Interfacial reaction between zirconium alloy and graphite mold/yttrium oxide ceramic mold

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Abstract: Zirconium alloys are active in the molten state and tend to react with the mold during casting. The casting technology of zirconium is not yet well established; especially in selecting the mold materials, which are difficult to determine. In the present work, the interfacial reactions between zirconium casting and casting mold were studied. The zirconium alloy was melted in a vacuum arc skull furnace and then cast into the graphite mold and ceramic mold, respectively. The zirconium casting samples were characterized using SEM, EDS and XRD with an emphasis on the chemical diffusion of elements. A reaction layer was observed at the casting surface. Chemical analysis shows that chemical elements C, O and Y from the mold are diffused into the molten zirconium, and new phases, such as ZrC, ZrO, YO$_{1.335}$ and Y$_6$ZrO$_{11}$, are formed at the surface. In addition, an end product of zirconium valve cast in a yttria mold has a compact structure and good surface quality.

Key words: graphite mold; yttrium oxide ceramic mold; zirconium alloy; reaction layer

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Known as the “most promising material in 21st century”, zirconium alloys have a wide range of applications in fields such as atomic energy, chemical industry, light industry, and machinery. Such wide applications are due to their superb combined properties, for example low density, low thermal neutron absorption capture cross section, high specific strength, good compatibility with nuclear fuel, excellent corrosion resistance and processability. Zirconium alloys are almost irreplaceable in the nuclear and chemical industry for making fuel clad tube, pressure tube, condenser, pump, impeller, valve and so on [1-4]. At present, most zirconium alloy products are forgings, the material utilization of which is low. This is mainly due to the fact that the casting technology of zirconium is unstable and not yet well established, especially in selecting the mold materials, which are difficult for users to determine.

Compared with titanium, zirconium is more active and prone to being oxidized. During the casting process, molten zirconium alloys can easily react with the mold materials and produce a surface contamination layer. Although the interfacial reactions between titanium and refractory materials have been studied and well documented [5-8], little work has been done or there have been few reports in the similar area for zirconium and its alloys. McDeavitt [9-10] heated the zirconium specimens to the melt state on the ceramic substrates and studied the interfacial reactions. Yet, this method does not duplicate the exact casting environment and the resultant surface contamination layer may be different.

In the present work, the most commonly used titanium alloy mold materials, for example graphite and Y$_2$O$_3$ ceramic [11-12], were used. Scanning Electron Microscope (SEM), Energy Diffraction Spectrum (EDS), X-Ray Diffraction (XRD), hardness measurement and other analytical testing techniques were employed to study the interfacial reaction between zirconium alloy casting and the mold.

1 Experimental procedure

Zirconium alloy Zr702C was used in this study. The nominal compositions and chemically analyzed compositions of the specimen are shown in Table 1 [13]. The dimension of the tested samples was 20 mm × 10 mm × 60 mm. The Y$_2$O$_3$ ceramic mold was made by investment casting method. Both the surface and back of the Y$_2$O$_3$ ceramic mold was coated prior to the casting, the compositions of the coatings are shown in Table 2. The graphite mold was prepared by machining high-purity synthetic graphite block and degassed at 1,100 °C [14]. The zirconium alloy was melted and
Table 1: Nominal compositions and tested compositions of Zr702C (wt.%)  

<table>
<thead>
<tr>
<th></th>
<th>Zr+Hf</th>
<th>Hf</th>
<th>Fe+Cr</th>
<th>H</th>
<th>N</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal compositions</td>
<td>$\geq 98.8$</td>
<td>$\leq 4.5$</td>
<td>$\leq 0.3$</td>
<td>$\leq 0.005$</td>
<td>$\leq 0.3$</td>
<td>$\leq 0.1$</td>
<td>$\leq 0.25$</td>
</tr>
<tr>
<td>Tested compositions</td>
<td>99.57</td>
<td>2.40</td>
<td>0.198</td>
<td>0.0014</td>
<td>0.031</td>
<td>0.015</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 2: Main compositions of ceramic coatings  

