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Reactions of Hf-Ag and Zr-Ag alloys with Al_2O_3 at elevated temperatures

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We are studying reactions of Ti, V, Zr, and Hf with ceramics as part of a program to understand fundamental reaction and bonding mechanisms in active metal brazing of ceramics. In this paper we present results of experiments with model systems comprising Ag alloys that contain different amounts of Hf or Zr that were reacted with sapphire or 99.6% alumina for different times and temperatures in a controlled atmosphere furnace. In these alloys the Ag functions as an inert solvent, which allowed us systematically to determine the effects of changes in concentration of the active element. We observed qualitative wetting and spreading tendencies of the alloys during heating and examined cross sections after cooling using electron analytical techniques. For all reaction times studied, the Hf/Ag alloys formed a discontinuous reaction layer, which was consistent with earlier high-resolution electron microscopy that showed sub-micrometer HfO_2 particles embedded in the surfaces of the Al_2O_3 grains. By contrast, initial reaction of the Zr/Ag alloys with Al_2O_3 produced a continuous interface layer. With longer reaction times, the ZrO_2 reaction product became much thicker and exhibited three distinct zones at the interface. The results suggest that the rate limiting step in the Zr/Ag reaction is the chemical reaction at the interface, whereas with Hf/Ag reaction diffusion of products away from the interface is rate limiting.

1. Introduction

Braze alloys that contain transition metals as so called active elements are widely used for ceramic joining. Commercial alloys usually contain 1–4% Ti, or less commonly, small amounts of Zr or V as the active element. Without the transition element addition, the molten alloys do not wet ceramics. With the active element additions, the braze alloys wet and then adhere after cooling to make practical joints with ceramics [1–7]. Many workers have observed that elemental additions to braze alloys that favor reaction also promote wetting [8, 9]. Thus, on the basis of their highly exothermic reactions with many oxides, V, Ti, Zr and Hf would be expected to promote wetting of oxide ceramics when they are added to otherwise nonwetting alloys [10], as is indeed the case.

The present work is part of a project that focuses on experimental Ag alloys that contain either Zr or Hf [11]. They are being developed as an alternative to Ti-containing alloys for making hermetic seals between alumina ceramics and the matched-expansion Fe-29Ni-17Co alloy (Kovar^{TM}). Ti in conventional braze alloys reacts preferentially with the Kovar^{TM}, which leads to non hermetic seals unless the metal is first coated with a diffusion barrier such as Mo [11]. The binary Hf/Ag and Zr/Ag alloys have fewer constituents than commercial active braze alloys and thus they might be expected to provide a simpler system for analysis of the details of reactions between active metals and ceramics. In this report, we discuss primarily our results from experiments with the Zr/Ag alloy, although a few experiments with the Hf/Ag alloys also are presented.

2. Experimental

Four different braze alloys were made by arc melting reagent grade Zr or Hf with Ag and casting the melt into ingots. Part of each alloy was rolled into foil and the rest was sliced into thin wafers with a band saw. The compositions are listed in Table I.

Reactions with two different commercial ceramic substrates are reported here. The ceramics, which were used with the surface finishes supplied by the manufacturer, were:

- Sapphire (optical polish)
- 99.6% alumina, balance Ca, Mg silicate glass (Coors Ceramics Co. electronic substrates)

The alloy specimens were cleaned sequentially in methanol, dilute hot detergent solution, and deionized

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TABLE I Compositions of Zr/Ag and Hf/Ag alloys

Active element	Weight %	Atomic %
Zr	2	2.4
Hf	2.5, 3.4 and 6.8	1.5, 2.1 and 4.2

water, then dried in air, placed on top of the ceramics and heated in one of two atmosphere-controlled furnaces for the reaction experiments. One furnace was heated by a tubular, graphite resistance element contained in a water-cooled, stainless steel vacuum chamber. The specimens were isolated from the heating element by a coaxial ceramic tube that was sealed by o-rings in the end flanges. Quartz windows in each flange allowed the sample to be observed during heating. Other experiments were conducted in a water cooled, stainless steel vacuum furnace heated by a tungsten resistance element. All the runs reported here were conducted in flowing Ar that had been passed through a Ti-Zr getter heated at 800°C. The specimens were heated to the reaction temperature at 20°C/min, held for the reported time and then were cooled by turning off the power to the furnace. Cooling rates for the first several hundred degrees were between 50 and 100°C/min. The cooling rates progressively decreased as the furnace cooled and we believe reaction rates were negligible below the eutectic temperature (∼940°C for Zr/Ag) [12]. The cooled specimens were cut perpendicular to the ceramic-metal interface, polished down to a 1 μm finish with diamond paste and then examined in a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Ion-thinned specimens were studied by transmission electron microscopy (TEM).

