Microstructural Evolution and Formation Mechanism of the Interface Between Titanium and Zirconia Annealed at 1550°C

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The diffusional reaction between titanium and zirconia was carried out isothermally at 1550°C in argon. The distinct reaction layers in the reaction-affected zone between Ti and ZrO₂ were investigated using analytical scanning electron microscopy, analytical transmission electron microscopy, and electron probe microanalyses. In the metal side, there existed five reaction layers in a sequence of α-Ti(O), Ti₂ZrO + α-Ti(O, Zr), Ti₂ZrO + α-Ti(O, Zr) + β′-Ti(O, Zr), α-Ti(O, Zr) + β′-Ti(O, Zr), and β′-Ti(O, Zr) after cooling. In the zirconia side, two reaction layers were found: near the original interface, β′-Ti coexisted with fine spherical c-ZrO₂-x, and Chinese-script-like c-ZrO₂-x, which dissolved a significant amount of Y₂O₃ in solid solution; further away from the original interface, the coarse-ordered intergranular α-Zr was excluded from metastable ZrO₂-x, resulting in the lenticular l-ZrO₂-x and ordered c-ZrO₂-x. An attempt was made to determine and propose the microstructural evolution and formation mechanism of the reaction layers between titanium and zirconia isothermally annealed at 1550°C.

I. Introduction

Extensive studies have been carried out on the interface reaction between titanium and zirconia in the last few decades.1–3 Weber et al. indicated that zirconia was blackened by a limited solid solution of titanium in zirconia, when the titanium melted react with the ZrO₂ crucible. In discussing the effect of limited solid solution of titanium in zirconia, when the titanium dissolved a significant amount of Y₂O₃ in solid solution; further away from the original interface, the coarse-ordered intergranular α-Zr was excluded from metastable ZrO₂-x, resulting in the lenticular l-ZrO₂-x and ordered c-ZrO₂-x. An attempt was made to determine and propose the microstructural evolution and formation mechanism of the reaction layers between titanium and zirconia isothermally annealed at 1550°C.

In order to shed light on the microstructural evolution of the various distinct reaction layers between titanium and zirconia, the Ti/ZrO₂ diffusion couple was isothermally annealed in argon at 1550°C for various periods in the present study, and the microstructures were characterized using analytical scanning electron microscopy (SEM), analytical transmission electron microscopy (TEM), and an electron probe microanalyzer (EPMA). Finally, the formation mechanisms, as well as microstructural evolution, of the reaction layers between titanium and zirconia were proposed.

II. Experimental Procedures

Bulk ZrO₂ specimens used in this study were prepared from the powder of 3 mol% Y₂O₃ partially stabilized zirconia (with a nominal composition of >94 wt% ZrO₂+H₂O₂ [H₂O₂ accounts for approximately 2%–3% of this total]), 5.4 wt% Y₂O₃, <0.001 wt% Fe₂O₃, <0.01 wt% SiO₂, <0.005 wt% Na₂O, <0.005 wt% TiO₂, <0.02 wt% Cl, <0.005 wt% SO₄₂⁻ (Toyo Soda Mfg. Co., Tokyo, Japan) by hot pressing (Model HPS0-MTG-5010, Thermal Techno. Inc., Santa Rosa, CA). The bulk ZrO₂ and commercially available titanium billets (with a nominal composition of 99.91 wt% Ti, 0.25 wt% O, 0.01 wt% H, 0.03 wt% N, 0.10 wt% C, 0.30 wt% Fe; Kobe Steel, Ltd., Tokyo, Japan) were cut and machined into dimensions of 14 mm × 14 mm × 5 mm. The sandwiched samples, one Ti in between two ZrO₂ specimens, were slightly pressed and annealed at 1550°C for 0.5, 3, and 6 h in an atmosphere of Ar. The hot-pressing procedures of bulk ZrO₂ and the sandwiched samples have been described in detail elsewhere.5

The cross-sectional SEM, TEM, and EPMA specimens perpendicular to the interface of titanium and zirconia were cut, ground, and polished by standard procedures. The microstructures at the interface were observed using an analytical SEM (Model JSM 6500F, JEOL Ltd., Tokyo, Japan) and an analytical TEM (Model JEM 2000FX, JEOL Ltd.). The quantitative composition analyses were carried out based on the principle of the Cliff–Lorimer standarless technique⁶ by an EDS (Mode ISIS300, Oxford Instrument Inc., London, U.K.) attached to the TEM. The backscattered electron images (BEI) had been characterized using analytical transmission electron microscopy (TEM), and an electron probe microanalyzer (EPMA). The measurement conditions for EPMA were as follows: the accelerating voltage was 15 kV, the probe current was 1.5 × 10⁻⁸ A, and the beam diameter was 1 μm.

