

Ti₂ZrO Phases Formed in the Titanium and Zirconia Interface After Reaction at 1550°C

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Hot-pressed 3 mol% Y₂O₃ partially stabilized ZrO₂ was reacted with titanium at 1550°C/30 min. The interface was characterized by analytical transmission microscopy (transmission electron microscopy/energy-dispersive spectroscopy). The lamellar and the spherical Ti₂ZrO as well as the orthorhombic β'-Ti were found to exist in the titanium side after cooling down to room temperature. The crystal structures of the lamellar and the spherical Ti₂ZrO were orthorhombic and hexagonal, respectively. On heating, the dissolution of a large amount of zirconium and oxygen into titanium gave rise to the metastably supersaturated disordered α-Ti(Zr, O) solid solution where two different Ti₂ZrO phases subsequently precipitated, while the β-Ti coexisting with α-Ti at high temperatures was transformed to the orthorhombic β'-Ti during cooling. The spherical hexagonal Ti₂ZrO was an ordered structure, with Zr and O occupying substitutional and interstitial sites, respectively. The orientation relations between α-Ti and the lamellae orthorhombic Ti₂ZrO were determined to be [0001]_{α-Ti}//[110]_{Ti₂ZrO} and (1010)_{α-Ti}//(110)_{Ti₂ZrO}; meanwhile, those between the α-Ti and the spherical hexagonal Ti₂ZrO were [0001]_{α-Ti}//[0001]_{Ti₂ZrO} and (1010)_{α-Ti}//(1010)_{Ti₂ZrO}.

I. Introduction

TITANIUM alloys have excellent properties such as high specific strength and corrosion resistance. However, they are very active and tend to dissolve some interstitial elements (e.g., C, N, O, H) of ceramic molds during casting. Saha and Jacob¹ showed that there was an oxidation–reduction reaction between titanium alloys and various oxide molds, and thus, the so-called α-case was formed at the surface of titanium casting, resulting in a hardening and brittle structure.^{2–6} That is to say, the oxygen was readily dissolved into the titanium to form α-Ti at the surface of titanium alloys and caused the deterioration of mechanical properties.

The reactions between titanium and zirconia have been subjected to an intensive investigation, indicating that zirconia became oxygen-deficient because of the interfacial reaction. Economos and Kingery⁷ revealed that titanium penetrated along the grain boundaries of ZrO₂ with the formation of the oxygen-deficient zirconia. Ruh⁸ reported that up to 4 at.% of titanium was retained in zirconia at room temperature, while up to approximately 10 mol% zirconia would be dissolved in titanium. Zirconium entered into the titanium lattice substitutionally and oxygen entered interstitial positions, but no evidence of other compounds except oxygen-deficient zirconia at the interface was provided.

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Some researchers have studied the existence of interfacial phases and the effects of titanium on the stabilization and mechanical properties of zirconia. Weber *et al.*⁹ indicated that zirconia, with Ti exceeding the solubility limit, showed good strength and thermal shock resistance. Lin *et al.*¹⁰ stated that zirconia was stabilized because of the dissolution of TiO, formed by the reaction between titanium and residual trace oxygen in the vacuum furnace. The improvement in the strength and the thermal shock resistance of zirconia was attributed to the dissolution of TiO as well. According to the pseudobinary diagram of Ti–ZrO₂ proposed by Domagala *et al.*,¹¹ (Ti, Zr)₃O could precipitate from the supersaturated solid solution of α-Ti(Zr, O) during cooling. However, Weber *et al.*⁹ and Lin *et al.*¹⁰ found neither (Ti, Zr)₃O nor α-Ti (Zr, O).

Recently, Lin and Lin¹² reported that the interfacial reactions between zirconia and titanium melt resulted in titanium oxides such as Ti₃O or TiO₂ after reaction at 1750°C/7 min. Meanwhile, the lamellae of Ti₂ZrO and α-Ti(Zr, O) were also found. In the present study, the titanium and zirconia diffusion couple was annealed at 1550°C/30 min. The interfacial microstructures were characterized by transmission electron microscopy/energy-dispersive spectroscopy (TEM/EDS).¹³ The orientation relations between α-Ti and Ti₂ZrO were determined using stereographic projection analyses.

