# EVALUATION OF THE α-CASE WITH $TiO_2$ IN MOLD FOR TITANIUM INVESTMENT CASTING

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## Abstract

*Molten titanium easily reacts with not only oxygen, carbon, and nitrogen but also the ceramic mold to form an α-case on the casting surface. However, the brittle α-case must be removed by chemical milling because it weakens the mechanical properties of the casting. The aim of this study is to evaluate and suppress the formation of the α-case by including $TiO_2$ in the mold. Titanium powder was added into the alumina mold in order to facilitate the formation of $TiO_2$ by the oxidation of titanium during mold firing. Another way to include $TiO_2$ in the mold was to simply add $TiO_2$ into the alumina mold. Optical microscopy and the micro-Vickers hardness test were used to characterize the α-case. The composition and morphology of the molds were confirmed using X-ray diffraction and field emission scanning electron microscopy. The mold with added titanium ($Al_2O_3$ + Ti) was effective in controlling the α-case. However, the interfacial reactions of the mold with the added $TiO_2$ ($Al_2O_3$ + $TiO_2$) exhibited distinct differences in α-case formation compared to the Ti-added mold ($Al_2O_3$ + Ti), while having almost identical compositions.*

***Keywords:*** *titanium, investment casting, ceramic mold, α-case*

## Introduction

The investment casting process shows outstanding reproducibility of castings within close dimensional limits.[1] Because of the poor machinability and workability of titanium, investment castings are widely used to produce complex and near-net-shaped products. However, titanium is extremely reactive with ceramic molds, resulting in the formation of the α-case. The α-case is formed by the diffusion of oxygen and metallic elements in the ceramic mold and is composed of titanium oxide and intermetallic compounds.[2] The formation of the α-case on castings degraded the fatigue and ductility by acting as surface crack initiation sites under the service temperature.[3] Therefore, the α-case is usually removed through chemical milling before use. However, the milling process is expensive and limits the dimensional tolerance. $Al_2O_3$ was selected for the mold material because $Al_2O_3$ is more cost effective than $ZrO_2$ and $Y_2O_3$. In addition, $Al_2O_3$ features suitable strength, permeability, and collapsibility, which can ensure dimensional accuracy of castings.[4] The aim of this study is to evaluate and control the formation of α-case by the inclusion of $TiO_2$ in the $Al_2O_3$ mold, which is a primary component of the α-case in the mold. The inclusion of $TiO_2$ in the mold was achieved by the oxidation of titanium during the mold firing processes or it was added during the mold manufacturing process.

## Experimental Procedures

Alumina ($Al_2O_3$, purity of 99 %, 325 mesh), titanium (Ti, purity of 99 %, 325 mesh), rutile titanium dioxide ($TiO_2$, purity of 99 %, 325 mesh), and colloidal $SiO_2$ (30 % $SiO_2$, 15 nm) were used as primary coating materials. In order to produce $TiO_2$ in the mold, 50 wt% of titanium or $TiO_2$ was added to the $Al_2O_3$ flour (denoted as $Al_2O_3$ + 50Ti and $Al_2O_3$ + 50$TiO_2$ respectively.) Subsequently, colloidal $SiO_2$ was added to the slurry until it achieved a viscosity in 40 s, as measured using a Zahn cup (ASTM D-4212). The primary coating process was repeated twice, and the manufacturing condition of the slurry is shown in Table 1. In addition, the chamotte ($Al_2O_3$·$SiO_2$, purity of 98 %, 325 mesh) and colloidal

*Table 1. Manufacturing Condition of Primary Coat*

| Mold | Primary coat | | | | |
|---|---|---|---|---|---|
| | Flour | Size (mesh) | Stucco | Size (mesh) | Mixing ratio (flour/binder) |
| $Al_2O_3$ | $Al_2O_3$ | 325 | $Al_2O_3$ | 200 | 100:32 |
| $Al_2O_3$ + 50$TiO_2$ | $Al_2O_3$, $TiO_2$ | 325 | | | 100:32 |
| $Al_2O_3$ + 50Ti | $Al_2O_3$, Ti | 325 | | | 100:34 |

