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# OXIDATION AND VOLATILIZATION FROM TANTALUM ALLOY DURING AIR EXPOSURE

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## ABSTRACT

Tantalum alloys are one of the refractory metals with renewed consideration for high temperatures in fusion reactor applications. Tantalum alloys perform well in protective environments but are oxidized readily in gases containing higher oxygen levels. In addition, the radioactive isotope Ta-182 would be produced in tantalum and could be a significant contributor to dose if mobilized. Other isotopes of importance are produced from tungsten and hafnium. Mobilization of activated products during an accident with air ingress is therefore a safety issue. In this study, we measured the extent of oxidation and mobilization from tantalum alloy T-222 oxidized in flowing air between 500 and 1200 degrees C. This alloy nominally contains 10 wt% tungsten, 2.5 wt% hafnium and 0.01 wt% carbon. We found that the mobilization of Ta and Hf was closely linked to the occurrence of oxide spalling. These elements showed no migration from the test chamber. Some W was mobilized by volatilization as evidenced by transport from the chamber. Tungsten volatilization could occur primarily during initial stages of oxidation before the formation of an oxide scale impedes the process. The mobilization of Ta and W are presented in terms of the mass flux ( $\text{g}/\text{m}^2\text{-h}$ ) as a function of test temperature. These measurements along with specific designs, activation calculations, and accident scenarios provide information useful for dose calculations of future fusion devices.

## I. INTRODUCTION

Extensive effort was directed during the mid-1960's to develop tantalum alloys for use for space nuclear reactor systems.<sup>1</sup> Minor oxygen contamination in the alloys promoted corrosion in liquid lithium. Improvements were achieved by alloying small concentrations of hafnium to combine with the oxygen. Alloy T-222 represents one of these improved alloys. Tungsten, hafnium and a small amount of carbon were added to improve high temperature creep strength. Such alloys have received renewed interest within the fusion community for use in liquid metal coolant systems. Potential mobilization of activated products during operation or accidents with air ingress is a

safety concern. Tantalum alloys readily dissolve oxygen and oxidize above 500°C. Oxidation kinetics are complexly influenced by oxygen levels, oxygen dissolution, and the nucleation and growth of various suboxides and several oxides from different oxidation states.<sup>2,3</sup> An oxide scale of a  $\beta$ -phase of  $\text{Ta}_2\text{O}_5$  ultimately forms at high temperatures and oxygen levels. Tantalum oxides have low vapor pressures. Volatilization has been reported to occur at low oxygen pressures, e.g.,  $1 \times 10^{-3}$  Pa and high temperatures (1600 to 1700°C). Vaporizing species at these conditions are TaO and  $\text{TaO}_2$ .<sup>2</sup> Internal oxidation behavior has also been studied in T-111, a low carbon alloy similar to T-222. These studies were conducted in oxygen pressures between  $1 \times 10^{-4}$  to  $4 \times 10^{-2}$  Pa.<sup>4,5,6</sup> Hafnium oxide is very stable with negligible vapor pressure. Tungsten forms various volatile  $\text{WO}_3$  polymeric species. We have measured volatilization from tungsten alloys.<sup>7,8</sup> The volatilization of  $\text{WO}_3$  is enhanced by even small amounts of water vapor. The objectives of this study are to characterize the nature of the oxide scales formed at various temperatures during the air exposures, to quantify mobilization of Ta, W, and Hf, and verify the mechanisms associated with the mobilization of each of these elements.

