Investigation of the interactions between titanium and calcium zirconium oxide \((\text{CaZrO}_3)\) ceramics modified with alumina

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Abstract

Powdered mixtures of \(\text{CaO}, \text{ZrO}_2\) and \(\text{Al}_2\text{O}_3\) in various ratios were hot pressed. The mixtures reacted with titanium at 1600°C for 30 min in argon to evaluate the suitable ceramic crucibles for casting of titanium. The interfacial microstructures between titanium and ceramic composites were characterized using X-ray diffractometer, scanning and transmission electron microscope. The produced hot pressed mixtures that were chemically bonded together, contained calcium aluminate \((\text{CaAl}_2\text{O}_4)\), calcium dialuminate \((\text{CaAl}_4\text{O}_7)\), cubic zirconia \((\text{c-ZrO}_2)\), and calcium zirconium oxide \((\text{CaZrO}_3)\). The increase in \(\text{Al}_2\text{O}_3\) amount led to the decrease in \(\text{CaZrO}_3\) amount and an increase in the amount of \(\text{CaAl}_2\text{O}_4\), \(\text{CaAl}_4\text{O}_7\) and \(\text{c-ZrO}_2\) due to the reaction of \(\text{CaO}\) and \(\text{Al}_2\text{O}_3\). At the end of the reaction of the ceramic mixtures with Ti at 1600°C for 30 min, the acicular \(\alpha\)-Ti and \(\beta'\)-Ti were formed at the interface of Ti and the composites containing up to 10 vol.% \(\text{Al}_2\text{O}_3\). In composites containing more than 20 vol.% \(\text{Al}_2\text{O}_3\), \(\text{Ti}_3\text{Al}_5\) was found at the interface instead of \(\alpha\)-Ti and \(\beta'\)-Ti. Furthermore, \(\text{CaZrO}_3\), \(\text{ZrO}_2\) and \(\text{Ca}_3\text{Al}_2\text{O}_6\) existed on the sides of the ceramic far away from the interface. \(\text{CaZrO}_3/\text{Al}_2\text{O}_3\) composites with less than 20 vol.% \(\text{Al}_2\text{O}_3\) could be a potential crucible or mould material for productive applications in titanium casting.

Keywords: titanium casting, \(\text{CaZrO}_3\), \(\text{Ca}_3\text{Al}_2\text{O}_6\), microstructure, phase identification

I. Introduction

Titanium and its associated alloys possess high tensile strength, excellent toughness and light weight [1]. There are some advantages of titanium over other metals: titanium has very high corrosion resistance and it is widely used in aerospace, jet engines, medical devices, computer industry and in the manufacturing of consumable parts, such as bicycle parts and the head of a golf club [2,3]. Titanium tends to react with ceramic crucible in the vacuum through induction melting [4]. Hence, titanium alloys are subjected to melting in a water-cooled copper crucible by the consumable electrode vacuum arc melting (VAR) technique [5]. However, there are some disadvantages of the VAR process, such as the high cost of VAR equipment, challenges associated with the recycling of scrap, and long cycle time. Furthermore, an abundant oxygen layer on the surface of titanium, called “\(\alpha\)-case” occurs as a result of the reaction between the oxide on the surface of the crucibles and titanium during casting. The \(\alpha\)-case will lead to degradation of titanium’s surface, hence, causing a deterioration in the mechanical properties of titanium. Therefore, the concept of determining how to control the interfacial reactions between molten titanium and some ceramic materials is of great interest.

