# Oxidation of Titanium and Ti/ (TiB+TiC) Composite

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## Abstract

Titanium and titanium matrix composite reinforced with 10 vol. % (TiB+TiC) (10TMC) were oxidized at 700, 800 and 900 °C for 30, 50 and 70 h, and their oxidation behavior was studied. Oxidation of Ti and 10TMC in air led to the formation of rutile-$TiO_2$ without any other oxides. The oxide scale thickened with an increase in the oxidation time and temperature. Significant growth of the rutile oxide caused thermal stresses which generated during oxidation and voids formed at the scale/matrix interface, and the oxide scales were susceptible to cracking.

**Keywords**: Titanium, Titanium matrix composite, Oxidation, Oxide scale

## 1. Introduction

Titanium and titanium alloys are light in weight, have high tensile strength, toughness, and excellent corrosion resistance. They are widely used for highly demanding structural parts such as aircrafts, chemical plants, automotive, ocean engineering, oil refinery, biomaterials, highly stressed components, and military applications [1-3]. Recently, the introduction of particulates or continuous fibers with low density and high elastic modulus into titanium alloys has further improved the specific modulus, specific strength, creep resistance, wear resistance, and the service temperatures [4-8]. In order to utilize the titanium matrix composites (TMC) for industrial purpose, the oxidation study is imperative. In this study, the oxidation behavior of titanium and titanium matrix composite reinforced with 10 vol.% (TiB+TiC) particulates (hereafter, designated as 10TMC) were investigated after isothermally oxidizing at 700-900 °C for 30-70 h in air. Particulate reinforced titanium matrix composites have attracted considerable attentions.

## 2. Experimental

Titanium and the mold for TMCs were prepared by a common casting technique [9]. Prepared mold was mounted in the vacuum induction melting furnace. After that, $B_4C$ (99% purity, 1500 mm, 150 mm and 0.5 mm) was added to pure Ti (99% purity, Grade 2), following which the synthesis of the TMCs was carried out using vacuum induction melting. The pressure of the furnace atmosphere was held at 1.33 X $10^{-1}$ Pa and charged with inert argon gas at a pressure of 4.9 X $10^{3}$ Pa. The oxide mold was super-heated sufficiently to overcome the problem of low viscosity of TMCs, and then 1.88 mass% $B_4C$ was added to the pure Ti in the graphite crucible in order to form the 10 vol% of (TiB+TiC) reinforcement [9].

Ti and 10TMC samples were cut to 10x10x2 $mm^3$ in size, mechanically polished, and ultrasonically cleaned with ethanol solution. Research materials were oxidized at 700, 800 and 900 °C for 30, 50 and 70 h in air. Following oxidation process, matrix phases and oxide scales were investigated using scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) using Cu-Kα radiation operated at 40 kV and 100 mA. The matrix grain sizes were measured through the conventional mean-linear-intercept method using SEM. The Vickers microhardness was measured with a load of 100 N for 5 sec for more than 5 points on each sample at ambient temperature.

## 3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the oxide scales formed after isothermal oxidation at 800 °C for 70 h.

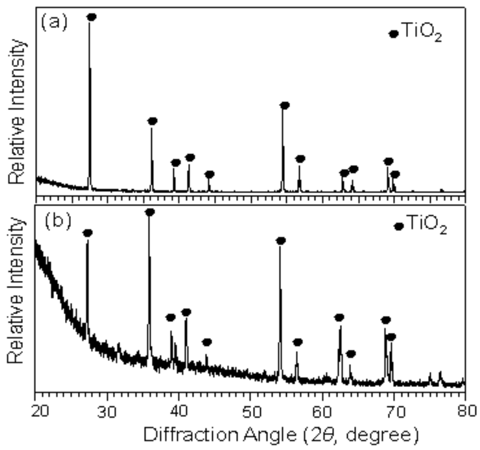


Fig. 1 X-ray diffraction patterns after oxidation at 800 °C for 70 h. (a) Titanium, (b) Titanium matrix composite rein-forced with 10 vol.% (TiB+TiC)