## II. EXPERIMENTAL PLAN

Specimens were prepared from a 0.1-in. thick plate of Alloy T-222. The Heat 650208 was produced by Wah Chang in 1997. Specimens (2.54 cm x 2.54 cm x 0.25 cm) were nominally 30 grams and had a surface area of about 15  $\text{cm}^2$ . They were polished to a 600-grit finish and cleaned with ethanol. The specimens were tested in a 4 cm diameter quartz chamber heated in a 36 cm long muffle furnace. Air supplied from a cylinder was flowed through a column of Drierite and preheated to 400°C. The air was vented to the atmosphere at the ambient pressure at the INEEL of about 650 mm Hg. A flow rate of one liter per minute (STP) was maintained during all tests. This flow rate and the atmospheric pressure at the INEEL pressure produced gas velocities at specimen surfaces ranging from 0.04 to 0.08 meters per second over the temperature range of 500 to 1200°C. The gas then flowed through a 1.5-cm diameter quartz tube packed with quartz wool. The latter components extended from the furnace reaching near

Table 1. Test matrix and results from tantalum alloy T-222 tested in air.

Specimen (a)	Temperature, °C	Time, h	Mass gain, g	Average rate of oxygen pickup, g/h	Average oxygen content, at%	Alloy loss per side, mm	Oxidation rate (b), mm/h
Ta1	500	81	0.0094	0.0001	0.4	0.07	9E-4
Ta2	600	55	1.9134	0.0348	41.9		
Ta3	700	55	0.5502	0.0100	19.2		
Ta4	800	48	3.9742	0.0828	60.0		
Ta5	900	8	1.7391	0.2174	39.6	0.27	3.4E-2
Ta6	1000	6	3.0939	0.5157	53.9		
Ta7	1100	4	2.1096	0.5274	44.3		
Ta8	1200	2	1.5479	0.7740	36.9	0.27	1.4E-1

(a) The nominal mass of the specimens is 30 g. (b) Assuming linear oxidation kinetics.

ambient temperatures at the outlet. The specific test temperatures and times are given in Table 1. Test durations were varied to provide longer exposures at lower temperatures. Mass changes of specimens were measured. The oxidized specimens were examined and photographed. Cross sections of selected specimens were prepared and metallographically examined. Oxidized specimens and spalled oxides were examined using scanning electron microscopy and XRD. Particle size distributions were obtained from image analysis of photomicrographs and a Coulter particle size analysis system. Particles of oxides transferred to the quartz components were removed and dissolved with solutions of hydrofluoric and nitric acid. These solutions were chemically processed and analyzed by ICP-AES. Distributions of mobilized elements within the test system were thus determined.

### III. EXPERIMENTAL RESULTS

The extent of visually apparent oxidation and oxide spalling from specimens and in the test chambers provided insight into mobilization rates. The specimen tested at 500°C had a very thin dark oxide. Transition to an advanced stage of oxidation as indicated by a voluminous light yellow oxide started to form at one edge. The specimen exposed at 600°C had developed a complete scale of yellow oxide. The flat sides and edges had spalled off as large pieces. There was also a fair amount of oxide powder released from beneath the scale. Some particles of this oxide were apparent in the test chamber. The yellow oxide that developed on the specimen at 700°C had turned completely into powder. Some of this powder was present in the reaction chamber. The specimen tested for 48 hours at 800°C developed a 2.5-mm thick oxide scale. The sides and edges spalled off as large pieces revealing a 1.28-mm thick dark gray core. This showed that the volume expansion as the metal converted to oxide was about a factor of four. Some fine yellowish powder was released along with some larger flat grayish particles from the zone near the oxide to metal interface. Less of the fine

yellowish powder was released when the oxide scales spalled from specimens exposed at 900°C and 1000°C. The pieces of scale appeared to be sintered into a harder oxide. Oxide scales remained mostly intact after the shorter exposures of 4 and 2 hours at 1100°C and 1200°C, respectively. The flat surfaces of the specimens remain light grayish in color and appeared partially translucent. This suggests that they are somewhat dense and adherent onto the metal core. Yellowish oxide had formed only at the cusp-shaped regions of higher oxidation at the corners of the specimen. There were only minor amounts of oxide particles evident in the quartz test chambers. A black deposit formed on the front end of the quartz wool during the 1200°C test. This was the only test to show such visually apparent deposit downstream from the specimen.