3. Results

3.1. Wetting and reaction at 965–1000°C

Both 2.5% Hf/Ag and 2% Zr/Ag wet and adhered to 99.6% alumina and sapphire at temperatures above 965°C, but they did not spread to the very low contact angles that are characteristic of Ti-containing braze alloys. In a wetting experiment, most conventional braze alloys initially melt and then retract to a hemispherical shape. With further heating, the drop spreads and the contact angle of the advancing edge decreases to some steady state value. The present alloys behaved differently. Immediately on melting, the molten Hf/Ag and Zr/Ag tended to stick to the Al_2O_3 substrate and, although they beaded up slightly, the initial rectangular shape of the alloy sample persisted. The observed contact angles varied along the periphery of the drop and it was impossible to obtain conventional wetting curves that show a uniform decrease in contact angle with time. For example, within a few seconds of reaching 1000°C, the 2% Zr/Ag specimens assumed a contact angle that varied from 60°–90° around the irregular circumference and then changed only slightly for heating times up to 30 min. The contact angle for the 2.5% Hf/Ag alloy exceeded 140° initially and only dropped to below 90° after about 20 min at 1000°C. Regardless of the variability in the contact angles, all the cooled alloys adhered strongly to the ceramic and, as discussed below, showed evidence for a reaction zone at the interface between the alloy and the ceramic.

Fig. 1 is a low magnification SEM image of an interface that formed after reacting 2% Zr/Ag on sapphire for 5 min at 965°C. The figure shows a reaction zone about 5 μm thick that is relatively uniform and continuous in the interior of the specimen, but that does not extend all the way to the edge of the drop. The cross section of the alloy has a somewhat unconventional shape with an acute contact angle near the Al_2O_3 surface that reverses to obtuse away from it. This shape seems to be the result of the upper part of the drop drooping or slumping more rapidly under gravitational forces than the footprint can spread under the balance of forces acting on the edge of the drop. Fig. 2 is a higher magnification view of the edge of the specimen illustrating that the advancing edge of the alloy drop extends about 10 μm beyond the first part of the reaction zone. The

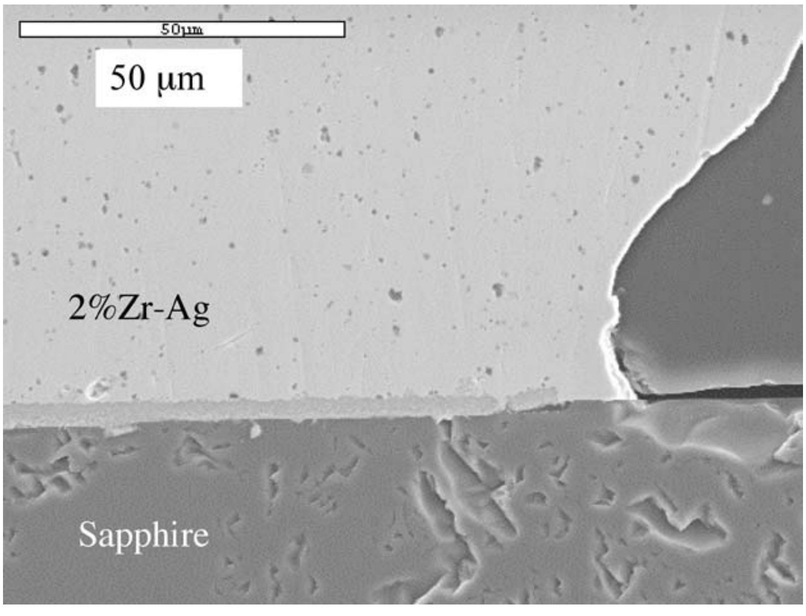

Figure 1 Interface between 2% Zr/Ag and sapphire after reaction for 5 min. at 965°C.