II. Experimental Procedures

Bulk zirconia specimens used in this study were prepared from the powder of 3 mol% Y₂O₃ partially stabilized zirconia (Toyo Soda Mfg. Co., Tokyo, Japan) by hot-pressing in a graphite furnace in vacuum (Model HP50-MTG-7010, Thermal Techno, Inc., Santa Rosa, CA). The specimens were heated to and held at 300°C for 3 min under 5 MPa at a heating rate of 30°C/min, while heating to and being held at 1450°C for 30 min under 30 MPa at a heating rate of 25°C/min. During cooling, pressure was released at 1100°C. The as-hot pressed samples were annealed at 1200°C/4 h so that the stoichiometric ZrO₂ samples were obtained. On the other hand, billets of commercially pure titanium (Cp-Ti) were used in this study. Nominal compositions of the starting materials, i.e., zirconia powder and titanium billets, were listed in Table I.

Both zirconia and titanium specimens were cut and machined to dimensions of 14 mm × 14 mm × 5 mm. Their surfaces were ground and polished to 0.5 μm with a diamond paste, and then ultrasonically cleaned in acetone. One titanium specimen was inserted in between two ZrO₂ specimens to produce a sandwiched sample, and then put in the graphite furnace mentioned above, preparatorily pressed under 5 MPa, evacuated to 2 × 10⁻⁴ Torr, and filled with argon to one atmospheric pressure. This cycle of evacuation and purging was repeated at least three times. The temperature was raised to 1000°C at a raising rate of 30°C/min, to 1550°C at 25°C/min, and then held at 1550°C for 30 min. Thereafter, the temperature was lowered to 1000°C at a cooling rate of 25°C/min, and then furnace cooled down to room temperature.

The microstructures at the interface between zirconia and titanium were characterized using an analytical transmission electron microscope (Model JEM 2000FX, JEOL Ltd., Tokyo,

Table I. Compositions of the Starting Materials

Material	Composition (wt%)
Ti	99.31 Ti, 0.3 Fe, 0.25 O, 0.1 C, 0.03 N, 0.01 H
3Y-ZrO ₂	>94 ZrO ₂ +HfO ₂ , [†] 5.4 Y ₂ O ₃ , <0.001 Fe ₂ O ₃ , <0.01 SiO ₂ , <0.005 Na ₂ O, <0.005 TiO ₂ , <0.02 Cl, <0.005 SO ₄ ²⁻

[†]Accounts for approximately 2~3% of this total.

Japan). Cross-sectional TEM specimens perpendicular to the interface of zirconia and titanium were cut into about 3 mm × 2 mm × 0.5 mm. They were ground, polished, and dimpled to 50 μm in thickness. The TEM specimens were then 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 technique¹³ by an EDS (Mode ISIS300, Oxford Instrument Inc., London, UK) attached to the TEM.

III. Results and Discussion

The lamellae of Ti₂ZrO and α-Ti as well as the orthorhombic β'-Ti were found to exist in the titanium side after cooling down to

room temperature, as shown in Fig. 1(a). Figure 1(b) shows a magnified micrograph of the inset area in Fig. 1(a), showing the elongated β'-Ti in the middle of the bright field image and the Ti₂ZrO lamellae precipitated in the α-Ti matrix. The spherical ordered Ti₂ZrO phase, showing high strain-field contrast because of the lattice distortion, precipitated in α-Ti matrix in the right lower corner (arrowed). It is believed that the ordering of Zr and O in α-Ti caused the lattice strain owing to the difference in atomic sizes.

Figures 2(a) and (b) display the selected area diffraction patterns (SADPs) of β'-Ti, with zone axes of [110] and [111], respectively, being identified as orthorhombic with lattice parameters $a = 0.585$ nm, $b = 0.847$ nm, and $c = 0.606$ nm. The EDS spectrum in Fig. 2(c) indicates that β'-Ti(Zr, O) contained