The amount of oxidation was obtained from changes in mass and thickness of the metal core observed with metallography. Mass changes showing oxygen pickup are given in Table 1. These values have been used to calculate average bulk rates of oxygen pickup (g/h), assuming linear kinetics, and overall average oxygen contents (at%). The average rates of oxygen pickup increased progressively with temperature except for the test at 700°C. The oxygen pickup of 0.5502 g, or rate of 0.0100 g/h, at 700°C was less than one-third of that measured at 600°C. This difference cannot be explained by a possible loss of some of the fine powdery oxide. Only 1 to 3 mg of tantalum plus tungsten was recovered from the test chambers and measured by ICP-AES for these two tests. The discontinuous trend instead agrees with inflections in the temperature dependence of oxidation rates observed for Ta and Nb by other studies.<sup>2,3,9</sup> The transformation of metallic suboxide phases to pentoxides has been suggested as a possible reason for this behavior. The oxygen in the thin layer formed at 500°C was less than 0.5 at% of the specimen mass. The specimen tested at 800°C with an oxygen content of 60 at% was the most completely oxidized. This suggests that much of the oxide was Ta<sub>2</sub>O<sub>5</sub> since 30 to 40 percent of the specimen core was not completely oxidized.

Cross sections showed evidence of interstitial gas diffusion into the alloy in addition to revealing oxide scales. The high adsorption, diffusion and solubility of oxygen, and also nitrogen, into tantalum are well known.<sup>2</sup> Oxygen distributions and increases in hardness have also been presented in the studies on alloy T-111.<sup>4,5,6</sup> We determined diamond pyramid hardness profiles from the edge to the center of specimens using a 50 gram weight. These hardness profiles for the specimens tested at 500, 900 and 1200°C are shown in Figure 1. All specimens showed an increase in hardness due to an apparent inward diffusion of some interstitial. The measurements within 0.05 mm of the surface were significantly higher. The depth of diffusion extended to about 0.2 mm in the 500°C specimen. Microhardness readings then remained constant from there to the center of the specimen. Microhardness continuously decreased from the surface to the center of the specimen for the 900°C test. The values at the center approached those of the base material at 500°C. The highest near-surface hardness was observed in the specimen tested at 1200°C. The hardness then decreased to nearly constant values at a depth of 0.5 to 0.75 mm. The hardness near the core remained higher than that of the other two specimens. Our hardness profiles for the 500 and 900°C exposures agree closely with those obtained by Stecura<sup>4</sup> from specimens doped with 0.9 to 2.4 at % oxygen at 820°C. The hardness profile obtained by Stecura from a specimen doped with 3 at % oxygen and then vacuum annealed for two hours at 1320°C matches both the shape and magnitude of the profile from our 1200°C test except for the outermost location. Reference 4 did not show the high near-surface hardness since oxygen was not supplied during the vacuum anneal. XRD analysis of extracted precipitates from Reference 4 also showed that as-doped specimens contained primarily tantalum oxides and minor amounts of tungsten and hafnium oxides. After annealing at 1320°C the precipitates were primarily hafnium oxides. Due to the similarities in hardness with our 1200°C test we might expect that hafnium oxides may also be instrumental for the higher hardness values near the center compared to the 500 and 900°C specimens. Liu, et al.<sup>5,6</sup> related hardness increases with oxygen content but reported somewhat flatter hardness profiles. This may have been due to the use of thinner specimens and lower oxygen pressures.

A consequence of oxygen uptake and increased hardness is an increase in brittleness. We observed cracks in the hardened outer regions in the specimens. These regions appeared as featureless zones in the alloy beneath the oxide scales with optical microscopy and SEM. These zones were about 0.05 mm thick in the specimen tested at 500°C and 0.2 mm thick in the specimens tested at 900 and 1200°C. The high oxygen levels of interstitial or oxide

precipitates likely influenced the polishing process resulting in the featureless appearance.

