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Growth mechanism of reinforcements in in-situ synthesized (TiB+ TiC)/Ti composites①

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[Abstract] The growth mechanism of reinforcement in in-situ synthesized (TiB+ TiC)/Ti composites was investigated. The results show that reinforcements nucleate and grow in a way of dissolution-precipitation. The morphologies of reinforcements are closely related to the solidification paths and crystal structure of reinforcements. TiB, as a reinforcement, is liable to grow along [010] direction and forms in short-fibre shape due to its B27 structure, whereas primary TiC is liable to form composition undercooling and grow in dendritic shape. TiC phases precipitated in binary eutectic and ternary eutectic reactions grow in equiaxial shape. The addition of aluminum element refines TiB and TiC particles, and makes TiC reinforcements grow into the equiaxial particles easily. The addition of graphite adjusts the solidification paths and forms more TiC with dendritic shape.

[Key words] TMCs; in-situ reaction; growth mechanism; solidification path; crystal structure
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1 INTRODUCTION

Titanium-based metal-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]. Compared with fiber reinforced TMCs, particle reinforced TMCs are very attractive for their properties such as isotropic behavior, easy to fabricate, economical and convenient to fabricate parts of complex shape. A series of methods are used to fabricate particle reinforced TMCs including outside doping and in-situ technique. The in-situ technique is free of contamination so that composites with better properties can be gained. Powder metallurgy[3, 4], casting[5, 6] and mechanical alloying technique[7] are used to fabricate particle reinforced TMCs. TiB and TiC reinforced TMCs have been produced by common titanium casting technique and self-propagation high-temperature synthesis (SHS) between titanium, B_4C and graphite powders[8]. Since the process is completely similar to that of common titanium alloy, it is possible to fabricate TiB whisker and TiC particle reinforced TMCs with high properties economically. The in-situ synthesis mechanism have been expounded[8, 9], however, there is not explicit discussion on the growth mechanism of the reinforcement. The investigation on the growth mechanism of reinforcements is valuable to control microstructures of in-situ synthesized composites and adjust its properties.

In this paper, the solidification paths of in-situ synthesized (TiB+ TiC)/Ti composites as well as the effects of crystal microstructure on the growth morphologies are highlighted. The effects of alloying element on microstructures of composites are also discussed.

2 EXPERIMENTAL

The raw materials were the second grade sponge titanium, B_4C powder with purity of 95% and average particle size of 5~ 10 μm, and graphite powder of 99.8% and 5~ 7 μm. B_4C, graphite powders and sponge titanium were blended, then compacted into pellets. Due to the sorption of holes in sponge titanium pellets, B_4C powder and graphite powder were easily distributed homogeneously in the micro-holes of sponge titanium without special blending process. In order to investigate the effect of alloying element, aluminum with purity of 99.8% was added. The chemical composition of the raw materials and their volume fraction are listed in Table 1. The casting technique of TMCs was completely similar to that of common titanium alloy. The various amounts of pellets were melted two times in a non-consumable vacuum arc remelting (VAR) furnace to produce (TiB+ TiC)/Ti composites. The casting samples were cut directly from ingots, then were polished and etched with a solution of 85% water + 10% nitric acid + 5% hydrofluoric acid. The microstructures of samples

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Table 1 Chemical composition of samples and volume fraction of reinforcements (φ_r)

Sample No.	w(Ti) /%	w(B_4C) /%	w(C) /%	w(Al) /%	φ_r /%	x(TiB): x(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

as well as the distribution and morphologies of reinforcements were characterized by Philips SEM515 scanning electron microscopy (SEM) equipped with energy dispersion X-ray spectrometer (EDS) analysis system. The samples for TEM were performed by argon ion milling and the microstructures of TMCs were observed by H-800 transmission electron microscopy operated at 200 kV. On the other hand, Netsch DSC404 instrument was used to measure thermodynamic curve in order to reveal the effects of alloying element on the solidification path of composites. The samples were heated at a rate of 10 ℃/min from ambient to 1600 ℃, subsequently cooling to ambient temperature at the same rate under dynamic high pure argon atmosphere (flow velocity of 80 mL/min).