$SiO_2$ were used as backup slurry materials. A backup coating was applied three times, at 4 h intervals, with chamotte slurry and $Al_2O_3$ stucco (purity of 99 %, 18–32 mesh). The mold was dewaxed in an autoclave at 150 MPa and fired in the furnace at 1200 K (927 °C/1700 °F) for 2 h in an air atmosphere. One hundred and twenty grams of commercial pure titanium (ASTM B-348, grade 2) was placed on top of a water-cooled copper crucible. The mold was located inside the copper crucible for dropping titanium melts. A titanium rod was melted in a plasma arc melting furnace (PAM), and the casting process is presented in Figure 1. Phase identification of molds was carried out by X-ray diffraction (XRD, M18XHF-SRA, Mac Science). The thickness of the α-case was determined by using a micro-Vickers hardness test (MVK-H2, Mitutoyo) and optical microscopy (OM, PME 3, Olympus). In our work, the micro-Vickers hardness test was performed at an interval of 50 μm from the casting surface to 1000 μm, applying a 100 g load. The microstructure and composition of the mold surface before and after casting were examined by field emission scanning electron microscopy (FE-SEM, JSM-7600F, JEOL). Also, the surface roughness of the before casting molds was confirmed using a profiler (Bruker DXT-A, Bruker).

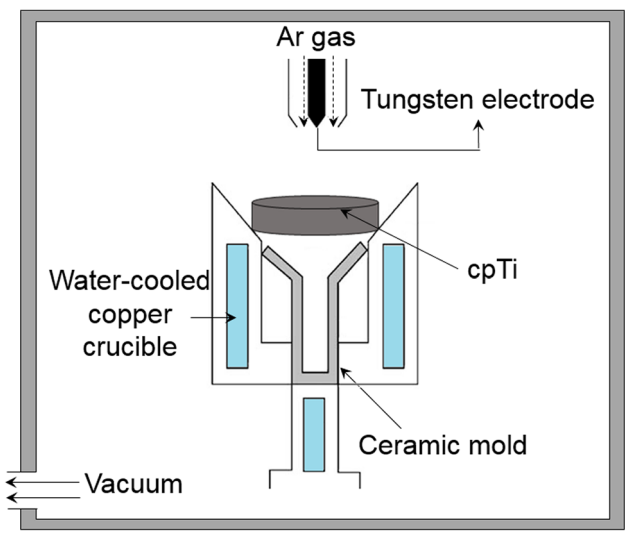


***Figure 1. Plasma arc melting furnace used to produce the titanium castings.***

## Results and Discussion

### Analysis of Mold Composition

Figure 2 shows the X-ray diffraction (XRD) spectra of the ceramic molds. The composition of the $Al_2O_3$ and $Al_2O_3$ + 50$TiO_2$ molds was unchanged, indicating that the $Al_2O_3$ and $TiO_2$ were in stable phases after mold firing. However, the large amount of $Al_2O_3$, $TiO_2$, and the small amount of $Ti_5Si_3$ were found in the $Al_2O_3$ + 50Ti mold. Most of the $TiO_2$ was formed by the reaction between atmospheric oxygen and titanium during mold firing. Also, the reaction between titanium and colloidal silica resulted in the formation of $Ti_5Si_3$ and $TiO_2$. The Gibbs free energy changes (ΔG) of $TiO_2$ and $Ti_5Si_3$ at 1200 K (927 °C/1700 °F) in the $Al_2O_3$ + 50Ti mold are shown in the following equation:[5]

$$Ti + O_2 \rightarrow TiO_2 \quad \Delta G = -440\,kJ/mol \qquad \text{Eqn. 1}$$

$$3SiO_2 + 8Ti \rightarrow Ti_5Si_3 + 3TiO_2 \quad \Delta G = -792\,kJ/mol \qquad \text{Eqn. 2}$$

Thermodynamic calculations indicated that the formation of $TiO_2$ and $Ti_5Si_3$ were spontaneous reactions. From the XRD results, the main composition of the $Al_2O_3$ + 50Ti