III. Results and Discussion

(1) Formation Mechanism of Various Reaction Layers

Figures 1(a), (b), and (c) display the backscattered electron images of the cross section normal to the interface between Ti and ZrO₂ after reaction at 1550°C for 0.5, 3, and 6 h, respectively. Titanium was on the left-hand side, while zirconia was on the
other side. The arrows in the upper middle of these figures indicated the original interface of Ti and ZrO₂. There were five reaction layers, designated as “A,” “B,” “C,” “D,” and “E,” on the metal side, while only two distinct reaction layers, designated as “F” and “G,” were found on the zirconia side. The thickness of the individual reaction layers increased with the annealing time. Moreover, in the reaction layer “G,” zirconia grains grew obviously and α-Zr (brighter) was coarsened and became isolated after reaction at 1550°C for 6 h (Fig. 1(c)). The existence of the pores in the ceramic side was attributed to the Kirkendall effect, as zirconium and oxygen diffused to the titanium side much faster than titanium diffused toward the zirconia side.

Figure 2(a) displays the backscattered electron image of the cross section normal to the interface between Ti and ZrO₂ after reaction at 1550°C/6 h. The distributions of Y, Ti, Zr, and O elements in the interface are demonstrated by X-ray mappings in Figs. 2(b)–(e), respectively. The original interface (the arrows) was deliberately located according to the results of the characteristic Kα X-ray map of yttrium (Fig. 2(b)), which was relatively immobile compared with the elements Zr, O, and Ti. Because Ti and Zr are isomorphous elements and the differences in their atomic radii are very small, they are readily substituted for each other. Figures 2(c) and (d) confirm that the interdiffusion of Ti and Zr was intense and the diffusion distance of Ti and Zr was nearly equal. Figure 2(e) shows that oxygen underwent a long-range diffusion into titanium, leading to the formation of the oxygen-containing α-Ti.

Figure 3 displays the backscattered electron image of the reaction layers “A,” “B,” and “C” between Ti and ZrO₂ after reaction at 1550°C/6 h. The reaction layer “A” was α-Ti, which dissolved a large amount of oxygen and a small amount of zirconium. The quantitative analyses by the EPMA showed that it contained 71.30 at.% Ti, 0.97 at.% Zr, and 27.72 at.% O. Original corresponding to α-Ti(O). α-Ti(O) was formed by the oxidation–reduction reaction of titanium and zirconia, and can be expressed as follows:

\[
\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_2 - x + \beta\text{-Ti(O)} \quad (1)
\]

\[
\beta\text{-Ti(O)} \xrightarrow{\text{cooling}} \alpha\text{-Ti(O)} \quad (2)
\]

The reaction layer “B” with a continuous lamellar morphology consisted of α-Ti (gray) and needle-like Ti₂ZrO (bright). The thin continuous layer, consisting of lamellar α-Ti and Ti₂ZrO, was first found in the present study. Unlike these continuous lamellar phases found in the present study, Lin and Lin⁵ reported that the Ti₂ZrO lamellae were precipitated from plate-like α-Ti (O, Zr) by a eutectoid reaction during cooling. The formation of lamellar α-Ti (O) and Ti₂ZrO in the thin continuous layer (the reaction layer “B”) can be expressed as follows:

\[
\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_2 - x + \beta\text{-Ti(Zr, O)} \quad (3)
\]

\[
\beta\text{-Ti(Zr, O)} \xrightarrow{\text{cooling}} \alpha\text{-Ti(Zr, O)} \xrightarrow{\text{cooling}} \alpha\text{-Ti(Zr, O)} + \text{Ti}_2\text{ZrO} \quad (4)
\]
The reaction layer “C” consisted of β'-Ti (bright) and the lamellae of Ti2ZrO and α-Ti (gray). At high temperatures, the primary α-Ti dissolved a large amount of zirconium and oxygen, forming metastable α-Ti(Zr, O), and thus resulted in the precipitation of the lamellae Ti2ZrO during cooling. Meanwhile, the β-Ti, which dissolved a large amount of Zr and O, transformed into orthorhombic β'-Ti(Zr, O) solid solution during cooling. The coexistence of α-Ti (O), Ti2ZrO, and β'-Ti (O, Zr) can be expressed by the following reactions:

\[
\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_{2-x} + \alpha\text{-Ti(Zr, O)} + \beta\text{-Ti(Zr, O)} \tag{5}
\]

\[
\alpha\text{-Ti(Zr, O)} + \beta\text{-Ti(Zr, O)} \xrightarrow{\text{cooling}} \alpha\text{-Ti(Zr, O)} + \text{Ti}_2\text{ZrO} + \beta'\text{-Ti(Zr, O)} \tag{6}
\]

