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High-temperature OM investigation of the early stage of (TiC + TiB)/Ti oxidation

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The initial oxidation behavior of titanium matrix composites (TMCs) was studied in a temperature range 550 to 650°C in a flow of purified oxygen at atmospheric pressure using thermogravimetry. The oxidation kinetics very initially follows approximately a linear rate law and then a parabolic rate law. The oxidation rate decreases gradually as the oxidation proceeds. The initial *in situ* oxidation was investigated by high-temperature optical microscopy in air. The oxide layer was examined by X-ray diffraction and scanning electron microscopy combined with an energy dispersive X-ray spectroscopy unit. It was found that the reaction products are predominantly rutile. The reinforcements of TiB and TiC can result in a decrease in the overall oxidation rate at 550, 600, and 650°C. This is attributed to the interface cohesion and the clean interfacial microstructure between reinforcements and the titanium matrix alloy, which is strong enough such that the reinforcements can act as barriers to solid-state diffusion.

1. Introduction

There continues to be widespread use of titanium and its alloy in the aerospace, petrochemical, gas/steam turbine, and automotive industries for a variety of structural applications. These materials are considered technically superior and cost-effective primarily because of their strength-to-weight ratio, strength at moderate temperatures, and good resistance to creep and fatigue. However, titanium matrix composites (TMCs) attract extensive attention owing to their high specific modulus, high specific strength, high strength at elevated temperature and wide potential application in the field of aviation, aerospace and automobile [1, 2]. In recent years, we have highlighted a novel *in situ* process in which traditional ingot metallurgy plus self-propagation high-temperature synthesis (SHS) techniques were used to produce (TiB + TiC)/Ti matrix composites [3]. The formation mechanism of *in situ* synthesized titanium matrix composites has been discussed [4]. The microstructure and mechanical properties at room temperature have also been investigated [5, 6]. The former results show that TiB grows in whisker shape while TiC grows in equiaxed or near-equiaxed shape. TiB whiskers distributed random in the titanium matrix alloy after casting. The main aim in developing the TMCs is to widen the utilization field at high temperature [7]. So, it is necessary to understand the oxidation behavior of TMCs at elevated temperatures, especially above 500°C, in air. Recently, several investigations on TMCs oxidation have dealt with the long-term oxidation behavior [8, 9]. By now, there is no research on the early stages of TMCs oxidation. However, the results of long-term oxidation indicate that the early stages of oxidation may play an important part in the later course of oxidation and in understanding oxidation mechanisms of TMCs.

In the present work the early stages of TMCs oxidation at temperatures of 550, 600 and 650°C in air were investigated. A characterization of the oxidation products, the structure and morphology of the oxide scale, was made in order to throw further light on the oxidation mechanisms of TMCs.

2. Experimental procedures

A common casting technique was used to fabricate the *in situ* synthesized (TiB + TiC)/Ti matrix composites. The reagents used were two grade sponge titanium (99%), B_4C powder (98%, average particle size, 5–10 μm) and graphite powder (99.8%, average particle size, 5–7 μm). The total volume percentage of reinforcements TiB and TiC was 0%, 5% and 8%, respectively. On the basis of a former paper [10], the titanium matrix composites reinforced with two different mole ratios between TiB and TiC (4:1 and 1:1) were *in situ* fabricated by consumable vacuum arc remelting. The compositions of the raw materials and the theoretical volume percentage of the reinforcements are listed in Table I.

In order to obtain information about the oxidation kinetics in the early stages of oxidation, coupons of about 10 × 10 × 3 mm were firstly cut out of the ingots and polished on a series of SiC polishing paper up to #1000, then ultrasonically washed in an acetone bath, dried in air, and weighed before oxidation. The isothermal oxidation kinetics were continuously followed by the

TABLE I Compositions and reinforcements volume percentage in (TiB + TiC)/Ti composites

