EFFECT OF THE ALUMINA CONTENT ON THE INTERFACIAL REACTIONS BETWEEN TITANIUM AND CALCIA/ZIRCONIA/ALUMINA COMPOSITES

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Powder mixtures of CaO, ZrO₂, and Al₂O₃ in various ratios were hot pressed and then reacted with titanium at 1600°C/30 min in Ar to evaluate the suitable ceramic crucibles for titanium casting. The interfacial microstructures between titanium and ceramic composites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and analytical transmission electron microscopy (TEM). In the hot pressing composites, the CaZrO₃, c-ZrO₂, CaAl₂O₄ and CaAl₄O₇ phases were existed when the sample contained 20% Al₂O₃. The amount of CaZrO₃ phase was decreased with increasing Al₂O₃, but that of c-ZrO₂ was in the opposite manner. In the original interface, Ti₃Al₅ were found in the samples containing more than 20 vol% Al₂O₃, and the amount of Ti₃Al₅ increased with increasing Al₂O₃. With increasing Al₂O₃ amount, the residual ZrO₂ participated on the ceramic side away from interface. When the amount of Al₂O₃ in the composites was above 20 vol.%, a large amount of CaZrO₃ was formed at the interface to form as a barrier layer and possible suppressed the diffusion of oxygen from ceramic to titanium.

I. Introduction

Titanium and its alloys have high tensile strength, excellent toughness, light weight, and extraordinary corrosion resistance and widely used in aerospace, jet engines, medical devices, computer industry and consumers, such as bicycles and golf club heads. Because the ceramic crucible reacts with titanium significantly in the vacuum induction melting,¹ titanium alloys are melted in a water-cooled copper crucible by the consumable electrode vacuum arc melting (VAR).² However, there are some disadvantages for the VAR process, for example, the high cost of the equipment, scrape recycle, and long cycle time. Furthermore, an abundant oxygen layer on the surface of titanium, so-called “α-case” resulted from the reaction between the ceramic crucibles and titanium during casting. The α-case will deteriorate the mechanical properties of titanium. Therefore, determining how to control the interfacial reactions between titanium melt and some ceramic materials is of great interest.

Several refractories, such as Y₂O₃, CaO, and ZrO₂ have been investigated as crucible materials for melting titanium alloys. In the last few decades, extensive studies have been carried out on the interfacial reactions between titanium melt and zirconia molds and/or crucibles.³⁻¹⁰ Saha and Jacob⁶ indicated that a brittle α-case was formed at the surface of titanium parts and thus adversely affected their mechanical properties. Economos and Kingery⁷ found that titanium penetrated along the grain boundaries of ZrO₂ to form black oxygen-deficient zirconia. Recently, Lin et al.¹¹⁻¹⁷ have thoroughly investigated the phase formation mechanisms and microstructural evolution at the interface between titanium (or titanium alloys) and 3Y-ZrO₂ (or various ratios of Y₂O₃/ZrO₂) using analytical electron microscopy. Both lamellar orthorhombic Ti₃ZrO and...
spherical hexagonal Ti$_2$ZrO were found in α-Ti(Zr, O) after reaction at 1550°C. Lin and Lin\textsuperscript{15} also found intergranular α-Zr, twinned t'-ZrO$_2$-x, lenticular t'-ZrO$_2$-x, and ordered c-ZrO$_2$-x on the zirconia side far from the interface between Ti and 3Y–ZrO$_2$ after annealing at 1550°C. The ZrO$_2$ was dissolved into Ti on the zirconia side near the original interfaces, Y$_2$O$_3$ reprecipitated in the samples containing 30%–70 vol% Y$_2$O$_3$. Furthermore, the Y$_2$O$_3$/ZrO$_2$ samples became more stable with increasing Y$_2$O$_3$, because the solubility of Y$_2$O$_3$ in Ti was very low.

As for CaO-ZrO$_2$ system, Kim et al.\textsuperscript{19–20} demonstrated that the surface coating of CaZrO$_3$ on crucibles is suitable for Ti alloys casting. The CaZrO$_3$ was comparable chemical inertness to ZrO$_2$ and low cost than yttria based systems. Thus, CaZrO$_3$ can be one of the potential refractory materials for titanium casting. According to Chang and Lin’s study,\textsuperscript{21} a diffusion zone featuring columnar CaZrO$_3$ was formed in the matrix of β'-Ti after reaction between Ti and the CaO/ZrO$_2$ composite at 1550°C. The CaZrO$_3$ was formed due to the outward diffusion of O and Zr away from metastable CaO fully stabilized ZrO$_2$. This result indicates that CaZrO$_3$ was a stable phase and was not significantly dissolved in Ti. Furthermore, Lin et al. had studied the CaZrO$_3$ as a crucible for Ti–6Al–4V and TiNi melts material. There are few amount of Ca, Zr, Ti, and Ni diffusion to the original interfacial reaction layer, which showed CaZrO$_3$ promising performance and a very good refractory resistance. In Schafföner et al. study,\textsuperscript{22} CaZrO$_3$ crucible can withstand several Ti6Al4V and TiAl melts and exhibited no cracking in crucible due to low thermal shock.