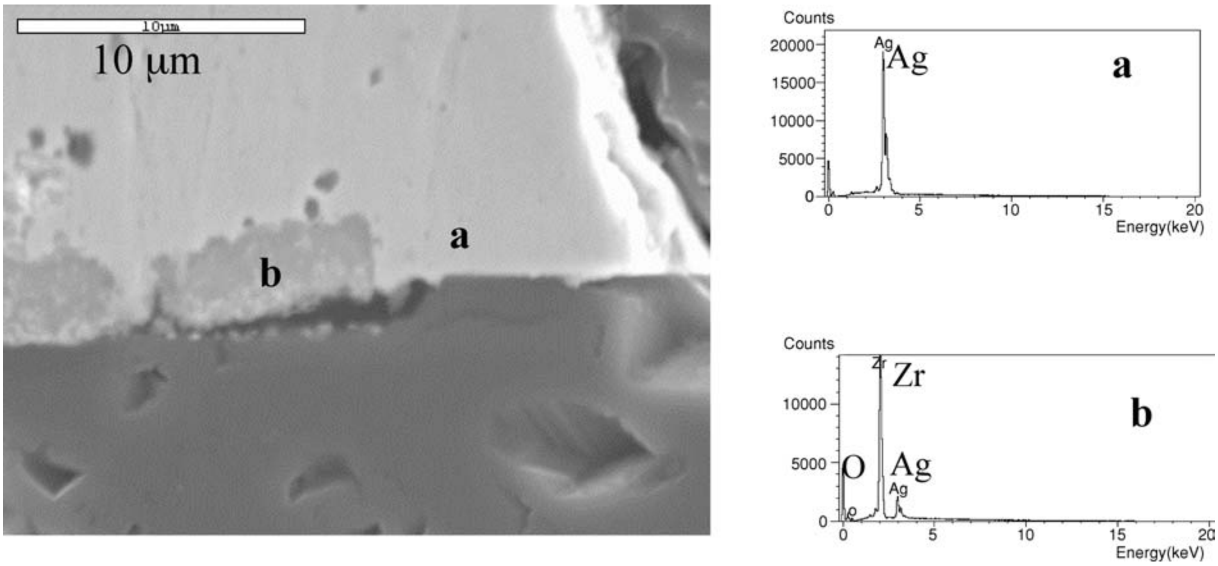

Figure 2 Higher magnification image of same specimen as in Fig. 1. The edge of the drop at position **a** contains only Ag. The reaction zone at **b** contains Ag and ZrO_2.

