FUNDAMENTAL STUDIES OF CERAMIC/METAL INTERFACIAL REACTIONS AT
ELEVATED TEMPERATURES

by

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Fundamental Studies of Ceramic/Metal Interfacial Reactions at Elevated Temperatures

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1.0 ABSTRACT
This work characterizes the interfaces resulting from exposing oxide and non-oxide ceramic substrates to zirconium metal and stainless steel-zirconium containing alloys. The ceramic/metal systems together were preheated at about 600°C and then the temperatures were increased to the test maximum temperature, which exceeded 1800°C, in an atmosphere of high purity argon. Metal samples were placed onto ceramic substrates, and the system was heated to elevated temperatures past the melting point of the metallic specimen. After a short stay at the peak temperature, the system was cooled to room temperature and examined. The chemical changes across the interface and other microstructural developments were analyzed with energy dispersive spectroscopy (EDS). This paper reports on the condition of the interfaces in the different systems studied and describes possible mechanisms influencing the microstructures.

2.0 INTRODUCTION
Ceramic/liquid metal interfaces play a significant role in the processing of metal matrix composites, development of reusable crucibles in reactive metal melting, and ceramic-metal brazing. The question of interface design and control for these systems is complex. The atomic or electronic structure of the metal is an important factor that affects the reactivity of the liquid metal in contact with the ceramic material. When ceramics and liquid metals are exposed to elevated temperatures, chemical reactions and formation of undesirable phases often occur at the interface.

The interfacial region that connects the metal with the ceramic material may adopt different forms, from a simple interface of atomic bonds to new reaction phases and/or interfaces located between the metal and the ceramic. Complex oxides, carbides, nitrides, and intermetallics frequently form at the interface between metals and ceramics during processing or service at elevated temperatures.

There are applications where wetting and the formation of a strong ceramic-metal interface are not desirable. In metal casting, a refractory crucible is used to handle the liquid metal, and ceramic porous bodies are used as filter materials. For such applications, interface development must be avoided, and the paradigms employed for brazing and composite processing need to be reversed.

Wetting can be considered a surface phenomenon and it has been shown to occur on the surface of the ceramic/metal reaction product [1]. Reactive alloy additions can be added to the metal or applied directly to the interface. Coatings of Ni, Ag, Cu, and Cr have been applied to the ceramic surfaces to enhance wettability, while the Na process is used to prepare Al₂O₃ for wetting by metallic liquids [2-4]. Chemical vapor deposition of titanium coatings onto Al₂O₃ has been shown to enhance its wettability [5]. The commercial Moly-Manganese process uses a reduction reaction to obtain a reliable braze [6, 7].

Most wetting investigations are based on the contact angle (Figure 1), first defined empirically by Young [8]:

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]

where \( \gamma_{SV} \), \( \gamma_{SL} \), and \( \gamma_{LV} \) are the solid-vapor, solid-liquid, and liquid-vapor interfacial energies respectively. A contact angle \( \theta \) of 90° or greater is non-wetting, while a contact angle between zero and 90° is partially wetting. The experimental measurement of the equilibrium contact angle, however, may be complicated by interfacial reactions. The formation of new phases at the interface is not accounted for in Equation 1; under that condition, the results become ambiguous. Interfacial reaction may partially dissolve the substrate, resulting in a non-horizontal surface by the triple point [9]. The resulting configuration no longer has the horizontal force balance assumed for the Young's equation, and determination of the contact angle is experimentally difficult. In addition, the nature of the surface is also unknown.

The work presented in this paper considers high-temperature reactions at ceramic-metal interfaces and the microstructures that develop after melting. Results are given for the interactions of pure liquid zirconium and liquid zirconium metal alloys with beryllia, yttria, zirconium nitride, and zirconium carbide.

3.0 EXPERIMENTAL WORK
A wide variety of oxides and non-oxide ceramics were fabricated from high purity powders by hot uniaxial pressing (HUP). All materials were cleaned with acetone, to remove dirt and other contaminants, prior to the high temperature exposures. The metal samples used were pure Zr and ferritic (HT9) stainless steel alloyed with 15 wt. % Zr. The composition of the ferritic stainless steel (HT9) in weight percent is 0.5Ni,
The metal/ceramic assemblage was heated in a tungsten mesh furnace in high purity argon with a sensing thermocouple placed about 0.5 cm beneath the samples. The materials were preheated to 600°C, continuously heated at a rate of about 20°C/min to 1600°C, and then at 10°C/min to about 2000°C. In most cases, the system was held at the peak temperature for 5 minutes, then cooled to room temperature at ~20°C/min. The wetting and high temperature interactions between the molten metals and ceramic substrates were monitored through an external video camera. In-situ observations were followed by post-test examinations using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

