

# Noncontaminating Plasma Arc Sprayed Crucible Coatings for Containing Molten Ceramic Oxides

D.J. Sordelet, T.W. Ellis, and I.E. Anderson

A study was performed to assess the suitability of several plasma arc sprayed coatings applied to graphite crucibles for melt processing  $\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  ceramics. Coatings of W, Ta over W, and Re over W were evaluated. Pressed compacts of  $\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  were each placed in refractory metal-coated graphite crucibles and heated to 2040, 2150, and 2200 °C, respectively. Compatibility of the coating/ceramic oxide systems was evaluated by optical and scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and combustion chromatography. The Ta over W coating system was chemically nonreactive with all three molten oxides studied.

## 1. Introduction

AMES Laboratory recently established the Ames Laboratory Plasma Spray (ALPS) Facility. The operation currently is focused on atmospheric and low-pressure plasma arc spraying of ceramic and advanced metal alloy systems for numerous applications. One major activity involves developing coating systems for containment crucibles used in high-temperature processing techniques such as high pressure gas atomization (HPGA), self-heating synthesis (SHS), and solidification studies. As new refractory materials are processed through molten or reaction routes, crucibles that are nonreactive to the materials being processed are required; furthermore, process temperatures of new materials under evaluation frequently exceed 2000 °C. For example, the Ames Laboratory HPGA system has been used to prepare powders of copper/refractory metal alloys.<sup>[1]</sup> However, during this study, attempts to contain a molten Cu-21Nb-2Mo alloy in a molybdenum alloy crucible at 2000 °C resulted in substantial selective dissolution of Mo from the crucible inner wall. Figure 1 highlights the crucible and atomization region of the HPGA system. The stringent demands placed on the containment crucible are quite clear. The crucible must first be noncontaminating to the molten material, which typically is heated to 200 to 400 °C above its liquidus temperature. Second, it must withstand the mechanical load of the molten charge. Third, it must survive the thermal stresses induced at the melt line. The inherent static thermal gradient developed during melting, together with the dynamic thermal gradient produced as the molten charge leaves the vessel, increases the crucible susceptibility to catastrophic thermal shock damage.

Refractory materials that provide the required high-temperature chemical stability described above, e.g., ceramic oxides and intermetallic compounds, typically are characterized by brittleness and very poor thermal shock resistance. Graphite is often used as a containment vessel material because of its high-tem-

perature mechanical stability and compatibility with many materials. However, systems that tend to form carbides cannot be used, nor can materials that suffer from interstitial carbon impu-

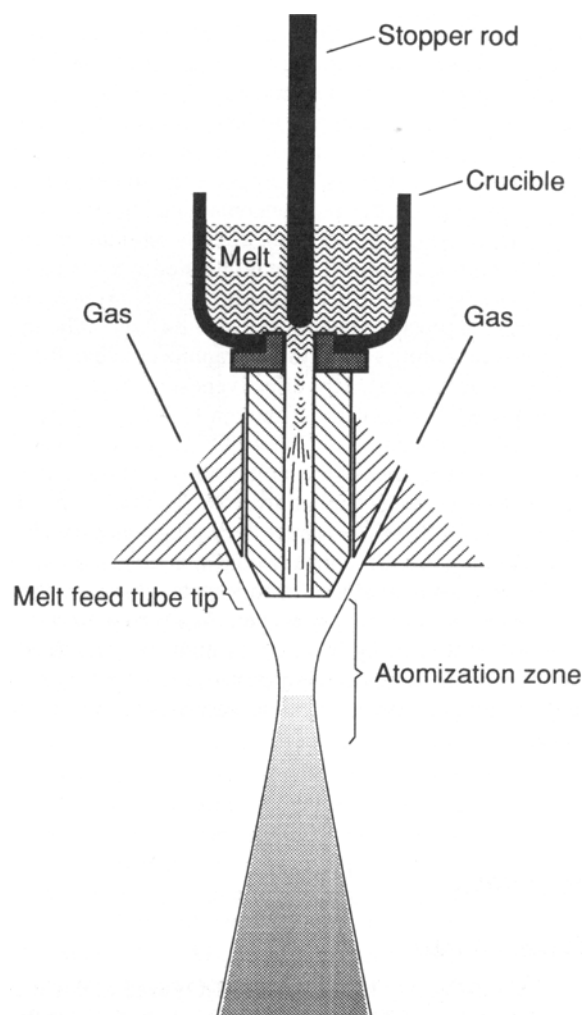
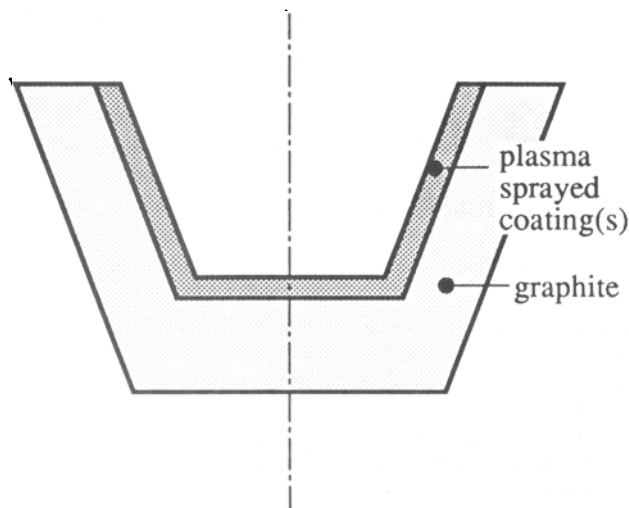


Fig. 1 General configurations of containment crucible and atomization regions of Ames Laboratory HPGA system.