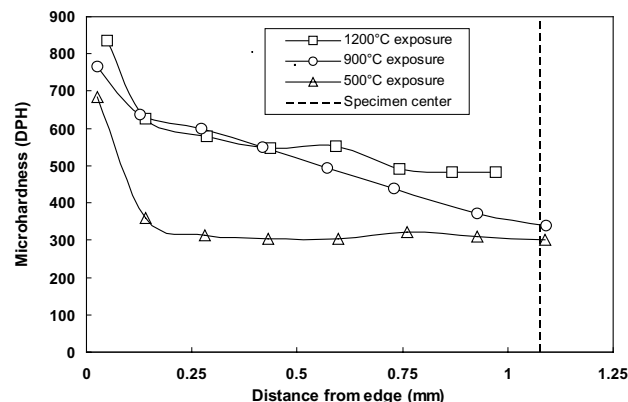


Figure 1. Microhardness profiles for specimens exposed at 500, 900 and 1200°C.

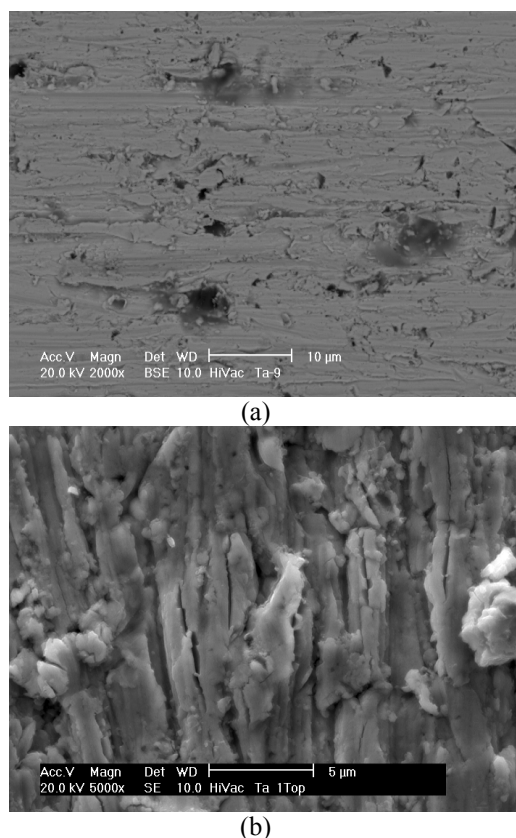


Figure 2. SEM images of the surfaces of T-222 specimens. (a) As-polished. (b) 500°C exposure for 81 hours.

SEM revealed changes in the oxide morphology on the specimens. Figure 2 shows a comparison between the surfaces of an untested as-polished specimen and the one tested at 500°C. The untested specimen shows deformed smears from polishing. Such smearing is indicative of

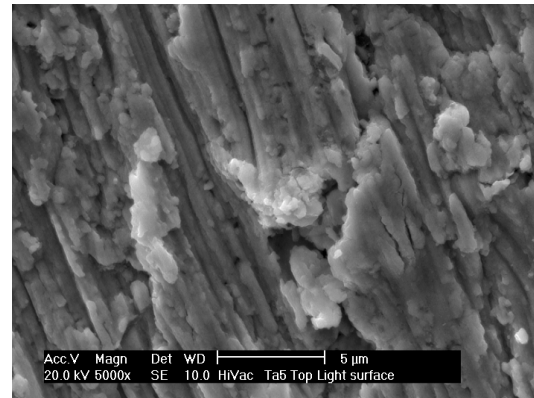
ductile material. The harder carbide inclusions stand out in relief. The SEM image of the specimen tested at 500°C shows small microcracks in laminated oxides formed along preexisting polishing marks. SEM showed progressive changes to oxide features with increasing temperature. The top and bottom of surfaces of the oxide spalled from the sides of the specimen at 900°C are shown in Figure 3. The top surface shows some small rounded nuclei beginning to form on oxide platelets. The bottom surface shows a fractured surface typical of a brittle material. The material shown may be the oxide scale or the alloy along the interface that has dissolved a high amount of oxygen. The appearance of this fracture prompts us to believe that the oxide spalled during cool down. An example of the oxide formed at 1200°C is shown in Figure 3(c). The oxide consists of round crystals 0.1 to 0.2 μm in diameter. The small crystals appear to be bonded together. The oxide seems relatively free of cracks and voids providing some impediment to mobilization as we discuss later in the interpretation of tungsten ICP measurements.