Refractory materials, such as \(\text{Y}_2\text{O}_3\), \(\text{CaO}\) and \(\text{ZrO}_2\), have been investigated as crucible materials for melting titanium alloys. In the past few decades, extensive studies have been conducted with regard to interfacial reactions between molten titanium and zirconia moulds and/or crucibles [6–13]. Saha and Jacob [9] indicated that a brittle \(\alpha\)-case was formed on the surface of titanium, thereby adversely affecting the mechanical properties of titanium. Economos and Kingery [6] discovered that molten titanium could penetrate through the grain boundaries of \(\text{ZrO}_2\) to form black oxygen-deficient zirconia. Recently, Lin et al. [14–20] thoroughly investigated the phase formation mechanisms and the microstructures formed at the interface be-
tween titanium (or titanium alloys) and 3Y-ZrO$_2$ (or varying Y$_2$O$_3$/ZrO$_2$ ratios) using analytical electron microscopy. Both lamellar orthorhombic Ti$_2$ZrO$_7$ and spherical hexagonal Ti$_2$ZrO$_4$ were found in α-Ti(Zr,O) after the reaction at 1550 °C [17,19,20]. Lin and Lin [18] also found intergranular α-Zr, twinned t-ZrO$_{2x}$, and lenticular t-ZrO$_{2x}$, and ordered c-ZrO$_{2x}$ 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$_3$ precipitates in the samples containing 30–70 vol.% Y$_2$O$_3$ [21]. 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. [22,23] demonstrated that the surface coating of CaZrO$_3$ on to the crucibles is suitable for Ti alloys casting. The CaZrO$_3$ possesses comparable chemical properties to ZrO$_2$ because CaZrO$_3$ is chemically inert to ZrO$_2$ and has lower cost compared to yttria-based systems. Thus, CaZrO$_3$ could be a potential refractory material for titanium casting. According to Chang and Lin [24], a diffusion zone featuring columnar CaZrO$_3$ was formed after reaction of Ti and CaO/ZrO$_2$ composites at 1550 °C. The CaZrO$_3$ was formed due to the outward diffusion of oxides and zirconia away from fully stabilized ZrO$_2$. This result indicates that CaZrO$_3$ was in a stable phase and it was not significantly dissolved in Ti. Furthermore, Lin et al. [25] studied CaZrO$_3$ as a crucible for Ti-6Al-4V (or TC4) and TiNi-alloy based melts material. Small amount of Ca, Zr, Ti and Ni diffused to the original interfacial reaction layer, indicating that CaZrO$_3$ has a promising performance and a very good refractory resistance [25]. In Schaffüner et al. study [26], CaZrO$_3$ crucible was able to withstand Ti-6Al-4V and TiAl melts, thereby not exhibiting any form of cracking due to the low thermal shock resistance.

The CaZrO$_3$ mixed with Al$_2$O$_3$, Y$_2$O$_3$, and MgO possess high chemical stability and a very good thermal stability against thermal shock [27]. The CaZrO$_3$/Al$_2$O$_3$ samples contained Al$_2$O$_3$ in various quantities, i.e. 10, 20, 30, and/or 40 vol.% of Al$_2$O$_3$ and the equimolar ratio (1:1) of CaO and ZrO$_2$ powders in a balanced reaction with commercially pure titanium (CP-Ti) melt at 1600 °C in 30 min. The macrostructures were characterized using X-ray diffractometer (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM) with an attached energy-dispersive X-ray spectroscopy (EDS). The phase formation mechanism and microstructural evolution between CP-Ti and CaZrO$_3$/Al$_2$O$_3$ composites were elucidated.

II. Experimental procedure

Ceramic composites were prepared from powdered zirconia (> 99.9 wt.% ZrO$_2$; the average particle size was smaller than 0.5 μm; Toyo Soda Mfg. Co., Tokyo, Japan), calcia (> 99.9 wt.% CaO 0.5 μm average particle size; Sigma Aidrich, Missouri, United States), and α-alumina (> 99.9 wt.% Al$_2$O$_3$; ≤ 10 μm average particle size; Sigma Aidrich, Missouri, United States). Powder mixtures of ZrO$_2$ and CaO containing 10, 20, 30, and 40 vol.% Al$_2$O$_3$ were prepared and designated as CZA10, CZA20, CZA30, CZA40, respectively. Ceramic powder mixtures were dispersed in ethanol and the pH of the suspension was adjusted to 11 by adding 0.2–0.7 wt.% ammonium hydroxide (NH$_4$OH). The suspension was subjected to ultrasonic vibration for 10 min, dried in an oven at 150 °C, ground with an agate mortar and pestle, and screened through an 80 mesh (sieve size is 0.177 mm). Bulk ceramic composites were fabricated by hot pressing in a graphite furnace at 1 atm argon. Then, the composite specimens were heated at 300 °C and held for 3 min under 5 MPa at a heating rate of 30 °C/min, followed by heating to 1300 °C and holding for 30 min under 30 MPa at a heating rate of 25 °C/min. During cooling, pressure was released at 1100 °C. The phase identification of CaZrO$_3$/Al$_2$O$_3$ composites was performed by XRD.