**Key Words:** applications, graphite crucibles, microscopy, tantalum coatings, tungsten coatings

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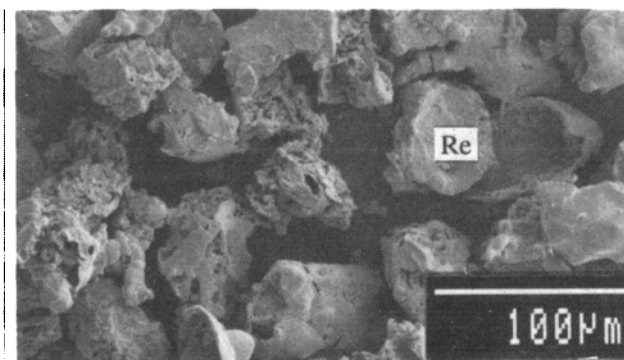
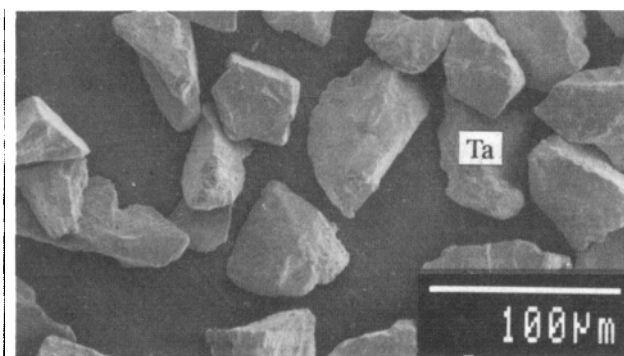
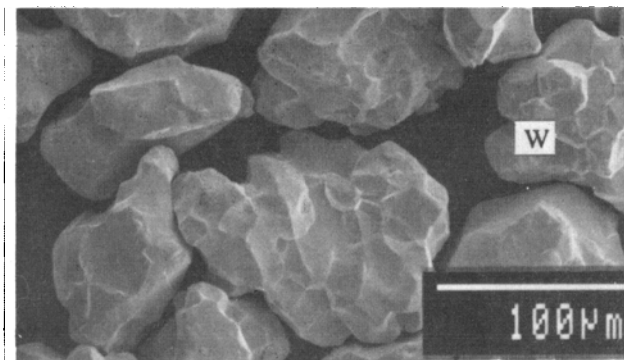
**Fig. 2** Schematic cross section of composite crucible design.

rities. Therefore, an approach has been devised that combines the chemical stability of various refractory materials with the physical stability of graphite. Figure 2 shows the composite crucible design that has been evaluated. The plasma sprayed coating system is chosen based on the thermodynamic stability of the interface between it and the process material. Because the coating is thin, thermal gradients are less steep, decreasing the potential of the coating for cracking or spalling by thermal shock. In addition, the authors' experience has shown that it is beneficial to precede the desired noncontaminating layer with a refractory metal layer, e.g., tungsten, directly onto the graphite surface.<sup>[2]</sup> The refractory metal layer is intended to block carbon migration from the graphite to the subsequently sprayed protective layer and the process material and also increase adherence of the composite coating system to the graphite crucible. Recent programs have demonstrated the effectiveness of this composite crucible approach for containing molten Cu-15Cr (vol%) alloys.<sup>[2]</sup> A coating system of  $ZrO_2 \cdot 8wt\%Y_2O_3$  over W was far more stable in the presence of the molten alloy at 1800 °C than a series of Ta-base coatings applied over W. A subsequent study found that the  $ZrO_2 \cdot 8wt\%Y_2O_3$  over W coating was quite effective in containing Cu-Cr alloys with Cr contents up to 90 vol%.<sup>[3]</sup> In the current study, refractory metal coating systems were evaluated for containing molten  $Al_2O_3$ -base ceramics. This work was motivated by the desire to study the solidification behavior of ceramic oxides in an attempt to understand the structure/property relationships of ceramic materials having tailored microstructures.

## 2. Materials

### 2.1 Ceramic Oxides

The  $Al_2O_3 \cdot ZrO_2$ ,  $Al_2O_3 \cdot Y_2O_3$ , and  $Al_2O_3$  used in this study were purchased from CERAC, Inc., Milwaukee, WI. All three oxides were reported to be 99.99% pure. The  $Al_2O_3 \cdot ZrO_2$  is a eutectic mixture of 60 at%  $Al_2O_3$ . The stoichiometric  $Al_2O_3 \cdot Y_2O_3$



**Fig. 3** SEM micrographs of refractory metal feedstock powders.

is 62.5 at%  $Al_2O_3$ , the yttrium aluminum garnet compound. The powders were dry mixed and isostatically pressed to form compacts for melting.

