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Microstructure of in-situ TiC particle reinforced titanium alloy matrix composites①

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[Abstract] TiC particle reinforced titanium alloy matrix composites with different aluminum content was prepared by the XD^{TM} method. The constitute phase and the microstructure of the composites were studied by XRD and SEM. The results show that the calculated lattice parameter of TiC there exists a diffraction peak shift for TiC, which may be due to the vacancies of C in TiC. The stoichiometry of TiC is $Ti_{62}C_{38}$. There exist two different kinds of TiC in the composites: dendritic primary TiC and short bar-shape eutectic TiC, respectively. Although TiC of macrostructure is homogeneously distributed in the matrix, the eutectic TiC of microstructure mainly segregates at the grain boundary, especially at the tri-angular grain boundaries. The aluminum content has a great influence on the morphology of TiC. With increasing aluminum content up to 25 %, the size of TiC becomes small although it is still in dendrite or short bar-shape. When the aluminum content is more than 35 %, TiC is changed into thin plate or particle and the size is about 2 ~ 5 μm.

[Key words] TiC; titanium matrix composites; microstructure; XD^{TM}

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1 INTRODUCTION

Titanium matrix composites are interesting for high temperature and high strength application. Usually, matrices are reinforced by continuous silicon carbide filaments. Three main problems have been identified in SiC/Ti composites materials: (1) unstability between the fiber and the matrix during the processing of the composite or in service; (2) tensile residual stresses in the matrix and in the reaction zone due to the coefficient of thermal expansion (CTE) mismatch between the constitutes; and (3) for brittle matrices such as alpha alloys or intermetallics the reinforcement diameter must be decreased and no other alternatives are available so far[1,2]. Recently, reaction synthesis has been used to synthesize reinforcements in the melt. Because the reinforcement is in-situ in the titanium melt, the reinforcement forms a clean interface and is thermodynamically stable. Many reinforcements have been synthesized in the titanium melt, including TiC, TiB, TiB_2 and $TiAl_3$[3~7]. As one of in-situ method, XD^{TM} has been widely used to prepare particulate metal matrix composites, including aluminum based and titanium based composites[3,8~12]. In this paper, XD^{TM} was used to prepare particulate Ti-based composites utilizing TiC as an alternative reinforcement because of its thermodynamic compatibility to titanium. Its elastic modulus of 420 GPa is almost 4 times that of Ti, and the coefficients of thermal expansion of Ti and TiC closely match. The microstructure of the composites and the effect of aluminum content on the morphology of TiC have been investigated in detail.

2 EXPERIMENTAL

High purity titanium powder (99.7 %, 45 μm), aluminum powder (99.6 %, 29 μm) and carbon black (99.8 %, < 0.05 μm) were ball-milled for 24 h. Then they were uniaxially pressed into green compacts with 50 % ~ 60 % theoretical density and heated in vacuum to synthesize an Al/TiC master alloy. To prepare composites, the master alloy and the sponge titanium were melted in non-consumable vacuum arc furnace equipped with a water-cooled copper crucible. To ensure chemical homogeneity of the melted alloy, electron magnetic agitation was used and the ingots were melted at least three times. Compositions of the composites determined by chemical analysis are listed in Table 1. Assuming that C has been completely converted into TiC, and TiC contents are also listed. X-ray diffraction (XRD) analyses were conducted in a Rikagu D/max-RB X-ray diffractometer. The microhardness was measured by a XDS-III microhardness instrument and the results are averages of at least three indents. The microstructure of the composites was observed by scanning electron microscopy (SEM).

3 RESULSTS AND ANALYSES

3.1 X-ray diffraction result

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Table 1 Compositions of composites (%)

Sample	Al	C	O	Expected TiC	Ti
Ti-6Al/10TiC	5.22	1.78	0.32	8.9	Bal.
Ti-10Al/10TiC	8.58	1.89	0.32	9.5	Bal.
Ti-25Al/10TiC	26.82	2.08	0.33	10.4	Bal.
Ti-35Al/10TiC	34.62	1.98	0.28	9.9	Bal.