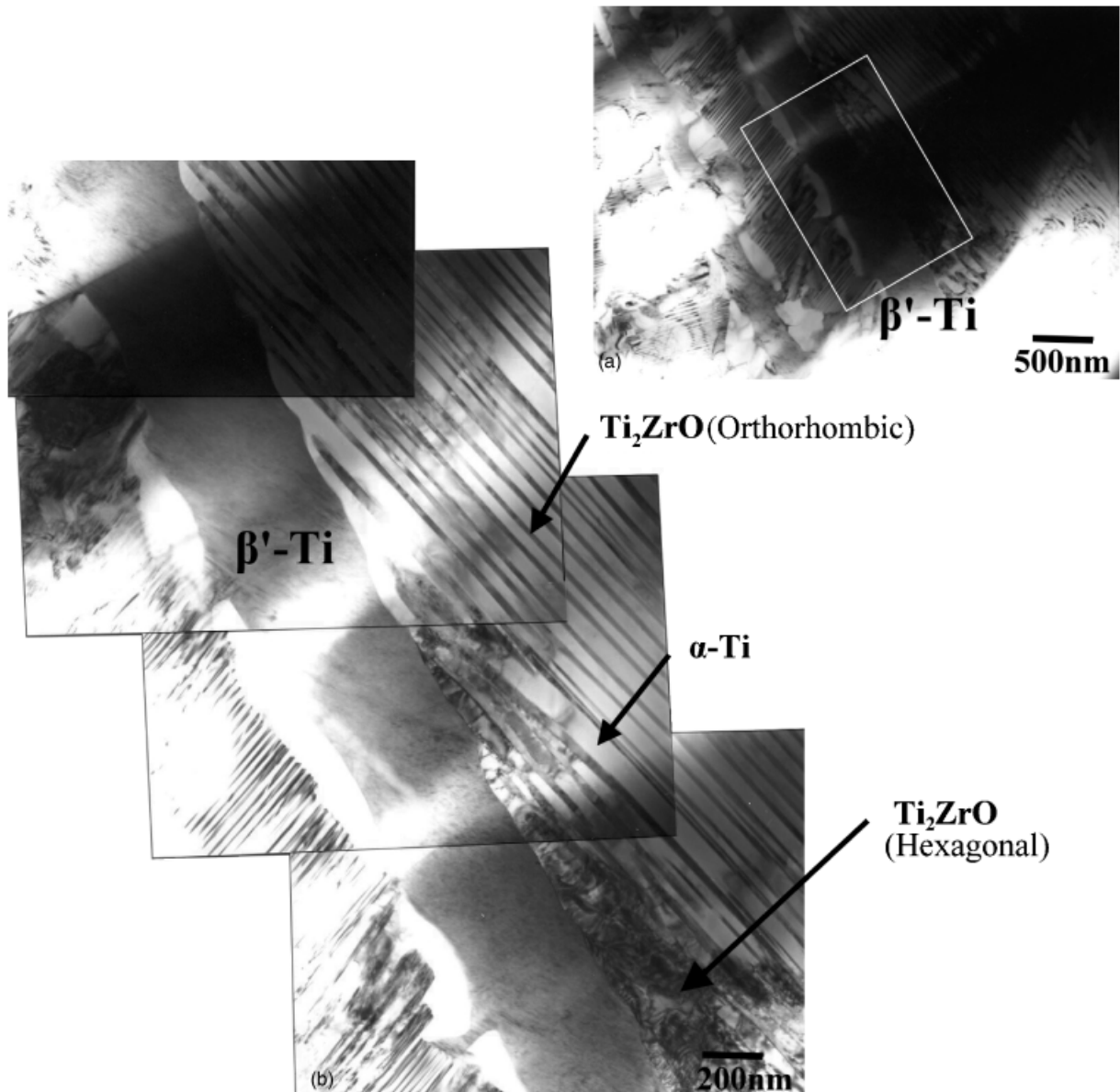


Fig. 1. (a) The transmission electron microscopy micrograph showing the interface between Cp-Ti and ZrO₂(3Y) after reaction at 1550°C/30 min; (b) A magnified micrograph of the marked region in (a), indicating the elongated β'-Ti and the lamellar structure of α-Ti and Ti₂ZrO on both sides of β'-Ti. The arrows in the lower right region indicate the spherical Ti₂ZrO.