We selected to characterize the powder from the 700°C test to due to the large amount that formed. The SEM image of the powder in Figure 4 shows that there are different types of particles. We determined a count-based size distribution using optical microscopy and image analyses. We obtained a geometric mean diameter (GMD) of 1.95 μm and a geometric standard deviation (GSD) of 2.92. Mass-based size distribution measured with laser diffraction using the Coulter counter showed bimodal characteristics. This may be due to the different types of particles, or the non-spherical, flakelike, features shown in Figure 4.

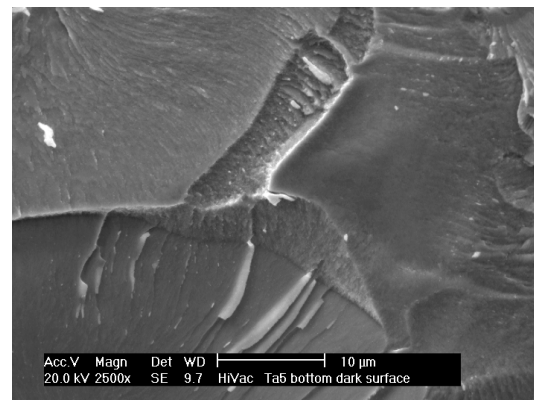
We performed x-ray diffraction (XRD) analyses of oxides from the 500, 700, 900, and 1200°C tests. The oxide scale was intact on the specimens tested at 500 and 1200°C. Oxide powders were used for the analyses for the 700 and 900°C exposures. A pattern expressed for a solid solution, Ta(O), formed from tantalum heated in air and oxygen between 470 and 520°C provided the best fit for the 500°C test.<sup>10</sup> There were some unidentifiable peaks that could result from lattice distortion due to dissolved oxygen. They did not match patterns for metallic Ta phases. Diffraction peaks became more distinct with higher temperatures. Other oxide patterns, e.g., Ta<sub>2</sub>O<sub>5</sub>, and Ta<sub>14.8</sub>W<sub>1.20</sub>O<sub>40.6</sub> provided fair fit to the peaks. The pentoxide fit the spectrum from the 1200°C test quite well.

We present average mass flux determinations of tantalum, tungsten and hafnium from the ICP-AES in Table 2 assuming linear release with time. Although the reported flux values are derived from test chamber, the collection tube, and filter measurements, tungsten was the only element found in significant quantities beyond the test

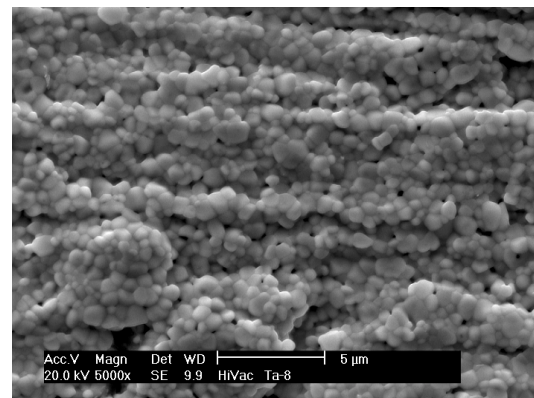
chamber. Hafnium was only detected within the test chamber at 600 and 700°C. Tantalum measurements were well above detection limits except for those for the 1100 and 1200°C tests. These were 20 to 40 percent above the detection limit. The mass flux determinations for tungsten were always greater than 10 times the uncertainty.



(a)



(b)



(c)

Figure 3. SEM images of oxide scales formed on T-222 specimens exposed at 900 and 1200°C. (a) and (b) the top and bottom surfaces of scale from the 900°C test, respectively. (c) Top surface of oxide formed at 1200°C.