Sample no.	Matrix alloy	B_4C (wt%)	C (wt%)	Reinforcements (vol%)	Mole Ratio (TiB:TiC)	TiB (vol%)	TiC (vol%)
TMCs1	Ti	0.96	0.68	8.00	1:1	4.17	3.83
TMCs2	Ti	1.53	0	8.00	4:1	6.50	1.50
TMCs3	Ti	0.96	0	5.00	4:1	4.17	0.83
Pure Ti	Ti	0	0	0	0	0	0

thermogravimetric method (TGA) with an autorecording thermobalance with a sensitivity of 0.01 mg, at the temperatures of 550, 600, and 650°C, respectively. A specimen was hung from a balance beam and the atmosphere was replaced with purified oxygen flowing at a rate of 6.7×10^{-4} $\text{l}\cdot\text{s}^{-1}$ under atmospheric pressure. The oxidation run was started by switching on the furnace with a heating rate of about $1.6°\text{C}\cdot\text{s}^{-1}$. The kinetics was measured from the beginning of the heating-up period. The performance of the oxidation was evaluated by generating weight-gain data as a function of time.

Samples of about 2 × 2 × 1 mm for optical microscopy (OM) were also taken from the ingots. Then they were prepared using conventional techniques of grinding and mechanical polishing. Their oxidation microstructures were characterized by *in situ* high-temperature optical microscopy (HTOM) in static air, at 550, 600, and 650°C, for up to 14.4 ks. The specimens after the HTOM tests were also similarly examined. Scanning electron microscopy (SEM) combined with an energy dispersive X-ray spectroscopy (EDX) unit and X-ray diffraction (XRD) techniques were employed to understand the nature and composition of the oxide scales formed during exposure to elevated temperatures.

3. Results and discussion

3.1. Thermo-gravimetry

In Fig. 1 weight gains per unit area, at 550, 600 and 650°C, are plotted against time. All specimens show almost the same oxidation trend at 550, 600 and 650°C. At the beginning of oxidation a strong increase in weight can be observed. After an oxidation time of about 0.8 ks, there is a gradually bend in the weight-gain curve, and the oxidation rate decreases up to about 28.8 ks.