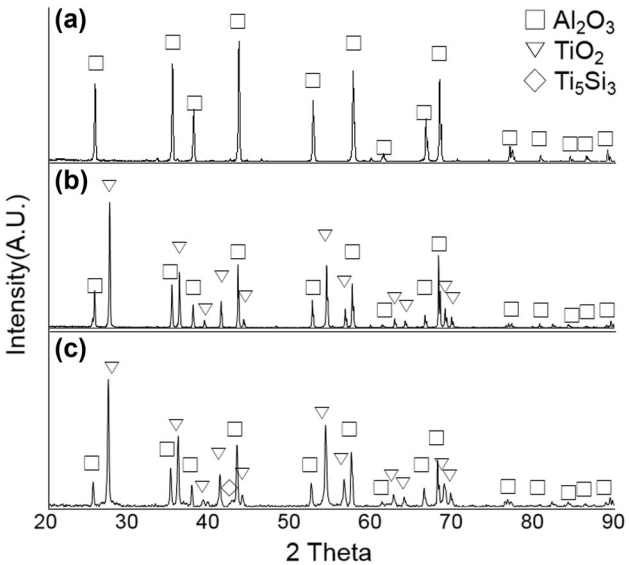


***Figure 2. XRD results of the ceramic mold (a) $Al_2O_3$, (b) $Al_2O_3$ + 50$TiO_2$, and (c) $Al_2O_3$ + 50Ti.***

mold was found to be very similar to that of the $Al_2O_3 + 50TiO_2$ mold, with $Al_2O_3$ and $TiO_2$ being present in both molds.

### Thickness of α-Case

Figure 3a and 3b shows a severe reaction layer that had Widmanstätten microstructures made from $Al_2O_3$ and $Al_2O_3 + 50TiO_2$ molds. However, the titanium surface made with the $Al_2O_3 + 50Ti$ mold (see Figure 3c) had the same microstructure as the inner side of the casting. This indicates that the use of the $Al_2O_3 + 50Ti$ mold effectively suppressed the formation of the α-case. Figure 4 exhibits a micro-Vickers hardness profile in titanium castings in relation to the depth from the surface. The depth of the α-case was revealed to be 350 μm when the castings were made using $Al_2O_3$ and $Al_2O_3 + 50TiO_2$ molds. However, for titanium castings made with the $Al_2O_3 + 50Ti$ mold, the thickness of the α-case was only 50 μm. The formation of the α-case was entirely different in the $Al_2O_3 + 50TiO_2$ and $Al_2O_3 + 50Ti$ molds although the compositions of the molds were almost similar.

### The Morphology of Mold Surface Before the Casting

The mold surface morphology and chemical compositions were analyzed by FE-SEM in order to understand the reason why $Al_2O_3 + 50Ti$ leads to less α-case formation. Figures 5 and 6 show FE-SEM images and energy dispersive spectroscopy (EDS) results of the mold surface before casting. Before casting, the $Al_2O_3$ mold surface contained homogeneously distributed, $Al_2O_3$ and $SiO_2$. Because the fine flour particles surrounded by colloidal silica formed a chemical bonding between the large flours. Contact between the larger ceramic particles is achieved through small bridges of binder and flour.[6]

The $Al_2O_3 + 50TiO_2$ mold surface also consisted of a mixture of $Al_2O_3$ and $SiO_2$ ($Al_2O_3 + SiO_2$) or $TiO_2$ and $SiO_2$ ($TiO_2 + SiO_2$) that could not be distinguished by their morphologies. In addition, $Al_2O_3 + SiO_2$ and $TiO_2 + SiO_2$ both had flat surfaces.