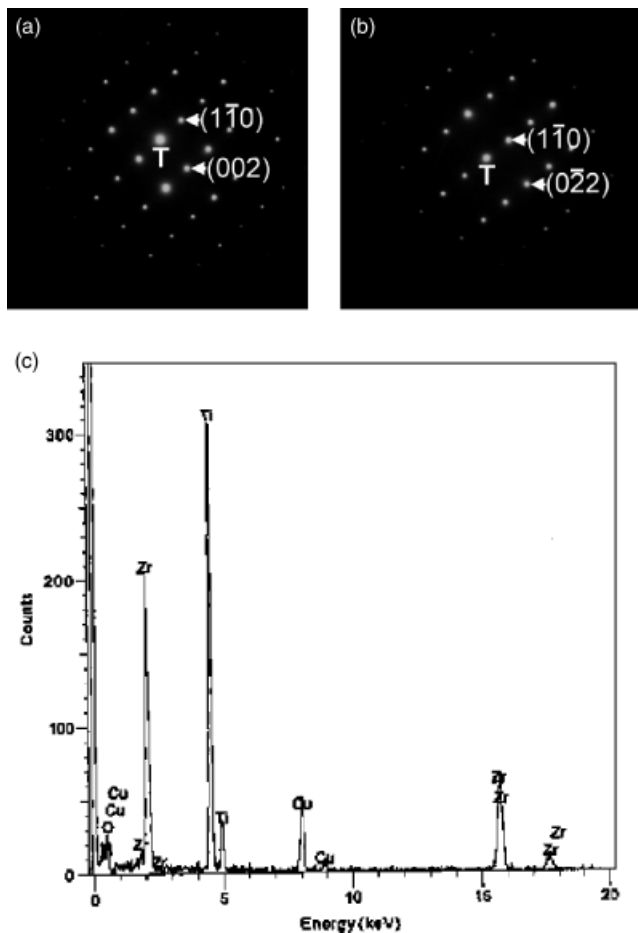


Fig. 2. (a) and (b) selected area diffraction patterns of β' -Ti, $Z = [110]_{\beta'-Ti}$ and $Z = [111]_{\beta'-Ti}$, respectively; (c) an energy-dispersive spectrum of β' -Ti.

57.9 at.% Ti, 30.7 at.% Zr, and 11.4 at.% O. From the Ti–ZrO₂ phase diagram,¹¹ it is known that hexagonal α -Ti and body-centered cubic β -Ti coexist in Cp-Ti at 1550°C, and the β -Ti will transform into α -Ti during cooling. Oxygen raises the transformation temperature of $\alpha \rightarrow \beta$,¹⁴ causing the α -phase to be stabilized. Despite the dissolution of a large amount of zirconium, which is a β -stabilizer, β -Ti did not survive but rather transformed to an orthorhombic β' -Ti(Zr, O) solid solution during cooling. The transformation of β -Ti to β' -Ti has been investigated in Ti–Al–Nb systems.¹⁵ However, the formation of β' -Ti in the titanium and zirconia system was first found in this study.

At high temperatures, α -Ti dissolved a large amount of zirconium and oxygen, forming a metastably supersaturated disordered solid solution α -Ti(Zr, O), thus resulting in the precipitation of the lamellae Ti₂ZrO during cooling. The interlacing lamellar phases were identified as orthorhombic Ti₂ZrO and hexagonal disordered α -Ti from the superimposed SADPs of these two phases shown in Fig. 3(a). The streaking of the diffraction spots was caused by the lamellar-shaped effect. The orientation relations were identified as $[0001]_{\alpha-Ti} // [110]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha-Ti} // (1\bar{1}0)_{Ti_2ZrO}$. Moreover, the lattice constants of Ti₂ZrO orthorhombic unit cell were calculated as follows: $a_o = 0.494$ nm, $b_o = 0.817$ nm, and $c_o = 0.309$ nm, and those of α -Ti hexagonal unit cell are $a_h = b_h = 0.301$ nm, $c_h = 0.468$ nm. Figure 3(b) shows the EDS spectrum of the α -Ti, revealing that it comprised 80.7 at.% Ti, 8.5 at.% Zr, and 10.8 at.% O. Figure 3(c) shows the EDS spectrum of the lamellar Ti₂ZrO, consisting of 56.1 at.% Ti, 22.9 at.% Zr, and 21.0 at.% O. Figure 3(d) displays the standard stereographic projection corresponding to Fig. 3(a) with $[0001]_{\alpha-Ti} // [110]_{Ti_2ZrO}$. It indicates that the $(10\bar{1}0)$ plane of α -Ti is parallel to the (110) plane of Ti₂ZrO, in agreement with the result presented by Lin and Lin.¹²

The crystallographic relation between α -Ti (solid line) and the lamellar Ti₂ZrO (dash line) inferred from Fig. 3(a) is schematically shown in Fig. 4. The habit planes of Ti₂ZrO and α -Ti are $(10\bar{1}0)_{\alpha-Ti}$ and $(1\bar{1}0)_{Ti_2ZrO}$, respectively. The stacking sequence of α -Ti is ABABAB. It reveals that the crystal structure of the orthorhombic Ti₂ZrO is based on that of hexagonal α -Ti with a stacking sequence of ABACABAC.