### 2.2 Graphite Crucibles

High-purity graphite crucibles were purchased from Beaumac Co., Epsom, NH. Total ash content for this material is reported to be <15 ppm by weight.

### 2.3 Plasma Arc Sprayed Powders

The coating systems evaluated were 0.025 in. (0.635 mm) W, 0.015 in. (0.381 mm) Ta over 0.010 in. (0.254 mm) W, and 0.015 in. (0.381 mm) Re over 0.010 (0.254 mm) W. Figure 3 shows SEM photomicrographs of the plasma spray feedstock powders.

### 3. Experimental Procedure

#### 3.1 Plasma Arc Spraying

The refractory metal coatings were applied to the graphite crucibles by Plasma Coating Corp., Gardena, CA. This outside vendor was used to expedite the evaluation of the current systems during construction of the ALPS facility. Prior to coating, the crucibles were grit blasted by 50- $\mu\text{m}$   $\text{Al}_2\text{O}_3$ . Spraying was performed in air using a Plasmadyne SG1B gun with a front feed powder injection port. Argon and helium were used as primary and secondary gases, respectively. Spraying was performed at 600 A and 30 V.

#### 3.2 Melt Processing

The pressed oxide compacts were placed inside the plasma sprayed graphite crucibles. The crucibles were covered with graphite tiles coated with the same system as the containment crucible. The materials and spraying parameters used to prepare the tiles were identical to the crucible coatings. The lids minimized the exposure of the molten oxide to the carbon present in the furnace atmosphere. The crucibles were heated in an induction furnace rated at 3 kHz and 50 kW power. The samples were placed in a larger graphite cylinder that served as the RF field susceptor. The furnace enclosure was evacuated to  $10^{-3}$  Pa and backfilled with argon to just below atmospheric pressure. The  $\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  samples were heated to approximately 2040, 2150, and 2200  $^\circ\text{C}$ , respectively, and held at temperature for 20 min. These temperatures are approximate,  $\pm 50$   $^\circ\text{C}$ , due to bridge formation over the optical pyrometer sight hole in the furnace insulation. The samples were cooled to room temperature before removing.

#### 3.3 Analytical Techniques

Following the melt processing experiments, the lids were removed, and the crucibles were sectioned axially to reveal the crucible/refractory metal coating(s)/ceramic interfaces. The sample sections were mounted in epoxy, ground, and polished with 1  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ . Optical microscopy was used to observe the as-polished surfaces. Subsequently, the samples were carbon coated and analyzed by SEM and EDS. Combustion chromatographic analysis was used to measure approximate carbon levels in several oxide samples after melting. Oxygen contents of feedstock powders and resulting coatings were determined by inert gas fusion.

### 4. Results

Figure 4 shows the ceramic oxide/refractory metal coating interfaces that developed during the melt processing experiments. Note that no micrograph is shown for the W-Re/ $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  system. This sample reacted to form a highly moisture-sensitive product that broke down into dust after brief exposure to water during metallographic sectioning.

#### 4.1 W-Coated Crucibles

The 100% tungsten coatings were penetrated by each of the molten oxides studied. The oxide/tungsten coating interfaces

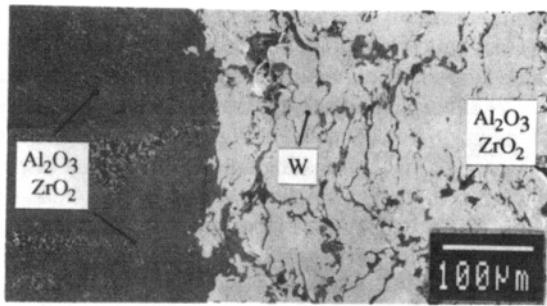
are highlighted in Fig. 5. The oxides have migrated into the porosity throughout the coating. The path of this migration appears to be along the splat boundaries. A significant structural change in the layer of tungsten adjacent to the  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  is readily observed in Fig. 4(d) and detailed in Fig. 5(b). The tungsten grains have coarsened, and the coating structure has been disrupted. Small pieces of the coating are visible in the bulk of the  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ . The penetration of the pure  $\text{Al}_2\text{O}_3$  into the tungsten is more severe than that of the other two oxide systems (see Fig. 4f). The pores in the coating are much larger, which suggests possible chemical reactivity between the coating and the molten oxide. It is not clear whether this increased penetration and possible reactivity results from the chemical properties of the pure  $\text{Al}_2\text{O}_3$  or the higher melt processing temperature (2200  $^\circ\text{C}$ ). Elemental analysis by EDS of the material within the large pores of the tungsten coating (Fig. 5c) identified the presence of both W and Al. A series of W-Al intermetallic phases exists with melting temperatures well below the 2200  $^\circ\text{C}$  melt processing temperature used for this system. However, additional diffraction studies would be necessary to characterize this material completely.

