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Effects of Annealing Temperature on Microstructural Development at the Interface Between Zirconia and Titanium

Kun-Lin Lin and Chien-Cheng Lin*,†

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan

The interfacial reaction layers in the Ti/ZrO_2 diffusion couples, isothermally annealed in argon at temperatures ranging from 1100° to 1550°C for 6 h, were characterized using scanning electron microscopy and transmission electron microscopy, both attached with an energy-dispersive spectrometer. Very limited reaction occurred between Ti and ZrO_2 at 1100°C. A β'-Ti(Zr, O) layer and a two-phase α-Ti(O)+β'-Ti(Zr, O) layer were found in the titanium side after annealing at $T \geq 1300$°C and $T \geq 1400$°C, respectively. A three-phase layer, consisting of $Ti_2ZrO+\alpha$-Ti(O, Zr)+β'-Ti (O, Zr), was formed after annealing at 1550°C. In the zirconia side near the original interface, β'-Ti coexisted with fine spherical c-ZrO_{2-x}, which dissolved a significant amount of Y_2O_3 in solid solution at $T \geq 1300$°C. Further into the ceramic side, the α-Zr was formed due to the exsolution of Zr out of the metastable ZrO_{2-x} after annealing at $T \geq 1300$°C: the α-Zr was very fine and dense at 1300°C, continuously distributed along grain boundaries at 1400°C, and became coarsened at 1550°C. Zirconia grains grew significantly at $T \geq 1400$°C, with the lenticular t-ZrO_{2-x} being precipitated in c-ZrO_{2-x}. Finally, the microstructural development and diffusion paths in the Ti/ZrO_2 diffusion couples annealed at various temperatures were also described with the aid of the Ti–Zr–O ternary phase diagram.

I. Introduction

THE interfacial reactions between titanium and zirconia have been studied in the past several decades.[1–3] It is generally accepted that the oxygen of zirconia is readily dissolved into the titanium to form α-Ti(O), resulting in the blackening of oxygen-deficient zirconia (ZrO_{2-x}). Various reaction layers in the interface between titanium and zirconia were found.[4,5] However, they were not fully explored because of the limitations of the analytical instruments. Meanwhile, some researchers[6,7] indicated that the titanium additive could improve the mechanical properties of zirconia including strength and thermal shock resistance.

Recently, Lin and colleagues[8–13] have thoroughly investigated the diffusional reactions between titanium (or titanium alloys) and zirconia. Using transmission electron microscopy (TEM)/energy-dispersive spectrometer (EDS) analyses, they indicated that the ordered titanium suboxide (Ti_3O) and the orthorhombic lamellae Ti_2ZrO were formed in the solid solution of α-Ti(O) between zirconia and titanium melt during cooling from 1700°C.[9] In addition, the orthorhombic β'-Ti(Zr, O) and a spherical-ordered Ti_2ZrO phase were also found in the metal side of the Ti/ZrO_2 diffusion couple after annealing at 1550°C.[11] The orientation relations between α-Ti(Zr, O) and lamellae

Ti_2ZrO were determined to be $[0001]_{\alpha-Ti}//[110]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha-Ti}//(1\bar{1}0)_{Ti_2ZrO}$; meanwhile, those between α-Ti(O) and spherical-ordered Ti_2ZrO were $[0001]_{\alpha-Ti}//[0001]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha Ti}//(10\bar{1}0)_{Ti_2ZrO}$.[11] Furthermore, the acicular α-Ti(O) was precipitated in the β'-Ti(O, Zr) matrix with two various orientation relations in the metal side.[13] One was determined to be $[2\bar{1}\bar{1}0]_{\alpha-Ti}//[001]_{\beta'-Ti}$ and $(0001)_{\alpha-Ti}//(100)_{\beta'-Ti}$ and the other $[2\bar{1}\bar{1}0]_{\alpha-Ti}//[021]_{\beta'-Ti}$ and $(0001)_{\alpha-Ti}//(1\bar{1}2)_{\beta'-Ti}$.[13] In the zirconia side, far away from the interface of Ti/ZrO_2, Lin and Lin[12] also observed twinned t'-ZrO_{2-x}, lenticular t-ZrO_{2-x}, and/or ordered c-ZrO_{2-x} as well as the intergranular α-Zr after annealing at 1550°C.

Even though extensive studies were carried out on the interface reactions between titanium and zirconia, the temperature effects on the microstructure evolution have not been well known to date. In order to shed light on the temperature effects on the microstructural evolution of the various distinct reaction layers between titanium and zirconia, the Ti/ZrO_2 diffusion couples were isothermally annealed in argon at 1100°, 1300°, 1400°, and 1550°C, respectively, for 6 h in the present study. Various microstructures were characterized using scanning electron microscopy (SEM) and TEM, both attached with an EDS. Through the comparison among various microstructures, an attempt was made to propose the microstructural development of the reaction layers between titanium and zirconia at various annealing temperatures, while diffusion paths were depicted in the Ti–Zr–O ternary phase diagram.

II. Experimental Procedures

(1) Sample Preparation

Bulk ZrO_2 specimens were prepared from the powder of 3 mol% Y_2O_3 partially stabilized zirconia by the hot press (Model HP50-MTG-7010, Thermal Technology Inc., Santa Rosa, CA). The nominal composition of the zirconia powder was supplied by the vendor (Toyo Soda Mfg. Co., Tokyo, Japan) as follows: >94 wt% ZrO_2+HfO_2 (accounting for approximately 2%–3% of this total), 5.4 wt% Y_2O_3, <0.001 wt% Fe_2O_3, <0.01 wt% SiO_2, <0.005 wt% Na_2O, <0.005 wt% TiO_2, <0.02 wt% Cl, and <0.005 wt% SO_4^{2-}. Both as-hot-pressed ZrO_2 specimens and commercially available titanium billets (with a nominal composition of 99.31 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 to the dimensions of 14 mm × 14 mm × 5 mm. One Ti billet was inserted in between two ZrO_2 specimens to form a sandwiched sample, which was then slightly pressed and annealed at 1100°, 1300°, 1400°, and 1550°C, respectively, for 6 h in an atmospheric argon. The hot-pressing procedures of both bulk ZrO_2 and the sandwiched samples have been described in detail elsewhere.[11]

(2) SEM/EDS Analyses

A SEM (Model JSM-6330F, JEOL Ltd., Tokyo, Japan) equipped with an EDS (Mode ISIS300, Oxford Instrument Inc., London, U.K.) was used for the microstructural observation on the interface between titanium and zirconia. Both

backscattering electron image (BEI) and secondary electron image (SEI) were acquired. Cross-sectional specimens were cut into about 3 mm × 2 mm × 1 mm, and then ground and polished using a diamond paste down to 1 μm. The specimens for the SEI observation were etched by the Kroll reagent (10 mL HF+30 mL HNO_3+60 mL H_2O) for 15 s. In order to avoid electric charging under the electron beam, specimens were coated with a thin layer of platinum.