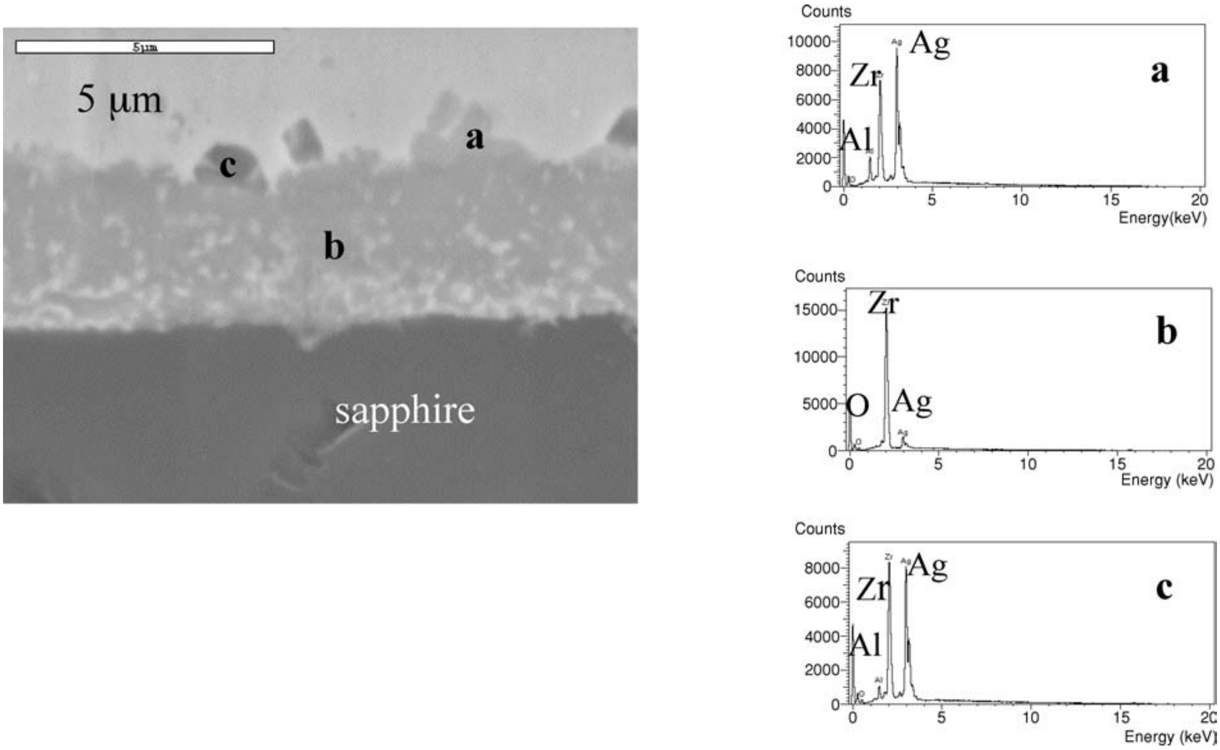

Figure 3 SEM image of the interior of the specimen shown in Figs 1 and 2 (2% Zr/Ag on sapphire, 5 min. at 965°C). Point **a** shows the presence of ZrO_2 and the Ag matrix; point **b** contains mostly ZrO_2 and a little intergranular Ag; point **c** contains ZrO_2, Ag, and Al_2O_3.

EDS spectra show there is only Ag in that part of the alloy. The reaction zone contains Zr, Ag, and O, as indicated by the other EDS spectrum in Fig. 2. Fig. 3 is a SEM image of the interface in the interior of the same alloy heated for 5 min at 965°C on sapphire. The EDS analysis shows the reaction zone has the same interpenetrating microstructure of Ag and ZrO_2 (inferred from the EDS spectra and TEM results presented below) as seen in Fig. 2, but it also contains Al, which is most likely present as Al_2O_3.

As mentioned above, in these experiments the Hf/Ag alloys do not wet Al_2O_3 as well as the Zr/Ag alloys do. In addition, interfacial reaction is less extensive with the Hf/Ag alloys and the reaction product is more dispersed than with Zr/Ag. Fig. 4 illustrates this point for 2.5% Hf/Ag reacted on sapphire for 5 min at 965°C. The interface shows evidence for three phases, which are most likely Ag, HfO_2, and an aluminum-containing phase, based on EDS analyses and thermodynamic considerations.

3.2. Wetting and reactions above 1000°C

We performed some experiments at higher temperatures to create more extensive reaction products. The Zr/Ag results are presented here; the Hf/Ag experiments at the higher temperatures are not yet complete. Fig. 5 is a series of three SEM images of the interface