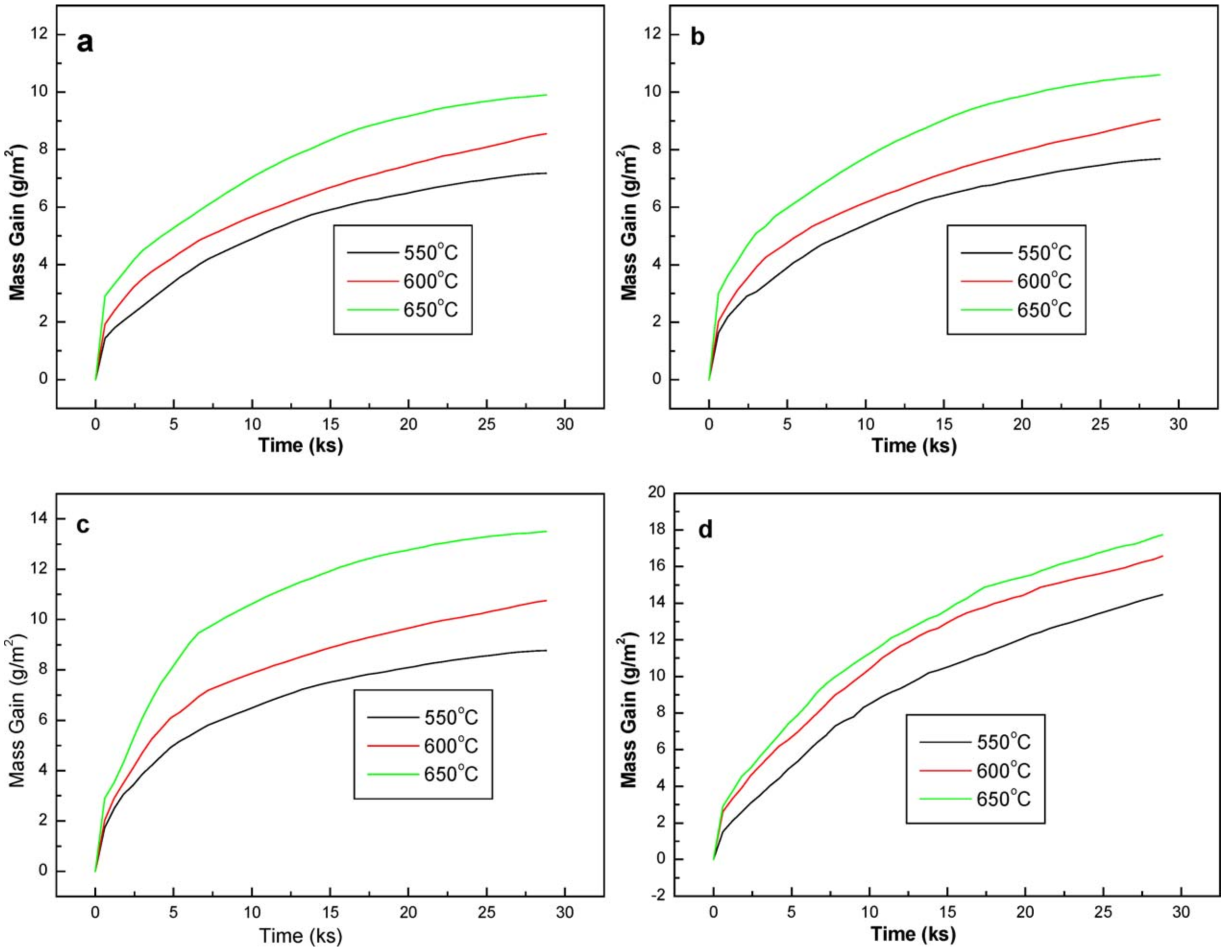

Figure 1 Mass gain-time relationship of (a) TMCs1, (b) TMCs2, (c) TMCs3, and (d) pure Ti in purified oxygen at 550, 600, and 650°C for 28.8 ks.

TABLE II Calculated values of the reaction index (n) for isothermal oxidation as a function of temperature

	Reaction index (n)			
Temperature (°C)	TMCs1	TMCs2	TMCs3	Pure Ti
550	2.1	2.3	2.4	2
600	2	2.1	2.2	1.87
650	1.8	2	2	1.73

Usually, the isothermal-oxidation kinetic are expressed as [11]:

$$(\Delta m)^{\mathrm{n}} = K_{\mathrm{n}} t$$

where, Δm, t, n, and K_{n} are the mass gain per unit area, time, reaction index, and rate constant, respectively. The values of n, obtained from the reciprocal of the gradient of the logarithmic plot of Δm versus t for a given set of reaction are listed in Table II.

If one considers, for example, the curves in Fig. 1a, one can successively find an almost linear portion during the initial 0.8 ks, followed by a slowing down and finally a parabolic kinetic (Table II). The slope of the linear period increases when the temperature increases. It is clear that the mass gains for the TMCs2 are lower than those of TMCs1 and TMCs3. This suggests that the reinforcements can improve the resistance, especially TiB providing better oxidation resistance than TiC. This good property of the reinforcements is attributed to the interface cohesion and the clean interfacial microstructure between reinforcements and the titanium matrix alloy [10],which is strong enough such that the reinforcements can act as barriers to solid-state diffusion of titanium upon exposure at 550, 600, and 650°C.

3.2. Metallography

Typical features of the outer surfaces of the specimens after oxidation at 650°C are shown in Fig. 2. At first glance no significant difference between the samples oxidized at the same time and temperature can be observed. All show a similar oxidized surface with almost the same morphology of the oxide scale. However, the oxidation period is short and the temperature is not so high, the oxides are loosely packed as shown in Fig. 2a, b and c. Kofstad *et al.* [12] asserted that from a thermodynamic standpoint one could reason the formation of various oxides in titanium including TiO, TiO_2, Ti_2O_3, and Ti_3O_5. EDX analysis (Fig. 2d) shows that oxide scale consists of oxide in titanium. Fig. 3 is XRD patterns of the specimens oxidized at 600°C for 28.8 ks. It