(3)   TEM/EDS Analyses

A TEM (Model JEM 2000Fx, JEOL Ltd.) equipped with an EDS (Mode ISIS300, Oxford Instrument Inc.) was also used for characterizing the interfacial microstructure between titanium and zirconia. Cross-sectional TEM specimens perpendicular to the interface of titanium and zirconia were cut, ground, and polished by standard procedures as mentioned previously.[11] The TEM specimens were dimpled and ion milled by a precision ion miller (Model 691, Gatan Inc., Pleasanton, CA). The quantitative composition analyses were carried out based on the principle of the Cliff–Lorimer standardless technique.[14]

III.   Results and Discussion

(1)   Distinct Microstructures at Various Temperatures

The microstructure of the Ti/ZrO_2 interface strongly depended on the annealing temperature. Figures 1(a)–(d) display the BEIs of the cross section normal to the Ti/ZrO_2 interface after annealing at 1100°, 1300°, 1400°, and 1550°C for 6 h, respectively. Titanium was in the left-hand side, while zirconia was on the other side. The vertical arrows in the upper side of individual figures indicate the original interfaces of Ti and ZrO_2. The original interfaces were deliberately located by the results of characteristic K_α X-ray maps of yttrium (not shown), which were relatively immobile compared with elements Zr, O, and Ti.

(A)   *Reaction Layer "I" of the Ti/ZrO_2 Interface:*   A gray thin layer (designated as the reaction layer "I") was formed in the interface between Ti and ZrO_2 at temperatures $T \geq 1400°C$ as shown in Figs. 1(c) and (d). The reaction layers "I" in Figs. 1(a) and (b) were invisible because of the limited resolution; however, they could be observed using SEM or TEM at a higher magnification [Figs. 2(a) and 3]. To the left of the reaction layer "I" was the α-Ti with oxygen in solid solution, designated as α-Ti(O) in this study.

Figure 2 displays the SEIs of the lamellar α-Ti (Zr, O) and Ti_2ZrO in the reaction layer "I" etched by Kroll reagent (10 mL HF+30 mL HNO_3+60 mL H_2O) after annealing at 1300°,

1400°, and 1550°C, respectively. The thickness of the reaction layer "I" increased with temperature. Figure 2 shows clearly, at a higher magnification, the very different microstructures developed at various anneal temperatures. For example, the sequence of the reaction layers I+IV+... [Fig. 2(a)] was formed after annealing at 1300°C, while the sequence of the reaction layers I+III+... [Fig. 2(b)] and the sequence of the reaction layers I+II+... [Fig. 2(c)] were formed after annealing at 1400° and 1550°C, respectively.

For the benefit of good resolution of TEM, a very thin reaction layer "I" was found in the Ti/ZrO_2 interface after annealing at 1100°C for 6 h. Figure 3(a) displays the TEM micrograph of the cross section between Ti and ZrO_2 after annealing at 1100°C for 6 h. The arrow indicates the original interface, with titanium and zirconia being in the upper and lower sides, respectively. Their morphologies were very different from results in previous studies after annealing at 1550° or 1700°C.[9,11] The SADPs as shown in Fig. 3(b) indicated that the lamellar phases were composed of orthorhombic Ti_2ZrO and hexagonal disordered α-Ti(Zr, O). The orientation relationship of Ti_2ZrO and α-Ti(Zr, O) could be expressed as follows: $[0001]_{\alpha-Ti}//[110]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha-Ti}//(1\bar{1}0)_{Ti_2ZrO}$. The EDS, shown in Fig. 3(c), indicated that the Ti_2ZrO consisted of 56.1 at.% Ti, 22.9 at.% Zr, and 21.0 at.% O.

(B)   *Reaction Layer "II" of the Ti/ZrO_2 Interface:*   The lamellar α-Ti(Zr, O) and Ti_2ZrO along with β'-Ti(Zr, O) (designated as the reaction layer "II"), as indicated previously,[11] were observed in the Ti/ZrO_2 interface after annealing at 1550°C/6 h [Fig. 1(d)]. In contrast, no such lamellar structure was found in the samples after annealing between 1100° and 1400°C.

(C)   *Reaction Layer "III" of the Ti/ZrO_2 Interface:*   The two-phase acicular α-Ti(Zr, O)+β'-Ti(Zr, O) layers (designated as the reaction layer "III") after annealing at 1400° and 1550°C are shown in Figs. 1(c) and (d), respectively. The reaction layer "III" appeared as a relatively minor layer at 1550°C compared with the reaction layer "II," as shown in Fig. 1(d). At a higher magnification, it was seen that the amount of acicular α-Ti(Zr, O) gradually decreased toward the original interface.[13] Lin and Lin[13] indicated that the acicular α-Ti was precipitated from the β'-Ti matrix by means of the ledge mechanism. In contrast, the reaction layer "III" was not found after annealing at 1100° or 1300°C.