The apparent densities and bulk densities of hot pressed CaZrO$_3$/Al$_2$O$_3$ samples were determined by the Archimedes principle using water as an immersion medium. The hot press conditions, compositions, relative densities, and designations of CaZrO$_3$/Al$_2$O$_3$ samples are listed in Table 1. The relative densities of the CZ (pure CaZrO$_3$), CZA10, CZA20, CZA30 and CZA40 were 98.0, 98.5, 98.2, 98.3 and 98.6% TD, respectively.

Hot pressed ceramic composites were cut and machined to the dimensions of about 10 mm × 10 mm × 5 mm. The composite CaZrO$_3$/Al$_2$O$_3$ was placed into the graphite crucible and tightly packed with commercially pure titanium powder. The crucible was placed in an electric resistance furnace having its heating element, made of tungsten. The chamber was evacuated at vacuum of about 10$^{-4}$ torr and refilled with argon. The cycle of vacuum evacuation and purging with argon was repeated three times. The temperature was increased to 1600°C at a heating rate of 10°C/min, where the composites were held at 1600°C for 30 min and cooled to room temperature in the furnace.

The phase identification was performed using an XRD Model D8 DISCOVER, Bruker AXS, Germany). The operating conditions of X-ray diffraction were CuKα radiation at 40 kV and 40 mA, and a scanning rate of 1.2°/min. SEM (Model JSM 6500F, JEOL Ltd., Japan) was used for the microstructural observation of the interfaces between Ti and CaZrO$_3$/Al$_2$O$_3$ samples. SEM specimens were cut and ground using a diamond matted disc, and polished using diamond pastes of sizes 6, 3, and 1 μm in sequence. The TEM specimens were prepared by focused ion beam (FIB) so that the thickness is less than 100 nm. Prior to the FIB milling, a layer of platinum approximately 1 μm thick was deposited on the specimen by ion beam chemical deposition using Trimethyl-methylcyclopentadienyl-platinum(IV) (C$_3$H$_5$Pt) as a precursor gas. The Pt layer served as
a marker and prevented the outer surface of the sample from being directly exposed to the gallium ion beam implantation during subsequent ion milling operations. The FIB milling was performed with a Ga\(^+\) ion beam at 30 keV. After rough milling (7–1 nA), polishing (0.5–0.1 nA), and final polishing (50–10 pA), a thin foil of (17 µm × 2 µm × 0.05 µm) was cut off and transferred to a TEM grid (Formvar/Carbon Coated-Copper 200 mesh) using a micromanipulator for subsequent TEM analyses.

The interfacial microstructures were then characterized using a TEM (Model JEM 2010F, JEOL Ltd.) equipped with an EDS (OXFORD INCA, X-Max\(^\text{N}\) Silicon Drift Detector, Oxford Instrument Inc.). The analyses of atomic configurations in various phases were performed using a computer simulation software for crystallography (CaRIne Crystallography 3.1, Divergent S.A., Compiègne, France). Chemical quantitative analyses for various phases were conducted by the Cliff-Lorimer standardless technique [28]. A conventional ZAF correction was done using the LINK ISIS software.

III. Results and discussion

3.1. CaZrO\(_3\)/Al\(_2\)O\(_3\) composites

Figure 1 shows the XRD spectra of various hot pressed CaZrO\(_3\)/Al\(_2\)O\(_3\) samples. Two phases, orthorhombic CaZrO\(_3\) (calcium zirconate) and cubic zirconia (c-ZrO\(_2\)), were found in CZ sample. When Al\(_2\)O\(_3\) was added to the composites, calcium aluminate (CaAl\(_2\)O\(_4\)) or calcium dialuminate (CaAl\(_4\)O\(_7\)) were formed, in addition to c-ZrO\(_2\) and CaZrO\(_3\). The amount of c-ZrO\(_2\) increases with increasing amount of Al\(_2\)O\(_3\) in the composites as indicated by the peak at 30° of XRD spectra. Furthermore, the amount of CaZrO\(_3\) decreases with increasing amount of Al\(_2\)O\(_3\). The XRD results were consistent with the phases indicated by the CaO-Al\(_2\)O\(_3\)-ZrO\(_2\) phase diagram at 1380°C [29] and are listed in Table 1.