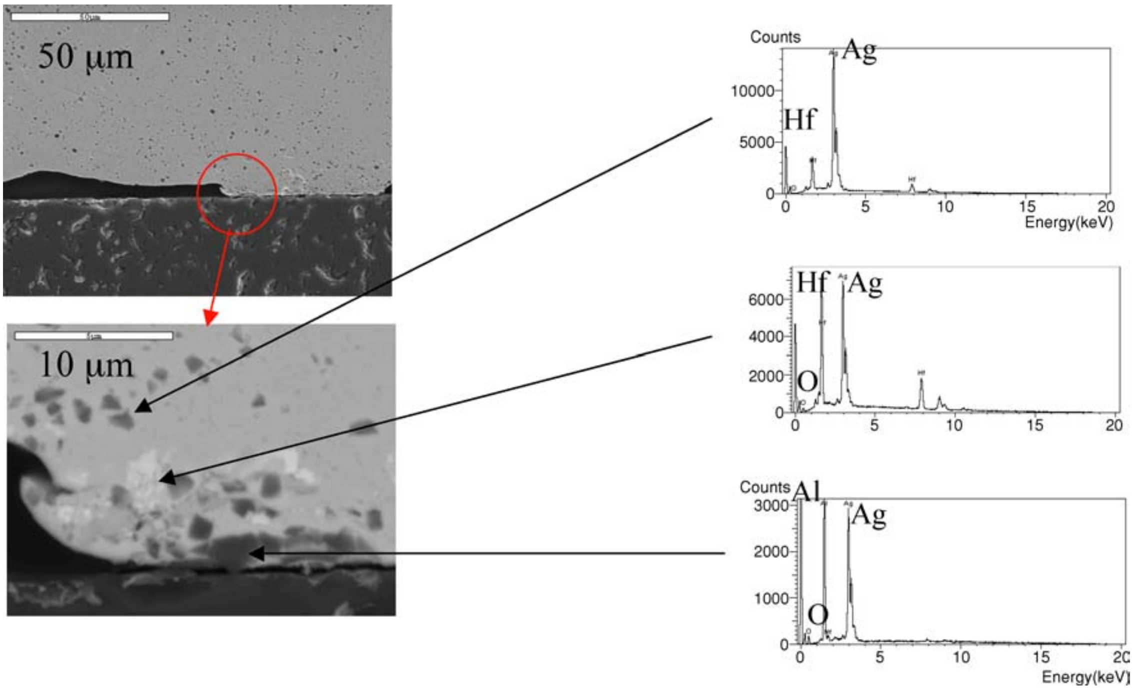

Figure 4 SEM images of the interface between 2.5% Hf/Ag and sapphire heated for 5 min. at 965°C.

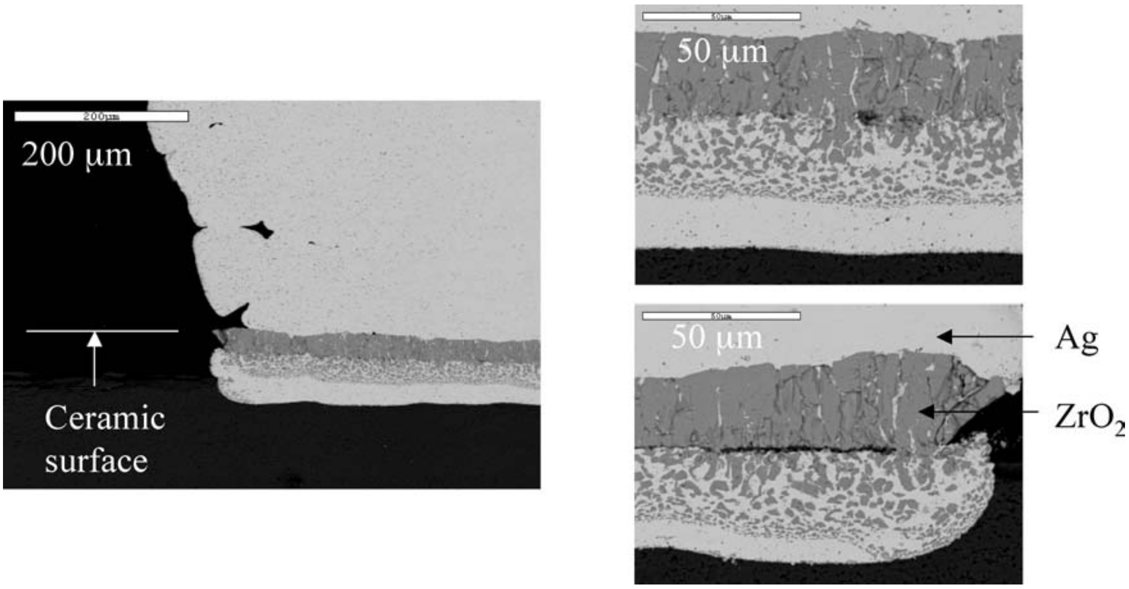

Figure 5 Three SEM images of the interface between 2% Zr/Ag and 99.6% Al_2O_3 heated for 1 min. at 1160°C. Note that the molten alloy penetrated about 100 μm into the alumina substrate.

between 2% Zr/Ag and 99.6% Al_2O_3 after reaction for one minute at 1160°C. Note that because of the 20°C/min heating rate, the specimen was above the 940°C eutectic temperature for 11–13 min. It is apparent that the reaction has caused the molten alloy to penetrate about 100 μm into the ceramic, indicating that a lot of Al_2O_3 has been removed by dissolution or reaction. The microstructure of the reaction zone contains three distinct regions and is very different from the lower temperature results. Nearest the Al_2O_3 is a layer that is mostly Ag with a composition similar to that of the bulk Zr/Ag alloy in the interior of the drop. Above the Ag layer is a zone that, according to our analyses, contains interpenetrating phases of Ag and ZrO_2. The top layer has a columnar microstructure of ZrO_2 grains with thin layers of Ag running vertically between them.