(D)   *Reaction Layer "IV" of the Ti/ZrO_2 Interface:*   The region to the nearest left of the original interface dissolved a higher concentration of Zr in Ti. No acicular α-Ti(Zr, O) was thus observed in this region as the zirconium was an effective stabilizer of β-Ti. Figures 1(b)–(d) show that a continuous
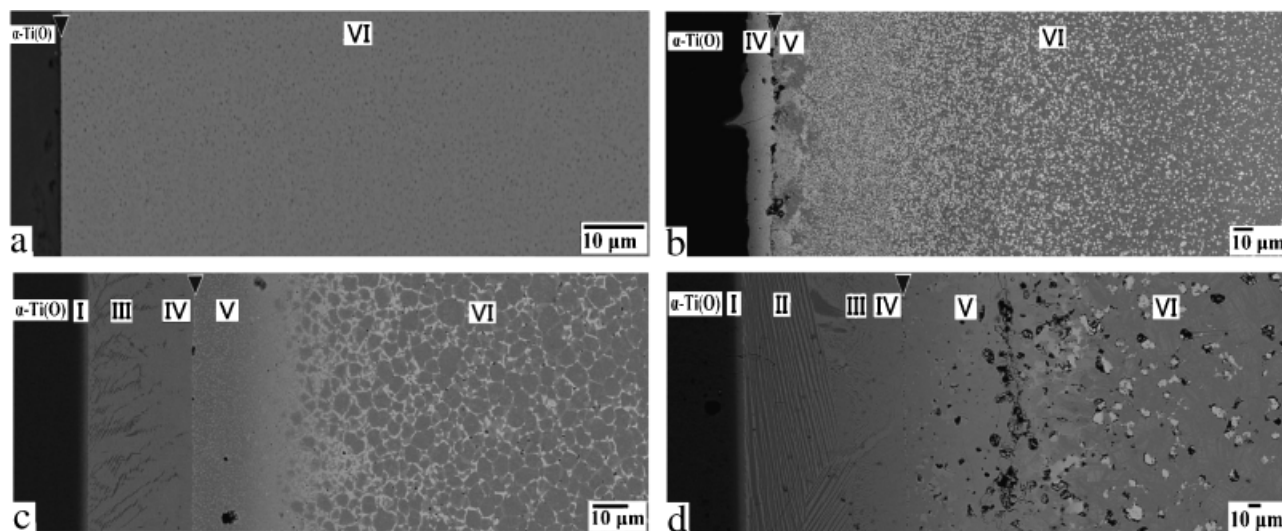

Fig. 1.   Scanning electron microscopy micrographs (backscattered electron images) showing the interface of Ti and ZrO_2 after annealing for 6 h at (a) 1100°C, (b) 1300°C, (c) 1400°C, and (d) 1550°C. The vertical arrows in the upper side indicate the original interface. The interface reaction layers were designated as the reaction layers "I," "II," "III," "IV," "V," and "VI," respectively.
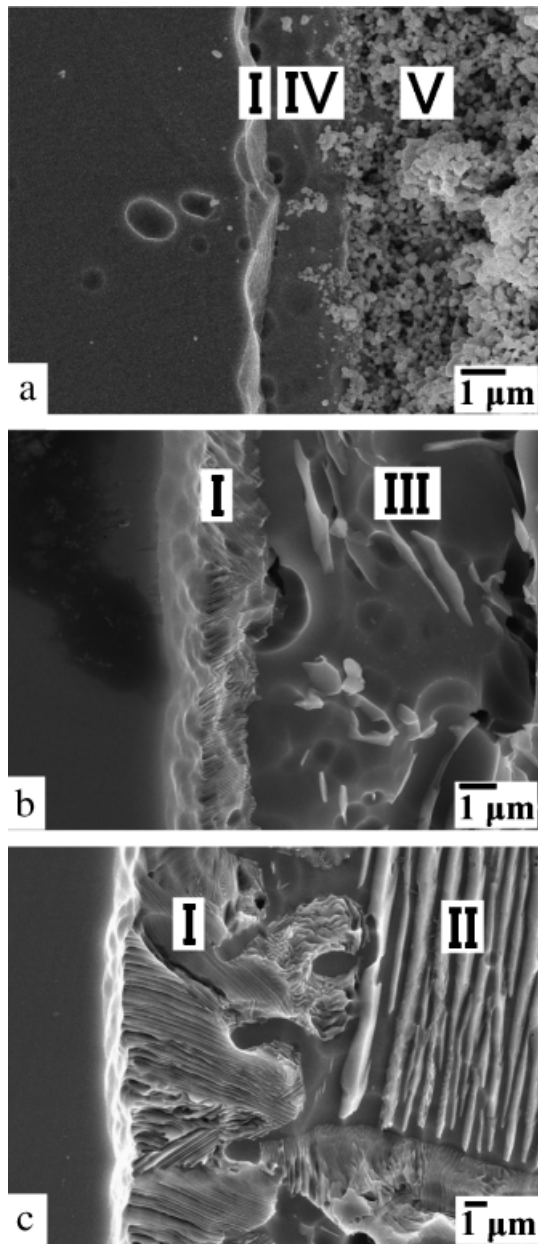
Fig. 2. Scanning electron microscopy micrographs (secondary electron images) showing the variation of the reaction layer "I" after annealing at (a) 1300°C, (b) 1400°C, and (c) 1550°C, respectively.

β'-Ti(Zr, O) layer (designated as the reaction layer "IV") was formed in the metal side abutting the original interface after annealing at temperatures ranging from 1300° to 1550°C. No reaction layer "IV" was observed after annealing at 1100°C as the reaction was quite limited.

(E) Reaction Layer "V" of the Ti/ZrO₂ Interface: Figure 1 also demonstrates very distinct microstructures in the ceramic side after annealing at various temperatures. At 1100°C, the anneal temperature was so low that no apparent interfacial reaction was noticeable. At $T \geq 1300$°C, zirconia was gradually dissolved in titanium so that residual fine spherical c-ZrO₂ existed in the matrix of β'-Ti(Zr, O). The spherical zirconia contained a significant amount of Y₂O₃, resulting in the stabilization of c-ZrO$_{2-x}$ (designated as the reaction layer "V") as shown particularly in Figs. 1(c) and (d). It was believed that, at high temperatures such as 1400° or 1550°C, the chemical reaction-enhanced dissolution of ZrO₂ into Ti was an important mechanism that dominated in the reaction layer "V."