CaZrO$_3$ doped with Al$_2$O$_3$, Y$_2$O$_3$, and MgO have possessed high chemical stability and very good tolerance against thermal shock.\textsuperscript{24} In the present study, the various amount of Al$_2$O$_3$ was added in the same volume ratio of CaO-ZrO$_2$ powders, formed as CaZrO$_3$, and then melted with Cp-Ti at 1600°C in 30 minutes. The microstructural characterization was used by X-ray diffraction (XRD), scanning emission microscopy (SEM) and analytical transmission electron microscopy (TEM) with an attached energy dispersive X-ray spectroscope (EDS). The formation mechanism for interfacial reaction phases between Cp-Ti and Al$_2$O$_3$/CaO/ZrO$_2$ composites is also discussed and elucidated.

II. Experimental Procedure

The ceramic composites were prepared from the powders of zirconia, calcia, and α-alumina. The CaO/ZrO$_2$/Al$_2$O$_3$ samples contained 10, 20, 30, or 40 vol% Al$_2$O$_3$, respectively, and a constant volume ratio of CaO and ZrO$_2$ mixture as the balance. The bulk ceramic composites specimens were fabricated by hot pressing in a graphite furnace at 1 atm argon. The phase identification of CaO/ZrO$_2$/Al$_2$O$_3$ composites was analyzed by XRD. The compositions, and designations of CaO/ZrO$_2$/Al$_2$O$_3$ samples are listed in Table I.

As hot-pressed ceramic composites were cut and machined to dimensions of about 10 mm × 10 mm × 5 mm. A bulk composite was placed into the graphite crucible, and then tightly packed with commercially pure titanium powder. The temperature was increased to 1600°C at a heating rate of 10°C/min, held at 1600°C for 30 min and then cooled to room temperature in the furnace.

The phase identification of Ti and CaO/ZrO$_2$/Al$_2$O$_3$ samples, respectively, was performed using an X-ray diffractometer. A scanning electron microscope was used for microstructural observation on the interfaces between Ti and various CaO/ZrO$_2$/Al$_2$O$_3$ samples.

Cross-sectional SEM specimens were cut and ground using a diamond matted disc and then polished using diamond pastes of 6, 3, and 1 μm in sequence. The TEM specimens were prepared by Focus ion beam (FIB) and the thickness is less than 100 nm enable electron transparent.
III. Results and Discussions

(1) Various CaO/ZrO$_2$/Al$_2$O$_3$ composites

Figure 1 shows the XRD spectra of various hot-pressed CaO/ZrO$_2$/Al$_2$O$_3$ samples. These spectra were arranged for CZA40, CZA30, CZA20, CZA10, and CZ, respectively, in a sequence from top to bottom. Two phases, orthorhombic CaZrO$_3$ (calcium zirconate) and cubic zirconia (c-ZrO$_2$), were found in the CZ composites. When Al$_2$O$_3$ added into the composites, the calcium aluminate (CaAl$_2$O$_4$) or calcium dialuminate (CaAl$_4$O$_7$) were formed, excepting c-ZrO$_2$, CaZrO$_3$. The amount of c-ZrO$_2$ increased with increasing Al$_2$O$_3$ in composites as indicated by the peak at 30° of XRD spectra. Furthermore, the amount of CaZrO$_3$ reduced with increasing Al$_2$O$_3$ in the composites. The XRD results are consistent with the phases indicated by the CaO-Al$_2$O$_3$-ZrO$_2$ phase diagram at 1380°C [25] and are resulted in the Table I.

(2) Joint of Cp-Ti with various CaO/ZrO$_2$/Al$_2$O$_3$ composites

Figures 2(a)–(e) display the cross sectional backscattered electron images of Ti and various CaO/ZrO$_2$/Al$_2$O$_3$ joints after reaction at 1600°C/30 min. Titanium is shown to the left of each micrograph, while the ceramic sample is on the right-hand side. Reaction layer I on the metal side close to the original interface is marked as "I" in Figs. 3(a–e), while reaction layer II on the ceramic side close to the original interface is marked as "II"; the zone within the ceramic side that was affected by the interface reaction is marked as "III". Arrows indicates the original interfaces, which were deliberately located according to the characteristic K$_α$ X-ray maps of calcium (not shown), since Ca was relatively insoluble in Ti with respect to Zr, O, and Al. The large pores in the interface near the ceramic, as shown in the region II, were attributed to the Kirkendall effect because Zr and O diffused to the titanium side more rapidly than that of Ti into the ceramic side.

