REACTIONS BETWEEN $\text{Al}_2\text{O}_3$/MgO CRUCIBLE MATERIALS AND A VACUUM MELTED Hf-BEARING SUPERALLOY

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Chemical reactions between a Hf-bearing superalloy melt and crucibles of three $\text{Al}_2\text{O}_3$/MgO base compositions were investigated. The Al, Zr, and Hf in the melt reacted with the oxygen generated by the breakdown of the crucible materials. The details of the reactions and the influence of crucible instability on the oxide content in the skull and in cast ingots are discussed.

INTRODUCTION

Melting superalloys under vacuum suppresses the normal oxidation of the alloying elements because of the low oxygen pressure in the furnace. However, the low furnace pressure, typically <10 x $10^{-3}$ torr, favors the decomposition of oxide crucible materials, which in turn, provides a steady flux of oxygen into the melt. Vaughn and Geiger showed that the aluminum in nickel-base alloys containing Al, Ti and C would react with this oxygen source to form $\text{Al}_2\text{O}_3$ particles in melts contained in either $\text{Al}_2\text{O}_3$ or MgO crucibles (1).

Hafnium, being a more powerful deoxidizer than Al, will directly reduce $\text{Al}_2\text{O}_3$ to form $\text{HfO}_2$ (2,3). Thus Hf-bearing alloys are more prone to form inclusions during melting. This paper presents the results of an investigation on the reactions which occurred between reactive alloying elements (Al, Ti, Hf, Zr) in melts of an advanced superalloy and crucibles of MgO, $\text{Al}_2\text{O}_3$, and MgAl$_2$O$_4$ (spinel) compositions.

EXPERIMENTAL PROCEDURE

The compositions of the materials used in this study are presented in Table I. A nickel melt was made in each of the crucibles to precondition them prior to melting the alloy.
One heat was melted without the reactive adds (Al, Ti, Zr, and Hf) to provide a base-line for comparison.

Table I. Composition of Materials Used in the Experiments

<table>
<thead>
<tr>
<th>Crucible</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$-P</td>
<td>99.55</td>
<td>--</td>
<td>0.07</td>
<td>--</td>
<td>0.09</td>
<td>--</td>
<td>0.25</td>
<td>21</td>
</tr>
<tr>
<td>MgO-R</td>
<td>6.5</td>
<td>92.0</td>
<td>1.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>20</td>
</tr>
<tr>
<td>Spinel-R</td>
<td>70.60</td>
<td>28.20</td>
<td>0.30</td>
<td>0.35</td>
<td>0.05</td>
<td>0.01</td>
<td>0.35</td>
<td>21</td>
</tr>
</tbody>
</table>

Approximately 136Kg (300 lb.) charges were made from the same lots of raw materials, and were all melted under the same conditions, 1500°C (2730°F), 5-8 x 10$^{-3}$ torr. The total melt time was about 100 minutes, and the reactive elements, Al, Ti, Zr, were added to the molten base charge about 35 minutes prior to the addition of the Hf. After the Hf add, the melts were poured into steel molds. The crucibles were allowed to cool under vacuum overnight, so that any metal or reactive products (skull) attached to the crucible would not be further oxidized. Additional details regarding the melting procedure and the characterization of the crucibles after use are discussed elsewhere (4).

All skulls from the alloy heats containing the reactive elements were removed and were examined by optical and SEM methods. The inclusion content of samples taken from cast ingots was determined by Pratt and Whitney using an electron beam remelting process to concentrate the oxides. These particles were then quantitatively extracted and weighed. The details of the inclusion analysis procedure have been reported previously (5), and are also described in this symposium (6).

RESULTS

Table II summarizes some of the experimental data. The oxygen content of the heat melted in the MgO crucible was significantly greater than that of the heats melted in the other two crucibles. The tendency of the alloy to wet the refractory materials was greatest in the case of the Al$_2$O$_3$ crucible, which could explain the strong adherence of the skull to the crucible.
Table II. Experimental Results

<table>
<thead>
<tr>
<th>Crucible</th>
<th>O N (ppm)</th>
<th>C</th>
<th>Hf</th>
<th>Zr (%)</th>
<th>Angle (°)</th>
<th>Dross (%)</th>
<th>Skull</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>4 11</td>
<td>.020</td>
<td>.81</td>
<td>.07</td>
<td>78</td>
<td>10%</td>
<td>A</td>
</tr>
<tr>
<td>MgO</td>
<td>11 9</td>
<td>.024</td>
<td>.78</td>
<td>.06</td>
<td>133(2)</td>
<td>10%</td>
<td>B</td>
</tr>
<tr>
<td>Spinel</td>
<td>3 9</td>
<td>.018</td>
<td>.82</td>
<td>.06</td>
<td>100</td>
<td>10%</td>
<td>B</td>
</tr>
</tbody>
</table>

(1) Sessile drop contact angle; 0 < 90° = wetting (Ref. 4).
(2) Based on crucible sample containing 97% MgO.
(3) Dross = % melt surface covered with floating oxides.
(4) A = thick in regions, strongly adherent to crucible.
B = thin and continuous, weakly bonded.