Figure 4(a) shows the bright-field image (BFI) of the reaction layer "V" after annealing at 1400°C for 6 h. The reaction
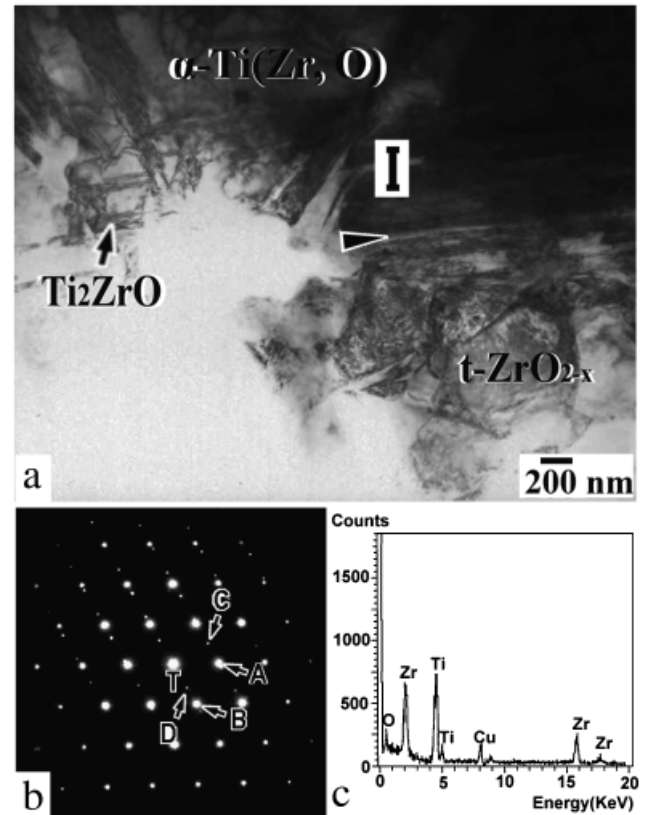

Fig. 3. (a) Transmission electron microscopy micrograph (bright-field image) showing the reaction layer "I" with the coexistence of α-Ti and Ti₂ZrO after annealing at 1100°C/6 h. (b) selected area diffraction patterns of the α-Ti and Ti₂ZrO, indicating that $[0001]_{\alpha-Ti}//[110]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha-Ti}//(1\bar{1}0)_{Ti_2ZrO}$ (A = $(01\bar{1}0)_{\alpha-Ti}$, B = $(10\bar{1}0)_{\alpha-Ti}$, C = $(00\bar{2})_{Ti_2ZrO}$, D = $(1\bar{1}0)_{Ti_2ZrO}$); (c) an energy-dispersive spectrum of Ti₂ZrO.

"V," in the outermost region of the original zirconia, consisted of β'-Ti(Zr, O) and c-ZrO$_{2-x}$. In this layer, zirconia was dissolved into titanium and became rounded in shape, resulting in β-Ti with oxygen and zirconium in solid solution. As the solubility of yttrium (or the stabilizer of ZrO₂ in the present study) in titanium was quite limited, yttrium was retained in the residual cubic zirconia. It was consistent with the results reported by Zhu *et al.*,[5] who found that yttrium element congregated and remained at the interface to form a high-Y₂O₃ content of ZrO₂, when ZrO₂ reacted with molten titanium. After annealing at 1550°C for 6 h, the β'-Ti(Zr, O) in the reaction layer "V" became an ordered phase during cooling. In Fig. 4(b), the ordered β'-Ti(Zr, O) phase displayed a high strain-field contrast because of the lattice distortion. Figures 4(c) and (d) show the SADPs of β'-Ti(Zr, O) with the incident electron beam along the zone axes of [021] and [$\bar{1}$12], respectively. The ordered structure was characterized by the $\{\bar{1}11\}$ superlattice reflections of β'-Ti(Zr, O). In contrast, the β'-Ti(Zr, O) phase in the layer "V," formed after annealing at 1400°C, did not experience the order–disorder phase transformation.

(F) Reaction Layer "VI" of the Ti/ZrO₂ Interface: At high temperatures, the oxidation–reduction reaction resulted in the formation of metastable oxygen-deficient zirconia (ZrO$_{2-x}$). Then, α-Zr would be excluded from this metastable ZrO$_{2-x}$ onto the grain boundaries of zirconia during the subsequent cooling. In the layer "VI" as shown in Figs. 1(b)–(d), the α-Zr co-existed with tetragonal and/or cubic zirconia. At 1300°C, the negligible grain growth of zirconia resulted in the very fine and dense α-Zr as shown in Fig. 1(b). For the sample after annealing at 1400°C, zirconia grains were delineated by the continuously distributed intergranular α-Zr [Fig. 1(c)], indicating a significant degree of grain growth. In addition to the apparent grain growth of
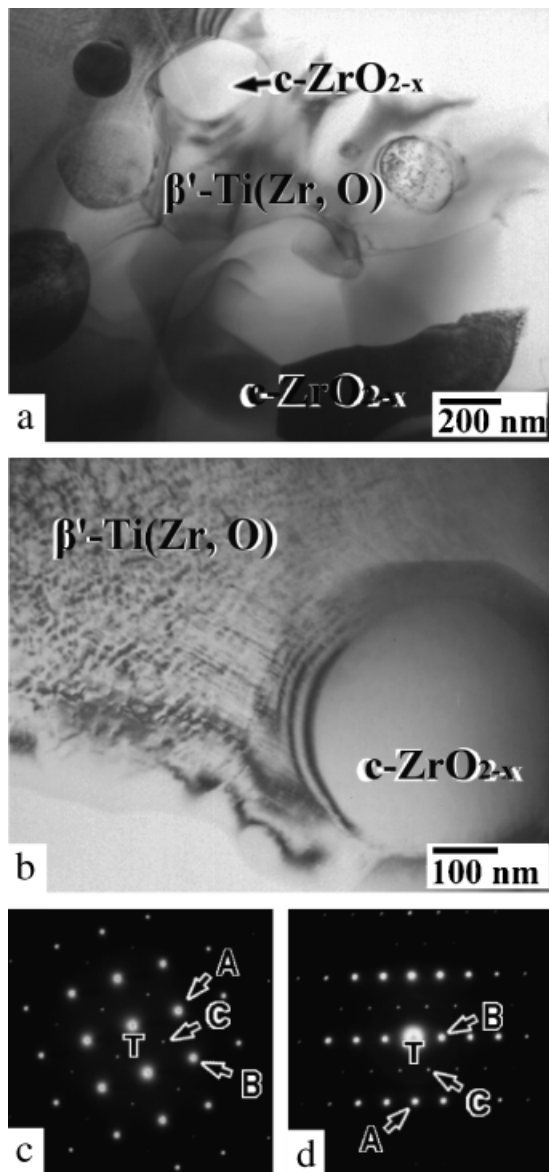
Fig. 4. Transmission electron microscopy micrograph (bright-field image) of the reaction layer "V" consisting of β'-Ti and c-ZrO$_{2-x}$ after annealing at (a) 1400°C/6 h; (b) at 1550°C/6 h; (c) a selected area diffraction pattern of β'-Ti in Fig. 4(b) (zone axis is [021], A = ($\bar{2}$00), B = ($2\bar{2}\bar{2}$), and C = ($\bar{1}1\bar{1}$)); (d) an SADP of β'-Ti in Fig. 4(b) (zone axis is [$\bar{1}$12], A = ($\bar{1}3\bar{2}$), B = ($\bar{1}\bar{1}$0), and C = ($\bar{1}$1$\bar{1}$)).