Figure 2 shows the backscattered electron images (BEI) of various CaZrO\(_3\)/Al\(_2\)O\(_3\) samples after they have been hot pressed at 1300°C for 30 min. The EDS analyses showed that the bright area was identified as c-ZrO\(_2\), the grey area was identified as CaZrO\(_3\), and the dark portion of the grains was identified as CaAl\(_2\)O\(_4\). Obvi-

![Figure 1. X-ray diffraction spectra of hot pressed CaZrO\(_3\)/Al\(_2\)O\(_3\) composites](image1)

![Figure 2. BEI of scanning electron microscopy of: a) CZ, b) CZA10, c) CZA20, d) CZA30, and e) CZA40 after hot pressing the composite at 1300°C for 30 min](image2)

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Composition [vol.%]</th>
<th>δ [%TD]</th>
<th>XRD phases</th>
</tr>
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<tbody>
<tr>
<td>CZ</td>
<td>44.45% CaO + 55.55% ZrO(_2)</td>
<td>98.0</td>
<td>CaZrO(_3), c-ZrO(_2)</td>
</tr>
<tr>
<td>CZA10</td>
<td>10% Al(_2)O(_3) + 90% (CaO/ZrO(_2))</td>
<td>98.5</td>
<td>CaZrO(_3), c-ZrO(_2), CaAl(_2)O(_4)</td>
</tr>
<tr>
<td>CZA20</td>
<td>20% Al(_2)O(_3) + 80% (CaO/ZrO(_2))</td>
<td>98.2</td>
<td>CaZrO(_3), c-ZrO(_2), CaAl(_2)O(_4)</td>
</tr>
<tr>
<td>CZA30</td>
<td>30% Al(_2)O(_3) + 70% (CaO/ZrO(_2))</td>
<td>98.3</td>
<td>CaZrO(_3), c-ZrO(_2), CaAl(_2)O(_4), CaAl(_4)O(_7)</td>
</tr>
<tr>
<td>CZA40</td>
<td>40% Al(_2)O(_3) + 60% (CaO/ZrO(_2))</td>
<td>98.6</td>
<td>CaZrO(_3), c-ZrO(_2), CaAl(_2)O(_4), CaAl(_4)O(_7)</td>
</tr>
</tbody>
</table>
ously, there were pores in CZ and CZA10 (Figs. 2a,b). When the content of Al2O3 in the composites was increased, the pores disappeared in CZA30 and CZA40 (Figs. 2d,e). Thus, the addition of Al2O3 improves densification of the composites due to the formation of calcium aluminate or calcium dialuminate and elimination of the pores.

The addition of divalent oxide (CaO and MaO) and trivalent oxide (Sc2O3, Y2O3, Al2O3) into zirconia can result in c-ZrO2 due to the formation of oxygen vacancies [17,21,24]. As for calcium zirconate (CaZrO3), the CaO reacts with ZrO2 to form CaZrO3 as demonstrated by the negative free energy in Eq. 1 [30]:

\[
\text{CaO + ZrO}_2 \rightarrow \text{CaZrO}_3 \Delta G = -54 \sim -71 \text{ kJ/mol (1)}
\]