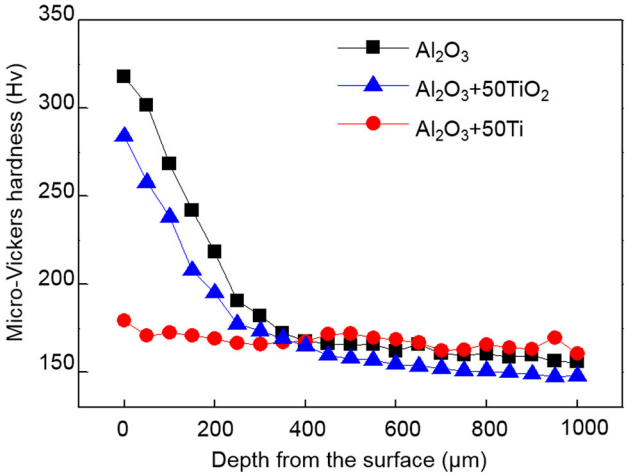


***Figure 4. Micro-Vickers hardness profile, as a function of depth from the surface, for titanium casting in ceramic molds.***

In the $Al_2O_3 + 50Ti$ mold, the $TiO_2$ phase had a flaky and rough surface, in conjunction with a flat surface of $Al_2O_3 + SiO_2$ layer. With an increase in temperature during mold firing, all surfaces of added titanium powder were covered by an oxide layer of flaky form because of titanium oxidation in $Al_2O_3 + 50Ti$ mold.[7] The roughness of mold surface was characterized by the average displacement from the mean height of asperities Ra for comparison between the added $TiO_2$ and formed $TiO_2$ (Ra = arithmetic average roughness). The average surface roughness of $Al_2O_3$ mold was 0.96 μm. And the Ra of $Al_2O_3 + TiO_2$ mold was 0.97 μm, which is approximately equal value to $Al_2O_3$ mold. However, the roughness of $Al_2O_3 + 50Ti$ mold was 1.18 μm and this value is slightly higher than $Al_2O_3$ and $Al_2O_3 + 50TiO_2$ molds. The titanium oxidation during mold firing results in the increase of surface roughness in $Al_2O_3 + 50Ti$ mold. However, increased roughness would not have a great effect on the dimensional tolerance because the augmented roughness was a low value.

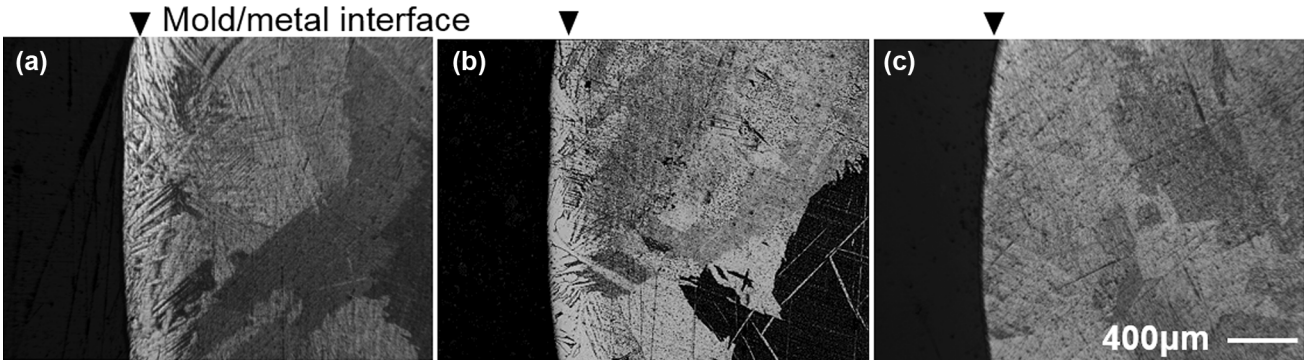


***Figure 3. Microstructure from titanium castings made in the ceramic molds (a) $Al_2O_3$, (b) $Al_2O_3 + 50TiO_2$, (c) $Al_2O_3 + 50Ti$.***