3 RESULTS AND DISCUSSION

3.1 Microstructure of composites

Microstructures of in-situ synthesized (TiB + TiC)/Ti composites are shown in Fig. 1. As reported by Refs. [8] and [9], TMCs reinforced with TiB and TiC can be produced by common casting technique utilizing the SHS reactions between titanium B_4C and graphite powders. The addition of aluminum element

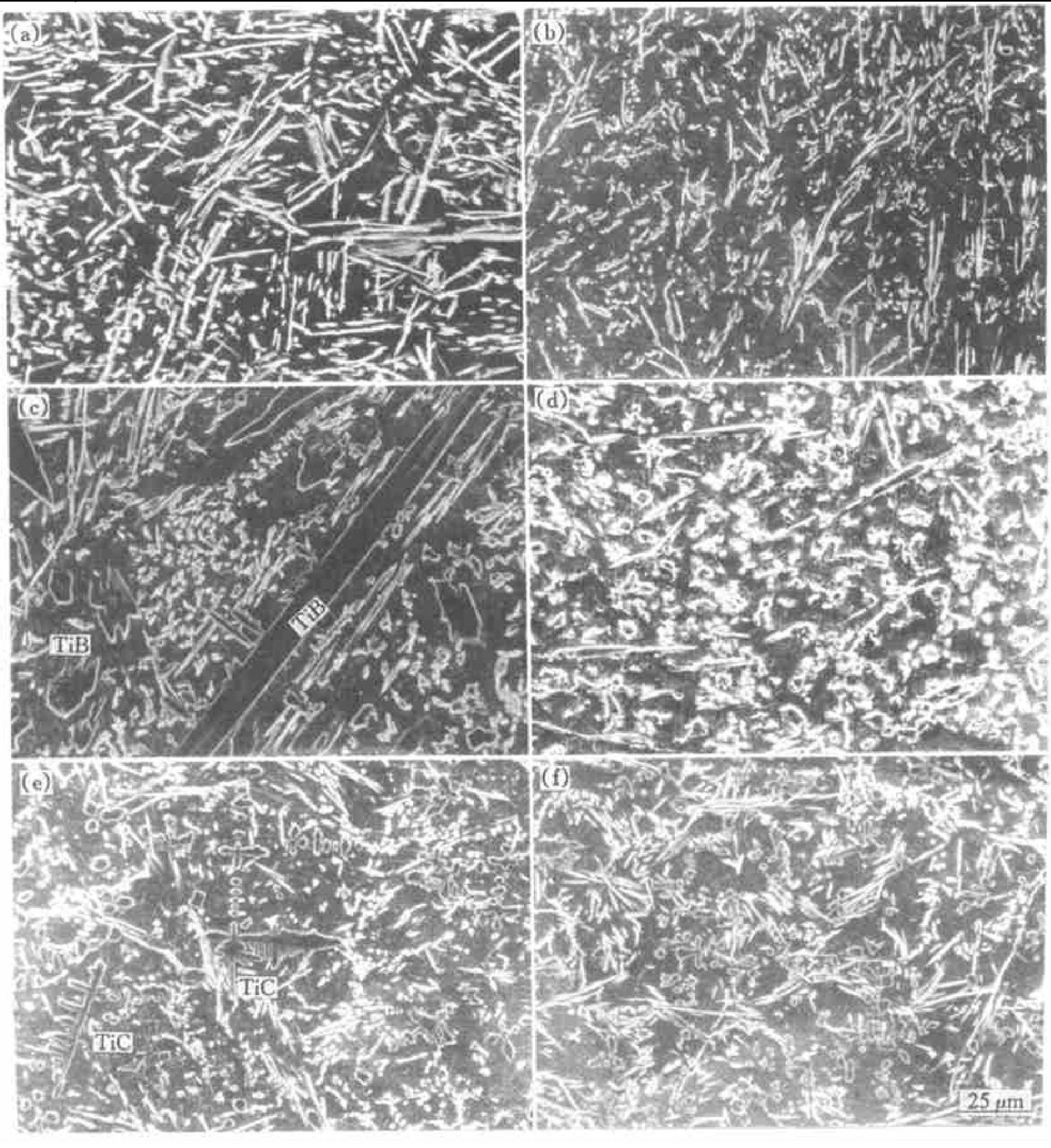

Fig. 1 SEM microstructures of in-situ synthesized TMCs
(a) —Sample 1; (b) —Sample 2; (c) —Sample 3; (d) —Sample 4; (e) —Sample 5; (f) —Sample 6