The free energies of the calcium aluminate phases, including CaAl2O4, CaAl4O7 and Ca12Al14O33, are shown in Eqs. 2-7 [31,32]:

\[
\begin{align*}
\text{Al}_2\text{O}_3 + \text{CaO} & \rightarrow \text{CaAl}_2\text{O}_4 \Delta G = -38 \text{ kJ/mol (2)} \\
2 \text{Al}_2\text{O}_3 + \text{CaO} & \rightarrow \text{Ca}_2\text{Al}_2\text{O}_7 \Delta G = -51 \text{ kJ/mol (3)} \\
7 \text{Al}_2\text{O}_3 + 12 \text{CaO} & \rightarrow \text{Ca}_7\text{Al}_2\text{O}_{12} \Delta G = -275 \text{ kJ/mol (4)} \\
\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 17 \text{Al}_2\text{O}_3 & \rightarrow 12 \text{CaAl}_2\text{O}_7 \Delta G = -26 \text{ kJ/mol (5)} \\
\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 5 \text{CaO} & \rightarrow 12 \text{CaAl}_2\text{O}_7 \Delta G = -14 \text{ kJ/mol (6)} \\
\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + \text{5CaAl}_2\text{O}_4 & \rightarrow 12 \text{CaAl}_2\text{O}_7 \Delta G = -7 \text{ kJ/mol (7)}
\end{align*}
\]

From the calculation of the Gibbs free energies of calcium aluminate phases, the most negative free energy was that of Ca12Al14O33, showing that the reaction is the most spontaneous when compared to the free energies of CaAl2O4 and CaAl12O37. However, Ca12Al14O33 phase was not part of the present study. Possibly, the Ca12Al14O33 phase reacted with Al2O3 to form CaAl2O4 and CaAl2O4 as shown in Eqs. 5 and 6, or the Ca12Al14O33 phase might have reacted with CaAl2O4 to form CaAl2O4 as indicated by Eq. 7. It is also possible that the Ca12Al14O33 phase was a transient phase, which was not observed in the study. In addition, CaAl2O4 was the main phase instead of CaAl12O37, although the free energy of CaAl12O37 was smaller than that of the CaAl12O37 phase. CaAl12O37 could react with Ca12Al14O33 phase to form CaAl2O4 phase as indicated by the Eq. 7 and reported by Iftekhar et al. [32].

3.2. Reactions of Cp-Ti with CaZrO3/Al2O3

Figures 3a-e display the cross sectional BEI of Ti and various composites of CaZrO3/Al2O3 after the occurrence of a reaction at 1600 °C for 30 min. Titanium is shown at 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. 3a-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 is affected by the interfacial reaction is marked as “III”. Arrows indicating the original interface are shown on the diagram according to the characteristic Kα X-ray maps of calcium (not shown), since Ca is relatively insoluble in Ti with respect to zirconium, oxygen and aluminium. The large pores in the interface near the ceramics, as shown in the region II, could be attributed to the Kirkendall effect be-

![Figure 3. BEI images of: a) CZ, b) CZA10, c) CZA20, d) CZA30, and e) CZA40, showing the cross section between Ti and CaZrO3/Al2O3 composites after the reaction at 1600 °C for 30 min (arrows indicate the original interface between Ti and CaZrO3/Al2O3 composites)

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cause zirconium and oxygen must have diffused to the titanium side more rapidly than the rate of diffusion of titanium into the ceramic side.

Reaction layer “I” - at the titanium side

Reaction layer “I” contains dark needle-like regions and bright regions near the interfaces of Ti/CZ and Ti/CZA10, as shown in Figs. 3a,b. The needle-like regions should be \(\alpha\)-Ti(Zr,O) phase and the bright regions should be the \(\beta^+\)-Ti(Zr,O) phase, which conforms to the previous reports by Lin and Lin studies [17,19,20]. The needle-like \(\alpha\)-Ti(O) phase and the \(\beta^+\)-Ti(Zr,O) phase are usually found in the titanium side of the micrograph because of the interfacial reactions between Ti and 3Y-ZrO\(_2\). An \(\alpha\)-Ti(O) phase with a small amount of oxygen in solid solution and \(\beta^+\)-Ti(Zr,O) dissolved a significant amount of zirconium (\(\beta^+\) stabilizer) and oxygen (\(\alpha\) stabilizer) in solid solution [17,19,20]. Moreover, the needle-like \(\alpha\)-Ti(O) and \(\beta^+\)-Ti(Zr,O) in reaction layer “I” were effectively suppressed at the titanium side of Ti/CZA20, Ti/CZA30 and Ti/CZA40.