4.0 RESULTS AND DISCUSSION

4.1 Zr/BeO System

During heating some surface crust developed in the Zr near the interface with BeO as the temperature approached 1500°C. At about 1550°C, a significant reaction was noticed between the Zr metal and the BeO substrate. This reaction intensified, and bubbling, or gas evolution, was observed at the solid-liquid boundary as the temperature reached 1580°C. At ~1605°C a liquid layer appeared at the interface, yet the Zr metal was far below its melting point, and the sample maintained its original parallelepiped shape. As the temperature reached 1735°C, the Zr metal became distorted and assumed a trapezoid-like shape. At about 1780°C, the Zr specimen deformed greatly because of the increased amount of liquid within the sample. At 1790°C, the Zr metal collapsed, and a hemispherical droplet formed. A wetting angle of ~60° was measured at 1795°C in a still video image. The contact angle decreased significantly at ~1825°C. The heating cycle continued up to 2000°C, where the system was held for five minutes.

A chemical reaction at the Zr/BeO interface was suggested by the gas evolution observed at the liquid-ceramic interface in the video at ~1605°C. It appears the Zr reduced the BeO. One possible chemical reaction is:

$$\text{BeO(s)} + \text{Zr(s)} = \text{Zr(O)} + \text{Be[Zr(O)]} \quad (2)$$

Evidence of such reaction was confirmed by the changes in the microstructure and composition of the pure Zr on top of the BeO after the system was cooled to room temperature (Figure 2). The microstructure consists of coarse, proeutectic, blocky-like particles and a eutectic structure in a matrix of α-Zr. The EDS standardless analysis revealed oxygen levels of about 10 at. % in the α-Zr. No Zr was found in the black proeutectic phase, only oxygen; this implies that Be must also be present, since it is too light to be detected by the EDS equipment. The fine acicular-like particles of the eutectic microstructure contained Zr and oxygen; but these fine particles were dark as the proeutectic phase and expected to contain Be. The presence of Zr indicates that the eutectic structure is a mixture of α-Zr and intermetallic or oxide particles of Be-Zr-O.

The dissolution of the BeO was also evident by the fact that the original Zr/BeO interface receded into the ceramic substrate. In addition, Zr metal was found to have infiltrated the beryllia. It appears that the drop in the contact angle at ~1825°C between the molten Zr and the BeO was caused by the infiltration of liquid Zr.

4.2 HT9-15Zr/BeO System

No chemical reactions or initial interfacial melting was observed in this system during the interaction test. Partial melting of the metal alloy occurred at ~1340°C, and a non-wetting hemispherical cap was formed at ~1350°C. This alloy has a eutectic temperature of 1335°C; thus the chemical reactions between Zr and BeO noted at higher temperatures in the Zr/BeO system could not be seen here. The contact angle between the Zr alloy and the BeO was always greater than 90°, even at 2000°C.

The interface in this system consisted of a reaction layer, about 150-200 μm thick, which separated the Zr alloy and the BeO (Figure 3). The EDS results show this band to be rich in Zr (~54.0 at. %) and oxygen (~45.0 at. %), but Be is also expected present. The excess Zr confirms the reduction of BeO by Zr. The Zr alloy infiltrated the BeO but only to the extent of the reaction band (Figure 3b). This reaction band (Region 2) separated from the rest of the droplet (Region 1), hinting differences in coefficients of thermal expansion.

The microstructure displayed by the metal droplet and the metal alloy infiltrated in the reaction band is the same, consisting of dendrites and eutectic structure.

4.3 Zr/Y2O3 System

With this system, partial melting of the Zr occurred at ~1850°C, and gas evolution was noted at the interface. The Zr almost immediately wetted the ceramic upon melting; a contact angle of ~50° was measured. As in the BeO case this chemical reaction at the interface may be caused by Zr reducing the Y2O3:

$$3 \text{Zr(s)} + \text{Y2O3(s)} = 3 \text{Zr(O)} + 2 \text{Y} \quad (3)$$

This reaction does not appear to be as vigorous as that involving Zr and BeO. The interface in this system had minor changes, and the Y2O3 was not easily dissolved. According to thermodynamic data Y2O3 is more stable than BeO, but the governing factor may be the Y solubility in Zr. This also explains why Zr melted near its melting point, since yttrium will decrease the Zr melting point.

The Zr/Y2O3 interface was continuous with no stable third phase formed. Zirconium did dissolve some of the yttria and experienced some discoloration near the interface (~25-μm band). A strong bond was formed. The EDS results of this region indicate an oxygen level of 14.0 at. %. The oxygen content of the α-Zr away from the interface was negligible; oxygen was not detected by the EDS instrumentation. The yttrium from the interfacial chemical reaction diffused into the Zr but segregated to the grain boundaries on
cooling because of its limited solubility in $\alpha$-Zr. The grain boundary material was found to contain Y (86-90 at.%) and Zr (14-10 at.%). But no oxygen was detected at the grain boundaries or in the adjacent $\alpha$-Zr matrix for regions away from the interface. Figure 4 shows the interface in this system and the yttrium that segregated to the zirconium grain boundaries. A few cracks were seen in the ceramic substrate near the interface. Cracking also occurred in the side of the $Y_2O_3$ opposite to the metal/ceramic interface. This is expected due to thermal mismatches between the materials in the system.