#### 4.2 Ta-W-Coated Crucibles

Similar penetration of the three molten oxides was observed in the tantalum portion of the Ta-W coatings. The oxide/tantalum coating interfaces are highlighted in Fig. 6. Again, the path of oxide migration appears to be along the splat boundaries. As the oxide material surrounds and isolates individual tantalum splats or grains, they tend to move into the bulk of the oxide. An interesting and consistent feature of the Ta-W coatings is shown in Fig. 4(b), (e), and (g). The coating appears to delaminate along the Ta/W interface. A thin layer of the oxide fills the void between the separated layers. This material was identified by EDS to contain the same oxide(s) present in the bulk region of the melt, i.e., there does not appear to be any preferential penetration of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , or  $\text{ZrO}_2$ . In addition to the detached tantalum grains visible in the oxide, the Ta coating material was also found surrounding the  $\text{Al}_2\text{O}_3$  grains. This is shown in Fig. 6(c).

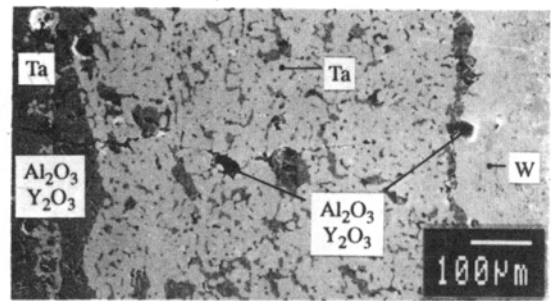
#### 4.3 Re-W-Coated Crucibles

The molten  $\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$  readily penetrated the Re layer (Fig. 7a). The movement of the eutectic mixture appears to be along the splat boundaries. This oxide also was detected by EDS to be present within the porosity of the tungsten coating. The behavior of the Re-W coatings in contact with  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  differed radically from their behavior with the other melt processing systems. The  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  reacted with the Re-W coating and formed a material that quickly broke down in the presence of water during subsequent metallographic sectioning. Also, this system generated a large amount of smoke within the fused silica furnace containment cylinder during heating at 2150  $^\circ\text{C}$ . This cylinder is used to contain a protective inert atmosphere around the susceptor and insulation. The deposit was removed and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and was found to contain mostly aluminum, with trace amounts of tungsten and rhenium. An oxygen leak into the argon atmosphere within the silica cylinder was first suspected. The melt processing experiment was repeated with new materials and again both the formation of a highly



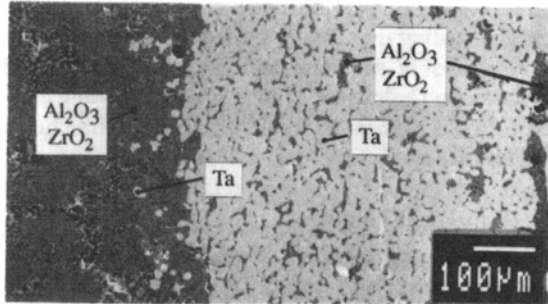
W/Al<sub>2</sub>O<sub>3</sub> • ZrO<sub>2</sub>

(a)



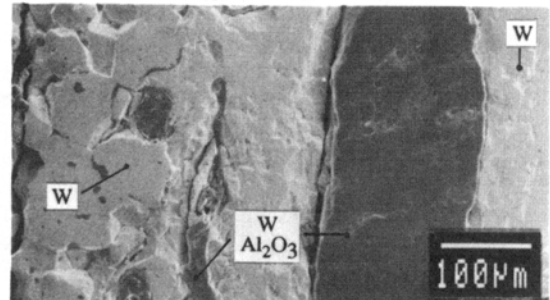
W • Ta/Al<sub>2</sub>O<sub>3</sub> • Y<sub>2</sub>O<sub>3</sub>

(b)



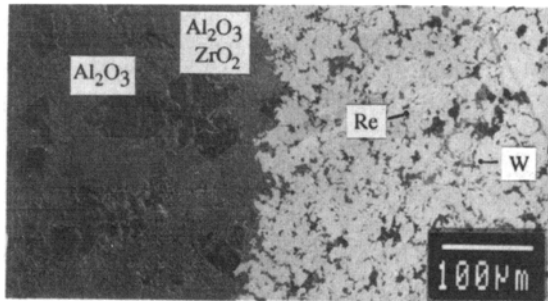
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(c)



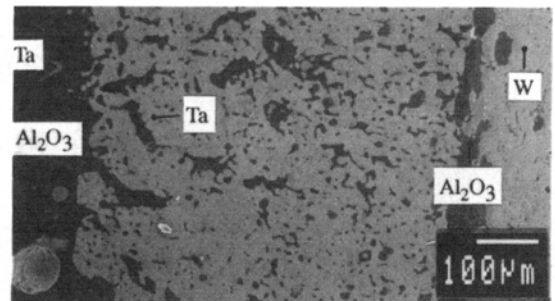
W/Al<sub>2</sub>O<sub>3</sub>

(d)



