Microstructure and Compressive Properties of *In Situ* Synthesized (TiB + TiC)/Ti Composites

Weijie Lu¹, Di Zhang¹, Xiaonong Zhang¹, Renjie Wu¹, Takao Sakata² and Hirotaro Mori²

¹State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China

²Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Yamadaoka, Suita 565 Japan

TiB and TiC reinforced titanium matrix composites have been produced by non-consumable arc-melting technology utilizing the self-propagation high-temperature synthesis reactions between titanium and B₄C, graphite. X-ray diffraction (XRD) was used to identify the phases in the composites. Microstructures of composites have been observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HREM). The results show that there are three phases in the composite: TiB, TiC and titanium matrix alloy. Reinforcements are distributed uniformly in the matrix. TiB grows in short-fiber shape and TiC grows in dendritic, equiaxed shapes. The interfaces between reinforcements and titanium matrix alloy are very clean. There is no any interfacial reaction. There are high-density dislocations around TiC particle. Mechanical properties have been improved due to the incorporation of reinforcements. The addition of aluminum not only strengthens the titanium matrix alloy by solid solution strengthening, but also improves the mechanical properties of composites by refining the reinforcements and matrix alloy.

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1. Introduction

Titanium-based metal-matrix composites (MMCs), reinforced with ceramic particles have considerable potential for improvements in properties and service temperature, while retaining isotropic behavior and ease of fabrication using conventional processing methods. Traditionally, titanium MMCs have been produced by such processing techniques as powder metallurgy^{1,2)} and casting technologies,^{3,4)} where the ceramic particles are directly incorporated into solid or liquid matrices, respectively. In this case, the scale of the reinforcement is controlled by the starting powder size, which is typically on the order of microns to tens of microns, and rarely below 1 μm . In recent years, novel processing techniques⁵⁻¹⁷⁾ based on the *in situ* production of MMCs have emerged. *In situ* techniques involve a chemical reaction resulting in the formation of a very fine and thermodynamically stable reinforcing ceramic phase within a metal matrix. As a result, this provides thermodynamic compatibility at the matrix-reinforcement interface. The reinforcement surfaces are also likely to be free of contamination and, therefore, a stronger matrix-reinforcement bond can be achieved. Some of these technologies include exothermic dispersion (XD), self-propagation high-temperature synthesis (SHS), and liquid-solid or liquid-liquid reactions.

Among the several techniques available to synthesize MMCs, the solidification processes are attractive due to their simplicity, economy and flexibility. TiB and/or TiC reinforced titanium matrix composites have been produced by solidification process,⁵⁻⁷⁾ where the reinforcing particles are formed *in situ* in the molten titanium prior to or during its solidification. The following SHS reactions have been used to fabricate TiB and/or TiC reinforced titanium matrix composites:

In the present work, we highlight a novel *in situ* process in which traditional ingot metallurgy plus SHS techniques utilizing reaction (1) and reaction (2) were used to produce (TiB + TiC)/Ti matrix composites. This paper focuses on the relationship between microstructure and compressive behavior of the *in situ* synthesized (TiB + TiC)/Ti composites.

2. Experimental Procedure

For preparing (TiB + TiC)/Ti MMCs, the raw materials were two grade sponge titanium, B₄C powder (98%, average particle size: 5 ~ 10 μm), graphite powder (99.8%, average particle size: 5 ~ 7 μm) and aluminum (98%). The stoichiometric amounts of sponge titanium, B₄C and graphite powder were blended, then they were compacted into pellets. The various amounts of pellets including the sponge titanium and/or aluminum were melted homogeneously in a non-consumable vacuum arc remelting (VAR) furnace to produce (TiB + TiC)/Ti composites via SHS reactions between titanium and B₄C, graphite. In order to ensure the chemical homogeneity of the composites, the ingots were melted at least three times. The compositions of the raw materials used to fabricate composites and the theoretical volume percentage of reinforcements are listed in Table 1. Two titanium alloys were also prepared for comparison, one without alloying element and the other with an Al content approximately equivalent to that of the metallic matrix in the composites (8 mass%).