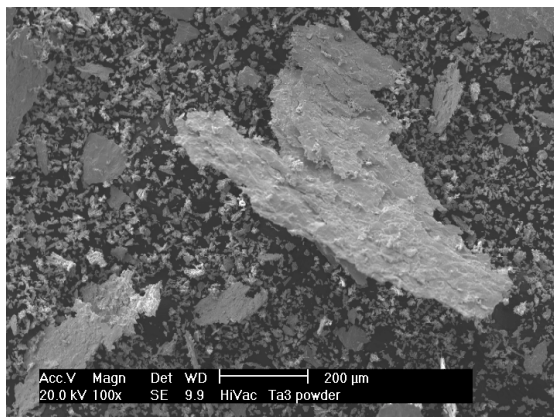


Figure 4. Powder released from T-222 specimen tested at 700°C.

Table 2. Mass flux determinations.

Temp., °C	Time, h	Hf (g/m <sup>2</sup> -h)	Ta (g/m <sup>2</sup> -h)	W (g/m <sup>2</sup> -h)
500	81	2.38E-5	1.12E-3	1.89E-4
600	55	2.48E-4	3.12E-2	2.64E-3
700	55	7.13E-5	1.30E-2	4.10E-4
800	48	8.04E-5	4.97E-3	5.09E-4
900	8	2.40E-4	5.76E-3	2.67E-3
1000	6	3.22E-3	4.04E-3	4.54E-3
1100	4	4.82E-4	2.41E-4	5.03E-3
1200	2	9.63E-4	4.81E-4	1.16E-1

We have plotted the mass flux of tantalum and tungsten with respect to temperature in Figure 5. The value for tungsten is approximately one-tenth of that for tantalum at 600°C whereas the mass flux of hafnium from Table 2 is about two orders of magnitude lower than tantalum. These correlations with alloy composition suggest that oxide spalled without migration out of the test chamber. There was evidence that tungsten was also mobilized by a volatilization mechanism. One-third of the tungsten mobilized at 500°C was found deposited downstream from the test chamber. About half of the W mobilized was found downstream of the test chamber at 800°C and about 85 percent at 1200°C. Increased tungsten volatilization above 800°C agrees with a report of a white condensate formed from T-111 at 990°C by Stecura.<sup>4</sup> The condensate was identified as WO<sub>3</sub>.

We have compared the mass flux of tungsten and tantalum from the T-222 alloy with values from our previous study of air oxidation of a powder metallurgy (PM) product.<sup>7</sup> The PM product contained 95 and 0.1 wt% tungsten and tantalum, respectively. Figure 6 shows that the mass flux of tungsten was quite comparable for the two

different studies at 500°C in spite of the fact that T-222 has one-tenth as much tungsten. Measurements from the T-222, however, are about two orders of magnitude

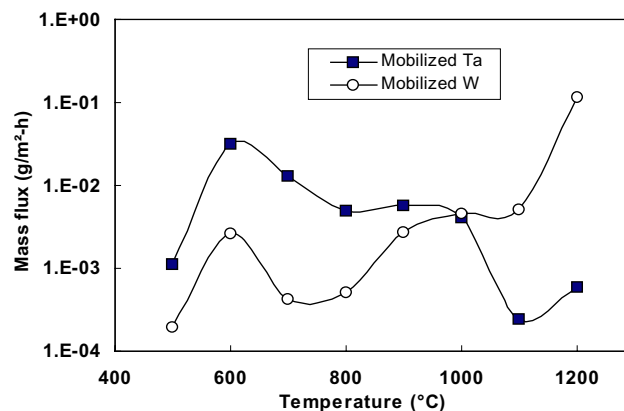


Figure 5. Mass flux of tantalum and tungsten from T-222 plotted with respect to temperature.