(2-1) Reaction Layer "I" at the Titanium Side

The reaction layer “I” consisted of dark needle-like region and bright region is found near the interfaces of Ti/CZ and Ti/CZA10 joints shown in Figs. 3(a, b). The needle-like region should be α-Ti (Zr, O) and the bright region is β’-Ti (Zr, O) supported by the previous reports.[11, 13, 14] The needle-like α-Ti(O) and β’-Ti(Zr, O) were usually found in the titanium side because of the interfacial reactions between Ti and 3Y–ZrO$_2$. An α-Ti (O) phase with a small amount of oxygen in solid solution and β’-Ti(Zr, O) dissolved a significant amount of zirconium (β stabilizer) and oxygen (α stabilizer) in solid solution.[11, 13, 14] Moreover, the needle-like α-Ti(O) and β’-Ti(Zr, O) in the reaction layer “I” were effectively suppressed at titanium side of the Ti/CZA20, Ti/CZA30, and Ti/CZA40 joints.

(2-2) Reaction Layer "II" at the Composites Side

Figure 3(a–e) show backscattered electron images of reaction layer "II" in the ceramic side of (a) Ti/CZ, (b) Ti/CZA10, (c) Ti/CZA20, (d) Ti/CZA30, and (e) Ti/CZA40 after reaction at 1600°C for 30 min. After joining, a large amount of titanium diffused and reacted with both ZrO$_2$ and CaZrO$_3$ of Ti/CZ and Ti/CZA10 composites to form as acicular α-Ti(Zr, O), β’-Ti (Zr, O), and residual CaZrO$_3$ shown in Figs. 4(a, b). Furthermore, the precipitation of the needle-like α-Ti(Zr, O) solid solution on the β’-Ti (Zr, O) substrate during the cooling process is very common at the interfacial reactions between Ti and ZrO$_2$. [15-17] However, Ti$_3$Al$_5$ instead two phases of α-Ti(Zr, O) and β’-Ti(Zr, O) in the reaction “II” were found when the Al$_2$O$_3$ increased above 20 vol. % of composites. Titanium reacted with Al of liquid CaAl$_2$O$_4$ (melting point ~ 1604 °C) of composites to form as Ti$_3$Al$_5$. The formation mechanism for the Ti$_3$Al$_5$ can be described as follow equation:

\[ 3\text{Ti} + 5\text{Al} \rightarrow \text{Ti}_3\text{Al}_5 \]  

(1)

Meanwhile, the ZrO$_2$ at the reaction layer “II” was dissolved into Ti$_3$Al$_5$ supported by the
EDS analysis (32.77 at% Ti, 52.85 at.% Al, 8.40 at.% Zr, 4.71 at.% O, 1.27 at.% Ca). Besides, when Al$_2$O$_3$ increased above 30 vol.% in Fig. 4(d, e), the morphology of both Ti$_3$Al$_5$ and CaZrO$_3$ changed into smooth and spherical due to the formation of a large amount liquid CaAl$_2$O$_4$. Excepting Ti$_3$Al$_5$ phase, Ca$_3$Al$_2$O$_6$ phase were also found shown in Figs. 4 (b–e). The formation mechanism of Ca$_3$Al$_2$O$_6$ phase could be described as follows:

$$\text{CaAl}_2\text{O}_4 + 2\text{CaZrO}_3 \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6 + 2\text{ZrO}_2$$  \hspace{1cm} (2) 

The phase identification for Ca$_3$Al$_2$O$_6$ will be discussed in the following TEM analysis.

Figures 4 show the FBI, SADPs and EDS of Ca$_3$Al$_2$O$_6$. Figure 6(a) shows the bright field image between reaction layer “II” and “III” of Ti/CZA40 after reaction at 1600°C for 30 min, indicating Ti$_3$Al$_5$, Ca$_3$Al$_2$O$_6$, and CaZrO$_3$ three phases. Figures 6(b) and (c) show the SADPs of Ca$_3$Al$_2$O$_6$ with [201] and [401] zone axes, respectively. The EDS spectrum in Fig. 6(d) shows that Ca$_3$Al$_2$O$_6$ composed of 22.41 at.% Ca, 23.16 at.% Al, 49.67 at.% O and 4.76 at.% Zr.