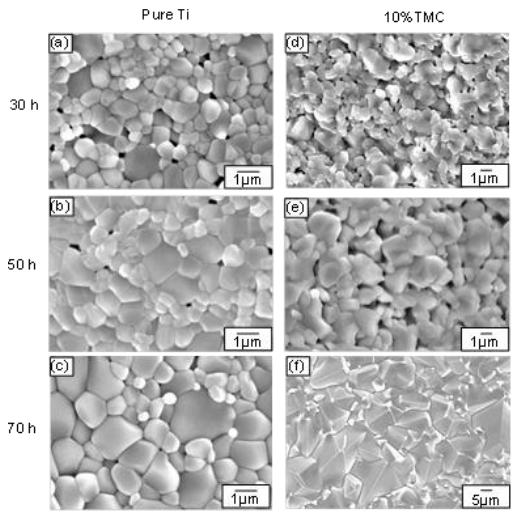


Fig. 2 SEM image after oxidation at 900 °C. Titanium for (a) 30 h, (b) 50 h, and (c) 70 h. Titanium matrix composite reinforced with 10 vol.% (TiB+TiC) for (d) 30 h, (e) 50 h, and (f) 70 h

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For titanium and 10TMC, the oxide scales consisted of rutile-$TiO_2$ without any other oxides. Apparently, boron and carbon in (TiB+TiC) evaporated during oxidation. SEM micrographs are shown in Fig. 2. The oxide grain size of 10TMC increased with an increase of an oxidation time more rapidly than that of pure titanium. Particularly, the coarse rutile-$TiO_2$ grains formed on 10TMC after oxidation at 900 °C for 70 h were noticeable.

Fig. 3 shows the grain evolution of oxide grains that formed on 10TMC as a function of the oxidation temperature. The grain size has increased proportionally to the oxidation temperature, owing to the increased reaction and diffusion rates at high temperature.

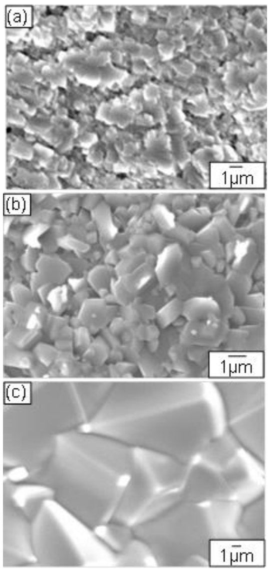


Fig. 3 SEM image of oxide scales formed on Titanium ma-trix composite reinforced with 10 vol.% (TiB+TiC) after oxidation for 70 h at (a) 700 °C, (b) 800 °C, and (c) 900 °C

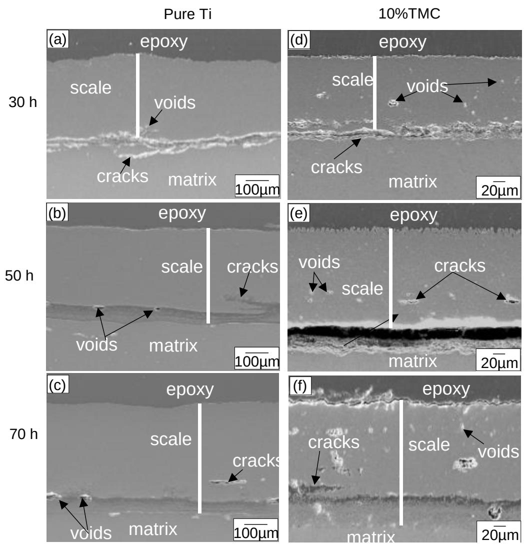


Fig. 4 SEM cross-section image after oxidation at 900 °C. Titanium for (a) 30 h, (b) 50 h, and (c) 70 h. Titanium matrix composite reinforced with 10 vol.% (TiB+TiC) for (d) 30 h, (e) 50 h, and (f) 70 h

Fig. 4 shows the cross-section of titanium and 10TMC after oxidation at 900 °C for 30, 50, and 70 h. As the oxidation reaction proceeded, oxide layer formation has generated stresses, which induced cracking and delamination of the oxide scale. These effects in voids formation at scale/metal interface that could act as stress concentration sites.

Voids apparently formed owing to the significant outward diffusion of Ti ions to form thick $TiO_2$ oxide scale. The average thickness of the oxide scale was 340 μm (Fig. 4(a)), 350 μm (Fig. 4(b)), 400 μm (Fig. 4(c)), 125 μm (Fig. 4(d)), 170 μm (Fig. 4(e)), and 190 μm (Fig. 4(f)). The addition of 10 vol. % (TiB+TiC) beneficially improved the oxidation resistance of the Ti metal. During the initial stage of oxidation, oxygen is absorbed on the surface of the metal by physisorption. The oxygen molecules dissociate creating oxygen anions through a chemisorption process until a monolayer of oxide is formed.

Fig. 5 shows the SEM/EDS analysis results of 10TMC after oxidation at 700 °C for 70 h. The oxide scale was 7 μm-thicks (Fig. 5(a)). Unlike in the Fig. 4, the oxide scale was dense, adherent, and crack-free owing to the slower growth rate and less thermal stresses generated during oxidation.