Figure 1 shows cross sections of the skull and crucibles, and the depth of the altered region within the crucibles after the melt had been completed.

Figures 2A and 2B show SEM micrographs of the metal side of the Al2O3-crucible skull. Metal dendrites are quite obvious and contain fine oxides dispersed across the surface. A dendrite tip comprises the entire field of view in Figure 2B, the larger oxides tend to be Al2O3, while smaller ones are HfO2.

The metal side of the Al2O3-crucible skull is distinctly different from that of the MgO-crucible skull shown in Figure 2C.

Figure 1. Melt-crucible reaction zones including the skull and altered regions within the crucible.
Figure 2. SEM of the melt side of the skull showing exposed oxides on solidified (dendritic) metal surface. Skull from: (A&B) Al₂O₃, (C&D) MgO, and (E&F) spinel crucibles. Note the various types of oxide morphologies. The calibration bar and number indicate the dimensional scale in µm.
Dendrite tips on the MgO-crucible skull are flat compared to the more angular dendrite tips from the Al2O3-crucible skull (Fig. 2A). Wormy HfO2 oxides cover the metal surface in both Figures 2C and 2D. The oxides are almost exclusively HfO2 and are imbedded in the metal surface. On the flat metal dendrite tips, the HfO2 has a wormy appearance, while the interdendritic regions, shown in Figure 2C, contain larger HfO2 particles.

Figure 2E shows the metal side of the skull from the spinel crucible. Flat metal dendrite tips are quite apparent. Several oxides are present on the metal surface. The HfO2 has two morphologies: wormy oxides deeply rooted in the metal dendrites and spherical particles. Figure 2F shows the wormy oxides in greater detail. The lighter wormy oxides appear to be HfO2, while the darker ones appear to be predominantly Al2O3. These oxides coexist in thin layers with the Al2O3 being closer to the metal skull surface, and the HfO2 existing on top of the Al2O3, towards the melt interior. All skulls contain varying amounts of the spherical or chunky HfO2 particles; however, the wormy HfO2 particles occur predominantly on the spinel-crucible skull surface.

Figure 3 shows the refractory side of the skull for all three crucibles. Figure 3A shows the surface of the alumina-crucible skull. A cauliflower structure is quite evident in the central and lower portion of the micrograph, which is actually a two-phase structure as shown in Figure 3B. The ZrO2 occurs as a thin, plate-like layer attached to a columnar Al2O3 phase (Fig. 3B). This ZrO2 layer forms a discontinuous boundary between the crucible and the skull.

Figures 3C and D reveal the oxide morphology on the refractory side of the MgO-crucible skull, which contain a smooth, semi-continuous ZrO2 layer that covers the surface. This region of the MgO-crucible skull has the same morphology as the Al2O3-crucible skull, with the Al2O3 product of reaction residing in a columnar morphology below the ZrO2 layer.

Figures 3E and F show the refractory side of the spinel-crucible skull. Figure 3E shows the Al2O3 columnar structure, which resides between the ZrO2 layer and the metal in the skull. The ZrO2 layer comprises the entire surface shown in Figure 3F.

Transverse sections of the skulls are shown in Figure 4. Figures 4A and B are typical of the MgO-crucible skull. Oxides appear to extend across the skull. The large globular oxides are
Figure 3. SEM of the crucible side of the skull surface showing heavy concentration of oxides. Skull from: (A&B) Al₂O₃, (C&D) MgO, and (E&F) spinel crucibles. Very little metal is present in this surface.
Figure 4. SEM of transverse section of the skulls from (A&B) MgO, (C) Al₂O₃, and (D) Spinel crucibles.

predominantly Al₂O₃, while the smaller spherical oxides are a combination of HfO₂ and Al₂O₃. The view of the skull shown in Figure 4D is dominated by the small spherical Al₂O₃ and HfO₂ particles, which occur throughout the cross section. Figure 4C shows the transverse section of the Al₂O₃-crucible skull; very few fine spherical oxides are present in the metal-side of the skull. The skull from the Al₂O₃-crucible contains few total oxides.

