests that excessive grain growth may be inhibited by oxidation of Th on grain boundaries interior to the sample. The formation of ThO<sub>2</sub> below 10-15 μm in depth was not observed in samples A and B.

## CONCLUSIONS

Chromium, Fe, and Ni migrate from the PuO<sub>2</sub> fuel to the Ir cladding and alter the chemistry of the near surface grains and grain boundaries. Although the effect of these impurities is not now known, they should probably be excluded from the Ir until their effect is understood. The observation that in situ oxidation of Th on grain boundaries seems to reduce grain growth should be investigated further. Currently no information is available concerning the effect of grain boundary ThO<sub>2</sub> on high temperature impact ductility. This study does suggest that this oxidation phenomena may be a way to stabilize the alloy against exaggerated grain growth and thereby improve its impact resistance.

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