## **List of Figures**

## **Chapter 1 Introduction**

Fig. 1.1 Unit cell of $\alpha$ -Ti.
<b>Fig. 1.2</b> Unit cell of β-Ti
Fig. 1.3 Effect of alloying elements on phase diagrams of titanium alloys
(schematically)15
Fig. 1.4 Schematic of a vacuum casting furnace used for making
titanium castings16
<b>Fig. 1.5</b> Low-yttria portion of proposed ZrO <sub>2</sub> -Y <sub>2</sub> O <sub>3</sub> phase diagram17
Chapter 2
Ti <sub>2</sub> ZrO Phases Formed in the Titanium and Zirconia
Interface after Reaction at 1550°C
Fig. 2.1 (a) The TEM micrograph showing the interface between Cp-Ti
and $ZrO_2(3Y)$ after reaction at 1550 °C /30min; (b) A magnified
micrograph of the marked region in (a), indicating elongated $\beta$ '-Ti and
the lamellar structure of $\alpha\text{-Ti}$ and $\text{Ti}_2\text{ZrO}$ in both sides of $\beta\text{'-Ti}$ .
The arrows in the lower right region indicate the spherical ordered
Ti <sub>2</sub> ZrO30
<b>Fig. 2.2</b> (a) and (b) SADP's of $\beta$ '-Ti, Z=[110] $_{\beta'$ -Ti} and Z=[111] $_{\beta'$ -Ti,
respectively; (c) EDS of β'-Ti31
<b>Fig. 2.3</b> (a) SADP's of the lamellar $Ti_2ZrO$ and $\alpha$ - $Ti$ , $Z=[0001]_{\alpha$ - $Ti}$

//[110] $_{Ti2ZrO}$ ; (b) EDS of $\alpha$ -Ti; (c) EDS of the lamellar $Ti_2ZrO$ ; (d) the standard stereographic projection with [0001] $_{\alpha$ -Ti //[110] $_{Ti2ZrO}$ 32
<b>Fig. 2.4</b> The lattice relation of the orthorhombic Ti <sub>2</sub> ZrO (dash line) and hexagonal α-Ti (soild line).
<b>Fig. 2.5</b> (a) SADP's of the spherical ordered Ti <sub>2</sub> ZrO and α-Ti, Z=[0001] $_{\alpha\text{-Ti}}$ //[0001] <sub>Ti2ZrO</sub> ; (b) the hexagonal Ti <sub>2</sub> ZrO unit cell <sup>17</sup> ; (c) EDS of the spherical ordered Ti <sub>2</sub> ZrO; (d) the standard stereographic projection with [0001] <sub>α-Ti</sub> //[0001] <sub>Ti2ZrO</sub> .
Chapter 3
Zirconia-Related Phases in the Zirconia/Titanium Diffusion
Couple after Annealing at 1100° to 1550°C
ESIN
Fig. 3.1 (a) TEM micrograph (bright field image, BFI) of zirconia far
away the ZrO <sub>2</sub> /Ti interface after reaction at 1100°C/6 h,
indicating $t$ -ZrO <sub>2-x</sub> with an average grain size $\sim$ 0.5 $\mu$ m; (b) SADP of the
<i>t</i> -ZrO <sub>2-x</sub>
Fig. 3.2 SEM micrograph (backscattered electron image, BEI) of the
zirconia side in the ZrO <sub>2</sub> /Ti diffusion couple after reaction at 1300°C/6 h, indicating the apprintment of a 7r (marked as "A") and
indicating the coexistence of $\alpha$ -Zr (marked as "A") and
t-ZrO <sub>2-x</sub> , (marked as "B"). Also shown is the coarsening of α-Zr
(arrowed)
Fig. 3.3 (a) TEM micrograph (bright field image, BFI) of $\alpha$ -Zr and
t-ZrO <sub>2-x</sub> in the ZrO <sub>2</sub> /Ti diffusion couple after reaction at 1300°C/6 h; (b)
SADP of the $\alpha$ -Zr along the [101] zone axis; (c) EDS of the $\alpha$ -Zr shown
in (b); (d) SADP of the t-ZrO <sub>2-x</sub> , along the [110] zone axis; (e) EDS of
the $t$ - $TrO_2$ shown in (d)