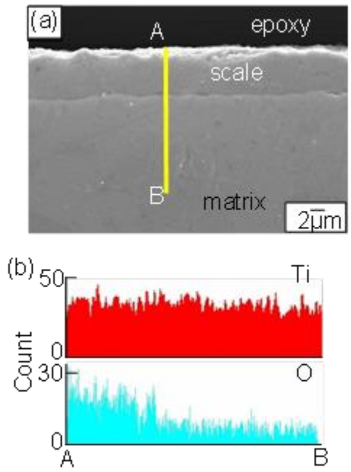


Fig. 5 Titanium matrix composite reinforced with 10 vol.% (TiB+TiC) after oxidation at 700 °C for 70 h. SEM cross-section, (b) EDS line profiles along A-B

Vickers microhardness of 10TMC was measured at the surface of the formed oxides as a function of the oxidation time and temperature, and presented in Fig. 6. During the early stage of oxidation, the microhardness increased at each temperature owing to the formation of thin hard oxide scale. The microhardness increased with higher oxidation temperature. However at the later stage of oxidation, the microhardness decreased to a certain extent.

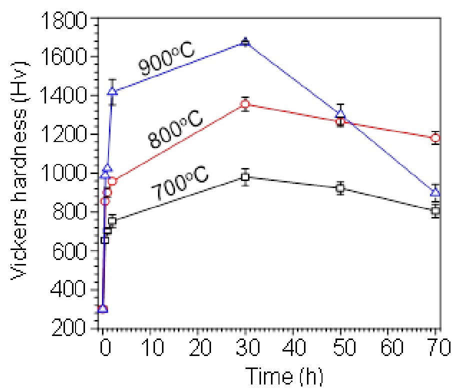


Fig. 6 Microhardness of Titanium matrix composite rein-forced with 10 vol.% (TiB+TiC) [top of the surface] as a function of oxidation time and temperature

It is clear that, the hardness increases with temperature as well as with the oxidation time, up to 30 hrs. Further oxidation causes the hardness to decrease; this may be attributed to stress relieving of the oxide grains arisen during heating stage of the oxidation process which induce cracking and delamination of the oxide scale. An evident matching with the results obtained from density; as the density increases, the hardness increases.

## 4. Conclusions

The oxidation behavior of titanium and 10TMC was investigated after isothermal oxidation at 700, 800 and 900$^oC$ up to 70 h. The XRD analysis revealed that the oxide scale consisted of rutile-TiO2.The scale thickness, growth and thermal stress increased with the increase in the oxidation time and temperature. The oxidation at 900 $^oC$ for 70 h led to the cracking and void formation in the oxide scale as well as around the oxide scale/matrix interface. Microhardness of the oxide scale increased for the short stage of oxidation (30 h) and decreased for at the longer oxidation times (70 h) due to the stress-relieving arisen by the oxide grain growth.

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## References

[1] M. Yamada, "An overview on the development of titanium alloys for non-aerospace application in Japan," Material Science and Engineering A, vol. 213, pp. 8-15, 1996.

[2] M. Peters, J. Hemptenmacher, J. Kumpfert, and C. Leyens, Titanium and Titanium Alloys: fundamentals and applications, Germany: WILEY-VCH, pp. 1-36, 2003.

[3] S. R. Seagle, "The state of the USA titanium industry in 1995," Material Science and Engineering A, vol. 213, pp. 1-7, 1996.

[4] S. Abkowitz, P. F. Weihrauch, S. M. Abkowitz, and H. L. Heussi, "The commercial application of low-cost titanium composites," Journal of Metals, vol. 47, pp. 40-41, 1995.

[5] S. Ranganath, "A review on particulate-reinforced titanium matrix composites," Journal of Materials Science, vol. 32, pp. 1-16, 1997.

[6] F. H. Froes, "Recent advances in titanium metal matrix composites," USA, TMS, Warrendale, PA, 1995.

[7] T. Yamamoto, A. Otsuki, and K. Ishihara, "Synthesis of near net shape high density TiB/Ti composite," Material Science Engineering A, vol. 239, pp. 239-240, 1997.

[8] D. B. Lee, Y. C. Lee, and D. J. Kim, "The oxidation of $TiB_2$ ceramics containing Cr and Fe," Oxidation of Metals, vol. 56, pp. 177-189, 2001.

[9] B. J. Choi and Y. J. Kim, "Effect of B4C size on tensile property of (TiB+TiC) particulate rein-forced titanium matrix composites by investment casting," Materials Transactions, vol. 52, pp. 1926-1930, 2011.

 