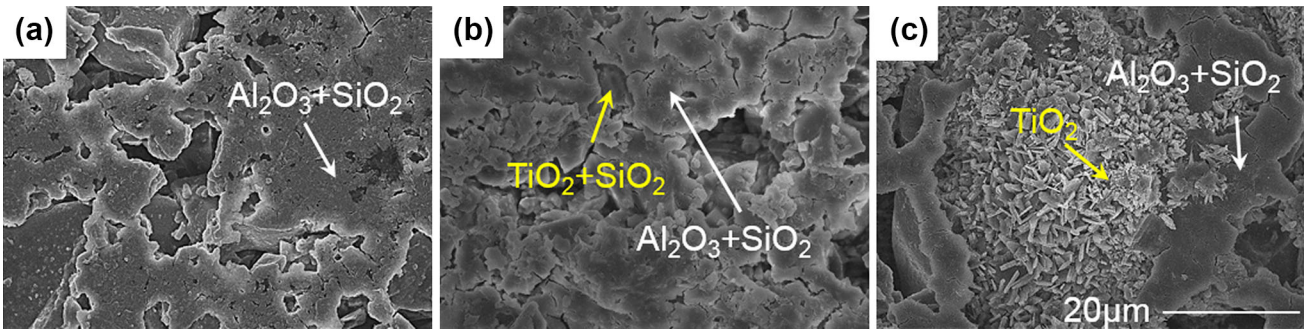


*Figure 5. FE-SEM images of the mold surface of before casting (a) $Al_2O_3$, (b) $Al_2O_3$ + 50$TiO_2$, (c) $Al_2O_3$ + 50Ti.*

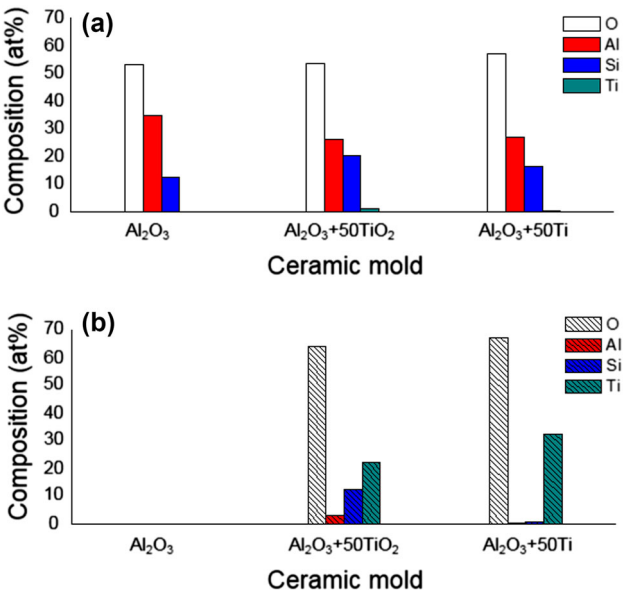


*Figure 6. EDS results of the ceramic mold surface before casting (a) the region of $Al_2O_3$ + $SiO_2$, (b) the region of $TiO_2$ or $TiO_2$ + $SiO_2$.*

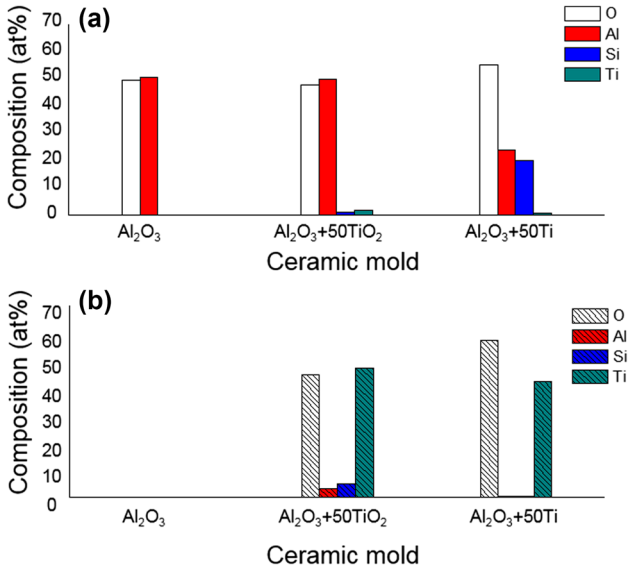


*Figure 8. EDS results of the ceramic mold surface after casting (a) the region of $Al_2O_3$ + $SiO_2$, (b) the region of $TiO_2$ or $TiO_2$ + $SiO_2$.*

## The Morphology of Mold Surface After the Casting

The morphology and composition analysis of molds after casting are presented in Figures 7 and 8. After casting in the $Al_2O_3$ mold, the primary coating layer of $Al_2O_3$ + $SiO_2$ was no longer observed because the titanium melt reacts with the $Al_2O_3$ mold by dissolving the $Al_2O_3$ + $SiO_2$ layer by penetration. The $Al_2O_3$ + $SiO_2$ layer was detached during the knockout, resulting in titanium that adheres to the $Al_2O_3$ + $SiO_2$. And the coarse $Al_2O_3$ flour in the $Al_2O_3$ mold had a ratio of aluminum to oxygen of one-to-one ratio.