Reaction Layer “II” - near the interface

BEI images of reaction layer “II” in the ceramic side of Ti/CZ, Ti/CZA10, Ti/CZA20, Ti/CZA30 and Ti/CZA40 after reaction at 1600 °C for 30 min are shown in Fig. 4. After reaction at 1600 °C for 30 min, a large amount of titanium diffused to the region occupied by ZrO\(_2\) and CaZrO\(_3\). The diffused titanium was also involved in a reaction with both ZrO\(_2\) and CaZrO\(_3\) of Ti/CZ and Ti/CZA10 composites to form acicular \(\alpha\)-Ti(Zr,O), \(\beta^-\)-Ti(Zr,O) and residual CaZrO\(_3\), as shown in Figs. 4a,b. Furthermore, the precipitation of the needle-like \(\alpha\)-Ti(Zr,O) solid solution on the \(\beta^+\)-Ti(Zr,O) substrate during the cooling process was very common at the interfacial reactions between Ti and ZrO\(_2\) [17,19,21,24]. However, two phases of \(\alpha\)-Ti(Zr,O) and \(\beta^+\)-Ti(Zr,O) in reaction layer “II” were found when Al\(_2\)O\(_3\) content increased above 20 vol.%. Titanium was involved in the reaction with Al from liquid CaAl\(_2\)O\(_4\) (melting point \(\sim1604^\circ\text{C}\), which is close to the reacting temperature of 1600°C) to form Ti\(_3\)Al\(_5\). The formation mechanism for Ti\(_3\)Al\(_5\) is shown in the equation below:

\[
3\text{Ti} + 5\text{Al} \rightarrow \text{Ti}_3\text{Al}_5 \quad (8)
\]

Meanwhile, the ZrO\(_2\) at reaction layer “II” was dissolved in Ti\(_3\)Al\(_5\), which is 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\(_3\) content increased above 30 vol.% in Figs. 4d,e, the morphology of both Ti\(_3\)Al\(_5\) and CaZrO\(_3\) changed into smooth and spherical shapes due to the formation of a large amount of liquid CaAl\(_2\)O\(_4\). In addition to the Ti\(_3\)Al\(_5\) phase, the CaAl\(_2\)O\(_3\) phase was also found as shown in Figs. 4b-e. The formation mechanism of CaAl\(_2\)O\(_3\) phase could be described as follows:

\[
\text{CaAl}_2\text{O}_4 + 2\text{CaZrO}_3 \rightarrow \text{Ca}_3\text{Al}_2\text{O}_8 + 2\text{ZrO}_2 \quad (9)
\]

The phase identification for Ca\(_3\)Al\(_2\)O\(_8\) is discussed in the TEM analysis below.

Figure 5 shows the bright field images (BFI), selected area diffraction patterns (SADPs), and EDS of CaZrO\(_3\) and Ti\(_3\)Al\(_5\) in reaction layer “II” of the ceramic side at the interface between Ti and: a) CZ, b) CZA10, c) CZA20, d) CZA30, and e) CZA40 after the reaction at 1600 °C for 30 min.

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that the composition of the TiAl was 27.97 at.% Ti, 50.63 at.% Al, 10.91 at.% O and 10.22 at.% Zr.

Figure 6a shows the bright field image between reaction layer “II” and “III” of TiCZA40 after reaction at 1600 ºC for 30 min. It indicates the formation of TiAl, CaAl2O4 and CaZrO3. Figures 6b,c show the SADPs of CaAl2O4 with [111] and [201] zone axes, respectively. The lattice parameters of the CaAl2O4 phase were measured and calculated to be \(a = 10.68\,\text{Å}, b = 10.85\,\text{Å}, c = 15.34\,\text{Å},\) and \(\alpha = \beta = \gamma = 90^\circ,\) which correspond to the parameters of the orthorhombic CaAl2O4 reported in JCPDS# 330251 \( (a = 10.8737\,\text{Å}, b = 10.8512\,\text{Å}, c = 15.1152\,\text{Å}, \alpha = \beta = \gamma = 90^\circ).\) The EDS spectrum in

Fig. 6d shows that Ca3Al2O7 is composed of 22.41 at.% Ca, 23.16 at.% Al, 49.67 at.% O and 4.76 at.% Zr.