Figure 5(a) shows the superimposed SADPs of the spherical ordered Ti₂ZrO phase and the α -Ti matrix with $[0001]_{\alpha-Ti} // [0001]_{Ti_2ZrO}$ and $(10\bar{1}0)_{\alpha-Ti} // (30\bar{3}0)_{Ti_2ZrO}$. From superimposed diffraction patterns, the spherical ordered phase was identified as hexagonal Ti₂ZrO, in agreement with the result presented by Fykin *et al.*¹⁶ The crystal structure of the hexagonal Ti₂ZrO was proposed as shown in Fig. 5(b). It indicates that the hexagonal Ti₂ZrO unit cell with space group $D_{6h}^{17}P6/mmm$ had one Zr atom at 0, 0, 0, and two Ti atoms at $1/3, 2/3, 1/2$, and $2/3, 1/3, 1/2$. Additionally, one O atom was statistically positioned at $1/2, 0, 0; 0, 1/2, 0; 1/2, 1/2, 0$.

In order to understand the reflection planes of Ti₂ZrO structure, its structure factor of Ti₂ZrO must be calculated. From the atomic positions of Ti₂ZrO by Fykin *et al.*,¹⁶ the structure factor was calculated as follows:

$$F = f_{Zr} + f_{Ti} [e^{2\pi i(h/3+2k/3+l/2)} + e^{2\pi i(2h/3+k/3+l/2)}] + f_O [e^{2\pi i(h/2)} + e^{2\pi i(k/2)} + e^{2\pi i(h/2+k/2)}]$$

Multiplication by the complex conjugate, however, would give the square of the absolute value of the resultant wave amplitude F .

$$\begin{aligned} |F|^2 = & [f_{Zr} + f_{Ti} \cos 2\pi \left(\frac{h+2k}{3} + l/2 \right) \\ & + f_{Ti} \cos 2\pi \left(\frac{2h+k}{3} + l/2 \right) + f_O \cos 2\pi(h/2) \\ & + f_O \cos 2\pi(k/2) + f_O \cos 2\pi(h+k/2)]^2 \\ & + [f_{Ti} \sin 2\pi \left(\frac{h+2k}{3} + l/2 \right) \\ & + f_{Ti} \sin 2\pi \left(\frac{2h+k}{3} + l/2 \right) \\ & + f_O \sin 2\pi(h/2) + f_O \sin 2\pi(k/2) \\ & + f_O \sin 2\pi(h+k/2)]^2 \end{aligned}$$

When all possible values of h, k, l were considered, the results were summarized as in Table II. The relative intensities of the diffraction spots in Fig. 5(a) were consistent with the results of calculated structure factors for Ti₂ZrO. The structure factors of the reflections $(4\bar{2}20)$ and $(2\bar{1}10)$ were $|F|^2 = [f_{Zr} + 2f_{Ti} + 3f_O]^2$ and $|F|^2 = [f_{Zr} + 2f_{Ti} - f_O]^2$, respectively. The reflection spot of the $(4\bar{2}20)$ plane was thus brighter than that of the $(2\bar{1}10)$ plane as shown in Fig. 5(a). Furthermore, the reflection spot of the $(30\bar{3}0)$ plane with $|F|^2 = [f_{Zr} + 2f_{Ti} - f_O]^2$ was visible. The (2020) and $(10\bar{1}0)$ reflections were absent, because its structure factor $|F|^2 = [f_{Zr} - f_{Ti} - f_O]^2$ was comparatively small and negligible.

The lattice constants of hexagonal Ti₂ZrO unit cell were calculated as follows: $a = b = 0.902$ nm and $c = 0.455$ nm, while those of the α -Ti hexagonal unit cell are $a = b = 0.301$ nm and $c = 0.468$ nm. Figure 5(c) displays the EDS spectrum of spherical ordered Ti₂ZrO consisting of 54.2 at.% Ti, 22.7 at.% Zr, and 23.1 at.% O. Figure 5(d) shows the standard stereographic projection of the spherical ordered Ti₂ZrO and α -Ti corresponding with Fig. 5(a), showing that the $(10\bar{1}0)$ plane of α -Ti was parallel to the $(30\bar{3}0)$ plane of the spherical ordered Ti₂ZrO.

Zirconia was highly soluble in titanium,¹¹ allowing the formation of a disordered solid solution of α -Ti(Zr, O) at high temperatures. The lamellar and spherical Ti₂ZrO phases with different crystal structures were precipitated from the supersaturated α -Ti(Zr, O) during cooling. In contrast, Lin and Lin¹² reported only one of the Ti₂ZrO phases in their previous study.