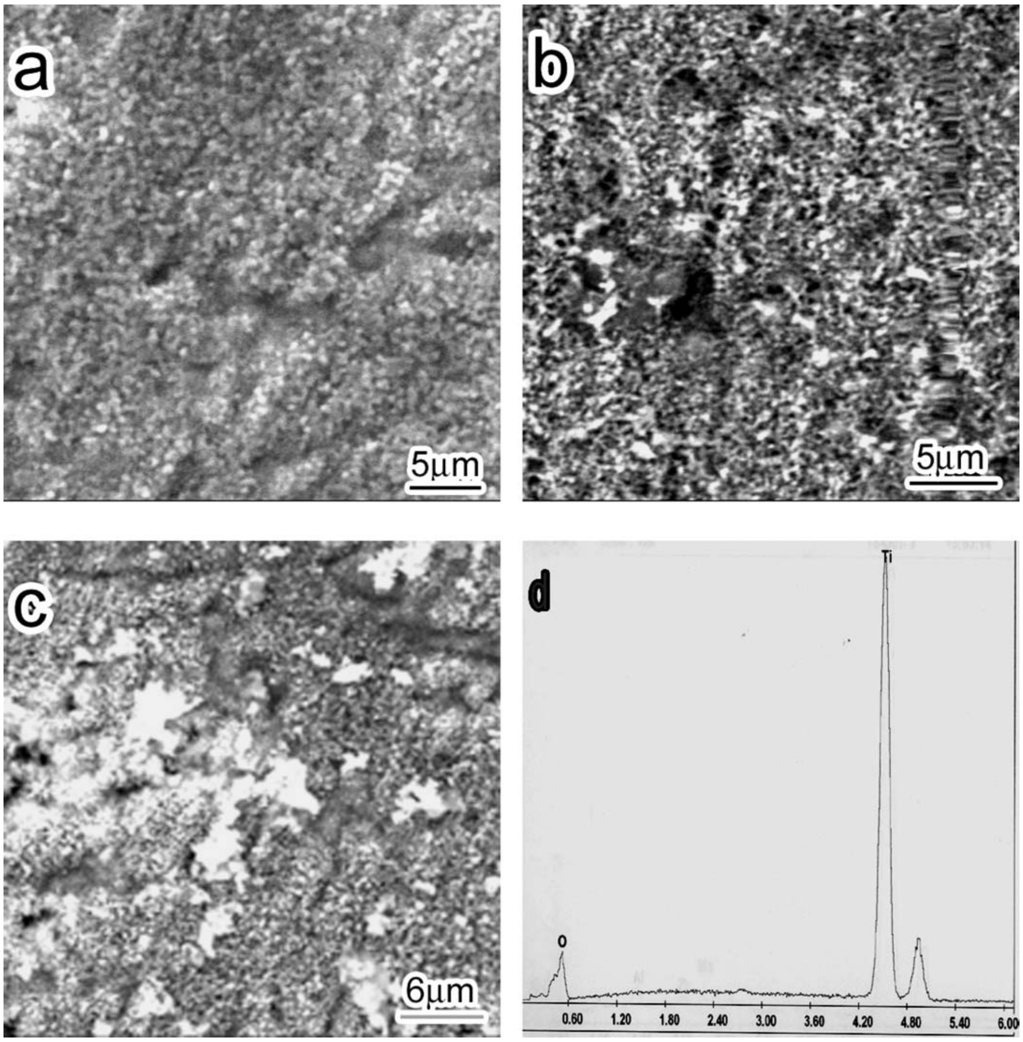

Figure 2 Outer surfaces of (a) TMCs1, (b) TMCs2, and (c) TMCs3 in purified oxygen at 650°C for 28.8 ks, and (d) EDX result of (a), (b), and (c).