As zirconium was the stabilizer of β-Ti, fewer acicular α-Ti was observed on the right-hand side of Fig. 4, where a higher concentration of Zr existed in titanium. Also shown in Fig. 4, the amount of the acicular α-Ti increased with the distance away from interface. The reaction layer “D,” which dissolved a significant amount of zirconium (β stabilizer) and oxygen (α stabilizer), was composed of α+β titanium with Zr and O in solid reaction at 1550°C/6 h. The original interface of titanium and zirconia was beyond the right-hand side of the micrograph.

The coexistence of α-Ti (O), Ti2ZrO, and β'-Ti (O, Zr) can be expressed by the following reactions:

\[
\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_{2-x} + \alpha\text{-Ti(Zr, O)} + \beta\text{-Ti(Zr, O)} \tag{3}
\]

\[
\beta\text{-Ti(Zr, O)} \xrightarrow{\text{cooling}} \alpha\text{-Ti(Zr, O)} + \beta'\text{-Ti(Zr, O)} \tag{7}
\]

Fig. 2. (a) Scanning electron micrograph (backscattered electron image, BEI) of the cross section between Ti/ZrO2 after reaction at 1550°C/6 h; (b)–(e) X-ray maps of Y, Ti, Zr, and O, respectively.
solution. For comparison, it is worth noting that the acicular-like α-Ti was also found in α+β titanium alloys such as Ti–6Al–4V or Ti–8Al–1Mo–1 alloys.

The orientation relationship of the acicular α-Ti and the β'-Ti has been subjected to an intense investigation. Figure 5(a) shows the TEM micrograph (bright-field image, BFI) of the reaction layer “D” viewed in the direction normal to the interface of Ti and ZrO₂ after reaction at 1550 °C/6 h. The acicular α-Ti and the β'-Ti were identified as hexagonal and orthorhombic crystal structures, respectively, from the superimposed selected area diffraction patterns (SADPs), as shown in Fig. 5(b). The SADPs in Fig. 5(b) were schematically redrawn in Fig. 5(c), with the diffraction spots being indexed. The orientation relations between α-Ti and β'-Ti were thus identified as follows: [2110]₀₀₀₁ // [001]β'-Ti, and (0001)₀₀₀₁ // (100)β'-Ti. Moreover, the lattice constants of the β'-Ti orthorhombic unit cell were calculated as follows: \( a_\beta = 0.58 \text{ nm}, b_\beta = 0.84 \text{ nm}, \) and \( c_\beta = 0.61 \text{ nm}, \) and those of the α-Ti hexagonal unit cell were \( a_\alpha = b_\alpha = 0.30 \text{ nm}, \) and \( c_\alpha = 0.46 \text{ nm}. \) Figure 5(d) shows the EDS spectrum of the acicular α-Ti, revealing that it comprised 54.0 at.% Ti, 13.4 at.% Zr, and 32.8 at.% O. Figure 5(e) shows the EDS spectrum of the β'-Ti, consisting of 58.1 at.% Ti, 30.7 at.% Zr, and 11.2 at.% O. As Zr is a stabilizer of β-titanium, it is not surprising that β'-Ti(Zr, O) contains much more Zr than α-Ti(Zr, O) does.