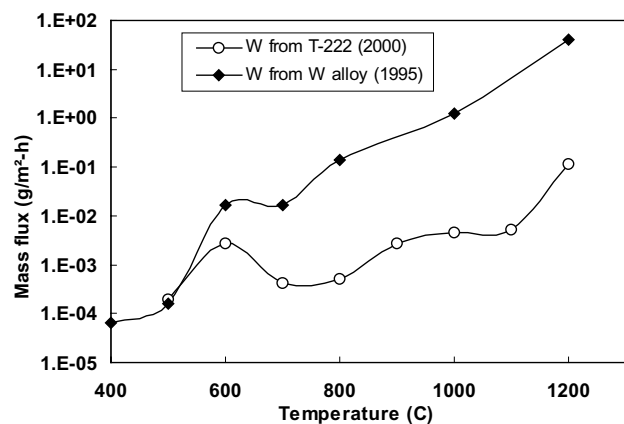


Figure 6. Mass flux of tungsten from T-222 and a previously tested PM products with 95 wt% tungsten.

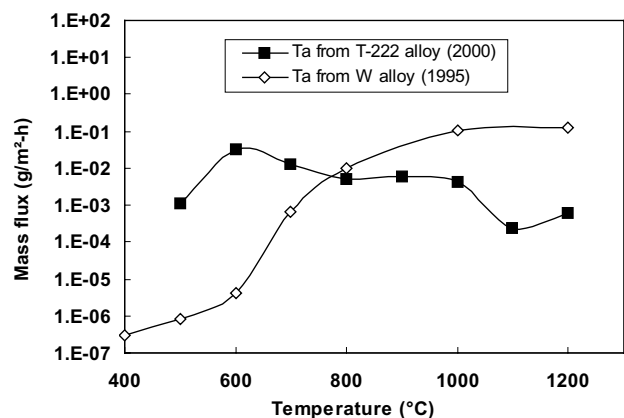


Figure 7. Mass flux of tantalum from T-222 and a previously tested PM products with 0.1 wt% tantalum.

lower above 800°C. This agrees with the temperatures at which we observed significant oxide formation on T-222. Perhaps much of the WO<sub>3</sub> volatilization occurred during the initial stages of the test and once an oxide scale formed this process was impeded by oxide scales similar to those shown in Figure 3. The plots for tantalum mass flux in Figure 7 show a different trend. The values of tantalum mobilization for the PM product with only 0.1 wt% Ta exceed those from T-222 above 800°C. Considering the apparent link between tantalum mobilization with oxide spalling the previous results must somehow be related to the spalling characteristics from the tungsten PM product.

#### IV. CONCLUSIONS

We have found mobilization processes in tantalum alloy T-222 to be linked to the character of the oxide. The development and growth of oxides on tantalum are complex and depend upon time, temperature and oxygen pressure. Oxide spalling appears to be a major contributor to the mobilization process. We believe that large pieces of oxide scale and oxide particles generally form during cool down. Oxides appear to be sintered into a harder scale at higher temperatures. This results in larger pieces being spalled with less particulate being generated. We observed a maximum in the amount of particulate generated from alloy T-222 at 600 and 700°C. The mobilization of tantalum and hafnium is linked to this spalling process. Although we observed an abundance of small, flake-like particles they were not transported out of the test chamber.

Tungsten was mobilized not only by spalling but showed an increasing contribution from volatilization with increasing temperature. Volatilization played a significant role even at the lowest temperature of 500°C. This may occur prior to the formation of the tantalum oxide scale. The mass flux at this temperature was actually very close to that which we observed from a previously tested tungsten alloy. The volatilization of tungsten actually decreases relative to its molar concentration in the alloy at higher temperatures. This suggests that an enhanced oxide scale slowed down the volatilization process of tungsten from the alloy.

We have determined mass flux values for tantalum, hafnium and tungsten from the T-222 alloy. These data can be used to estimate mobilization and activated product releases. However, since the processes are largely driven by oxidation spalling potential influences of thermal cycling with additional particulate formation should be kept in mind. We observed influences from internal oxidation in the tantalum alloy. Hardness increases render some specimens quite brittle. This is an issue that should be considered in future applications of such alloys that could potentially be exposed to oxidizing conditions.

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