within amount of α phase doesn't result in formation of new phase. It can be seen from Fig. 1 that the reinforcements are distributed uniformly in the titanium alloy matrix. However, there are large differences in the morphologies of reinforcements with different shapes as short-fiber shape, dendritic shape and equiaxed shape. The results of EDS show that the reinforcement with dendritic shape and equiaxed shape are TiC phases, whereas the reinforcements with short-fiber shape are TiB phases. Comparing Fig. 1 (a) with Fig. 1(c), it can be seen that TiB in sample 3 grows into a great short-fibre shape with a long axis of more than 100 μm. The primary TiC in sample 5 grows into large dendritic shape. It can be seen that the addition of aluminum element make reinforcements grow in more fine shape, as showed in Figs. 1 (b), (d) and (f).

SEM microstructures of the reinforcements deeply etched are shown in Fig. 2. The typical TiB with short-fibre shape and TiC with dendritic shape can be seen obviously. The appearance of TiB is highly flat and straight. The interfaces of TiB are hexagonal shapes paralleled with each other. The TEM bright field image and respective selected area diffraction (SAD) of TiB are shown in Fig. 3. It can be concluded that the growth direction of TiB whisker is in the [010] direction, which means that TiB is liable to grow along the [010] direction.

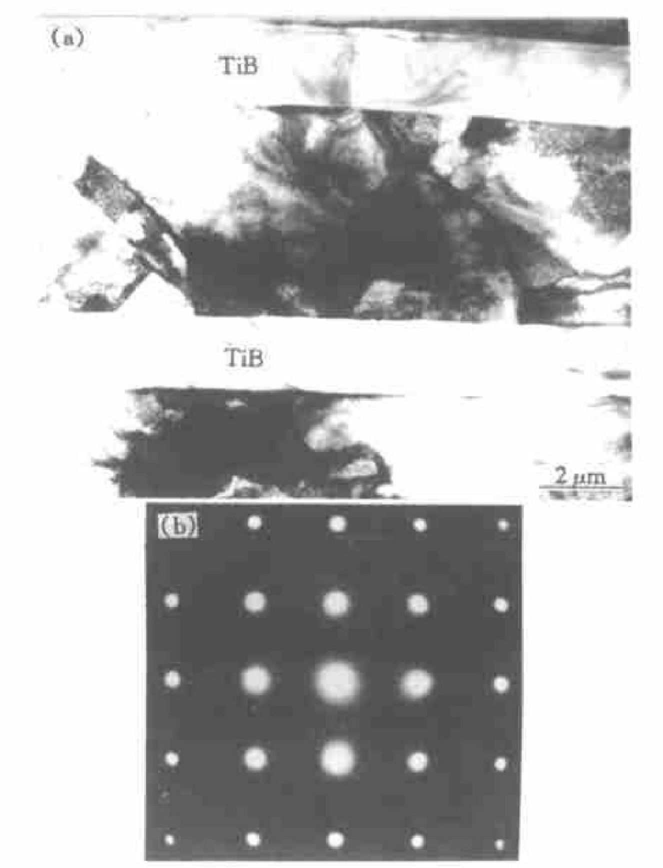

Fig. 3 TEM bright field images of TiB (a) and respective selected area diffraction (b) (Z. A. = [001])

3.2 Growth mechanism of reinforcements

Fig. 2 Typical morphologies of TiB (a) and TiC (b) in TMCs

The growth mechanism of reinforcements is related to the highest processing temperature. It can be classified into two mechanisms according to the highest temperature: diffusion mechanism and dissolution precipitation mechanism. When processing temperature is lower than liquid phase line, the growth mechanism of reinforcements is diffusion mechanism. For example, the reinforcements in TiB/Ti and TiC/Ti composites fabricated by powder metallurgy form by diffusion mechanism. If the processing temperature is higher than liquid phase line, the growth mechanism is dissolution-precipitation mechanism. It is suitable for the reinforcements in TiB/Ti[10], TiC/Ti[11] composites fabricated by casting technique.