zirconia, the intergranular α-Zr was coarsened and became isolated, as shown in Fig. 1(d), after annealing at 1550°C.

In the reaction layer "VI," the oxidation–reduction reaction rather than dissolution is the predominant mechanism in the reaction layer "VI." The dissolution played an insignificant role in the formation of the reaction layer "VI" as titanium was not detected by EDS in this layer. Figures 5(a)–(d) show the BFIs of the reaction layer "VI" after annealing at 1100°, 1300°, 1400°, and 1550°C for 6 h, respectively. After annealing at 1100°C/6 h, the limited reaction resulted in t-ZrO$_{2-x}$, as it was in as-hot-pressed samples, with no intergranular α-Zr and insignificant grain growth of zirconia [Fig. 5(a)]. At 1300°C/6 h, the t-ZrO$_{2-x}$ remained with a slight grain growth (grain size about 1–2 μm), while the dense fine α-Zr was formed by the exsolution of Zr from the metastable t-ZrO$_{2-x}$ [Fig. 5(b)]. After annealing at 1400° or 1550°C, it was found that the lenticular t-ZrO$_{2-x}$ with two variants precipitated in the ordered c-ZrO$_{2-x}$ [Figs. 5(c) and (d)], which was stabilized by the extensive oxygen vacancies. The ordered c-ZrO$_{2-x}$ was recognized by the 1/5{113} superlattice reflections. The grain sizes of zirconia after annealing at 1400°

and 1550°C were about 8–10 and 20–30 μm, respectively, indicating rapid grain growth on annealing.

The microstructures of the reaction layer "VI" strongly depended upon annealing temperature in the following respects: (1) the grain growth of zirconia; (2) the exsolution of α-Zr onto the grain boundaries of zirconia; and (3) the morphologies and crystal structures of zirconia. The microstructural features of the reaction layer "VI" are summarized in Table I.

It was also noted that a large amount of the pores existed in the ceramic side after annealing at $T \geq 1300$°C. The formation of these pores was attributed to the Kirkendall effect, because zirconium and oxygen diffused to the titanium side much faster than titanium did toward the zirconia side in the opposite direction.

(G) Formation of the Ti$_3$O Suboxide in α-Ti(O): In contrast to a limited diffusion range of zirconium (up to the reaction layer "I"), oxygen showed a relatively long diffusion range (well beyond the reaction layer "I"). Rather than forming a distinct layer with a specific thickness, the oxygen concentration of α-Ti(O) decayed gradually across a wide region. During cooling, the hexagonal phases of ordered titanium suboxides such as Ti$_2$O, Ti$_3$O, and possibly Ti$_6$O might be formed within an extended range, as shown in the Ti–O phase diagram.[15] In this study, only the ordered Ti$_3$O resulted from the transformation of α-Ti(O) during cooling because of the extended reaction between titanium and zirconia at 1400° or 1550°C. However, no such suboxide was found in those samples after annealing at 1100° or 1300°C.

Figure 6 shows that Ti$_3$O contained stacking faults and dislocations in α-Ti(O) abutting the reaction layer "I" after annealing at 1550°C for 6 h. The inset in the upper right corner shows the SADP of the hexagonal Ti$_3$O with the electron beam parallel to the zone axis of [1$\bar{2}$10]. The superlattice reflections (0002), (10$\bar{1}$1), and (20$\bar{2}$1) indicate that cell dimension along the c-axis of the superlattice should be twice that of the Ti cell, but not three times as proposed by Jostsons and Malin[16] and Lin and Lin.[9] The ordered structure of Ti$_3$O observed in this study coincided with the model proposed by Holmberg[17] and Yamaguchi.[18] It revealed that the lattice parameters of Ti$_3$O were $a = \sqrt{3}a_o$ and $c = 2c_o$, where a_o and c_o were those of the Ti unit cell.

(2) Temperature Effect on Microstructural Development

The microstructural development between titanium and zirconia can be explained by the isothermal Ti–Zr–O ternary phase diagram at 1450°C, as shown in Fig. 7, because the compositions of the solid phases are approximately constant between 1300° and 1550°C.[19] The solid, dashed, and dotted lines (marked as "1," "2," and "3," respectively) in Fig. 7(a) are the diffusion paths, which connect all gross compositions at various cross sections along the longitudinal direction perpendicular to the interface of Ti/ZrO$_2$ on annealing at 1550°, 1400°, and 1300°C, respectively.

The diffusion path 3 at 1300°C (dotted line) crosses the fields of β-Ti, β-Ti+t-ZrO$_2$, α-Zr+β-Ti+t-ZrO$_2$, and α-Zr+t-ZrO$_2$. It is noted that the region of α-Zr+β-Ti+t-ZrO$_2$ in the Ti–Zr–O ternary phase diagram corresponds to the interface between the layers of β-Ti+t-ZrO$_2$ and α-Zr+t-ZrO$_2$. The reaction layers of β-Ti, β-Ti+t-ZrO$_2$, and α-Zr+t-ZrO$_2$ are in sequence from Ti to ZrO$_2$ in the Ti/ZrO$_2$ diffusion couple on annealing at 1300°C, as shown on the left of Fig. 7(b). The final microstructure after cooling from 1300°C is schematically shown on the right of Fig. 7(b).