Figure 6(a) also shows the TEM micrograph (BFI) of the reaction layer “D” viewed in the direction normal to the interface of Ti and ZrO₂ after reaction at 1550 °C/6 h. Another orientation relationship of the acicular α-Ti and the β'-Ti was identified by the superimposed SADPs (Fig. 6(b)). The SADPs were redrawn and indexed in Fig. 6(c). The orientation relations were recognized as follows: [2110]₀₀₀₁ // [021]β'-Ti, and (0001)₀₀₀₁ // (112)β'-Ti. Figure 6(d) displays the image, taken from the high-resolution transmission electron microscopy (HRTEM), of the acicular α-Ti and the β'-Ti. The \( d \)-spacing of the plane (0110) for α-Ti was equal to 0.50 nm, while that of the (312) plane for β'-Ti was equal to 0.28 nm. The high-resolution image, as shown in Fig. 6(e), of the marked area in Fig. 6(d) was simulated by a computer program (Digital Micrograph 3.3, Gatan Inc., Pleasanton, CA). It indicated that the ledge mechanism (labeled as “L”) was probably the favorable precipitation mechanism of α-Ti from the matrix of β'-Ti. The ledge mechanism was frequently encountered in the partially coherent interface, consisting of many sets of edge dislocations or misfit dislocations. When the crystal structures of the matrix and the precipitate were different to a signif-
Based alloy. It was likely that the acicular phase dissolved a large amount of zirconium and oxygen, which can be expressed as follows:

$$\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_{2-x} + \beta'\text{-Ti(Zr, O)} \quad (3)$$

$$\beta'\text{-Ti(Zr, O)} \xrightarrow{\text{cooling}} \beta'\text{-Ti(Zr, O)} \quad (8)$$

In contrast, $\beta'$-Ti (gray) and $c\text{-ZrO}_{2-x}$ (bright, either rounded or Chinese script like) coexisted in the reaction layer “F.” On performing EPMA analyses, it was found that this $\beta'$-Ti contained 46.72 at.% Ti, 27.00 at.% Zr and 26.28 at.% O; meanwhile, the Chinese-script-like $c\text{-ZrO}_{2-x}$ contained 2.36 at.% Ti, 20.92 at.% Zr, 66.87 at.% O, and 9.84 at.% Y, displaying a large amount of yttrium, an effective stabilizer of $c\text{-ZrO}_{2-x}$. This is the reason why the zirconia was cubic symmetric in crystal structure. A few small rounded $c\text{-ZrO}_{2-x}$ grains were scattered near the interface, as $c\text{-ZrO}_{2-x}$ grains were extensively dissolved into titanium. On the right-hand side of Fig. 7, a Chinese-script-like $c\text{-zirconia phase (resembling the stroke of a calligraphic brush) was surrounded by the } \beta'\text{-Ti. The reason why } c\text{-ZrO}_{2-x} \text{ became Chinese script like was still unclear at present. It was believed that zirconium was excluded from the metastable oxygen-deficient zirconia during cooling. However, no } \alpha\text{-Zr was found in the reaction layer “F” like in the reaction layer “G,” as zirconium went into the solid solution in } \beta'\text{-Ti } (O, \text{ Zr). The formation mechanisms in the reaction layer “F” can be expressed as follows:}$

$$\text{ZrO}_2 + \text{Ti} \xrightarrow{\text{heating}} \text{ZrO}_{2-x} + \beta'\text{-Ti(Zr, O)} \quad (3)$$

$$\text{ZrO}_{2-x} \xrightarrow{\text{cooling}} \alpha\text{-Zr} + c\text{-ZrO}_{2-y(y<x)} \quad (9)$$

$$\alpha\text{-Zr} + c\text{-ZrO}_{2-y(y<x)} + \beta'\text{-Ti(Zr, O)} \quad (10)$$

Figure 8 displays the backscattered electron image and various characteristic X-ray maps of the reaction layer “F” after reaction at 1550°C/6 h. The X-ray mapping of Y in Fig. 8(b) indicates that yttrium was hardly dissolved in titanium and then remained in both small spherical and Chinese-script-like zirconia. This is consistent with the results reported by Zhu et al., who found that the yttrium element congregated and remained at the interface to form a high Y$_2$O$_3$ content of ZrO$_2$ when ZrO$_2$ reacted with molten titanium. The distributions of Ti, Zr, and O elements in the reaction layer “F” (Figs. 8 (c)-(e)) indicate that a significant amount of titanium diffused into the ceramic side and reacted with zirconia to form $\beta'$-Ti(Zr, O).

Figure 9(a) displays the backscattered electron image of the reaction layer “G” in the zirconia side far away from the interface after reaction at 1550°C/6 h. The distributions of Y, Ti, Zr, and O elements in the interface are demonstrated by individual characteristic X-ray mappings in Figs. 9(b)-(e), respectively. It
indicates that a significant amount of oxygen was dissolved in α-Zr (bright), with both yttrium and titanium being hardly dissolved in α-Zr. From the EMPA analyses, the α-Zr in the reaction layer “G” contained 1.05 at.% Ti, 57.54 at.% Zr, 40.73 at.% O, and 0.68 at.% Y, corresponding with α-Zr (O). Because the content of Zr in c- or t-ZrO_{2-x} declined as the temperature decreased, as shown in the Zr–O phase diagram, the α-Zr was segregated on grain boundaries during cooling by the exsolution of zirconium from ZrO_{2-x}, causing an increase in the O/Zr ratio of oxygen-deficient zirconia.