4.4 HT9-15Zr /$Y_2O_3$ System

This alloy melted at $\sim$1340°C due to its low melting point, making it difficult to observe interfacial reactions at higher temperatures. The molten alloy, as in the case of the BeO substrate, did not wet the $Y_2O_3$ ($\theta\sim110^\circ$). The contact angle was observed to vary unexpectedly with temperature; it measured 140° at 1950°C, it dropped to 90° when the temperature reached 2000°C, but then it declined to $\sim$60° after 5 minutes at this peak temperature. Figure 5a shows the final contact angle after solidification.

Bonding was evident between the metal alloy and the $Y_2O_3$, but this broke at the interface on cooling. Cracks in the yttria close to the interface are further evidence of such bonding. A thin and irregular transition layer developed at the interface (Figure 5b), rich in yttrium. The levels of Y at this location were measured as 11.0-13.0 at.%; the other two major elements were Zr (85.0-81.0 at.%) and Fe (2.0-3.0 at.%). This implies that the reduction of the $Y_2O_3$ was localized at the interface, and the reduced yttrium just remained in this region, since the EDS did not detect yttrium anywhere within the metal droplet. On the ceramic side of the interface there was Zr diffusion only, but near the interface.

The next three systems to be discussed include non-oxide ceramic substrates: two nitrides and a carbide. Thermodynamic data indicate that the stability of this type of ceramic is not as firm as that of oxides in general. However, because of the new non-oxide ceramics developed for structural engineering applications, such as metal matrix composites, or as ceramic/metal braze joints, it is important to understand the stability of the interface between metal and these ceramics to further extend their use.

4.5 Zr/ZrN System

As this system was heated to elevated temperatures, Zr did not melt at 1855°C, its melting temperature, but at 1975°C. Melting first occurred at the interface. The deviation of the melting temperature implied that nitrogen from ZrN dissociation had reacted with the pure Zr. This indicates that a chemical reaction at the interface between the Zr metal and the ZrN must have occurred before melting. According to the equilibrium phase diagram of Zr and N [10], $\beta$-Zr has a maximum nitrogen solubility of about 0.8 wt. %. This composition should melt at $\sim$1880°C. When the N content in Zr is between 3 and 5 wt. %, the alloy is $\alpha$-Zr, and the melting temperature ranges between $\sim$1880°C and $\sim$1985°C, respectively. The metal sample melted fully at 2000°C, and wetted the substrate (a contact angle of $\sim$37° was measured).

A reaction layer developed between the Zr metal and the ZrN substrate (Figure 6). The reaction layer is $\sim$40 μm thick and is a new ZrN<sub>4</sub> structure formed between the Zr metal and N. The EDS measurements of this band showed levels of N at about 15.0 at.%, with Zr ($\sim$15 at.%) as the other element. The reaction layer, however, showed continuity across the interface with the Zr metal, as well as with the original ZrN substrate. This transition band had a large crack parallel to the interface between the metal and ceramic joint, apparently caused by differences in the thermal expansion of Zr and ZrN.

The area of the ceramic substrate adjacent to the reaction layer appears to have been involved in the chemical reaction at the interface (Figure 6a). The size of this region was similar to the new ZrN precipitated reaction layer on the metal side of the interface. And its composition included N ($\sim$18.0 at.%) and Zr ($\sim$82.0 at.%). The N diffusion into the metal droplet was not only confined to the interface, it also diffused further into the Zr metal on top of the substrate. Lath-type precipitates of ZrN had formed throughout the $\alpha$-Zr matrix, as seen in Figure 6b. Standardless EDS measurements showed the N content in these dark precipitates to be $\sim$13 at. %.

4.6 HT9-15Zr/ZrN System

Similar to previous oxide ceramic systems, the alloy HT9-15Zr melted early at the eutectic temperature, and the molten metal did not wet the ZrN substrate. In this case a wetting angle larger than $\sim$140° was measured.