Samples for phase identification and microstructure observation were prepared following conventional metallographic techniques. The samples were cut directly from ingots and

Table 1 Compositions and reinforcements volume percentage in (TiB + TiC)/Ti composites.

Sample	Ti (mass%)	B ₄ C (mass%)	C (mass%)	Al (mass%)	Reinforcements (vol%)	Moles ratio (TiB : TiC)
1	98.12	1.88	0	0	10	4 : 1
2	91.00	1.75	0	7.25	10	4 : 1
3	96.25	3.75	0	0	20	4 : 1
4	90.46	3.53	0	6.01	20	4 : 1
5	98.00	1.16	0.84	0	10	1 : 1
6	90.87	1.08	0.79	7.26	10	1 : 1

were polished and etched with a solution of water, nitric acid, and hydrofluoric acid in proportion of 85 : 10 : 5. The microstructures of all samples were characterized by Philips SEM515 scanning electron microscopy (SEM) equipped with EDS analysis system. Phase identification was carried out via XRD using a D-max IVA automatic X-ray diffractometer.

Samples for TEM observation were cut from the cast ingots. Then they were thinned to 100 μm by polishing with SiC paper. The samples were punched to discs with a diameter of 3.0 mm. The disc samples were then dimple ground to 20 μm in thickness. The final stage of thinning was performed by argon ion milling (Gatan) with an incident angle of 10 deg until perforation occurred. TEM observation was performed by means of H-800 transmission electron microscopy and H-9000 high-resolution transmission electron microscopy. The microscopes were operated at 200 and 300 kV, respectively.

The compression specimens with sizes of $5 \times 5 \times 10 \text{ mm}^3$ were prepared by electro-discharge machining (EDM) and grinding. Compression tests were conducted in MTS-810 materials test machine. The strain rate is 0.01 s^{-1} . The HRC values of composites and matrix alloys were detected by HR-150A hardness test.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns for cast samples. They all indicate that the phases in the composites are titanium (hcp), TiB (B27, FeB type) and TiC (B1, NaCl type). The results of the X-ray diffraction analysis confirm that Ti matrix composites reinforced with different mole ratios of TiB and TiC can be produced by common casting technique utilizing the SHS reactions between Ti and B₄C, graphite powder. The addition of alloying element *i.e.* aluminum did

not form other phases when the composition of aluminum is equal to or less than 8 mass%. Compared with different compositions, there are no significant differences in the X-ray diffraction patterns except that there is a difference in the peak intensities of reinforcements. It is clear that the addition of graphite increases the quantity of TiC, *i.e.*, the peak intensity of TiC increases with the addition of graphite. At the same time, the peak intensity of TiB and TiC increases when the volume percent increases from 10 to 20%.

The microstructures of titanium matrix composites are shown in Fig. 2. It shows that the TiB and TiC reinforcements are distributed uniformly in the titanium alloy matrix. These reinforcements are on a large scale ranging from less than 1 μm to over 100 μm . Moreover, the reinforcements morphologies mainly exhibits following shapes: short-fiber shape, dendritic shape and near-equiaxed shape. The results of energy dispersion X-ray spectrometer (EDS) show that the reinforcements with short-fiber shape are TiB whereas the reinforcements with dendritic shape and equiaxed shape are TiC. Compared with sample 1, sample 3 and sample 5, it can be seen that the TiB in sample 3 grows into a coarser short-fiber shape whereas the primary TiC in sample 5 grows into coarser dendritic shape. The coarser TiB reinforcements are a product of unconstrained (primary) growth from the melt, prior to nucleation of the metallic phase. The smaller TiB reinforcements often appear in eutectic-like packets suggestive of coupled growth with the matrix. The coarser TiC reinforcements with dendritic shape are also a product of unconstrained (primary) growth from the melt. The smaller TiC reinforcements are formed during binary and ternary eutectic reaction. It can be seen from Figs. 2(e) and (f) that TiC is liable to grow in equiaxed shape due to the addition of aluminum. Compared with sample 1 and sample 2, we can

Fig. 1 X-ray diffraction patterns of *in situ* synthesized (TiB + TiC)/Ti composites (a) Sample 1, (b) Sample 6.