<table>
<thead>
<tr>
<th></th>
<th>Refractory materials</th>
<th>Binder</th>
<th>Sand</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface layer</td>
<td>Y$_2$O$_3$</td>
<td>Zirconium acetate</td>
<td>Y$_2$O$_3$</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>Back layer</td>
<td>Bauxite</td>
<td>Silica sol</td>
<td>Bauxite</td>
<td>-</td>
</tr>
</tbody>
</table>

cast centrifugally at 150 r-min$^{-1}$ in the 80 kg vacuum arc skull furnace. The samples were sectioned using wire cutting. In order to maintain the integrity of the reaction layers, no surface treatment (for example sand-blasting and acid-washing) was applied and the samples were inlaid in the bakelite during cutting. Subsequent polishing was necessary to remove the oxide formed during cutting. The etched samples (using 10vol.%HF+20vol.%HNO$_3$+70 vol.%H$_2$O etchant) were characterized using a Hitachi S-3400N scanning electronic microscope (SEM) equipped with energy dispersive analysis (EDS). X-ray diffraction (XRD) analysis was performed on a Shimadzu XRD-7000X to determine the phase structure in the compounds formed in the reaction layers. The samples were scanned using a Cu Kα radiation at 40 kV and 30 mA. The scanning speed (2θ) was 4 ℃·min$^{-1}$. The hardness profile of the samples was measured using a MH-50 digital micro-hardness tester under a load of 25 g.

2 Results and analysis

2.1 Macrostructure

The surface morphologies of zirconium alloy samples using graphite and Y$_2$O$_3$ molds are shown in Fig. 1. Both castings were intact from the mold and there was no sign of sand burn on the surface. It can be seen that the sample cast in the graphite mold is rough with flow marks and cold laps while the sample cast in the Y$_2$O$_3$ mold has a smoother surface with no obvious defects.

![Fig. 1: As-cast zirconium alloy samples cast in graphite mold (a) and Y$_2$O$_3$ mold (b)](image)

2.2 Interface reaction layers

The cross sectional microstructure of the as-cast zirconium alloy sample cast in graphite mold and Y$_2$O$_3$ mold are shown in Fig. 2. It can be seen from Fig. 2 that an obvious reaction layer (transition layer) is formed on the surface during the casting process, 20–30 μm thick for the casting using graphite mold and 40–50 μm for the one using Y$_2$O$_3$ mold.

It is well known that the surface of the casting always has a higher hardness than the matrix due to: A. the cooling effect of the mold and therefore refined grain structure can be obtained; and B. the permeation of the mold elements into the casting.
The hardness profile of the sample can be used to assess the thickness of the reaction layers. As shown in Fig. 3, the hardness of Zr/\textit{Y}_2\textit{O}_3 decreases monotonically with the distance away from the surface and no significant variation was found after 40–60 $\mu$m. This result agrees approximately with the SEM observation (40–50 $\mu$m transition layer in Fig. 2b). In contrast, the surface of Zr/Graphite sample has relatively lower hardness with a narrow transition layer (<30 $\mu$m), and the surface hardness profile flattens afterwards. It is also noted from Fig. 3 that the matrix hardness is higher in Zr/Graphite than in Zr/\textit{Y}_2\textit{O}_3, which might indicate a better chilling effect in graphite mold than in \textit{Y}_2\textit{O}_3 mold.

2.3 Diffusion of mold elements

The distribution of elements in the sample near the surface region was studied with SEM/EDS. Line scanning of C and Zr in the Zr/Graphite sample, and Y, O and Zr in the Zr/\textit{Y}_2\textit{O}_3 sample from the surface to the matrix were performed and results are shown in Fig. 4. It can be seen that EDS intensities of the mold element C in Zr/Graphite and Y and O in Zr/\textit{Y}_2\textit{O}_3 decrease from the reaction layer to the matrix, and then stay constant within the matrix. The semi-quantitative chemical analysis at different regions is summarized in Table 3. Though there is an obvious chemical segregation of C, Y and O in these samples, the matrix is still almost zirconium alloy (i.e. C, Y and O become tracing elements). In the reaction layer of the Zr/Graphite sample, the atomic fraction of C is 41.94% which indicates that nearly half of the zirconium is replaced by carbon from the graphite mold by diffusion. In the reaction layer of Zr/\textit{Y}_2\textit{O}_3 sample, the atomic fraction of O is 33.28% and Y is only 5.59%. So the reaction layer is mainly formed by the diffusion of O.
2.4 Phase analysis of interface reaction layer

The oxide or intermetallic phase formed at the sample surface were studied with XRD. As shown in the diffraction patterns in Fig. 5, there is ZrC in the surface of the Zr/Graphite sample without any free carbon identified; and there are four oxides Zr3O, Y2O3, YO1.335, and Y6ZrO11 in the surface of the Zr2O3 sample. The diffraction pattern of the Zr3O is more significant in the Zr/Y2O3 sample.

| Table 3: Results of spot scanning of reaction layer (at.%) |
|-----------------|-----|-----|-----|
|                 | C   | Y   | O   |
| Matrix (graphite mold) | 3.75 | -   | -   |
| Reaction layer (graphite mold) | 41.94 | -   | -   |
| Matrix (Y2O3 mold) | -   | 6.17 | -   |
| Reaction layer (Y2O3 mold) | 5.59 | 33.28 | -   |

Fig. 5: XRD analysis of reaction layer of zirconium alloy samples cast in graphite mold (a) and Y2O3 (b)

3 Interface reaction mechanism

The thermal conductivity of graphite is higher than Y2O3. The molten zirconium will then have a higher solidification rate in the graphite mold, which reduces the element diffusion rate and inhibits the interfacial reaction[15]. Therefore, the reaction layer of the Zr/Graphite is thinner. Yet, higher solidification rate also leads to the flow marks and cold laps on the surface. The Y2O3 ceramic mold has a good compactness and chemical stability, and the sample cast in the Y2O3 mold has smooth surface with less defects.