The formation of β-Ti on annealing at 1300°C as well as its transformation during cooling can be described as follows: on annealing at 1300°C, O and Zr were dissolved into Ti, leading to the formation of β-Ti(Zr, O) in the titanium side. While O diffused deeply into Ti beyond the reaction layers I, resulting in a long range (up to several hundreds of micrometers) of α-Ti(O), very little Zr diffused into Ti beyond the reaction layer I. As O diffused much faster than Zr in Ti, Zr tended to accumulate in the β-Ti(Zr, O) layer (up to several tens of micrometers), causing relatively rich Zr than O in the β-Ti(Zr, O) layer. Seeing that O and Zr are the stabilizers of α and β phases, respectively, the
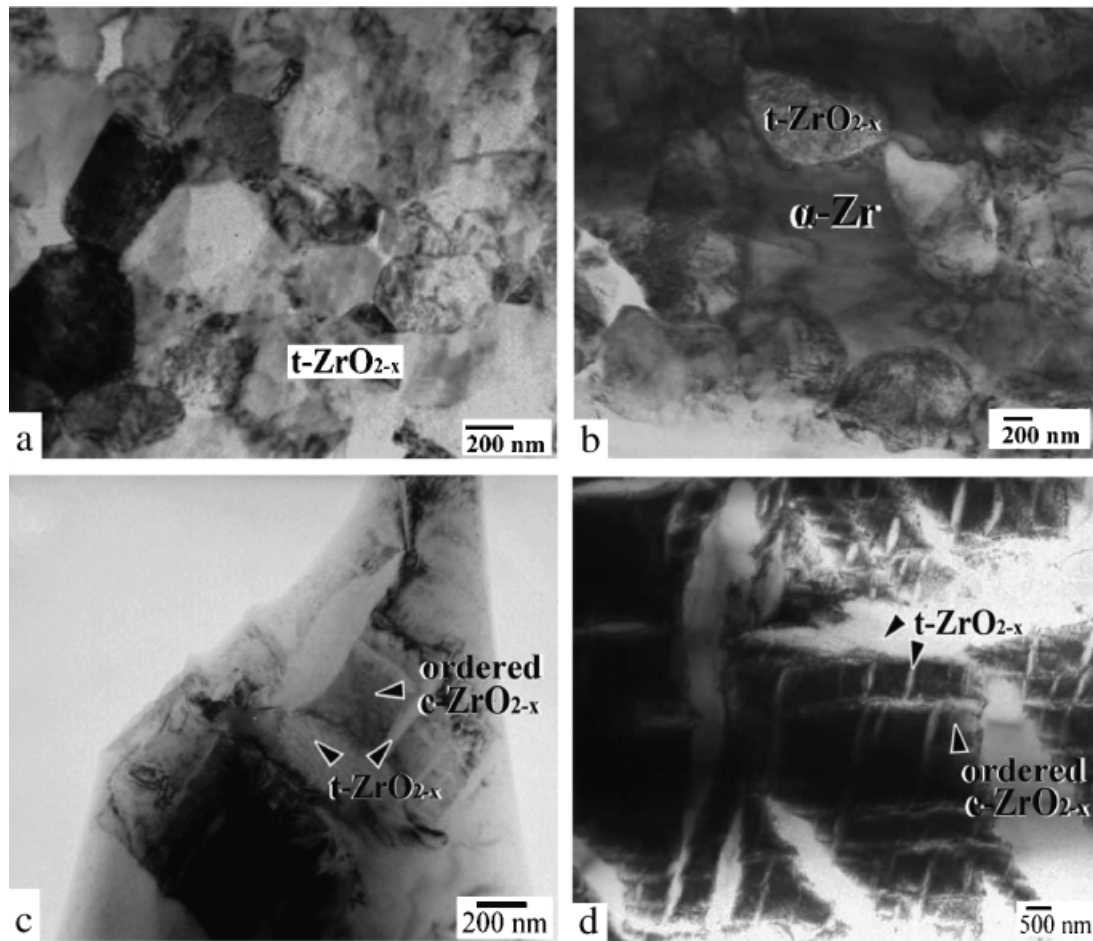
Fig. 5. Transmission electron microscopy micrograph (bright-field image) of the reaction layer "VI" far away from the original interface after annealing at (a) 1100°C, (b) 1300°C, (c) 1400°C, and (d) 1550°C, respectively, for 6 h.

Table I. Zirconia and Intergranular α-Zr in the Reaction Layer "VI"

Annealing conditions	Grain growth of zirconia and its size	Intergranular α-Zr	Morphology and crystal structure of zirconia
1100°C/6 h	Insignificant about 0.3–0.4 μm	Not found	Equiaxed t-ZrO_{2-x}
1300°C/6 h	Insignificant about 1–2 μm	Fine and dense	Equiaxed t-ZrO_{2-x}
1400°C/6 h	Significant about 8–10 μm	Continuously distributed on grain boundaries	t-ZrO_{2-x} (lenticular)+ ordered c-ZrO_{2-x}
1550°C/6 h	Significant about 20–30 μm	Isolated and coarsened on grain boundaries	t-ZrO_{2-x} (lenticular)+ ordered c-ZrO_{2-x}

Fig. 6. Transmission electron microscopy micrograph (bright-field image) of the suboxide Ti_3O near the reaction layer "I" after annealing at 1550°C for 6 h; the inset SADP of Ti_3O along the $[1\bar{2}10]$ zone axis ($A = (0004)$, $B = (30\bar{3}0)$, $C = (10\bar{1}1)$, and $D = (20\bar{2}1)$).

β-Ti(Zr, O) with a high concentration ($\approx$30 wt% in this study) of Zr remained as a distorted β phase (designated as β′) during cooling, but transformed into the α phase otherwise. In the fact that the β-Ti(Zr, O) layer was relatively rich with Zr at 1300°C, as indicated by the diffusion path 3 in Fig. 7(a), layer IV (β′) rather than layer III (α+β) was observed after cooling.