Fig. 3.4 (a) SEM micrograph (backscattered electron image, BEI) of
zirconia side in the $ZrO_2/Ti$ diffusion couple after reaction at $1550^{\circ}C/6\ h,$
indicating the coarsening of intergranular $\alpha\text{-}Zr$ (marked as "A") and
t-ZrO <sub>2-x</sub> (marked as "B") in the $c$ -ZrO <sub>2-x</sub> matrix (marked as "C"); (b)
SEM micrograph (secondary electron image, SEI) of as hot-pressed
zirconia after annealing at 1550°C/6 h in Ar54
Fig. 3.5 (a) TEM micrograph (bright field image, BFI) of zirconia in the
$ZrO_2/Ti$ diffusion couple after reaction at $1550^{\circ}C/6$ h, indicating the
twined $t'$ -ZrO <sub>2-x</sub> in $t'$ -ZrO <sub>2-x</sub> matrix; (b) and (c) are microdiffraction
patterns from the twined $t'$ -ZrO <sub>2-x</sub> and the $t'$ -ZrO <sub>2-x</sub> matrix along the zone
axes of [111], respectively
<b>Fig. 3.6</b> (a) TEM micrograph (bright field image, BFI) of zirconia in the ZrO <sub>2</sub> /Ti diffusion couple after reaction at 1550°C/6 h, displaying {100} type of variants of the lenticular $t$ -ZrO <sub>2-x</sub> in $c$ -ZrO <sub>2-x</sub> matrix; (b) A magnified image of the $c$ -ZrO <sub>2-x</sub> matrix in (a), showing the ordered structure; (c) EDS of the ordered $c$ -ZrO <sub>2-x</sub> , (d) and (e) are SADP's of the ordered $c$ -ZrO <sub>2-x</sub> matrix with zone axis being [110] and [310], respectively.
Fig. 3.7 Schematic diagrams showing the microstructural evolution of
the zirconia side in the $ZrO_2/$ Ti diffusion couple annealed at $1300^{\circ}C/6~h.$
(a) as hot-pressed; (b) grain growth on heating to 1300°C; (c) exclusion
of $\alpha$ -Zr from ZrO <sub>2-x</sub> during cooling57
Fig. 3.8 Schematic diagrams showing the microstructural evolution of
the zirconia side in ZrO <sub>2</sub> /Ti diffusion couple annealed at 1550°C/6 h. (a)
as hot-pressed; (b) apparent grain growth on heating to 1550°C; (c)
exclusion of $\alpha$ -Zr during cooling; (d) formation of twined $t'$ -ZrO <sub>2</sub> ; (e) the
formation of lenticular $t$ -ZrO $_2$ and ordered $c$ -ZrO $_{2-x}$

cross-sectional between Ti/ZrO <sub>2</sub> after reaction at 1550°C/6 h; (b) and (c)
selected area diffraction patterns of the $\alpha$ -Ti and $\beta$ '-Ti, Z=[2 $\overline{1}$ $\overline{1}$ 0] $_{\alpha$ -Ti //
$[021]_{\beta'\text{-Ti}}$ and its schematic diagram ( $\Delta$ : $\alpha\text{-Ti}$ , $\circ$ : $\beta'\text{-Ti}$ ), respectively; (d)
images taken form the high resolution transmission electron microscopy
(HRTEM) of acicular $\alpha$ -Ti and $\beta$ '-Ti; (e) the computer simulation in the
marked area of Fig. 4.3(d).
Fig. 4.7 SEM micrograph (backscattered electron image, BEI) of the
reaction layers "D", "E", and "F" in the interface between Ti/ZrO2 after
reaction at 1550°C/6 h83
Fig. 4.8 (a) SEM micrograph (backscattered electron image, BEI) of the
reaction layers "F" in the interface between Ti/ZrO <sub>2</sub> after reaction at
1550°C/6 h; (b)~(e) X-ray maps of Y, Ti, Zr, and O, respectively84
Fig. 4.9 (a) SEM micrograph (backscattered electron image, BEI) of the
reaction layer "G" in the zirconia side away from the interface after
reaction at 1550°C/6 h; (b)~(e) X-ray maps of Y, Ti, Zr, and O,
respectively85
Fig. 4.10 Schematic diagrams showing the microstructural evolution of
the Ti/ZrO <sub>2</sub> diffusion couple annealed at 1550°C. (a) as hot-pressed;
(b) the Ti-Zr-O ternary system at 1450°C <sup>19</sup> ; (c) the structure of the
Ti/ZrO <sub>2</sub> diffusion couple annealed at 1550°C, and (d) the structure on
cooling

## **Chapter 5**

Temperature Dependence of the Interfacial Reaction between Titanium and Zirconia Annealed between  $1100^{\circ}$  and  $1550^{\circ}$ C