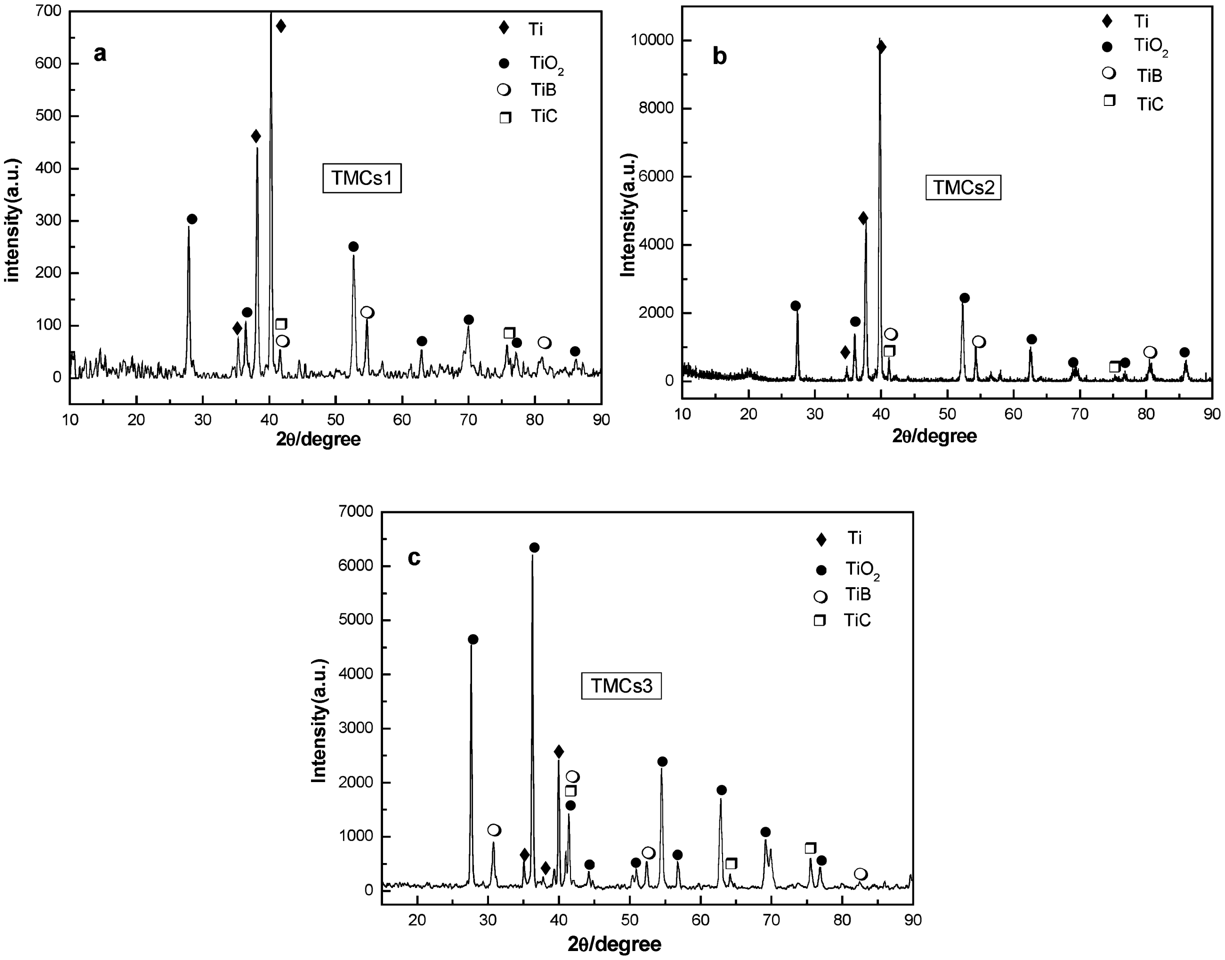

Figure 3 X-ray diffraction patterns of (a) TMCs1, (b) TMCs2, and (c) TMCs3 in purified oxygen at 600°C for 28.8 ks.

can be concluded that the reaction products are predominantly rutile. Other oxide phases were not detected by the XRD. Kofstad *et al.* [12] also concluded that only the rutile modification of TiO_2 has generally been observed for oxidation in oxygen below 1000°C.

3.3. High-temperature *in situ* OM investigations of TMCs

The *in situ* oxidation tests by HTOM were carried out to study the nucleation and the growth of the nuclei and any variation of the sample surface at the beginning of oxidation. However, a visual inspection of the exterior features of the oxide revealed that initially a thin slate gray-colored scale was formed on the titanium matrix composite substrate. As time proceeded, its color changed from yellow, blue, blue-green to gray, due to light interference depending upon thickness of the oxide film. From Fig. 4, it can be seen that at the very beginning of oxidation, the color of the crystal boundary region changed, then intra-crystalline changed. About 0.3 ks later, TiC reinforcements began to be colored, and TiB subsequently was colored. The color of the reinforcements changed from yellow to white, which was different from that of the crystals. These show that the appearance of the oxidation phases developed depends on the position on the sample. The oxide scale varies distinctly from the crystal boundary to intra-crystalline region. This is probably due to the oxidation of the crystal boundary prior to intra-crystalline and the reinforcements. After an oxidation time of only 1.8 ks at 600°C in air a considerable number of oxidation products can be observed on the surface of the samples (Fig. 4c and d). HTOM micrographs oxidized at 600°C for 5.4 ks are shown in Fig. 4e and f, respectively. It can be seen that much more oxidation products occurred on the surface of the samples. Moreover, the morphology of the reinforcements was not changed.