Fig. 2 SEM micrographs of (TiB + TiC)/Ti composites (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, (e) Sample 5, (f) Sample 6.

see that the addition of aluminum makes reinforcements to grow in more fine shape. The growth mechanisms of reinforcements are related to their crystal structure and solidification paths. As discussed in paper,¹⁸⁾ TiB grows in short-fiber shape due to its B27 crystal structure whereas TiC grows in dendritic shape and near-equiaxed shape due to its B1 crystal structure.

Figure 3 shows the typical TEM bright field images of titanium matrix composites (Sample 6). From the Fig. 3, it can be concluded that there is no any interfacial reaction and impurity segregation at the interfaces between reinforcements and matrix alloy. So the interfaces between reinforcements and matrix alloy are very clean. However, there are some apparent differences in matrix alloy around the TiB reinforcements and TiC reinforcements. There are a large number of dislocations in the matrix alloy around the TiC reinforcements whereas there are no dislocations in matrix alloy around TiB

reinforcements. The generation of high-density dislocations in matrix alloy is due to the difference in thermal expansion coefficient of reinforcements and matrix alloy. Because the thermal expansion coefficient of TiB is close to that of titanium matrix alloy, few dislocations are generated in matrix alloy around TiB reinforcements. Otherwise, a large number of dislocations will be generated in the matrix alloy around the TiC reinforcements. Figure 4 shows HREM image of TiB/Ti interface. The figure confirmed that the interface between TiB and titanium matrix alloy is very clean.

The room temperature stress-strain behavior of the composites is depicted in Fig. 5. The mechanical properties of *in situ* synthesized titanium matrix composites and titanium matrix alloy are listed in Table 2 (The strengthening ratio, S , is generally defined as the ratio of composite-to-matrix flow stresses at the same strain.). It can be concluded that the incorporation of reinforcements improves the mechanical prop-

Fig. 3 TEM bright field image of *in situ* synthesized (TiB + TiC)/Ti composites (a) showing TiB whisker (b) showing TiC reinforcement and high-density dislocations in matrix alloy around TiC (c) and (d) are respective selected area diffractions.

erties of composites. Moreover, the mechanical properties of composites improve with the increase of reinforcements content. HRC value of pure titanium alloy can not be detected by HR-150A hardness test because the value is too low. However, compared with Ti-8 mass%Al alloy, the increase of HRC values is evident due to the incorporation of reinforcements. In all, the mechanical properties improved with the incorporation of reinforcements although some reduction in ductility was observed.

Room-temperature compression tests reveal that the addition of reinforcements to matrix alloy increases the flow stress of the composites by a factor of $1.35 \leq S \leq 1.57$ for 10 vol% (TiB + TiC)/Ti composites. The observed increase in flow stress can be compared with values predicted from various continuum models which ascribe the strengthening to preferential load sharing by the stiffer, elastic reinforcements, arising from the inhomogeneous plastic flow of the matrix around the reinforcements.^{19,20} While these models are not fully applicable to the present composites, they cover a wide variety of reinforcement shapes and configurations and may be used to estimate upper and lower bounds for the strengthening effect. For the purposes of illustration the *in situ* composite is viewed as consisting of rigid reinforcements perfectly bonded to an elastic-perfectly plastic matrix. It should also be noted that none of the models considered here contains a microstructural length scale, allowing different reinforcements to be treated in the same manner.