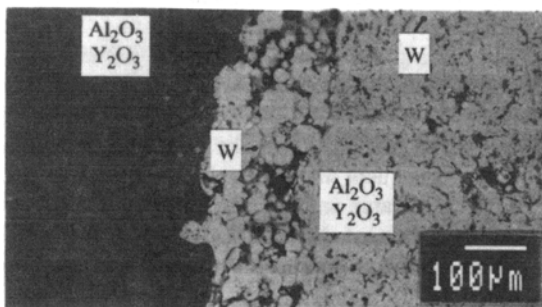
W • Re/Al<sub>2</sub>O<sub>3</sub> • ZrO<sub>2</sub>

(e)



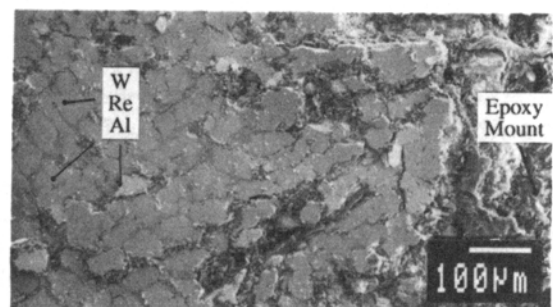
W • Ta/Al<sub>2</sub>O<sub>3</sub>

(f)



W/Al<sub>2</sub>O<sub>3</sub> • Y<sub>2</sub>O<sub>3</sub>

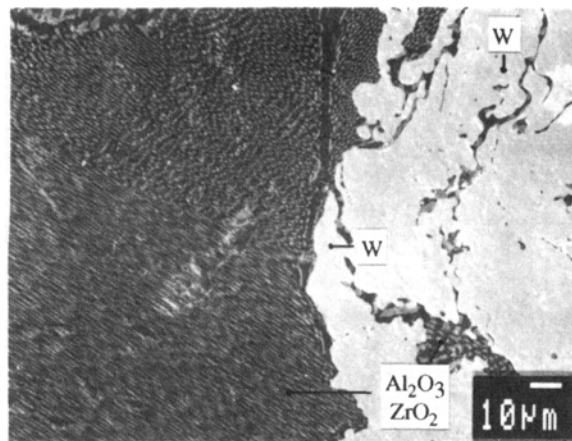
(g)



W • Re/Al<sub>2</sub>O<sub>3</sub>

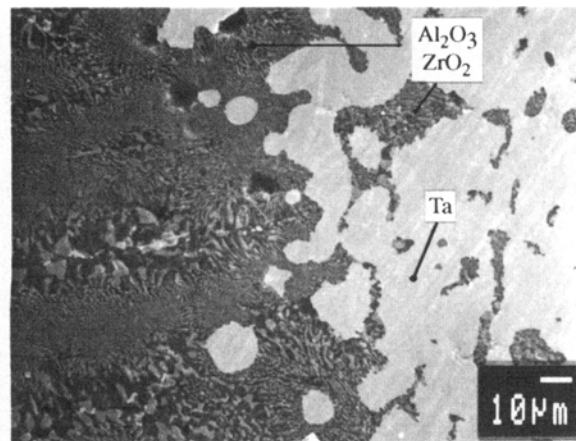
(h)

**Fig. 4** SEM micrographs of refractory metal coating/ceramic oxide interfaces.



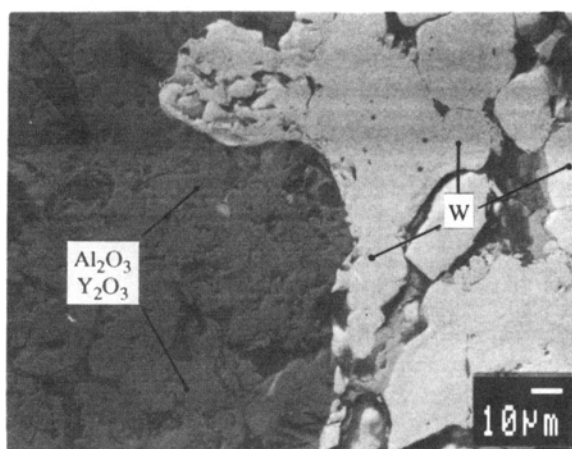
W/Al<sub>2</sub>O<sub>3</sub> · ZrO<sub>2</sub>

(a)



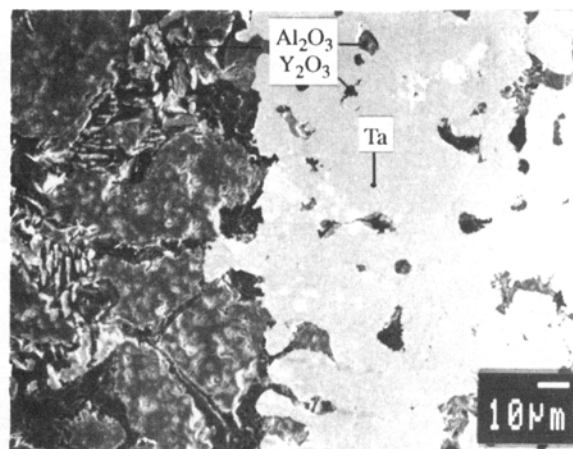
W · Ta/Al<sub>2</sub>O<sub>3</sub> · ZrO<sub>2</sub>