In an attempt to understand what is occurring at the reinforcements, typical features of the outer surface of the TiB after oxidation are shown in Fig. 5. Basically, the morphology of the reinforcements was not changed. Table III shows the measured values of EDX. It can be concluded that the oxygen content of crystal boundary is higher than that of intra-crystalline and reinforcements. Moreover, the oxidation process during the initial stage is dominated by the diffusion of oxygen. So

TABLE III Results of EDX in Fig. 5

		Atomic fraction of element (%)	
Site	Phase area	O	Ti
1	Intra-crystalline	46.32	53.68
2	Crystal boundary	57.91	42.09
3	TiB	38.26	61.74
4	TiB edge	43.28	56.72

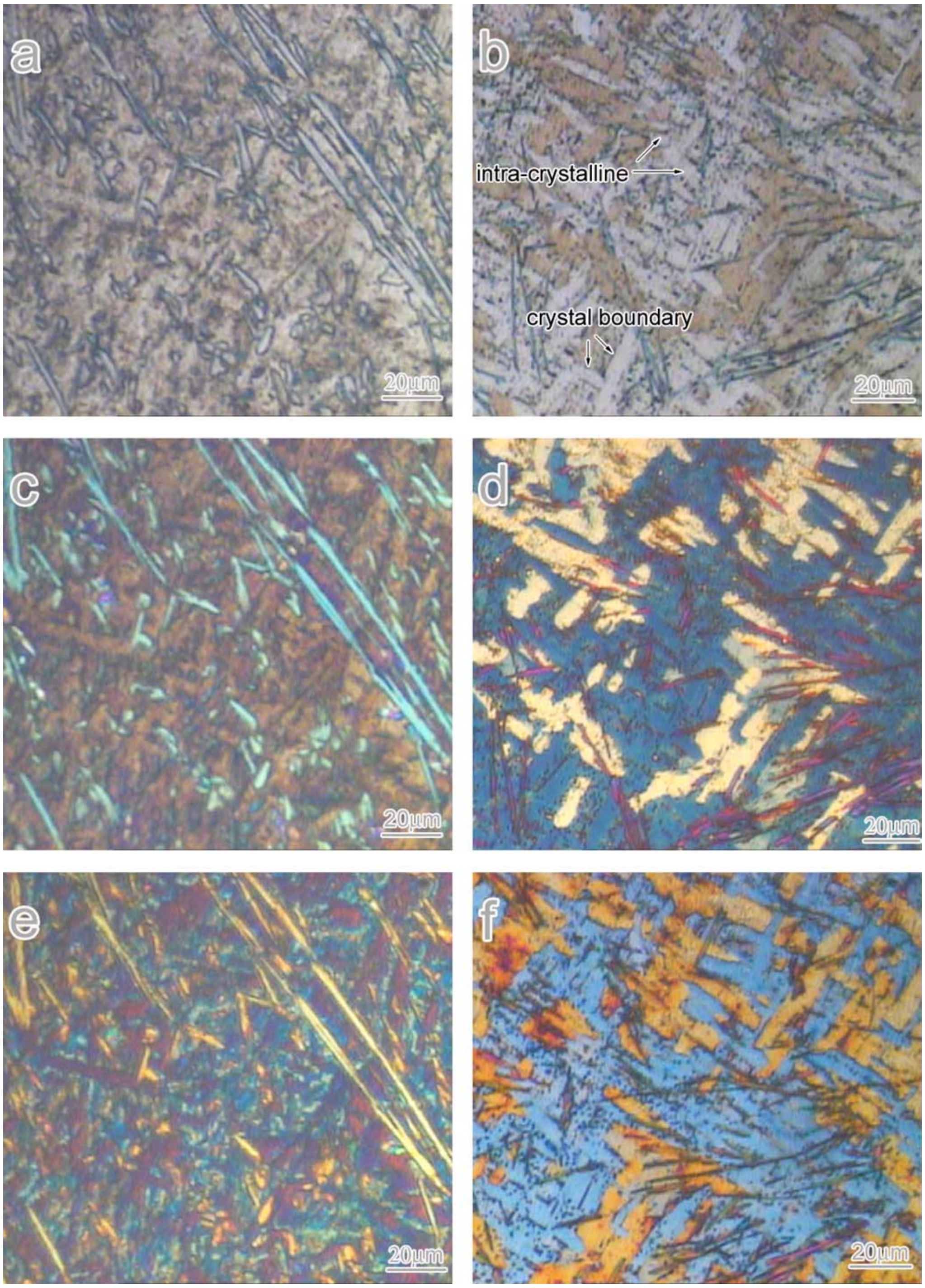

Figure 4 HTOM results of (a) TMCs1, (b) TMCs2 at 600°C for 0.3 ks, (c) TMCs1, (d) TMCs2 at 600°C for 1.8 ks, and (e) TMCs1 (f) TMCs2 at 600°C for 5.4 ks.

it is easier for diffusion of oxygen by crystal boundary than that by intra-crystalline. This evidence suggests that during very initial periods of oxidation, the oxidation is prone to take place in the crystal boundary, then the oxidation take place in the intra-crystalline, and lastly the reinforcements are oxidized.

3.4. Analysis

The oxidation in titanium is dominated by the diffusion of oxygen in both the scale and the metal core and that scale growth is dependent upon the oxygen concentration gradient in the 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. Depending upon the oxygen concentration gradient in the metal, oxygen ions either pass through the thin film or dissolved into the hexagonal-titanium lattice at octahedral interstitial locations or produce fresh oxide. Continued growth of the oxide film is restricted by the need for the chemical potential of oxygen in the oxide film and the reacting titanium to be in equilibrium. If a nonequilibrium condition exists, the rate of oxygen dissolution becomes the prevailing mechanism. However, once the titanium at the metal-oxide interface becomes saturated with oxygen, the rate-determining reaction is