Fig. 6 is a high magnification TEM image of the interface between 2% Zr/Ag and 99.6% Al_2O_3 heated at 1100°C for 30 min. The Al_2O_3 surface is rough, as might be expected if it has reacted with the alloy. Small grains of ZrO_2 (monoclinic by electron diffraction) appear to be growing from the Al_2O_3, but the grains are separated by Ag. One interesting result from the electron diffraction analysis is that all the Ag along the interface in the TEM specimen has the same crystallographic orientation, suggesting that it is a single crystal that extends over many separate Al_2O_3 grains along the interface.

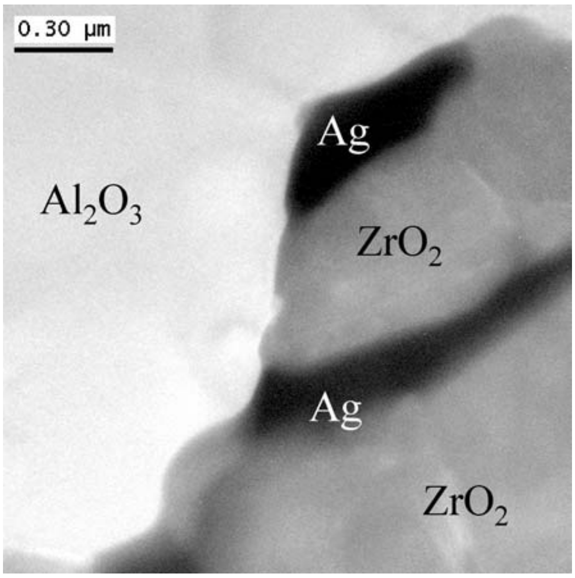

Figure 6 TEM image of the interface between 2% Zr/Ag and 99.6% Al_2O_3 after reaction for 30 minutes at 1100°C. Electron diffraction analysis shows that the ZrO_2 is monoclinic and that all the Ag is a single crystal.

4. Discussion

The unusual wetting behavior exhibited by the two alloys implies they rapidly form an interface with Al_2O_3 during the ramp to the 965°C hold temperature that pins the alloy to the ceramic. This would explain the failure of the alloys initially to retract to form hemispherical drops on the Al_2O_3, as well as the large variation in contact angle around the alloy periphery. Such behavior precluded the gathering of conventional wetting curves. The interfacial microstructures we observed do not have any detectable reaction products at the triple line that could be the source of the pinning, for example those shown in Figs 1 and 2 where the ZrO_2 reaction product is approximately 10 μm from the advancing edge of the drop. One possibility is that the initial reaction products are at too fine a scale to be seen in the SEM images presented in the figures. A second possibility is that the pinning is from a wetting interaction that precedes any reaction. The absence of reaction products at the triple line suggests the latter explanation is more likely, although it requires further experiments to confirm it.

As mentioned above, Figs 1 and 2 show that wetting of the Al_2O_3 by the Zr/Ag alloy precedes any interfacial reaction. The clearly defined ZrO_2 reaction layer is at least 10–20 μm from the advancing edge of the drop and no reaction product can be detected near the alloy-Al_2O_3-atmosphere triple line at the scale of our SEM observations. The observed microstructure implies that for this system wetting is faster than reaction. It has been suggested [13] that there is an initial interval in reactive wetting where the liquid wets the solid before any reaction can be detected. Later, when a continuous reaction product covers the solid, the liquid may form a new equilibrium contact angle on the reaction layer. The Zr/Ag-Al_2O_3 system studied here shows the expected microstructure in which wetting precedes the interfacial reaction. Our results support the idea that reaction between Zr/Ag and Al_2O_3 starts when Zr dissolved in the Ag reacts with the Al_2O_3 surface according to: $Zr + Al_2O_3 = ZrO_2 + Al$. The reaction is thermodynamically favored since the Gibbs energy for reaction is negative, ΔG°_r (1400 K) = − 49.9 kJ [10]. Previous TEM results have shown that the ZrO_2 crystallizes epitaxially on the Al_2O_3 grains with at least six different crystallographic orientation relationships [14]. The TEM studies done for the present work show that the ZrO_2 is initially arrayed along the Al_2O_3 interface as discontinuous grains that are surrounded by the alloy. Those alloy regions are the channels through which the Zr needed to continue the reaction diffuses to the Al_2O_3 interface. With further reaction, the ZrO_2 layer thickens and develops the interpenetrating microstructure shown in Figs 1–3. As the reaction proceeds, the upper part of the ZrO_2 reaction layer consolidates into a columnar ZrO_2 microstructure with thin Ag channels between the grains, such as shown in Fig. 5 for the 1160°C experiments. Eventually, the ZrO_2 layer lifts away from the Al_2O_3 surface, probably because of buoyant forces from the lower density of ZrO_2 ($\rho = 5.7$ g/cm^3) relative to Ag ($\rho = 10.5$ g/cm^3) and more of the Zr/Ag liquid flows under the ZrO_2 from the edges and perhaps through the Ag channels between the ZrO_2 columns.