The lowest estimation for the strengthening effect is obtained by assuming that the reinforcements are equiaxed, *i.e.* as if they were spheres or unit cylinders. Conversely, an up-

per limit would correspond to an array of uniformly spaced cylinders of high aspect ratio aligned in the direction of the applied stress. Using calculations on unit-cell models, Bao *et al.*¹⁹ found the strengthening ratio to vary approximately linearly with volume fraction, f , for relatively dilute loading ($f \leq 0.2$). The strengthening ratio can thus be expressed in a simplified form as:

$$S = 1 + Kf \quad (4)$$

where $k \approx 0.375$ for spheres. For aligned cylinders and elliptical needles of aspect ratio λ :

$$K_{\text{cylinders}} \approx 1.06\lambda + 0.64/\lambda - 0.95 \quad (5)$$

$$K_{\text{needles}} \approx 0.69\lambda + 0.44/\lambda - 0.75 \quad (6)$$

where the differences between cylinders and needles with same aspect ratio arise from the additional constraint to matrix flow around the corners of the former. Bao *et al.* also derived solutions for randomly oriented packets of elliptical needles and disks, which showed that the strong effect of aspect ratio for aligned reinforcements is largely diminished with misorientation.¹⁹

The strengthening effects of different reinforcement shapes estimated from the models for loadings of $f = 0.1$ or $f = 0.2$ are compared with the experimental results for room temperature strengthening in Table 3. It is clear that the experimental results are properly bounded by the upper and lower limits estimated from the models.

From theoretical analysis, the strengthening effect of reinforcements with short-fiber shape should be larger than that of

Fig. 4 High-resolution transmission electronic image of TiB/Ti interface in *in situ* synthesized (TiB + TiC)/Ti composites.

Fig. 5 Room-temperature compressive stress versus strain curves of titanium matrix composites at strain rate of $1 \times 10^{-2} \text{ s}^{-1}$.

particles, *i.e.* the strengthening effect of TiB whisker should be larger than that of TiC particle. However, compared with the experimental results of the volume fraction of each reinforcement (the measured volume percents of TiB whisker and TiC particle are listed in Table 2) and yield strength, the experimental results didn't conform that. The discrepancy may be attributed to various factors not included in this model. Not

only the reinforcements exercise their effect on strength of composites, but also the microstructures of matrix alloy may play an important role in strengthening the composites. According to Arsenault,²¹⁾ the dislocations will be generated due to a difference in coefficient of thermal expansion between the matrix and the reinforcement. The dislocation density can be expressed as following:

$$\rho = \frac{12\Delta T(\alpha_f - \alpha_m)V_f}{bd} \quad (7)$$

Where ρ is the dislocation density, α_f , α_m are the coefficient of thermal expansion of reinforcement and matrix alloy, respectively. V_f is the volume of reinforcement, b is Burgers vector of dislocation in matrix, d is the size of reinforcement, ΔT is the change of temperature.

For the strengthening due to the presence of dislocations generated by the differential thermal contraction, the following equation may be used:²¹⁾

$$\Delta\sigma_{\text{dis}} = \alpha G b \rho^{1/2} \quad (8)$$

Where $\Delta\sigma$ is the increase in yield strength, G is the shear modulus of the matrix and α is a geometric constant.

It can be concluded from above equations that more dislo-

Table 2 Mechanical properties of as-cast titanium matrix composites.

Sample	Matrix alloy	Volume percent (%)	Measured volume percent (%)		Yield strength (MPa)	Strengthening ratio S	Compressive ductility (%)	HRc
			TiB	TiC				
1	Ti	10	7.83	2.04	631	1.35	36.8	25.4
2	Ti-8 wt%Al	10	7.79	2.07	1300	1.57	22.6	46.1
3	Ti	20	15.76	4.07	794	1.70	31.1	33.7
4	Ti-8 wt%Al	20	15.71	4.05	1460	1.77	17.3	51.4
5	Ti	10	5.11	4.78	688	1.47	32.5	30.5
6	Ti-8 wt%Al	10	5.08	4.80	1253	1.52	21.9	45.8
7	Ti	0			467	/	47.6	/
8	Ti-8 wt%Al	0			825	/	26.3	25.3

Table 3 Comparison of experimental strengthening with model predictions.

