Chapter 6

Summary

The diffusional reaction between titanium and zirconia was conducted isothermally in argon at temperatures range from 1100° to 1550°C. The distinct reaction layers between titanium and zirconia were developed at various temperatures. The microstructures in the titanium and zirconia interface were characterized using electron probe microscopy (EPMA), analytical scanning electron microscopy/energy dispersive spectrometer (SEM/EDS) and transmission electron microscopy/energy dispersive spectrometer (TEM/EDS). The microstructures and reaction mechanisms at various temperatures were described in the following sections.

6.1 Interface structures and reaction mechanisms at 1100°C

A lamellar of Ti_2ZrO and α -Ti(O, Zr) phases first developed in the interface between Ti/ZrO_2 , while zirconia grains did not grow conspicuously. Even though only a limited reaction took place, the α -Ti dissolved a significant amount of zirconium and oxygen, forming supersaturated disordered solid solution α -Ti(Zr, O), which resulted in the precipitation of the lamellae Ti_2ZrO during cooling. The lamellar phases were identified as orthorhombic Ti_2ZrO and hexagonal disordered α -Ti from and the orientation relations were identified as $[0001]_{\alpha$ - $Ti}$ // $[110]_{Ti2ZrO}$ and $(10\overline{1}0)_{\alpha$ - $Ti}$ // $(1\overline{1}0)_{Ti2ZrO}$.

6.2 Interface structures and reaction mechanisms at 1300°C

Two reaction layers in the sequence of lamellar $Ti_2ZrO + \alpha$ -Ti(O, Zr) and the β '-Ti(Zr, O) were found in the titanium side. Because of the dissolution of a large amount of zirconium in titanium side, which is a β -stabilizer, β -Ti was transformed to orthorhombic β '-Ti(Zr, O), not α -Ti, during cooling. In the zirconia side near the interface, the β '-Ti(Zr, O) and the high- Y_2O_3 containing c- ZrO_2 were formed. Yttrium would be congregated and remained in zirconia due to the low solubility of yttrium in titanium. In the zirconia side away from the interface, the solubility of α -Zr in tetragonal ZrO_{2-x} declined as the temperature decreased. Hence, the α -Zr(O) tends to segregated from the supersaturated solid solution of t- ZrO_{2-x} during cooling, leading to the increase in the O/Zr ratio of the oxygen-deficient zirconia.

6.3 Interface structures and reaction mechanisms at 1400°C

Three reaction layers in the sequence of lamellar $Ti_2ZrO + \alpha$ -Ti(O, Zr), acicular α - $Ti(O, Zr) + \beta$ '-Ti(O, Zr), and β '-Ti(Zr, O) were found in the titanium side. The acicular α -Ti was precipitated from the β '-Ti matrix by means of the ledge mechanism. The acicular α -Ti and the β '-Ti showed two different orientation relations: one was $[2\,\overline{1}\,\overline{1}\,0]_{\alpha$ - $Ti}$ // $[001]_{\beta$ - $Ti}$ and $(0001)_{\alpha$ - $Ti}$ // $(100)_{\beta$ - $Ti}$ and the other was $[2\,\overline{1}\,\overline{1}\,0]_{\alpha$ - $Ti}$ // $[021]_{\beta$ - $Ti}$ and $(0001)_{\alpha$ - $Ti}$ // $(1\,\overline{1}\,2)_{\beta$ - $Ti}$. In the zirconia side, two reaction layers were found: near the original interface, β '-Ti coexisted with fine spherical c- ZrO_{2-x} and Chinese-script-like c- ZrO_{2-x} , which dissolved a significant amount of Y_2O_3 in solid solution; further away from the original interface, the coarsened intergranular α -Zr was excluded from metastable ZrO_{2-x} , resulting in the lenticular t- ZrO_{2-x} and

6.4 Interface structures and reaction mechanisms at 1550°C

Four layers in a sequence of $Ti_2ZrO + \alpha - Ti(O, Zr)$, $Ti_2ZrO + \alpha - Ti(O, Zr) +$ β' -Ti (O, Zr), α -Ti (O, Zr) + β' -Ti (O, Zr), and β' -Ti (Zr, O) were formed in the titanium side after cooling. The lamellar and the spherical Ti₂ZrO, which were orthorhombic and hexagonal, respectively, were found. The spherical hexagonal Ti₂ZrO was an ordered structure, with zirconium and oxygen occupying substitutional and interstitial sites, respectively. orientation relations between α-Ti and the lamellae orthorhombic Ti₂ZrO were determined to be $[0001]_{\alpha,Ti}$ // $[110]_{Ti2ZrO}$ and $(10\overline{1}0)_{\alpha-Ti}$ // $(1\overline{1}0)_{Ti2ZrO}$; meanwhile those between the α-Ti and the spherical hexagonal Ti₂ZrO were $[0001]_{\alpha-\text{Ti}} // [0001]_{\text{Ti}2ZrO}$ and $(10\overline{1}0)_{\alpha-\text{Ti}} // (10\overline{1}0)_{\text{Ti}2ZrO}$. In the zirconia side, near the original interface, β' -Ti and spherical or Chinese-script-like c-ZrO_{2-x} with high content of Y₂O₃ were in coexistence. Away the interface, zirconia grains grew rapidly to about $20 \sim 30 \mu m$ in size. The α -Zr was segregated on grain boundaries during cooling by the exsolution of zirconium from ZrO_{2-x} , while twinned $t'-ZrO_{2-x}$ or lenticular $t-ZrO_{2-x}$ in ordered c-ZrO_{2-x}, was found. The ordered c-ZrO_{2-x} was identified by the $\frac{1}{5}$ {113} superlattice reflections of its electron diffraction patterns.