The interfacial microstructure for Hf/Ag reaction with Al_2O_3 is substantially different from the Zr/Ag case just discussed. As shown in Fig. 4, the interface between the alloy and Al_2O_3 after reaction for 5 min at 965°C shows a dispersion of discrete particles rather than the continuous reaction layer seem for Zr/Ag on Al_2O_3. EDS analysis indicates the darker particles that are found throughout the solidified metal (**a** in Fig. 4) contain Hf and Ag. The as-melted alloy also contained particles that have a similar microstructure and composition, which suggests they are a Hf/Ag composition that segregated on cooling and not the result of reaction with Al_2O_3. No Hf-Ag phase diagram is available so we cannot quantitatively identify the stoichiometry of that Hf/Ag phase. The lightest colored particles in Fig. 4 (e.g., **b**) show EDS peaks for Hf, Ag and a smaller one for O. This implies to us that they are HfO_2 and that the Ag signal is from the surrounding Ag matrix. This conclusion is supported by the highly negative Gibbs energy for reaction between Hf and Al_2O_3, ΔG°_r(1400 K) = − 217.9 kJ for $3Hf + 2Al_2O_3 = 3HfO_2 + 4Al$, [10] and by the previous identification of HfO_2 after reaction between Al_2O_3 and a Hf/Ag/Cu alloy [15]. Hf-Al_2O_3 reaction should produce Al, which is detected in the larger, dark particles found along the interface, e.g., **c** in Fig. 4.

The Gibbs energy for Hf-Al_2O_3 reaction is greater than four times more negative than for reaction between Zr and Al_2O_3, and thus the kinetics for the Hf reaction are expected to be much faster than for the Zr reaction, even after allowing for the difference in molar concentrations of Hf and Zr in Ag. However, for equivalent times and temperatures, the Zr-Al_2O_3 reaction is much more extensive. Formation of a reaction product depends on three sequential steps: diffusion of the reactants to the interface, chemical reaction at the interface, and diffusion of products away from it. One possible explanation for the difference in reactivity is that Hf and Zr have different thermodynamic activities. That is, reaction of Hf with Al_2O_3 could be slower than the reaction between Zr and Al_2O_3 if Hf in Ag did not behave ideally and its activity coefficient were significantly less than unity. However, Hf and Zr are so similar chemically that it would be surprising if they would differ substantially in any deviation from ideality in Ag. The most parsimonious interpretation of the results presented here is that kinetics of reaction between Hf and Al_2O_3 are limited by the rate of diffusion of reactants to the interface or products away from it, but that the rate limiting step for Zr-Al_2O_3 reaction is the chemical reaction itself at the interface.

5. Summary and conclusions

The results of this study show that the Zr/Ag and Hf/Ag alloys adhere to the Al_2O_3 substrates for all heating times at 965°C and above. The alloys stick to Al_2O_3 almost immediately on reaching the liquidus temperature and do not retract to form uniform hemispherical drops as in conventional wetting experiments. The observed interfacial microstructures are the result of redox reactions between the Al_2O_3 and Zr or Hf. The Hf/Ag alloy produces a very thin and discontinuous reaction product on Al_2O_3. By contrast, the Zr/Ag alloy produces a continuous reaction layer that is at the interface initially, but that thickens and moves away from the Al_2O_3 with more extensive reaction. The initial ZrO_2 reaction product also is observed to grow epitaxially on Al_2O_3 grains. The results of these experiments suggest that the reaction rate is controlled by interface kinetics for $Zr + Al_2O_3 = ZrO_2 + Al$ (ΔG_r° (1400 K) = 49.9 kJ) and that diffusion of reactants to the interface or products away from it limits reaction for $3Hf + 2Al_2O_3 = 3HfO_2 + 4Al$ (ΔG_r° (1400 K) = − 217.9 kJ). From a practical standpoint, both alloy systems are useful for ceramic joining and the observed differences in Zr and Hf behavior may allow interfaces to be tailored for specific properties.

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