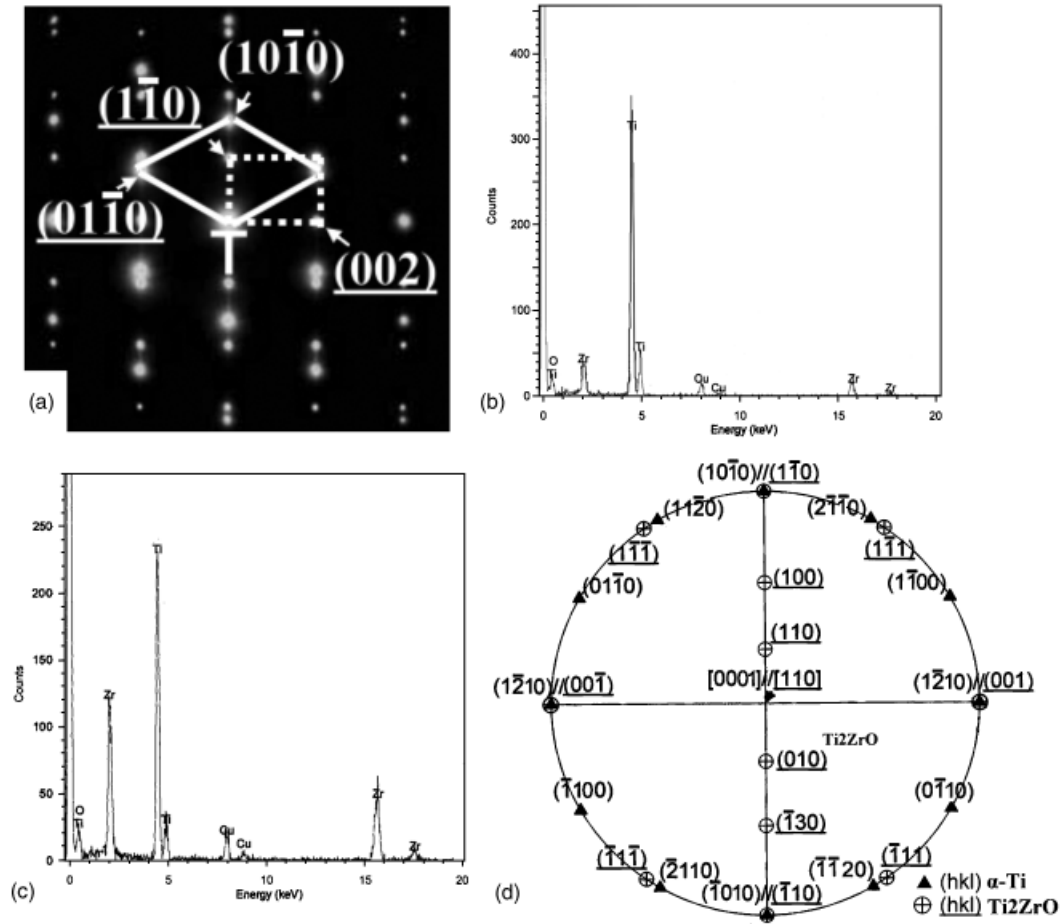


Fig. 3. (a) Selected area diffraction patterns of the lamellar Ti₂ZrO and α -Ti, $Z = [0001]_{\alpha\text{-Ti}} // [110]_{\text{Ti}_2\text{ZrO}}$; (b) an energy-dispersive spectrum of α -Ti; (c) an energy-dispersive spectrum of the lamellar Ti₂ZrO; (d) the standard stereographic projection with $[0001]_{\alpha\text{-Ti}} // [110]_{\text{Ti}_2\text{ZrO}}$.

According to the Ti–ZrO₂ phase diagram,¹¹ the solubility of ZrO₂ in titanium could exceed 20 at.%. In the present study, α -Ti dissolved a large amount of Zr and O at 1550°C, forming a supersaturated solid solution α -Ti(Zr, O), whereby Ti₂ZrO precipitated. However, a wide two-phase region (23–75 wt% ZrO₂)

of α -Ti(Zr, O) and (Ti, Zr)₃O in the Ti–ZrO₂ phase diagram is inconsistent with the coexistence of α -Ti(Zr, O), Ti₂ZrO, and β' -Ti in this study.

Lin and Lin reported¹² that the reaction at 1750°C/7 min between zirconia and titanium melt caused the formation of the lamellae Ti₂ZrO and α -Ti(Zr, O). However, whether Ti₂ZrO was formed during solidification or by precipitation from α -Ti(Zr, O) during cooling could not be confirmed. Because no liquid α -Ti(Zr, O) existed in this study, it is concluded that the lamellae Ti₂ZrO phase was not formed in the Ti melt but rather precipitated from α -Ti(Zr, O). Furthermore, Lin and Lin's report¹² did not find the spherical ordered Ti₂ZrO phase and the β' -Ti in the interface of zirconia and titanium reaction.