(a)



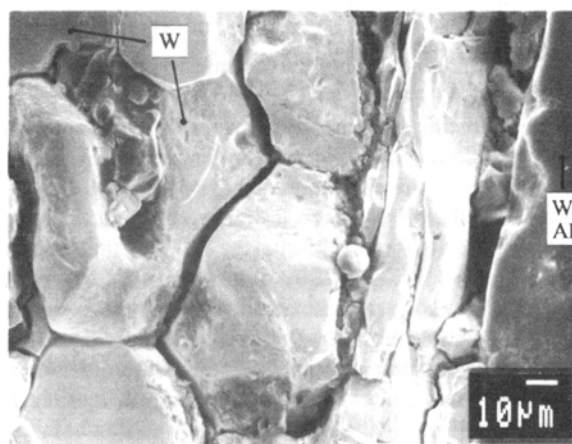
W/Al<sub>2</sub>O<sub>3</sub> · Y<sub>2</sub>O<sub>3</sub>

(b)



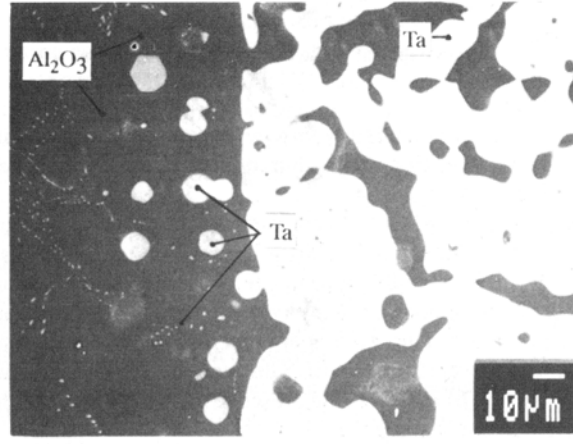
W · Ta/Al<sub>2</sub>O<sub>3</sub> · Y<sub>2</sub>O<sub>3</sub>

(b)



W/Al<sub>2</sub>O<sub>3</sub>

(c)

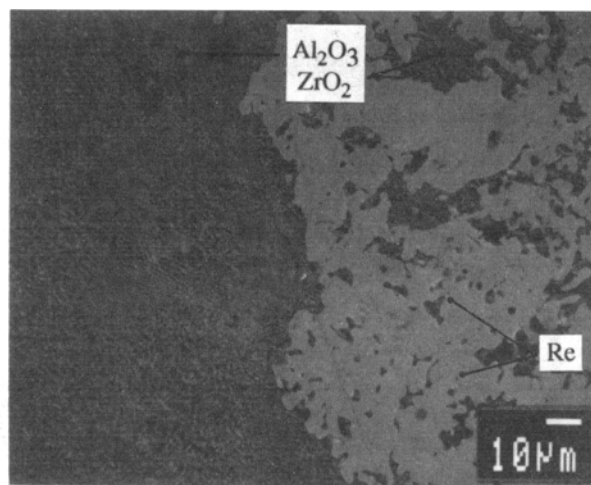


W · Ta/Al<sub>2</sub>O<sub>3</sub>

(c)

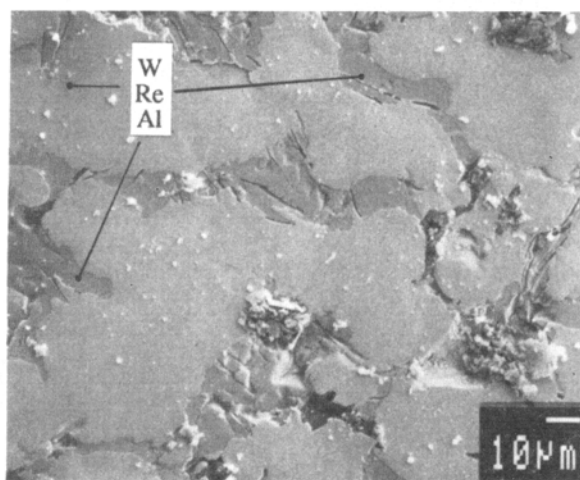
**Fig. 5** SEM micrographs of W/ceramic oxide interfaces.

**Fig. 6** SEM micrographs of W · Ta/ceramic oxide interfaces.



W • Re/Al<sub>2</sub>O<sub>3</sub> • ZrO<sub>2</sub>

(a)



W • Re/Al<sub>2</sub>O<sub>3</sub>

(b)

Fig. 7 SEM micrographs of W-Re/ceramic oxide interfaces.

moisture-sensitive material within the plasma sprayed graphite crucible and deposition of the aluminum-rich smoke on the silica cylinder were observed.

The residual Al<sub>2</sub>O<sub>3</sub> melt in contact with the graphite containment crucible is shown in Fig. 6(b). The resulting material has a very shiny silver metallic appearance in contrast to the normal white-gray appearance of many ceramic oxides. The rhenium and tungsten layers are no longer present. Tungsten, rhenium, and aluminum were found by EDS throughout the solidified material. Figure 7(b) indicates the presence of two phases, but the material was not characterized further.