The reaction layer III existed in the interface after annealing at 1400°C, but not at 1300°C. As the β-Ti(Zr, O) formed on annealing had relatively rich O at 1400°C than at 1300°C, as
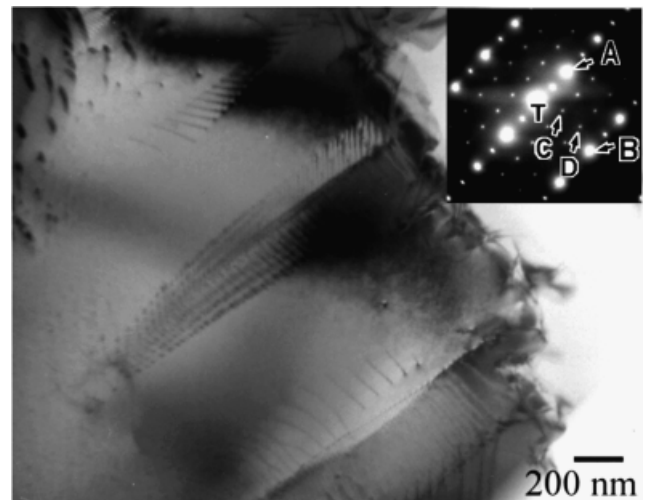
compared with diffusion paths 2 and 3, two cases took place in the β-Ti(Zr, O) during cooling from 1400°C: (1) the Zr concentration away from the original interface was so low that the acicular α phase was precipitated along with β′ (layer III); and (2) the Zr concentration close to the original interface was high enough that the β phase was stabilized and the phase transformation of β→β′ occurred (layer IV).
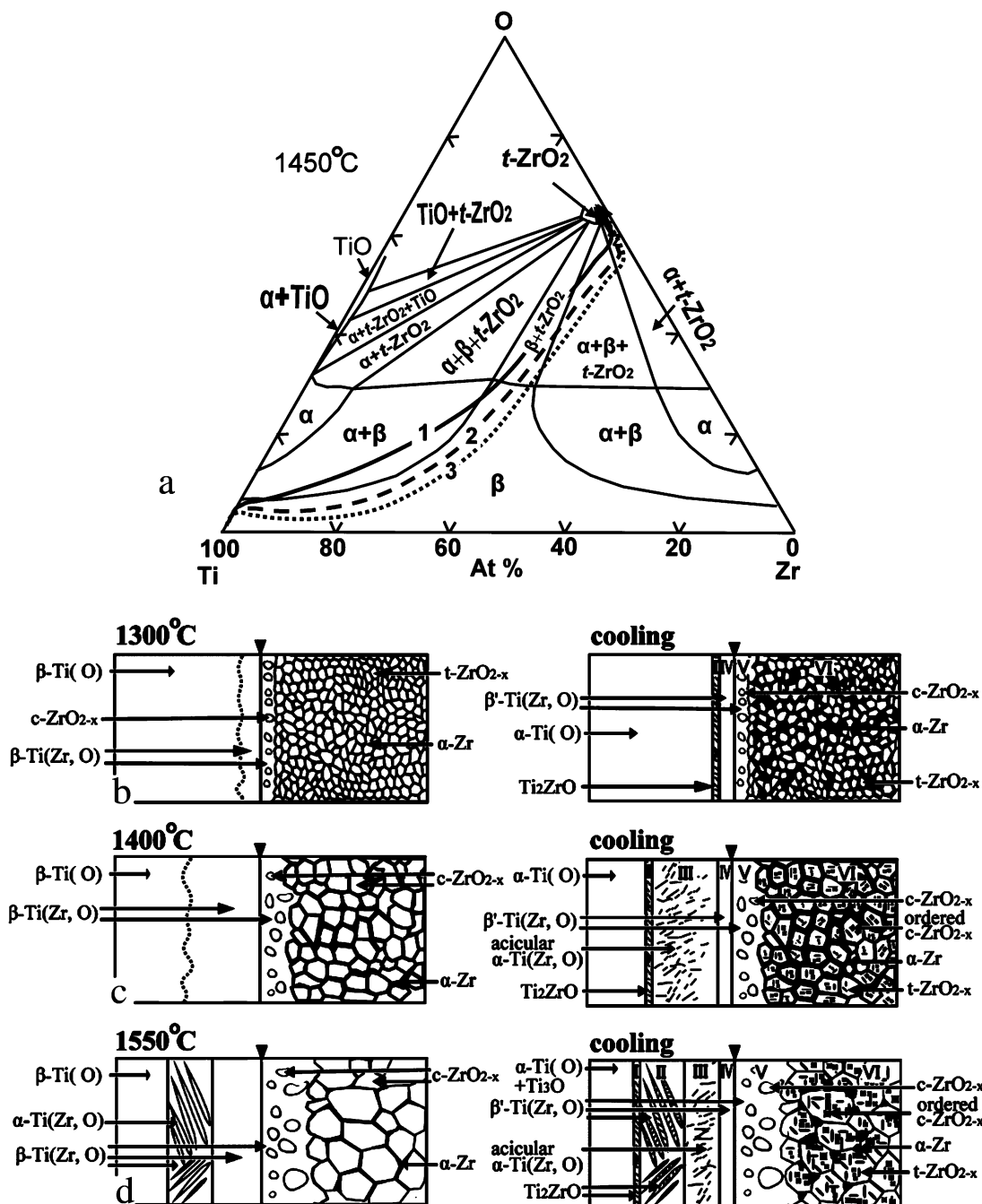
Fig. 7. Schematic diagrams showing the microstructural evolution and diffusion paths of the Ti/ZrO$_2$ diffusion couple annealed at various temperatures. (a) Various diffusion paths in the Ti–Zr–O phase diagram[19]; (b)–(d) the microstructures of Ti/ZrO$_2$ diffusion couple on annealing at 1300°, 1400°, and 1550°C and after subsequent cooling, respectively.

The zirconia in the Ti–Zr–O ternary phase diagram, shown in Fig. 7(a), would be in the cubic phase instead of the tetragonal phase when the Ti/ZrO$_2$ diffusion couple was isothermally annealed at temperatures above 1400°C, because of the dissolution of the stabilizer yttria. In the ceramic side, t-ZrO$_{2-x}$, ordered c-ZrO$_{2-x}$, and intergranular α-Zr existed in the reaction layer "VI" after annealing at 1400°C. The microstructures developed on annealing at 1400°C and after subsequent cooling are schematically shown in Fig. 7(c).