Fig. 5.1 SEM micrographs (backscattered electron image) showing the
interface of Ti and ZrO <sub>2</sub> after reaction for 6 h at (a) 1100°; (b) 1300°; (c)
1400°; and (d) 1550°C. The vertical arrows in the upper side indicated
the original interface. The interface reaction layers were designed as
the layers "I", "II", "IV", "V", and "VI," respectively108
Fig. 5.2 SEM micrographs (secondary electron image) showing the
variation of the layer "I" after reaction at (a) 1300°; (b) 1400°; and (c)
1550°C, respectively
Fig. 5.3 (a) A TEM micrograph (bright field image, BFI) showing the
layer "I" with the coexistence of α-Ti and Ti <sub>2</sub> ZrO after reaction at
1100°C/6 h; (b) selected area diffraction patterns of the α-Ti and Ti <sub>2</sub> ZrO,
indicating that $[0001]_{\alpha\text{-Ti}}$ // $[110]_{\text{Ti2ZrO}}$ and $(10\overline{1}0)_{\alpha\text{-Ti}}$ // $(1\overline{1}0)_{\text{Ti2ZrO}}$ (A =
$(01\overline{1}0)_{\alpha\text{-Ti}}, B = (10\overline{1}0)_{\alpha\text{-Ti}}, C = (00\overline{2})_{\text{Ti2ZrO}}, D = (1\overline{1}0)_{\text{Ti2ZrO}}); (c) \text{ the}$
energy-dispersive spectrum of Ti <sub>2</sub> ZrO110
Fig. 5.4 TEM micrograph (bright field image, BFI) of the layer "II"
showing the lamellae $\alpha$ -Ti + Ti <sub>2</sub> ZrO and $\beta$ '-Ti after reaction at 1550°C
for 6 h; the inset selected area diffraction patterns indicate $[0001]_{\alpha\text{-Ti}}$ //
$[110]_{Ti2ZrO}$ and $(10\overline{1}0)_{\alpha\text{-Ti}}$ // $(1\overline{1}0)_{Ti2ZrO}$ (A = $(01\overline{1}0)_{\alpha\text{-Ti}}$ , B = $(10\overline{1}0)_{\alpha\text{-Ti}}$ , C
= $(00\overline{2})_{Ti2ZrO}$ , D = $(1\overline{1}0)_{Ti2ZrO}$ ); (c) the energy-dispersive spectrum of
Ti <sub>2</sub> ZrO
Fig. 5.5 TEM micrograph (bright field image, BFI) of the reaction layer
"III" showing the coexistence of $\beta$ '-Ti and $\alpha$ -Ti after reaction at (a)
$1400^{\circ}\text{C/6} \text{ h } (A = (0001)_{\alpha\text{-Ti}}, \ B = (01\overline{1}0)_{\alpha\text{-Ti}}, \ C = (\overline{1}\overline{1}0)_{\beta'\text{-Ti}}, \ \text{and} \ D = (0001)_{\alpha'$
$(\overline{1}10)_{\beta'-T_i})$ in the inset selected area diffraction pattern (SADP) and (b)
$1550^{\circ}\text{C/6} \text{ h } (A = (0001)_{\alpha\text{-Ti}}, B = (01\overline{1}0)_{\alpha\text{-Ti}}, C = (\overline{1}1\overline{2})_{\beta\text{'-Ti}}, \text{ and } D = (01\overline{1}0)_{\alpha\text{-Ti}}$
$(11\overline{2})_{\beta'-T_i}$ ) in the insert SADP)

Fig. 5.6 TEM micrograph (bright field image, BFI) of the reaction layer

"V" consisting of $\beta$ '-Ti and $c$ -ZrO <sub>2-x</sub> after reaction at (a) 1400°C/6 h; (b)
at $1550^{\circ}\text{C/6}$ h; (c) a selected area diffraction pattern (SADP) of $\beta$ '-Ti in
Fig. 5.6(b) (Zone axis is [021], $A = (\overline{2}00)$ , $B = (\overline{2}2\overline{2})$ , and $C = (\overline{1}1\overline{1})$ ;
(d) a SADP of $\beta$ '-Ti in Fig. 5.6(b) (Zone axis is $[\overline{1}12]$ , $A = (\overline{1}3\overline{2})$ , $B =$
$(\overline{1} \overline{1} 0)$ , and $C = (\overline{1} 1 \overline{1})$
Fig. 5.7 TEM micrograph (bright field image, BFI) of the layer "VI" far
away from the interface after reaction at (a) 1100°C, (b) 1300°C, (c)
1400°C, and (d) 1550°C for 6h
Fig. 5.8 (a) TEM micrograph (bright field image, BFI) of the suboxide
Ti <sub>3</sub> O near the reaction layer "I" after reaction at 1550°C for 6 h; (b) the
energy-dispersive spectrum of Ti <sub>3</sub> O; (c) the selected area diffraction
pattern (SADP) along the $[2\overline{1}\overline{1}0]$ zone axis (A = (0002) and B =
$(0\overline{1}11)$ ; (d) a SADP of Ti <sub>3</sub> O along the $[1\overline{1}00]$ zone axis. (A = (0002), B
= $(11\overline{2}0)$ , C = $(\frac{1}{3}\frac{1}{3}\frac{\overline{2}}{3}\frac{1}{2})$ , and D = $(\frac{22\overline{4}}{3333}\frac{1}{2})$ )
Fig. 5.9 The crystal structure of Ti <sub>3</sub> O. The dash line indicates that the
Ti <sub>3</sub> O structure is based on the Ti <sub>2</sub> O structure (solid line). ⊙: oxygen
position, ●: titanium position, ●: unoccupied oxygen position. 15116
Fig. 5.10 Schematic diagrams showing the microstructural evolution of
the $Ti/ZrO_2$ diffusion couple annealed at $1550^{\circ}C$ . (a) as hot-pressed; (b)
the relation between the Ti-Zr-O phase diagram. <sup>20</sup> ; (c), (d), and (e) the
microstructure of Ti/ZrO <sub>2</sub> diffusion couple on annealing at 1300°, 1400°,
and 1550°C and their cooling stages, respectively