## 5. Discussion

The EDS analysis performed on the oxide portions of the samples generally did not reveal any chemical reactivity be-

**Table 1 Oxygen contents of feedstock powders and coatings determined by inert gas fusion**

Sample description	Oxygen content, ppm by weight
W powder before spraying .....	448
Ta powder before spraying .....	847
W coating .....	4 113
W-Ta coating.....	16 200

tween the molten ceramic and the refractory metal coatings. The W/Al<sub>2</sub>O<sub>3</sub>, Re-W/Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, and Re-W/Al<sub>2</sub>O<sub>3</sub> did exhibit reactivity as described above. The refractory metal coating observed at the ceramic oxide interface showed no traces of the oxide cations. Similarly, spot analysis of the oxide adjacent to the oxide/coating interface did not reveal the presence of any of the three refractory metal coating elements. However, substantial mass movement of molten material into the pores of the coating degrades the coating at the liquid interface, as shown in Fig. 6(c), and may also lead to liquid contact with the graphite crucible. This behavior intuitively seems to be a capillary or surface tension effect. The wetting phenomenon may be described by the following equation:<sup>[4]</sup>

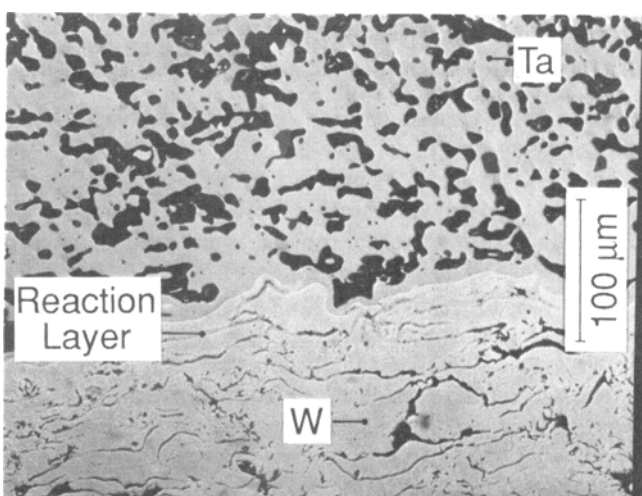
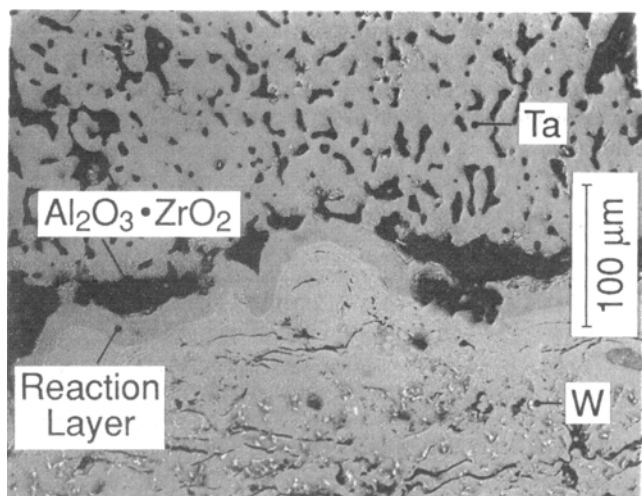
$$\gamma_{sl} \leq \gamma_{sv} - \gamma_{lv}$$

where  $\gamma_{sl}$  is the energy of the solid/liquid interface;  $\gamma_{sv}$  is the energy of the solid/vapor interface; and  $\gamma_{lv}$  is the energy of the liquid/vapor interface.

The equation describes the wetting of the refractory metal coating by the ceramic melt, in which case the surface energy of the solid/liquid interface is lower than that of the solid/vapor interface after removal of the liquid/vapor interface energy. Reference to surface energy data for ceramic melts and solid refractory metals shows that the surface energy values for molten Al<sub>2</sub>O<sub>3</sub> and solid tantalum are 700 and 2100 Nm/m<sup>2</sup>, respectively.<sup>[5,6]</sup> Although specific experimental determination of surface energies was not made for the systems studied during this investigation, the references are consistent with the observed penetration of the molten ceramic into the refractory metal coatings.

By eliminating the porosity network, low-pressure plasma spraying could reduce penetration of the coating by the molten liquid. Although this is a technically promising approach, less expensive methods were more desirable for this particular application. The results above show that the W-Ta coating system was chemically stable with the three oxides studied. Close observation of the Ta coating microstructure after melt processing (Fig. 4b, e, and g) shows substantial grain coarsening and porosity rearrangement. Furthermore, an interesting feature developed in all of the W-Ta coatings after melt processing. A dense layer approximately 50-μm wide formed at the interface between the two coatings. This layer is slightly visible in Fig. 4(e) and (g) and is shown in more detail in Fig. 8(a). No penetration by the molten oxides that permeated the porosity of the Ta coating was observed to extend beyond this reaction layer. In addition, no evidence of any chemical reactivity between the layer and the oxides was detected by EDS spot analysis. Attempts to deter-