Figure 7(a) reveals that the solid line or the diffusion path 1 at 1550°C crosses the fields of β-Ti, α-Ti+β-Ti, β-Ti, β-Ti+c-ZrO$_2$, α-Zr+β-Ti+c-ZrO$_2$, and α-Zr+c-ZrO$_2$. The reaction layers of β-Ti, α-Ti+β-Ti, β-Ti, β-Ti+c-ZrO$_2$, and α-Zr+c-ZrO$_2$ would be observed in the Ti–ZrO$_2$ diffusion couple on annealing at 1550°C as shown on the left of Fig. 7(d). By comparing various diffusion paths, it is worth noting that the two-phase α-Ti(Zr, O)+β-Ti

(Zr, O) region, where the diffusion path passes through, is found neither at 1300° nor at 1400°C. This region is corresponding to the reaction layer "II" in Fig. 1(d), consisting of β'-Ti and the lamellar Ti$_2$ZrO+α-Ti. The microstructural development on annealing at 1550°C and after subsequent cooling has been described previously[11,13] and schematically shown in Fig. 7(d).

It was worth noting that there existed a wide α-Ti(O) solid solution region, neighboring the reaction unaffected Ti, in all the diffusion couples after annealing at temperatures ranging from 1100° to 1550°C. As the relative concentration of oxygen was much larger than that of Zr in this α-Ti(O) solid solution region, all the diffusion paths near the Ti corner of the Ti–Zr–O ternary phase diagram should be bowed to the Ti–O edge as Fig. 7(a) indicated.

According to the foregoing discussion, the reaction layers formed in the interface of titanium and zirconia at various

Table II.   Reaction Layers Formed in the Interface of Ti/ZrO₂ at Various Temperatures

	Phases	Reaction layers	1100°C	1300°C	1400°C	1550°C
Metal side	α-Ti(O)		●	●	▲	▲
	α-Ti(Zr, O)+Ti₂ZrO	I	●	●	●	●
	α-Ti(Zr, O)+Ti₂ZrO+β'-Ti(Zr, O)	II	x	x	x	●
	α-Ti(Zr, O)+β'-Ti(Zr, O)	III	x	x	●	●
	β'-Ti(Zr, O)	IV	x	●	●	●
Ceramic side	β'-Ti(Zr, O)+c-ZrO₂₋ₓ	V	x	●	●	#
	α-Zr(O)+t-ZrO₂₋ₓ+c-ZrO₂₋ₓ	VI	x	†	●	●
	t-ZrO₂₋ₓ		●	●	●	●

●, observed; x, none; ▲, with sparsely distributed Ti₃O; #, with ordered β'-Ti(Zr, O); †, no c-ZrO₂₋ₓ was observed.

temperatures are summarized in Table II. In brief, a very limited interfacial reaction took place at temperatures as low as 1100°C, merely leading to the formation of the α-Ti(O) and oxygen-deficient zirconia t-ZrO₂₋ₓ. In the titanium side, a thin α-Ti(O)+Ti₂ZrO layer (or layer I) existed after annealing at $T \geq 1100$°C; the β'-Ti(Zr, O) layer (or layer IV) was formed after annealing at $T \geq 1300$°C; a two-phase α-Ti(O)+β'-Ti(Zr, O) layer (or layer III) was observed after annealing at $T \geq 1400$°C; and a three-phase Ti₂ZrO+α-Ti(O, Zr)+β'-Ti (O, Zr) layer (or layer II) was found after annealing at 1550°C. In the zirconia side, near the original interface (or layer V), β'-Ti co-existed with fine spherical c-ZrO₂₋ₓ, which dissolved a significant amount of Y₂O₃ in solid solution at $T \geq 1300$°C. Further into the ceramic side (or layer VI), the zirconia grains grew significantly with the lenticular t-ZrO₂₋ₓ, being precipitated in the c-ZrO₂₋ₓ matrix at $T \geq 1400$°C. However, no cubic zirconia was found in the reaction layer "VI" after annealing at 1100° or 1300°C. The exsolution of Zr out of the metastable ZrO₂₋ₓ led to the formation of α-Zr, which was finely dense after annealing at 1300°C, continuously distributed along grain boundaries at 1400°C, and became coarsened at 1550°C. It is also noted that the suboxide Ti₃O was found in the α-Ti(O), to the left of the reaction layer "I," after annealing at 1400° and 1550°C, while an ordered β'-Ti(Zr, O) phase existed in the reaction layer "V" after annealing at 1550°C.

IV. Conclusions

(1) The diffusional reactions between titanium and zirconia were carried out isothermally in argon at temperatures ranging from 1100° to 1550°C for 6 h. It was found that the microstructure in the Ti/ZrO₂ interface strongly depended on the annealing temperature.

(2) In the titanium side, a thin α-Ti(O)+Ti₂ZrO layer (or layer I) existed after annealing at $T \geq 1100$°C; the β'-Ti(Zr, O) layer (or layer IV) was formed after annealing at $T \geq 1300$°C; a two-phase α-Ti(O)+β'-Ti(Zr, O) layer (or layer III) was observed after annealing at $T \geq 1400$°C; and a three-phase Ti₂ZrO+α-Ti(O, Zr)+β'-Ti (O, Zr) layer (or layer II) was found after annealing at 1550°C.

(3) In the zirconia side near the original interface, β'-Ti co-existed with fine spherical c-ZrO₂₋ₓ, which dissolved a significant amount of Y₂O₃ in solid solution at temperatures ranging from 1300° to 1550°C, due to the reaction-enhanced dissolution mechanism.

(4) Further into the ceramic side, the zirconia grain grew significantly at 1400° and 1550°C. α-Zr was excluded out of the metastable ZrO₂₋ₓ after annealing $T \geq 1300$°C: α-Zr was densely distributed along with t-ZrO₂₋ₓ at 1300°C, continuously located at 1400°C, and became coarsened at 1550°C. The lenticular t-ZrO₂₋ₓ was precipitated in c-ZrO₂₋ₓ after annealing at 1400° and 1550°C, while the limited reaction resulted in t-ZrO₂₋ₓ as it was in as-hot-pressed samples after annealing at 1100° or 1300°C.

(5) Finally, the microstructural development in the Ti/ZrO₂ annealed at various temperatures was described by the aid of the Ti–Zr–O ternary phase diagram.

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