**Conclusions**

1. When the amount of Al$_2$O$_3$ was lower than 20 vol.%, CaZrO$_3$ was the primary crystallization phase on the hot-press samples. With increasing Al$_2$O$_3$ amount, the CaAl$_2$O$_4$ content and the c-ZrO$_2$ content increased, but the proportion of CaZrO$_3$ decreased. While c-ZrO$_2$ was the primary crystallization phase when the amount of Al$_2$O$_3$ exceeded 30 vol.%. 
2. During the interface reaction, when the amount of Al$_2$O$_3$ was 0 and 10 vol.%, the Ti side was $\alpha$-Ti solid solution with precipitated $\beta$-Ti on the grain boundary. With increasing alumina content, the $\alpha$-Ti solid solution increased, while the $\beta'$-Ti disappeared. On the amount of Al$_2$O$_3$ exceeded 20 vol.%, a Ti$_3$Al$_5$ was found on the original interface.
3. On the interface reaction, when the Al$_2$O$_3$ content was 0 and 10 vol.%, a reaction layer in which $\beta'$-Ti, needle-like $\alpha$-Ti, and CaZrO$_3$ coexisted was found on the ceramic side. In addition, dense CaZrO$_3$ was discovered in the area far from the interface. 
4. When the amount of Al$_2$O$_3$ exceeded 20 vol.%, no $\alpha$-Ti was discovered on the original interface; in addition, CaZrO$_3$ did not react with Ti, indicating that when the amount of Al$_2$O$_3$ exceeded 20 vol.%, the specimens could effectively inhibit interface reactions.
5. On the amount of Al$_2$O$_3$ exceeded 20 vol.% , Ti solid dissolved the Al and O of CaAl$_2$O$_4$ in the composite material, enabling the residual CaO to react with ZrO$_2$ and form CaZrO$_3$. With increasing Al$_2$O$_3$ amount, the proportion of the residual ZrO$_2$ that did not participate in the reaction increased on the ceramic side far away.

**References**


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**Table I.** Designations, Compositions, Hot-pressing condition and XRD Phase of Hot-pressed CaO/ZrO₂/Al₂O₃ samples

<table>
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<tr>
<th>Specimens</th>
<th>Composition (vol%)</th>
<th>XRD Phases</th>
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<tr>
<td>CZ</td>
<td>44.45% CaO +55.55% ZrO₂</td>
<td>CaZrO₃(S), c-ZrO₂(W)</td>
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<tr>
<td>CZA10</td>
<td>10% Al₂O₃ +90% (CaO/ZrO₂)</td>
<td>CaZrO₃(S), c-ZrO₂(M), CaAl₂O₄(W)</td>
</tr>
<tr>
<td>CZA20</td>
<td>20% Al₂O₃ +80 % (CaO/ZrO₂)</td>
<td>CaZrO₃(S), c-ZrO₂(M), CaAl₂O₄(W)</td>
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<tr>
<td>CZA30</td>
<td>30% Al₂O₃ +70 % (CaO/ZrO₂)</td>
<td>CaZrO₃(W), c-ZrO₂(S), CaAl₂O₄(M), CaAl₂O₇(W)</td>
</tr>
<tr>
<td>CZA40</td>
<td>40% Al₂O₃ +60 % (CaO/ZrO₂)</td>
<td>CaZrO₃(W), c-ZrO₂(S), CaAl₂O₄(M), CaAl₂O₇(W)</td>
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*The X-ray intensity: (S) Strong, (M) Medium, (W) Weak.*

![Fig. 1. X-ray diffraction spectra of as hot-pressed Al₂O₃/CaO/ZrO₂ samples.](image)
Fig. 2. (a)–(e) Backscattered electron images of the cross section between Ti and Al₂O₃/CaO/ZrO₂ samples after reaction at 1600°C for 30 min. Arrows indicate the original interfaces between Ti and Al₂O₃/CaO/ZrO₂ samples.

Fig. 3. Backscattered electron images of reaction layer "II" in the ceramic side at the interface between Ti and (a) CZ, (b) CZA10, (c) CZA20, (d) CZA30, and (e) CZA40 after reaction at 1600°C for 30 min.
Fig. 4. (a) The bright-field image of reaction layers II and III at the Ti/CZA40 interface after reaction at 1600°C for 30 min; (b) and (c) selected area diffraction patterns (SADPs) of Ca$_3$Al$_2$O$_6$ along the [201] and [401] zone axes, respectively; (d) an energy-dispersive spectrum of Ca$_3$Al$_2$O$_6$.

Fig. 5. Backscattered electron images of reaction layer "III" in the ceramic side at the interface between Ti and (a) CZ, (b) CZA10, (c) CZA20, (d) CZA30, and (e) CZA40 after reaction at 1600°C for 30 min.