The c-ZrO_{2-x} and the lenticular t-ZrO_{2-x} were observed in the gray region (Fig. 9(a)). It was believed that the specimen was cooled down from the two-phase (c+t) region in the ZrO_{2}-Y_{2}O_{3} phase diagram. The fact that the lenticular t-ZrO_{2} with three variants was transformed in the c-ZrO_{2-x} had been reported by several previous studies. Lin and Lin further found that the lenticular t-ZrO_{2-x} was formed in an ordered c-ZrO_{2-x}. It was worth noting that zirconia grains with a concentrated yttrium (Fig. 9(b)) had a cubic symmetry in crystal structure. The formation mechanisms in the reaction layer “G” can be expressed as follows:

\[
\begin{align*}
\text{ZrO}_2 + \text{Ti} & \xrightarrow{\text{heating}} \text{ZrO}_{2-x} + \beta-\text{Ti(O)} \\
\text{ZrO}_{2-x} & \xrightarrow{\text{cooling}} \alpha-\text{Zr(O)} + c-\text{ZrO}_{2-y(\gamma < x)} + t-\text{ZrO}_{2-y(\gamma < x)}
\end{align*}
\]  

Based upon the foregoing results and discussion, the individual phases and formation mechanisms of the distinct reaction layers in the reaction-affected zone between titanium and zirconia have been summarized in Table I.

(2) Proposed Model of Microstructural Evolution

Even though extensive studies were carried out on the interface reaction between titanium and zirconia, the microstructure
evolution has not yet been elucidated to date. The information with regard to the relationships between the ternary constitution and the microstructures produced by isothermal diffusion among three elements is very sparse. In the present study, an attempt has been made to infer the microstructure resulting from isothermal diffusion among titanium and zirconia with the aid of the Ti–Zr–O ternary phase diagram. However, only the isothermal Ti–Zr–O ternary phase diagram at 1450°C (not 1550°C) has been found in the literature. Assuming that the compositions of the solid phases are approximated as constant between 1450° and 1550°C, the interpretation of the microstructure at the interface between Ti and ZrO2 in terms of the Ti–Zr–O phase diagram can be reasonably determined. The Ti–Zr–O phase diagram and the diffusion couple are somewhat different chemically. The ZrO2 contains 3 mol% Y2O3, so it is out of the Ti–Zr–O ternary system. However, this probably does not have much effect on the results, and the effect may be negligible in this study.

Figure 10 shows the microstructural evolution at the interface between a titanium and zirconia diffusion couple after annealing at 1550°C based upon the observation and analyses mentioned above. Figure 10(a) illustrates the titanium and zirconia diffusion couple prior to the anneal heat treatment, indicating the original interface and finely distributed ZrO2 grains. When titanium was held in contact with zirconia at high temperatures, various diffusion layers developed.

By cross examining the experimental results and the ternary phase diagram, it was proposed that all gross compositions, in various vertical slices along the longitudinal direction perpendicular to the interface, lay upon the line a–b–c–d–e, or the so-called diffusion path, in the Ti–Zr–O ternary system at 1450°C. As shown in Fig. 10(b), the diffusion path crosses the fields of β-Ti, α-Ti+z-Ti, β-Ti, β-Ti+t–ZrO2, α-Zr+β-Ti+t–ZrO2, and α-Zr+t–ZrO2.

It is well known that the ddivariant or three-phase regions in the ternary phase diagram are simply in correspondence to the
that the diffusion path passed the region of two-phase region when the Ti/ZrO₂ diffusion couple was isothermally annealed at 1550°C. As a result, in the Ti-ZrO₂ diffusion couple, the layers of β-Ti, α-Ti+β-Ti, β-Ti, β-Ti+i-Ti-ZrO₂, and α-Zr+i+ZrO₂ would have been observed in sequence from Ti to ZrO₂, but not the layers of α-Zr+β-Ti+i-Ti-ZrO₂. The region of α-Zr+β-Ti+i-Ti-ZrO₂ in the Ti–Zr–O ternary phase diagram was represented in the diffusion couple by the interface between the layers of β-Ti+c-ZrO₂ and α-Zr+c-ZrO₂ as shown in Fig. 10(c). Furthermore, as illustrated in Fig. 10(b), the β-Ti layer, corresponding to the layer “A,” varied in composition from Ti to βₐ. The α in the α-Ti+β-Ti layer should vary from αₐ to αₜ, and the β from βₐ to βₜ.