Bonding developed between the metal droplet and the ZrN (Figure 7), but no transition phase was seen at the interface. There was continuity between the bright intermetallic phase of the HT9 alloy, Zr(Fe, Cr, Ni)₂+X[11], and the ZrN substrate, as seen in Figure 7b. The EDS spot analysis of this bright intermetallic near the interface with ZrN revealed the following composition in at. %: 42.0Fe, 6.0Cr, 22.0Ni, 25.0Zr, and 4.7N. The composition of the spot on the ZrN side of the interface contained just Cr ($\sim$53.0 at.%) and N ($\sim$46.0 at.%). The dark iron solution matrix near the interface had chemistry consisting of the following elements (at. %): 71.0Fe, 23.0Cr, and 5.0Ni. This lack of N and Zr solubility with the iron-rich matrix explains why the continuity of the metal/ceramic interface was just between the bright intermetallic phase and the ZrN, which is the compatibility of their compositions.

The cracking of the ZrN in this system was more serious compared to the Zr/ZrN combination, which may be attributed to a larger thermal expansion mismatch, plus the large volume of the brittle intermetallic. It was observed that the cracking was localized to the interface, but the major separation of the metal droplet occur inside the ZrN and away from the immediate metal/ceramic interface, as shown in Figure 7a.

4.7 Zr/ZrC System
The zirconium metal in this system melted completely at \(-1910^\circ C\), and no chemical reactions were detected in the video before melting. Furthermore, following melting the molten Zr flowed readily over the ZrC surface and spilled over to the sides of the ZrC specimen. The liquid metal finally rested on the tungsten dish that held the ZrC substrate. It also penetrated in between the tungsten holder and the ZrC, and bonded these two materials together (Figure 8), resulting in a true high-temperature ceramic-metal braze joint.

The top surface of the ZrC was clean and smooth, with no evidence of chemical reaction between the Zr metal and the ZrC. This lack of chemical reaction of this system is in significant contrast to that of the ZrN substrate. From standard thermodynamics data, the stability of the ZrN is greater than that of ZrC up to temperatures of about 1200°C. However, the rate of decrease in stability with increasing temperature is higher for ZrN than for ZrC. Review of the Zr-C equilibrium binary phase diagram indicated that both \(\alpha\)-Zr and \(\beta\)-Zr have limited solubility for carbon, but either phase is in equilibrium with ZrC.

The braze joint between the ZrC substrate and the W metal holder was metallographically analyzed to establish the extent of the Zr/W/ intermetallic interaction at the bottom of the ZrC. There was a strong bonding at the interface of the W and the ZrC. Also no cracking was observed in either material or in the Zr/W braze metal. Figure 8b gives more detail of the ZrC-W joint, which corresponds to the circle in Figure 8a. The interface between the \(\alpha\)-Zr and the ZrC is smooth, and it does not show any form of degradation or extensive chemical reaction. The microstructure at this Zr/ZrC interface is consistent with what is presented in the Zr and C equilibrium phase diagram.

On the opposite side of the braze metal, the molten Zr reacted with W. In examining the Zr-W equilibrium phase diagram, we observed that eutectic exists at Zr – 16.6 wt. % W with a melting temperature of about 1735°C. The microstructure encountered in the joint agrees with what is described in that phase diagram. That is, the braze metal consists of a matrix of \(\alpha\)-Zr with a eutectic consisting of W\(_2\)Zr intermetallic; closer to the W metal there is a layer of the same W\(_2\)Zr intermetallic attached to the base metal. An EDS analysis of the intermetallic particles confirmed their composition.

5.0 CONCLUSIONS
The concept of wetting as a parameter to assess indirectly the stability of a ceramic substrate in contact with a liquid metal at elevated temperatures is misleading.

The results of this study showed that chemical reactions occurred at elevated temperatures between Zr and HT9-15Zr metals and the oxide and non-oxide ceramic materials. Some of these reactions occurred before melting of the metallic samples. In some cases, high-temperature interaction phenomena influenced the melting point of the pure Zr, by either lowering or increasing it. In the Zr/BeO system, the Be lowered the melting point of Zr. For the Zr/N system, nitrogen from the dissociation of ZrN diffused into the metal Zr before melting and resulted in alloying of the pure Zr, thus elevating the melting temperature.

It was also found that even the most stable oxides that were expected to remain non-reactive at these high temperatures, e.g., BeO and Y\(_2\)O\(_3\), were at least partially reduced.

The molten metal did not always wet the ceramic substrate even when a transition phase was formed between them. This occurred primarily with the systems having the HT9-15Zr alloy. In other cases no transition phase developed, yet a strong bond developed between the metal and the ceramic substrate, as was the case of the Zr/N system.

The results of this investigation can be summarized in five specific conclusions:
1. Zirconium is the reactive element in these metal/ceramic systems. It provokes wetting of stable ceramics at high temperatures.
2. The interface chemical reaction byproducts dissolve in the pure Zr and affect its melting point. They also play a role in the wetting mechanics.
4. No transition phases form across the Zr/Y\(_2\)O\(_3\), Zr/ZrC, and Zr/HfC interfaces; however, there is continuity across this boundary, and a strong bond is achieved.

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