There have been two major mechanisms governing interface reaction during casting and solidification process. The first mechanism hypothesizes the replacement reaction between the liquid metal and the mold materials, during which liquid metal oxidizes and the compounds in the casting mold are deoxidized. Both the oxidation and deoxidization processes pollute the casting alloy. The other mechanism assumes that the compounds from the mold decompose into the atoms and then dissolve into the liquid metal. It is noted that the latter mechanism has become more popular and supported by more research[10,16,17].

When the molten zirconium is poured into the graphite mold, C atoms from the graphite mold diffuse into the molten zirconium. According to the Zr-C binary phase diagram[18] (Fig. 6), C has a small solubility in Zr (approximately 1%). As the content of C exceeds the solid solubility limit, intermediate phase ZrC precipitates. In the current study, atomic fraction of C in the reaction layer was measured as about 42% and the casting temperature was around 1,900 °C, which corresponds to the single phase region of ZrC in the phase diagram (Fig. 6). This is consistent with the results of X-ray analysis (Fig. 5). It can be concluded that, in addition to zirconium, ZrC is the only phase existing in the reaction layer.

Fig. 6: Binary phase diagram of Zr and C

Standard Gibb's Energies of oxide formation for Zr and Y as a function of temperature are shown in Fig. 7[19]. It can be seen that Y2O3 is more stable than ZrO2, which indicates that even at a high temperature it is also difficult to have a replacement reaction between Zr and Y2O3. Y2O3 can only decompose into O and Y atoms and dissolve into the molten Zr at high temperatures. As shown in the Zr-O and Y-Zr binary phase
diagram [17] (Fig. 8 and Fig. 9), both O and Y have a finite solid solubility in the Zr. According to the results of EDS in the reaction layers, more O diffuses into the Zr substrate. This is because O has a higher solid solubility in the Zr and a smaller atomic radius than Y (and therefore a higher diffusivity). When O content exceeds the solid solubility in the Zr, ZrO is formed in the diffusion layer.

Although the sample cast in Y2O3 mold has a relatively thicker diffusion layer than that cast by graphite mold, it has a smooth surface without any sign of sand burn. So the Y2O3 mold is more suitable for casting commercial products.

4  Casting case using Y2O3 mold

Zirconium valve castings were cast using a Y2O3 mold after being melted in the 80 kg vacuum arc skull furnace (the current was about 13,000 A and the voltage was about 45 V). The castings cast in the Y2O3 mold have a good surface quality. One representative casting is shown in Fig. 10. The mechanical properties shown in Table 4 meet the requirements, but this casting technology of zirconium alloys is worthy of further research for massive production.

5 Conclusions

We studied the effect of different mold materials (mainly graphite and Y2O3) on the casting of zirconium alloys. The interface reaction layer was found in both cases with different thickness, and the chemical compositions and phases in the reaction layer were also identified with SEM/EDS and XRD. The following conclusions were made:

(1) Graphite is a good thermal conductor and the zirconium alloy cast in graphite mold has a higher
cooling rate with a thin reaction layer but rough surface. In contrast, the same alloy cast in the \( \text{Y}_2\text{O}_3 \) ceramic mold has a smooth surface without any sign of sand burn. However, there is a diffusion layer of \( O \) (within the surface transition layer) in this casting.

(2) All elements in the mold materials can diffuse to the molten zirconium. Intermetallic phases (such as \( \text{ZrC} \) in \( \text{Zr}/\text{Graphite} \) and oxides \( \text{Zr}_2\text{O}_3, \text{YO}, \text{YO}_1.335 \) and \( \text{Y}_6\text{ZrO}_{11} \) in \( \text{Zr}/\text{Y}_2\text{O}_3 \)) can be formed due to the limited solid solubility of \( O, C \) and \( Y \) in \( \text{Zr} \). The XRD analytical results agree with the phases predicted by the phase diagrams.

(3) Qualified zirconium products can be produced using \( \text{Y}_2\text{O}_3 \) mold.

References


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