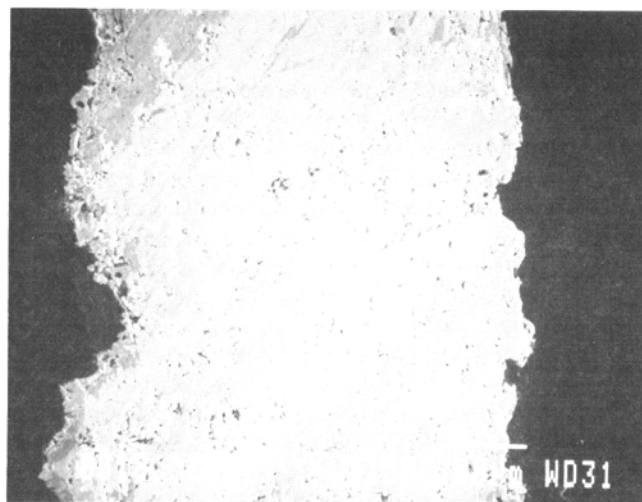


(b)

**Fig. 8** Optical micrograph highlighting the reaction layer formed during the following processing: (a) melt processing of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  eutectic mixture at 2040 °C and (b) heating to 2000 °C in the absence of any molten oxides.

mine the exact composition of the interfacial reaction layer, however, were inconclusive.

Because the dense reaction layer combined the necessary chemical stability along with the desired low porosity to inhibit liquid penetration, several additional experiments were performed to try and recreate the reaction layer throughout an entire coating. Initially, it was suspected that the presence of the molten oxide was a factor in the formation of the reaction layer and the microstructural change of the Ta coating. However, a sample of a W-Ta coating heated alone to 2000 °C, shown in Fig. 8(b), shows a nearly identical microstructure to the ones developed while in contact with the molten oxides. The Ta layer shown in Fig. 4(b), (e), and (g) has the appearance of a liquid phase sintered material. Tantalum has an oxide that melts just above 1500 °C and is far less volatile than the oxides of tungsten. Oxygen analysis by inert gas fusion was performed on several W and Ta



**Fig. 9** SEM micrograph of polished cross section of coating formed with a 1:1, by weight, blend of W and Ta powder.

**Table 2** Carbon content of selected ceramic oxides

Coating/oxide	Carbon content, ppm by weight		
	Sample No. 1	Sample No. 2	Sample No. 3
W/ $\text{Al}_2\text{O}_3\text{-ZrO}_2$ .....	55	62	97
W-Ta/ $\text{Al}_2\text{O}_3\text{-ZrO}_2$ .....	85	76	61
W-Ta/ $\text{Al}_2\text{O}_3$ .....	181	138	164

feedstock powders and coatings. The results are shown in Table 1. As would normally be expected, both W and Ta readily oxidized during plasma spraying. The higher oxygen content of the Ta coating is presumably due to the different vapor pressures of  $\text{Ta}_2\text{O}_5$  and  $\text{WO}_3$ .

Based on the assumption that the formation of the dense layer formed at the W-Ta interface was related to the oxidation of the particles during spraying, a powder blend of equal weights of W and Ta was plasma sprayed using parameters similar to those used to form the individual coatings. The cross section of the resulting coating is shown in Fig. 9(a). Comparing this to the microstructure of the individual W-Ta coating revealed that a much denser coating is formed with the blended powder. Although the exact mechanism producing the reaction layer at the W-Ta interface or the dense coating structure is not fully understood, the coating structure shown in Fig. 9 appears very promising as a containment barrier for melt processing the  $\text{Al}_2\text{O}_3$ -base ceramics evaluated in this study. Studies are underway to improve the coating structure formed from the blended W-Ta powders and to evaluate this refractory metal coating system for containing these and other molten ceramic alloys.

Samples of the bulk ceramic oxide from the W/ $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , W-Ta/ $\text{Al}_2\text{O}_3$ , and W/ $\text{Al}_2\text{O}_3$  system were analyzed for carbon content by combustion chromatography. The results are shown in Table 2. The absence of reactivity between the oxides and the coating systems, together with the ability of these coating systems to stop carbon migration from the graphite crucibles, strongly suggest that these systems are compatible for melt processing under the conditions studied.

## 6. Conclusion

A series of refractory metal plasma-sprayed coatings (W, Ta-W, and Re-W) applied to graphite crucibles were tested as containment barriers for melt processing  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ,  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ . The molten ceramics migrated along the splat boundaries into the porosity of the coatings. Despite the undesirable wetting of the coatings, there did not appear to be any chemical attack of the tungsten or tantalum by the oxides. In contrast, the Re-W coatings reacted with molten  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .

Future work is continuing at the Ames Laboratory Plasma Spray Facility on these and many other coatings for containment of high melting temperature reactive materials in advanced processing and solidification studies. The current study will be expanded to include the role of coating porosity on molten material penetration and to incorporate additional characterization techniques to better analyze the interfaces developed.

## Acknowledgment

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