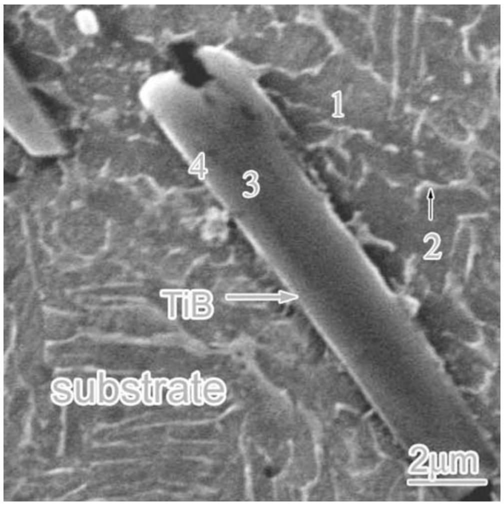

Figure 5 SEM photographs of TiB reinforcement oxidized at 600°C for 14.4 ks.

diffusion of oxygen ions through the oxide scale. The TiO_2 scale has been characterized as an n-type semiconductor, having an oxygen-deficient structure that produces oxygen ion vacancies rather than interstitial titanium ions. Thus, there is an inward passage of oxygen produced by anion-vacancy diffusion through the rutile lattice. It has also been known that the activation energy for titanium-ion diffusion is much greater than that of oxygen-ion diffusion in TiO_2. Therefore, for temperature below 650°C, it is generally believed that diffusion of titanium ions outward through the oxide layer is negligible. Solid-state diffusion of titanium would be difficult because the interface cohesion between reinforcements and the titanium matrix alloy is strong enough and which act as barriers to solid-state diffusion [3]. The clean interfacial microstructure between reinforcements and the titanium matrix alloy can also be attributed of this [13]. These indicate that the reinforcements can improve the oxidation resistance.

4. Conclusions

(1) The oxidation kinetics of TMCs at temperatures between 550 and 650°C in purified oxygen follows approximately linear rate laws during the very initial oxidation periods of 0.8 ks, then the oxidation rate decreases gradually as the oxidation proceed. It later follows the parabolic rate law.

(2) The oxide scale consists of rutile.

(3) The reinforcements, especially TiB, can improve the oxidation resistance at elevated temperature due to the enough strong interface cohesion and the clean interfacial microstructure between reinforcements and the titanium matrix alloy, which can act as barriers to solid-state diffusion.

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