Similarly, the primary coating layers of $Al_2O_3$ + $SiO_2$ and $TiO_2$ + $SiO_2$ were not observed, along the same lines as the $Al_2O_3$ mold. The exposed $TiO_2$ and $Al_2O_3$ were coarse

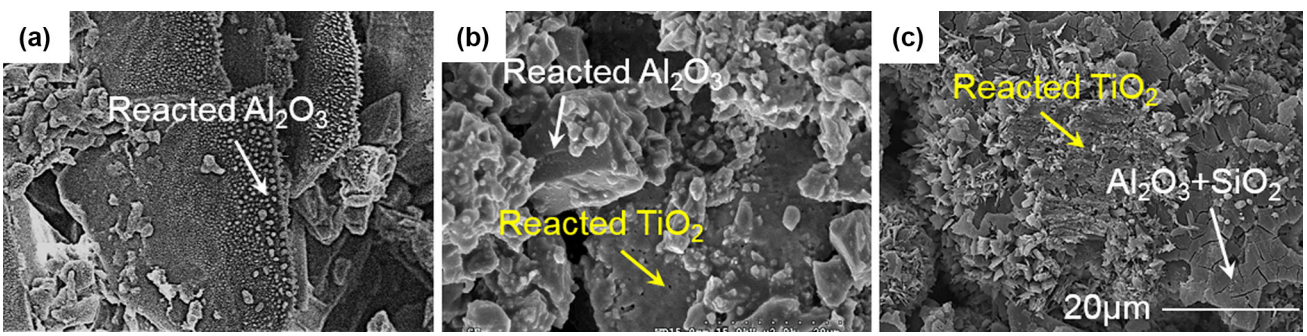


*Figure 7. FE-SEM images of the mold surface of after casting (a) $Al_2O_3$, (b) $Al_2O_3$ + 50$TiO_2$, (c) $Al_2O_3$ + 50Ti.*