In the case of a Ti-ZrO₂ diffusion couple where the reaction was predominant in the initial stage and the diffusion velocities of the three components were markedly different, the diffusion path deviated from the direct path between the compositions of the end points, i.e., Ti and ZrO₂ in the present study. It was believed that the oxidation–reduction reaction in the initial stage shifted the end point in the cubic side to the two-phase region of α-Zr+β-Ti+i-Ti-ZrO₂, presumably to point e. Besides, it was unlikely that the diffusion path passed the region of α-Ti+β-Ti+i-Ti-ZrO₂ as it was impossible for such an interface to exist in between the layers of α-Ti+β-Ti and β-Ti+i-Ti-ZrO₂. It was also noted that the layer of α-Zr+β-Ti was not observed in the present study. As a consequence, the ternary diffusion path a–b–c–d–e provided the best approximation that could be made at present.

In reality, the high chemical affinity of titanium to oxygen led to the formation of oxygen-deficient zirconia (ZrO₂₋ₓ), indicating that the oxidation–reduction reaction predominated in the initial stage before the diffusion prevailed. A significant increase in oxygen vacancies, as a consequence of the oxidation–reduction reaction between titanium and zirconia, triggered the stabilization effect of zirconia. The zirconia in the Ti–Zr–O ternary phase diagram, shown in Fig. 10(b), was in the cubic phase instead of tetragonal phase when the Ti/ZrO₂ diffusion couple was isothermally annealed at 1550°C.⁶

The various layers formed during the cooling stage are displayed in Fig. 10(d). The β-Ti layer abutting the reaction-affected Ti, with a small amount of Zr in solid solution, was transformed to α-Ti (designated as layer “A”) on cooling, and the continuous lamellar Ti₃ZrO₅+α-Ti (designated as layer “B”) is attributed to the precipitation of Ti₃ZrO₅ in the metastably transformed α-Ti matrix. Ti₃ZrO₅ was precipitated from α-Ti in the α-Ti+β-Ti layer during cooling, leading to the existence of

Table I. Microstructural Features and Formation Mechanisms of Various Phases at the Interface of Ti and ZrO₂ at 1550°C

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<td>“D”</td>
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<td>“G”</td>
<td>α-Zr(O)</td>
<td>Eqs. (1) and (11)</td>
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IV. Conclusions

1. The diffusional reaction between titanium and zirconia was carried out at 1550°C in argon. On the metal side, there existed five reaction layers in a sequence of α-Ti(O), Ti₃ZrO₅+α-Ti(O, Zr), Ti₃ZrO₅+α-Ti(O, Zr)+β'-Ti(O, Zr), α-Ti(O, Zr)+β'-Ti (O, Zr), and β'-Ti(Zr, O) after cooling.
2. On the zirconia side, two reaction layers were found: near the original interface, \(\beta'-\text{Ti}\) coexisted with fine spherical \(c-ZrO_2\), and Chinese-script-like \(c-ZrO_2\), further away from the original interface, coarsened intergranular \(\alpha'-\text{Zr}\), lenticular \(c-ZrO_2\), and ordered \(c-ZrO_2\), were found.

3. The acicular \(\alpha'/\gamma\) and the \(\beta'/\gamma\) showed different orientation relations. One of the orientation relations was determined to be \([2110]_{\alpha'/\gamma} / / [001]_{\beta'/\gamma}\) and \((0001)_{\gamma} / / (100)_{\beta'/\gamma}\) and the other was \([2110]_{\alpha'/\gamma} / / [021]_{\beta'/\gamma}\) and \((0001)_{\gamma} / / (112)_{\beta'/\gamma}\).

4. Based upon the experimental results in this study, the diffusion path, connecting phases formed by the reaction between Ti and ZrO\(_2\), was drawn on the Ti–Zr–O ternary phase diagram, and the microstructures produced by isothermal diffusion between Ti and ZrO\(_2\) at 1550 °C has been provided.

Acknowledgments

The authors would like to thank Mr. Chi-Ming Wen at the Chung-Shan Institute of Science and Technology for preparing the hot-pressed specimens.

References