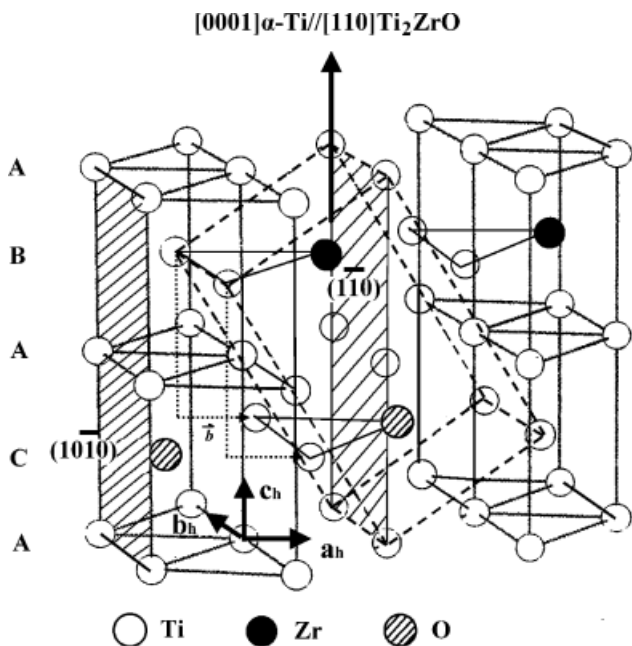


Fig. 4. Lattice relation of the orthorhombic Ti₂ZrO (dash line) and the hexagonal α -Ti (solid line).

IV. Conclusions

1. In the zirconia/titanium diffusion couple annealed at 1550°C/30 min, titanium readily dissolved a large amount of zirconium and oxygen, resulting in a metastably supersaturated solid solution.

2. The lamellar and the spherical Ti₂ZrO phases were precipitated from the supersaturated α -Ti solid solution, while the β -Ti coexisting with α -Ti at high temperatures was transformed to the orthorhombic β' -Ti during cooling.

3. The lamellar Ti₂ZrO had an orthorhombic crystal structure with the (110) planes being stacked in the ABACABAC sequence. In contrast, the spherical Ti₂ZrO had a hexagonal crystal structure, with Zr and O orderly occupying substitutional and interstitial sites, respectively.

4. The orientation relations between α -Ti and the lamellae orthorhombic Ti₂ZrO were determined to be $[0001]_{\alpha\text{-Ti}} // [110]_{\text{Ti}_2\text{ZrO}}$ and $(10\bar{1}0)_{\alpha\text{-Ti}} // (1\bar{1}0)_{\text{Ti}_2\text{ZrO}}$; meanwhile, those be-