Reinforcement	Aspect ratio (λ)	Strengthening effect			Reference (Model)
		K	$S (f = 0.10)$	$S (f = 0.20)$	
Spheres	1	0.375	1.04	1.08	19)
Transverse Fibers	1	1.1	1.11	1.22	20)
Aligned cylinders	1	0.75	1.08	1.15	19)
	10	9.7	1.97	2.94	
	20	20.3	3.03	5.06	
Aligned elliptical needles	1	0.38	1.04	1.08	19)
	10	6.2	1.62	2.24	
	20	13.1	2.31	3.62	
Random elliptical needles	10	1.6	1.16	1.32	
Titanium matrix composites	10-40		1.28-1.57	1.70-1.77	

cations in matrix will be generated if the difference in coefficient of thermal expansion of reinforcement and matrix alloy is larger. The strengthening due to the presence of dislocations will be larger. The difference in coefficient of thermal expansion between TiC and titanium matrix alloy is larger than that between TiB and titanium matrix alloy. So the more dislocations will be generated around the TiC reinforcements than that around the TiB reinforcements. The microstructure observation confirms the result (Shown in Fig. 3(b)). Moreover, as discussed in paper,¹⁸⁾ the addition of graphite changes the solidification paths and TiC firstly nucleates and grows from melt. Then the matrix alloy nucleates and grows in binary eutectic and ternary eutectic. The primary TiC particles may act as nucleation sites of titanium alloy, it will decrease the grain size of matrix alloy. According to Hall-Petch equation:

$$\Delta\sigma = kd^{-\frac{1}{2}} \quad (9)$$

Where K is Hall-Petch coefficient, d is grain size.

The strengthening effect of matrix alloy will increase with the refinement of grain size, which is beneficial to improve the mechanical properties of composites.

In all, the addition of graphite forms more TiC. The formation of TiC will generate more dislocations in matrix alloy around TiC reinforcements due to the difference in coefficient of thermal expansion between TiC and titanium matrix alloy. Moreover, primary TiC acts as nucleation sites of titanium

matrix alloy that will refine the grain size of matrix alloy. The above changes of microstructures are valuable to improve the mechanical properties, so the difference in the strengthening effect of TiB whisker and TiC particle is very limited.

It also can be concluded that the strengthening effect of composites with aluminum addition is larger than that of composites without aluminum addition. The strengthening effect of alloying element can be expressed as following. The addition of alloying element aluminum decreases the size of reinforcements that will generate more dislocations. Moreover, it will decrease the grain size of matrix alloy because the more fine primary reinforcements act as nucleation sites. They all will improve the mechanical properties. So the addition of aluminum not only strengthens the matrix alloy by solution strengthening but also improves the mechanical properties by refining the size of reinforcements that will generate more dislocations and decrease the grain size of matrix alloy.

4. Conclusions

In the present work, the microstructures and mechanical properties of *in situ* synthesized (TiB + TiC)/Ti composites have been studied, the following results were obtained:

(1) The titanium matrix composites reinforced with different volume percent and different mole ratio of TiB and TiC can be produced by common casting technique utilizing the SHS reactions between Ti and B_4C , graphite.

(2) The reinforcements are distributed uniformly in titanium matrix alloy. TiB grows in whisker shape whereas TiC grows in dendritic shape and near-equiaxed shape.

(3) The mechanical properties of *in situ* synthesized (TiB + TiC)/Ti composites improved due to the incorporation of reinforcements. The strengthening mechanisms mainly include the following factors: (1) undertaking load of TiB whiskers and TiC particles, (2) refinement of titanium matrix alloy's grain size, (3) intrinsic strengthening of the matrix alloy by high-density dislocations.

(4) The addition of graphite forms TiC reinforcements and generates a large number of dislocations in matrix alloy around TiC reinforcements due to the difference in coefficient of thermal expansion of TiC and matrix alloy. Moreover, primary TiC acts as nucleation sites of titanium matrix alloy that will decrease the grain size of matrix alloy. The changes of microstructures are valuable to improve the mechanical properties, so the difference in the strengthening effect of TiB whisker and TiC particle is very limited.

(5) The addition of alloying element aluminum decreases the size of reinforcements that will generate a large number of dislocations and decrease the grain size. It also will improve the mechanical properties. So the addition of aluminum not only strengthens the matrix alloy by solution strengthening but also improves the mechanical properties by refining reinforcements and matrix alloy.

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