**Reaction Layer “III” - at the composites side**

Figures 7a-e display the backscattering electron image of the reaction layer “III” in the Ti/Al composites joint after reaction at 1600 ºC for 30 min. It was observed that the shape of CaZrO3 changed to spherical form when amount of Al2O3 increased above 20 vol.% due to the formation of the liquid phase, i.e. Ca3Al2O7.

The liquid phase, CaAl2O4, would penetrate between CaZrO3 grains, exerting an attractive force, thereby pulling the grains together. Furthermore, the content of CaAl2O4 increases with an increase in the amount of Al2O3 on the ceramic side. A large amount of liquid CaAl2O4 tended to enhance the shrinkage and increase in density of CaZrO3, resulting in the reduction of the pores and grain growth in reaction layer “III”. During the reaction, liquid CaAlO2 dissolved CaZrO3 and ZrO2 at 1600 ºC. When the solution reached the saturation concentration, CaZrO3 and ZrO2 precipitated again in the solution during cooling.

To evaluate the effect of titanium on the composites, the composites were annealed at 1600 ºC for 30 min without reacting with titanium. Figure 8 shows the BEI images of the investigated composites after annealing at 1600 ºC for 30 min. By the EDS analyses of SEM (not shown), the bright area was identified as c-ZrO2, the grey area was CaAl2O4, and the dark portion of the grains was CaAl3Si7. Obviously, there were lots of pores in the CZ and CZA10 samples (Figs. 8a,b) (arrows in figure). When the content of Al2O3 in the composites increased, the pores gradually disappeared and were filled with CaAl1.6O2 supported by CZA0, CZA30, and CZA40 specimens (Figs. 8c,d). Thus, the addition of Al2O3 contributed to the increase in the density of the composites due to the formation of CaAl1.6O2 at 1600 ºC.

Figures 9 shows the BFI, SADPs, and EDS of CZA40 after annealing at 1600 ºC for 30 min. Figure 9a shows
presence of c-ZrO₂, CaAl₂O₇ and CaZrO₃. Figures 9b,c show the SADPs of CaAl₂O₇ with [113] and [111] zone axes, respectively. The lattice parameters of the CaAl₂O₇ phase were measured and calculated to be $a = 13.27 \, \text{Å}$, $b = 9.01 \, \text{Å}$, $c = 6.65 \, \text{Å}$, and $\alpha = \gamma = 90^\circ \neq \beta$, which corresponded to the parameters of monoclinic CaAl₂O₇ reported in JCPDS# 070082 ($a = 12.897 \, \text{Å}$, $b = 8.879 \, \text{Å}$, $c = 5.454 \, \text{Å}$, $\alpha = \gamma = 90^\circ \neq \beta$, space group is $C2/c$). The EDS spectrum in Fig. 9d shows that CaAl₂O₇ composed of 7.12 at.% Ca, 35.01 at.% Al, 57.6 at.% O and 0.18 at.% Zr.

Figure 10 shows the XRD spectra of CZA40 after annealing at 1300°C, CZA40 after reacting with Ti at 1600°C, and CZA40 after annealing at 1600°C in a sequence from the bottom to the top. Four phases, CaZrO₃ (o), c-ZrO₂ (c), CaAl₂O₄ (m), and CaAl₂O₇ (#) were found both in the CZA40 at 1300°C and 1600°C. The amount of CaAl₂O₇ increased as indicated by the peak at 21° of XRD spectra and the CaAl₂O₄ decreased as indicated by the peak at 37° XRD peak for CZA40 annealed at 1600°C. The formation mechanism for the CaAl₂O₇ could be described as the Eq. 10:

$$2 \text{CaAl}_2\text{O}_4 + \text{ZrO}_2 \rightarrow \text{CaAl}_4\text{O}_7 + \text{CaZrO}_3 \quad (10)$$
However, when CZA40 undergoes a reaction with Ti, both CaAl$_2$O$_4$ and CaAl$_4$O$_7$ disappear leaving behind the Ca$_3$Al$_2$O$_6$ phase (▼).