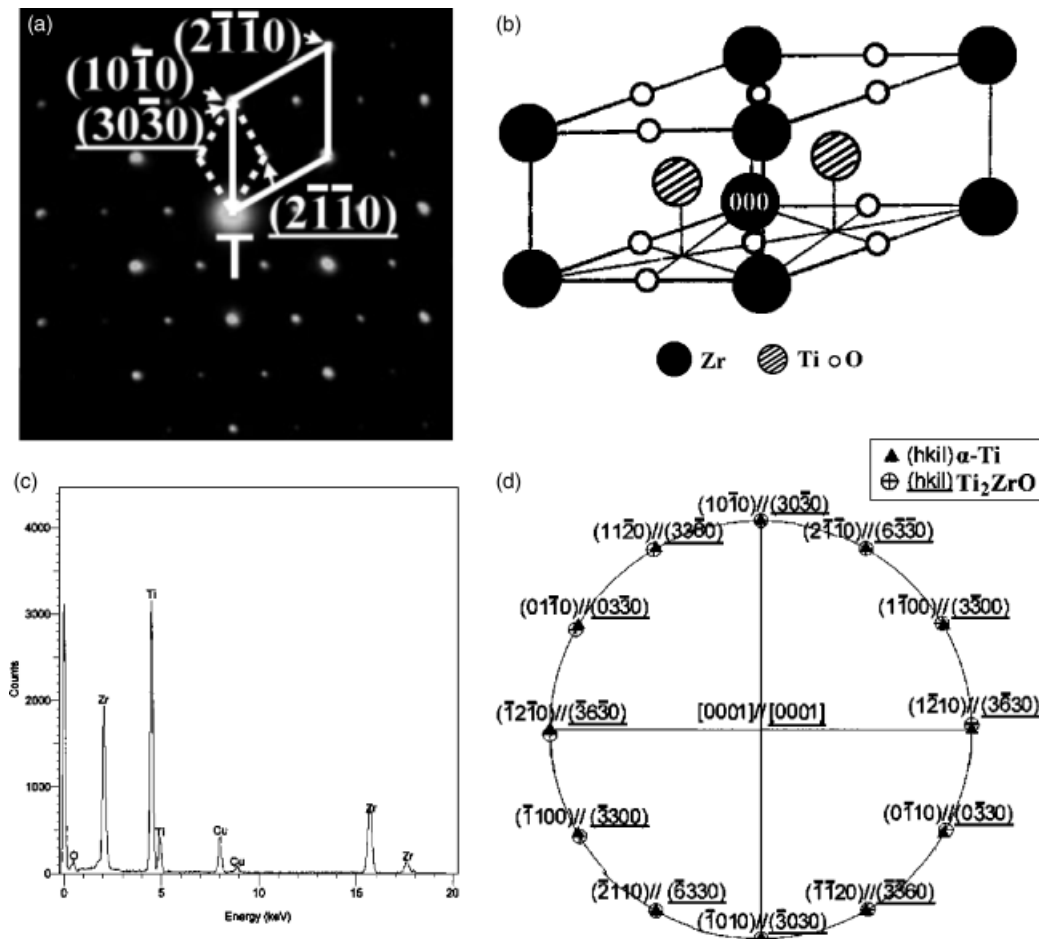


Fig. 5. (a) Selected area diffraction patterns of the spherical ordered Ti_2ZrO and the $\alpha\text{-Ti}$, $Z = [0001]_{\alpha\text{-Ti}}/[0001]_{\text{Ti}_2\text{ZrO}}$; (b) the hexagonal Ti_2ZrO unit cell;¹⁶ (c) an energy-dispersive spectrum of the spherical ordered Ti_2ZrO ; (d) the standard stereographic projection with $[0001]_{\alpha\text{-Ti}}/[0001]_{\text{Ti}_2\text{ZrO}}$.

Table II. Calculated Results of the Hexagonal Ti_2ZrO Structure Factor

$h+2k$ (or $2h+k$)	h and k	l	$ F ^2$
$3m, m = \text{even}$	Even	Even	$(f_{\text{Zr}} + 2f_{\text{Ti}} + 3f_{\text{O}})^2$
$3m, m = \text{even}$	Even	Odd	$(f_{\text{Zr}} - 2f_{\text{Ti}} + 3f_{\text{O}})^2$
$3m, m = \text{even}$	Mixed	Even	$(f_{\text{Zr}} + 2f_{\text{Ti}} - f_{\text{O}})^2$
$3m, m = \text{even}$	Mixed	Odd	$(f_{\text{Zr}} - 2f_{\text{Ti}} - f_{\text{O}})^2$
$3m, m = \text{odd}$	Odd or mixed	Even	$(f_{\text{Zr}} + 2f_{\text{Ti}} - f_{\text{O}})^2$
$3m, m = \text{odd}$	Odd or mixed	Odd	$(f_{\text{Zr}} - 2f_{\text{Ti}} - f_{\text{O}})^2$
$3m \pm 1, m = \text{even}$	Odd or mixed	Even	$(f_{\text{Zr}} - f_{\text{Ti}} - f_{\text{O}})^2$
$3m \pm 1, m = \text{even}$	Odd or mixed	Odd	$(f_{\text{Zr}} + f_{\text{Ti}} - f_{\text{O}})^2$
$3m \pm 1, m = \text{odd}$	Mixed	Even	$(f_{\text{Zr}} - f_{\text{Ti}} - f_{\text{O}})^2$
$3m \pm 1, m = \text{odd}$	Mixed	Odd	$(f_{\text{Zr}} + f_{\text{Ti}} - f_{\text{O}})^2$
$3m \pm 1, m = \text{odd}$	Even	Even	$(f_{\text{Zr}} - f_{\text{Ti}} + 3f_{\text{O}})^2$
$3m \pm 1, m = \text{odd}$	Even	Odd	$(f_{\text{Zr}} + f_{\text{Ti}} + 3f_{\text{O}})^2$

h, k, l , and m are integers.

tween the $\alpha\text{-Ti}$ and the spherical hexagonal Ti_2ZrO were $[0001]_{\alpha\text{-Ti}}/[0001]_{\text{Ti}_2\text{ZrO}}$ and $(10\bar{1}0)_{\alpha\text{-Ti}}/(10\bar{1}0)_{\text{Ti}_2\text{ZrO}}$.

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