Since the processing temperature of non-consumable remelting furnace used to fabricate (TiB+ TiC)/Ti composites in this experiment is far higher than 2 000 ℃, TiB and TiC reinforcements are completely melt in liquid titanium during fabricating according to the projection of liquidus surfaces in Ti-B-C ternary phase diagram[12] (Fig. 4). Therefore, TiB and TiC precipitate and grow from titanium melt in the way of nucleation and growth during solidification. Namely, TiB and TiC can be synthesized by the SHS reactions between sponge titanium, B_4C and graphite powders as the temperature increases during melting process. TiB and TiC are molten thoroughly in liquid titanium

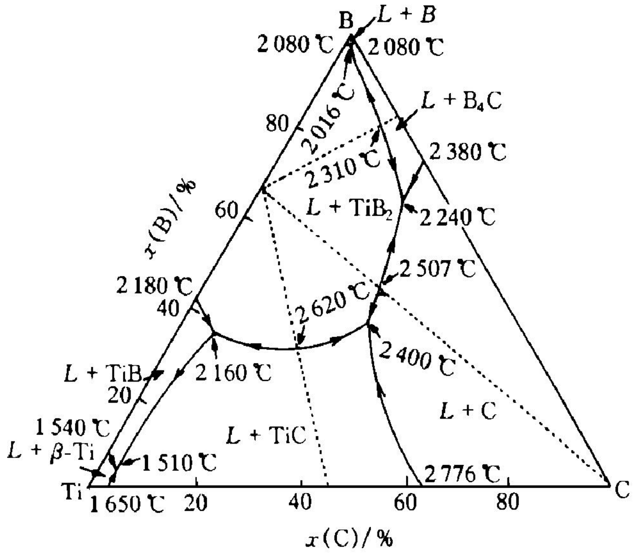

Fig. 4 Projection of liquidus surfaces in Ti-B-C ternary phase diagram

when the raising temperature exceeds the liquid phase line. During cooling, TiB and TiC reinforcements precipitate and grow from liquid titanium. The morphologies of reinforcements are related to the solidification paths.

As shown in Fig. 4, there is a ternary eutectic reaction among Ti, TiB and TiC at 1510 ℃, namely $L \longrightarrow Ti + TiB + TiC_{(1-x)}$. Moreover, there are three binary eutectic reactions in the rich-titanium corner. There are differences in solidification paths for TMCs reinforced with different reinforcements. The solidification paths of samples 1, 3 and 5 are shown in Fig. 5. The main difference in solidification paths of different TMCs is the formation of primary TiB and primary TiC. The primary TiC in sample 5 firstly disperses, so there are many TiC with dendritic shape. The primary TiB in sample 3 grows into a great short-fibre shape. On the other hand, since the density of reinforcements TiB and TiC that disperse during solidification is similar to that of titanium matrix alloy, reinforcements TiB and TiC distribute uniformly in matrix alloy.

The growth mechanism of reinforcements can be further confirmed by the DSC results of sample 2, as shown in Fig. 6. There are three endothermal peaks which counterpart with ternary eutectic reaction, binary eutectic reaction and one phase dissolution during heating procedure between 1400~ 1600 ℃. During solidification, there is only two exothermal peaks caused mainly by the delaying effect of solidification that makes exothermal peaks of primary crystal solidification and binary eutectic reaction overlap. It shows the broadening of the first solidification peak in DSC curve. It also indicates that the addition of aluminum element does not change the solidification paths and result in formation of other new phases. However, the addition of alloying element affects the nucleate and growth of reinforcements and makes the reinforcements grow finer, while TiC is liable to grow in equiaxed or near-equiaxed shape.

3.3 Effects of crystal structures on morphologies

The different growth morphologies of reinforcements are also attributed to their different crystal structures. A slight tendency toward anisotropic growth results from the anisotropy of the interfacial energy and the atomic attachment kinetics, and this leads to the appearance of crystallographically determined dendrite trunk and arm directions along low-index directions, as illustrated in Fig. 7(a). In contrast, other substances with highly directional bonding or strongly bonded complex crystal structures form crystals with angular, planar facets, as shown in Fig. 7(b)[13].