Figure 11a displays the proposed model of microstructural evolution in reaction layers II and III in Ti/CZ at 1600 °C for 30 min. Before hot pressing, the composite is composed of ZrO$_2$, CaZrO$_3$, and minor pores, but after hot pressing near the interface of reaction layer “II”, titanium diffuses into the composite and dissolves a relatively large amount of O and Zr to form β-Ti(Zr,O) solid solution. As the solubility of Ca in Ti was quite limited, Ca was retained in the original CaZrO$_3$. After cooling, the precipitation of the needle-like α-Ti(Zr,O) solid solution occurred on the β'-Ti(Zr,O) substrate. As for reaction layer “III”, which is the ceramic side located slightly away from the interface, the phases were ZrO$_2$, CaZrO$_3$, and minor pores formed after cooling. Figure 11b shows the formation mechanism for reaction layers II and III in the Ti/CZ-Al$_2$O$_3$ additive at 1600 °C for 30 min. Before hot pressing, the composite is made of ZrO$_2$, CaZrO$_3$, CaAl$_2$O$_4$, CaAl$_4$O$_7$ and minor pores after hot pressing. When the volume percentage of Al$_2$O$_3$ increased above 20 vol.%, Ti tends to diffuse toward the composites and a reaction occurs between titanium and aluminium present in the liquid CaAl$_2$O$_4$ to form Ti$_3$Al$_5$ close to the reaction layer “II”. After cooling, the formation of Ca$_3$Al$_2$O$_6$ occurs due to CaZrO$_3$ reacting with liquid CaAl$_2$O$_4$. At some distance slightly away from the ceramic side (reaction layers “III”) ZrO$_2$, CaZrO$_3$ and Ca$_3$Al$_2$O$_6$ were found and no Ti$_3$Al$_5$ was formed. The reaction layers of each of the samples and their corresponding crystal phases are all marked in Table 2.

IV. Conclusions

1. Ceramic composites of CaO, ZrO$_2$ and Al$_2$O$_3$ in various ratios were used with titanium at 1600 °C for 30 min in Ar. The interfacial microstructures between titanium and ceramic composites were characterized by using XRD, SEM and TEM.

2. Before the addition of titanium, calcium aluminate (CaAl$_2$O$_4$) or calcium dialuminate (CaAl$_4$O$_7$), c-

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Figure 11. Schematic showing the microstructural evolution of reaction layer “II” and “III” in:
(a) Ti/CZ and (b) Ti/CZ-Al$_2$O$_3$ additive
ZrO$_2$ and CaZrO$_3$ were formed in the ceramic composites. The amount of CaZrO$_3$ was reduced with an increase in the amount of Al$_2$O$_3$ in the composites. Meanwhile, the amounts of calcium aluminate (CaAl$_2$O$_4$), calcium dialuminate (Ca$_2$Al$_2$O$_5$) and c-ZrO$_2$ increase with an increase in the amount of Al$_2$O$_3$ due to the abundance of CaO to react with Al$_2$O$_3$.

3. After joining titanium and ceramic composites, the acicular α-Ti and β′-Ti are formed at the interface of the ceramic composites with 0 and 10 vol.% Al$_2$O$_3$. When the amount of Al$_2$O$_3$ in the ceramic composites exceeded 20 vol.%, the Ti$_3$Al$_5$ was formed at the interface rather than α-Ti and β′-Ti. Far from the interface, three phases of CaZrO$_3$, ZrO$_2$ and Ca$_3$Al$_2$O$_6$ existed in the ceramic side. In addition, the pores gradually disappeared on the ceramic side due to the formation of Ca$_3$Al$_2$O$_6$.

4. The incorporation of more than 20 vol.% Al$_2$O$_3$ in CaZrO$_3$/Al$_2$O$_3$ ceramic composites significantly suppressed the formation of the reactional phases at the interface at 1600 °C for 30 min. Conversely, an extensive reaction occurred at the interface between Ti and CZ as well as CZA10. Thus, CaZrO$_3$/Al$_2$O$_3$ ceramic composites with more than 20 vol.% Al$_2$O$_3$ could be suitable for the titanium casting.

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