DISCUSSION

When reactive elements, such as Al, Ti, Zr are added to a melt, a complex sequence of reactions occurs, involving the oxidation of these elements at the melt-crucible interface and within the melt. These elements compete with one another for the available oxygen, and the most stable ones (lowest free energy of oxide formation) become oxidized first. In this study, a layer of ZrO₂ was formed first on the grains of
the crucible oxides, as shown in Figure 3B. This is expected, since Zr in a nickel melt will directly reduce pure Al₂O₃ to form a ZrO₂ surface layer (7). Figure 3B indicates that once the ZrO₂ layer reaches a thickness of 1-3μm, an interwoven network of columnar Al₂O₃ forms and grows from the ZrO₂ base into the melt. This sequence is shown schematically in Figure 5, and holds true for the skull build-up in all three crucibles.

The Hf was added late in the melt so that its entry as HfO₂ into the skull occurred only in the outer regions (melt side) as shown in Figure 5. There are several morphologies of the HfO₂ particles, indicating several sources of formation. The HfO₂ particles occur as wormy (Fig. 2C & E), crab-like (Fig. 2F), and rock-like (Fig. 2B & D) structures. Many of the HfO₂ particles are clustered, indicating that they originated as individual particles.
within the melt, and then coalesced, forming clusters during the stirring of the melt. Eventually they came in contact with the particles in the skull and remained attached as a network of particles. This is indicated in Figure 5 by the numerous HfO₂ particles located on the melt-side of the Al₂O₃ columnar crystals. The clustering phenomenon has been described in a recent publication which shows its effectiveness in removing individual particles from a melt (8). Figure 5 shows some massive HfO₂ particles on the melt-side surface of the skull, where Hf reacted with earlier-formed Al₂O₃ clusters and films. Some of these appear to have originated in the dross, and later became attached to the skull during pouring. Also in Figure 5 are some fine oxide particles rich in Al, Mg, and Cr, which remained attached to the skull surface.

The amount of oxide in the skull varied considerably between the three melts, as shown in Table III. The heat melted in the MgO crucible had the highest level of oxygen (11 ppm) and also had the greatest percent of oxides (50%) in the skull surface facing the melt. The oxides consisted mainly of HfO₂ in the melt-side, and of mixtures of HfO₂ and HfO₂- and ZrO₂-altered Al₂O₃ particles on the crucible side. On the other hand, the skull from the Al₂O₃ crucible was 95% metal with very few HfO₂ crystals (+ clusters) in the melt-side surface. Also a scattering of fine Al₂O₃ particles on the melt-side surface were observed (Fig. 2A).

Table III. Data on Skulls and Inclusions

<table>
<thead>
<tr>
<th></th>
<th>Skull Surface</th>
<th>Skull-Transverse</th>
<th>Inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melt Side</td>
<td>Section</td>
<td></td>
</tr>
<tr>
<td>Cruible</td>
<td>% % Hf/Al</td>
<td>Avg. Metal Oxide</td>
<td>Content</td>
</tr>
<tr>
<td>MgO</td>
<td>95 5 0.1</td>
<td>700μm 95 5(2)</td>
<td>1.3ppm</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>50 50 8.0</td>
<td>1250μm 80 20(3)</td>
<td>6.5ppm</td>
</tr>
<tr>
<td>Spinel</td>
<td>90 10 0.5</td>
<td>350μm 80 20(4)</td>
<td>5.9ppm</td>
</tr>
</tbody>
</table>

(1)EDX Peak Ratio; (2) 5% HfO₂+Tr. Al₂O₃; (3) Mixture of HfO₂, HfO₂/Al₂O₃+ZrO₂/Al₂O₃; (4) 10% HfO₂+10% Al₂O₃; (5) Test performed by PWA; Inclusion oxides ~ to skull oxides, and inclusion content with no reactive adds = 0.35ppm.

CONCLUSIONS

The type and quantity of oxides forming in the melt or at the melt-crucible interface (skull) depend largely on the available oxygen (type of crucible material) and on the amount and types of reactive alloying elements. The
stability (to chemical reduction or dissociation) of the crucible materials decreases in the order: $\text{Al}_2\text{O}_3 > \text{MgAl}_2\text{O}_4 > \text{MgO}$. Thus, the heat melted in the $\text{Al}_2\text{O}_3$ crucible had the least amount of oxides in the skull (predominately $\text{HfO}_2$) and had the lowest inclusion content (1.5ppm, $\text{HfO}_2$). The heat melted in the MgO crucible exhibited the greatest at-pour oxygen, had the greatest amount of oxides in the skull ($\text{HfO}_2$, $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$), and had the greatest inclusion content (6.5ppm, $\text{HfO}_2 + \text{Al}_2\text{O}_3$). The performance of the heat melted in the $\text{MgAl}_2\text{O}_3$ crucible fell between that of the other two crucibles.

ACKNOWLEDGEMENTS

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REFERENCES