The crystal structure of TiB is B27. The chemical bonds are combined by electron between boron atoms and titanium atoms, and covalent bonds among boron atoms. Since the occupation of atoms and chemical bonds is asymmetry, reinforcements grow in a way of asymmetry, characterized by high directionality (as shown in Fig. 7(b)). As reported by Ref. [10], TiB is liable to grow along the [010] direction and form in short-fibre shape.

The crystal structure of TiC is NaCl type. Ti atoms array fcc sub-lattice, while carbon atoms occupy the free place of octahedral configuration forming another fcc sub-lattice. It can be concluded that both

(a)
L
↓
$\beta\text{-Ti}_p + L_m$
↓
$(\beta\text{-Ti} + \text{TiB})_m + L_e$
↓
$(\beta\text{-Ti} + \text{TiB} + \text{TiC})_e$
↓
α-Ti

(b)
L
↓
$\text{TiB}_p + L_m$
↓
$(\text{TiC} + \text{TiB})_m + L_e$
↓
$(\beta\text{-Ti} + \text{TiB} + \text{TiC})_e$
↓
α-Ti

(c)
L
↓
$\text{TiC}_p + L_m$
↓
$(\beta\text{-Ti} + \text{TiC})_m + L_e$
↓
$(\beta\text{-Ti} + \text{TiB} + \text{TiC})_e$
↓
α-Ti

Fig. 5 Solidification paths of in-situ synthesized TMCs
(a) —Sample 1; (b) —Sample 3; (c) —Sample 5

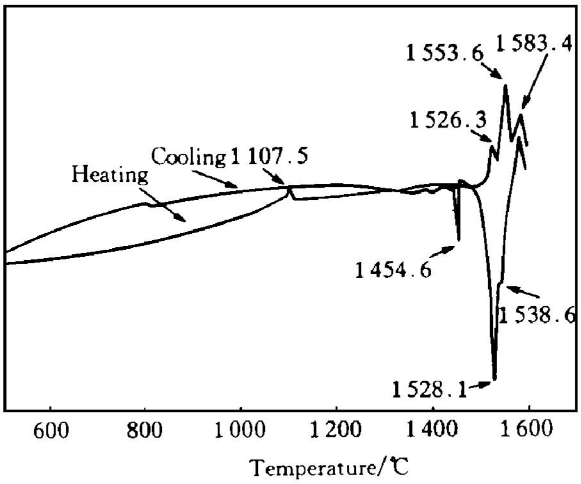

Fig. 6 DSC curve of in-situ synthesized TMCs

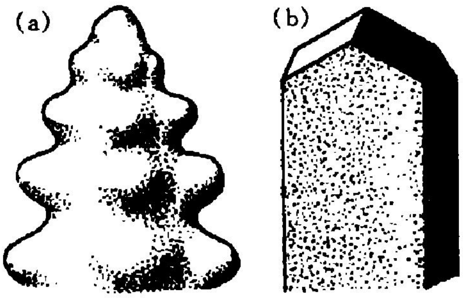

Fig. 7 Schematic diagram of facet (a) and non-facet (b) growth morphologies of crystals

titanium atom and carbon atom are surrounded by six next neighbor atoms of the respective other species in an octahedral configuration. Hence the unit cell consists ideally of two atoms of each species, i. e. of two formula units. The chemical bonds of TiC include C—C covalent bond, Ti—C ionic bond and Ti—Ti metal bond. It can be concluded that they are also completely symmetry with sub-lattice of Ti and carbon, indicating that unit cell of TiC is complete symmetry without preferential growth crystal facet no matter what geometric configuration and chemical bond are. TiC particles are precipitated from melt in a form of sphericity with least interfacial energy, therefore TiC is liable to grow in equiaxed shape. Due to the poor thermal conductivity of titanium melt and short melting time, there is no enough time to release the energy including reaction heat between Ti, B_4C and graphite, and crystal heat of TiC during solidification. So the temperature under-cooling is liable to form. Moreover, the component of carbon occupied the free places of octahedral configuration in the crystal structure changes in the range of 0.5~ 0.97 according to the occupation of carbon. Based on the Ti-C binary diagram, the liquid line is relatively steep and composition undercooling is liable to form. Thus, the primary TiC grows in typically dendritic shape due to composition undercooling and temperature undercooling during the solidification, while TiC dispersed from binary eutectic and ternary eutectic reactions grows in equiaxed shape or near-equiaxed shape.

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