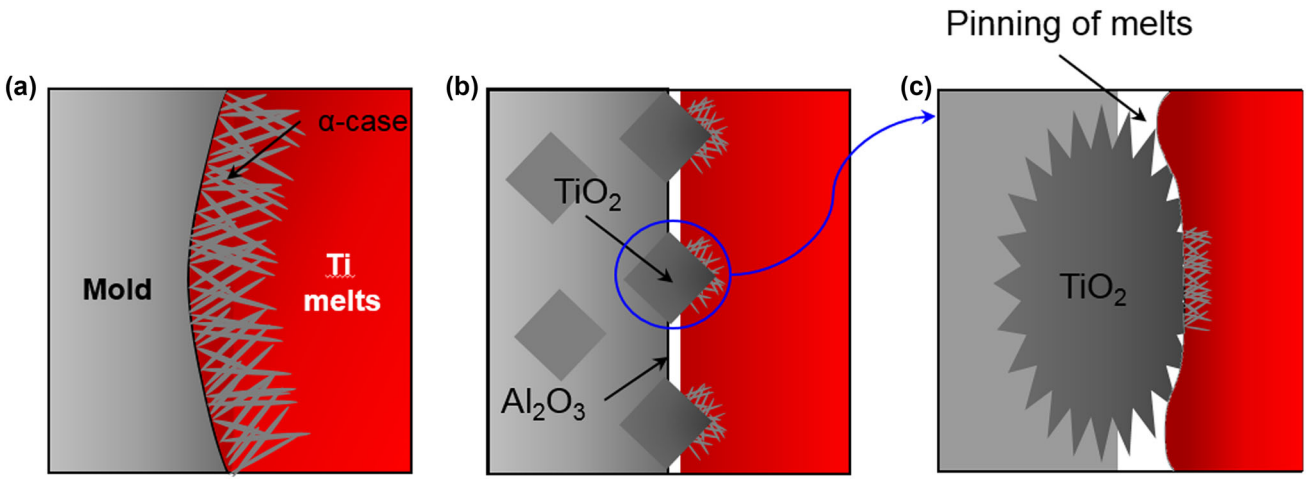


***Figure 9. Diagram illustrating the reactions of titanium with (a) $Al_2O_3$ and $Al_2O_3$ + 50$TiO_2$, (b) $Al_2O_3$ + 50Ti, (c) macrophotography of $TiO_2$ region in $Al_2O_3$ + 50Ti.***

refractory flours that existed inside the primary coating layers, and the ratio of metal to oxygen was almost 1:1.

In addition, the morphology of the $TiO_2$ phase was changed in the $Al_2O_3$ + 50Ti mold. Since the $TiO_2$ in $Al_2O_3$ + 50Ti was in contact with the titanium melt, the shape of $TiO_2$ surface flattens. However, inner coarse flour was not exposed, unlike the $Al_2O_3$ or $Al_2O_3$ + 50$TiO_2$ mold. The ratio of titanium to oxygen was decreased, due to the rapid diffusion of oxygen into the titanium melts in the $Al_2O_3$ + 50Ti mold. As a result, a change in the ratio of mold composition occurred during casting. However, the shape and chemical composition of the primary coating layer of $Al_2O_3$ + $SiO_2$ remained intact in the $Al_2O_3$ + 50Ti mold. And this result considered that the $Al_2O_3$ + $SiO_2$ had no contact with the titanium melt.

### Effect of Formed $TiO_2$ in $Al_2O_3$ + 50Ti mold on α-Case Formation

The surface morphology change (depending on the before and after casting), formed $TiO_2$ in the $Al_2O_3$ + 50Ti mold, that had a rougher surface than the $Al_2O_3$ + $SiO_2$ layer, due to the titanium oxidation. The rough surface results in an increase of wetting angle or resistance between the melts and substrate due to the reduction of contact area. Thus, the reaction rate may decline with rough surface.[8] Also, Sobczak et al.[9] have reported that rough surface may pin the triple line and strongly influence the wetting angle without notably influencing Ra, which may lead to $\Delta\theta$ values as high as 30°. (Triple line is the line of contact between the solid, liquid & atmosphere). As a result, the surface roughness could affect the wetting angles by decreasing reaction rate. Furthermore, the refractory materials that have good resistance to wetting by melts are worthwhile because the reaction can only occur if both make contact. A refractory which has good resistance to wetting has a tendency to increase its resistance to reaction.[10] Therefore, the formed $TiO_2$ by increasing surface roughness suppressed the contact of titanium melts with $Al_2O_3$ + 50Ti mold. A schematic showing the reactions that lead to the formation of the α-case is illustrated in Figure 9. When the titanium melts were poured into the $Al_2O_3$ and $Al_2O_3$ + 50$TiO_2$ molds, the titanium melts were exposed to the entire area of the mold surface. The molds decomposed into Al, O, Si, or Ti, and then these elements diffused into the titanium melt to form the α-case.[11–13] However, titanium was mainly in contact with formed $TiO_2$ because the morphology of $TiO_2$ was rougher and protruded more than the $Al_2O_3$ + $SiO_2$ layer.

## Conclusions

The composition of $Al_2O_3$ + 50Ti and $Al_2O_3$ + 50$TiO_2$ molds was found to be nearly identical due to titanium oxidation during mold firing. However, the morphology of the $Al_2O_3$ + 50$TiO_2$ mold resembled that of the $Al_2O_3$ mold. Further, the reactivity of titanium with $Al_2O_3$ + 50$TiO_2$ was similar to that with the $Al_2O_3$ mold. However, a reaction between the $Al_2O_3$ + 50Ti mold and titanium rarely occurred. These results indicate that the formed $TiO_2$ inhibits contact with the melt due to the increase in surface roughness.

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