The XRD result of Ti-6Al/10TiC composites is given in Fig.1. It has been shown clearly that the present phases are titanium and TiC. The lattice parameter value of TiC, a, associated with each peak position was calculated and plotted as a function of $1/2 \cdot (\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ in order to determine the least line as in the following equation:

$$a = a_0 + K \cdot \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \quad (1)$$

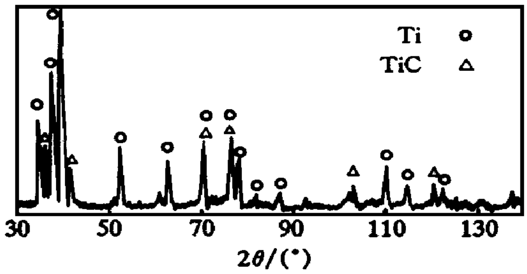

Fig.1 XRD pattern of Ti-6Al/10TiC composites

where a_0 is the extrapolated true value of a when θ approaches 90°, θ is the diffraction angle and K is the slope of the least lines.

The calculated lattice parameter of TiC is 0.43149 nm, slightly less than the standard value, 0.43283 nm, which indicates that there exists peak shift of TiC. According to the Ti-C phase diagram (Fig.2), TiC exists over a large range of stoichiometry from $Ti_{67}C_{33}$ to $Ti_{51}C_{49}$, which has also been confirmed by Kerans et al[14]. Referenced with the research results[15], the stoichiometry is $Ti_{62}C_{38}$. Previous studies have suggested that in this carbon-deficient structure, the titanium sublattice is relatively perfect, whereas the carbon sublattice is only partially filled[16].

The XRD analysis results of the composites with different aluminum content are listed in Table 2. With increasing aluminum content, Ti_3Al and TiAl will also form in the matrix besides TiC. However, the peak shift of TiC has also been observed in these XRD patterns.

3.2 Microstructure

Fig.3 shows the microstructures of Ti-6Al/10TiC composites. In Fig.3(a), there exist two different morphologies of second phase in the matrix: dendritic (Fig.3(b)) and spherical (Fig.3(c)). While the spherical phases are too small to be measured, microhardness measurement could be made on the dendritic phase and the alloy matrix. The results are listed in Table 3. For comparison, the microhardnesses of Ti-6Al-4V alloy and TiC obtained from the Metal Handbook are also given in Table 3. Combined with the XRD results, the dendritic phases are confirmed to be TiC. In addition, the spherical phases are also confirmed to be TiC by the energy spectrometer.

Table 2 Phase constituents of composites with different Al contents

Material	Constitute phase
Ti-6Al/10TiC	TiC, Ti
Ti-10Al/10TiC	TiC, Ti
Ti-25Al/10TiC	TiC, Ti_3Al, Ti
Ti-35Al/10TiC	TiC, Ti_3Al, TiAl

Table 3 Microhardnesses of Ti matrix dendritic phase, Ti-6Al-4V and TiC ceramic

Material	Microhardness /9.8 MPa	Material	Microhardness /9.8 MPa
Ti matrix	274	Ti-6Al-4V	220 ~ 280
Dendritic phases	881.8 ~ 1287.5	TiC	880 ~ 1600

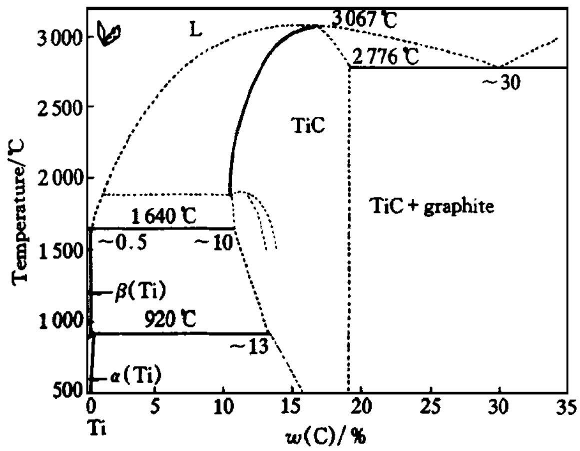

Fig.2 Phase diagram of Ti-C system[13]

From Fig.3(a), it is found that TiC particles are homogeneously distributed in the matrix. But in high magnification microstructure (Fig.3(c)), the spherical TiC particles segregate mainly at the grain boundary, especially at the triple-point grain boundary (Fig.3(d)), which indicates that TiC particles can not be a site for the nucleation of Ti during solidification process.

Microstructures of the deeply etched Ti-6Al/10TiC composites are shown in Fig.4. The coarse and developed dendritic structure of TiC is shown in Fig.4(a). Unfortunately, it was found that the presumed "spherical" TiC particles are in thin plate or particle (Fig.4(b) and (c)).

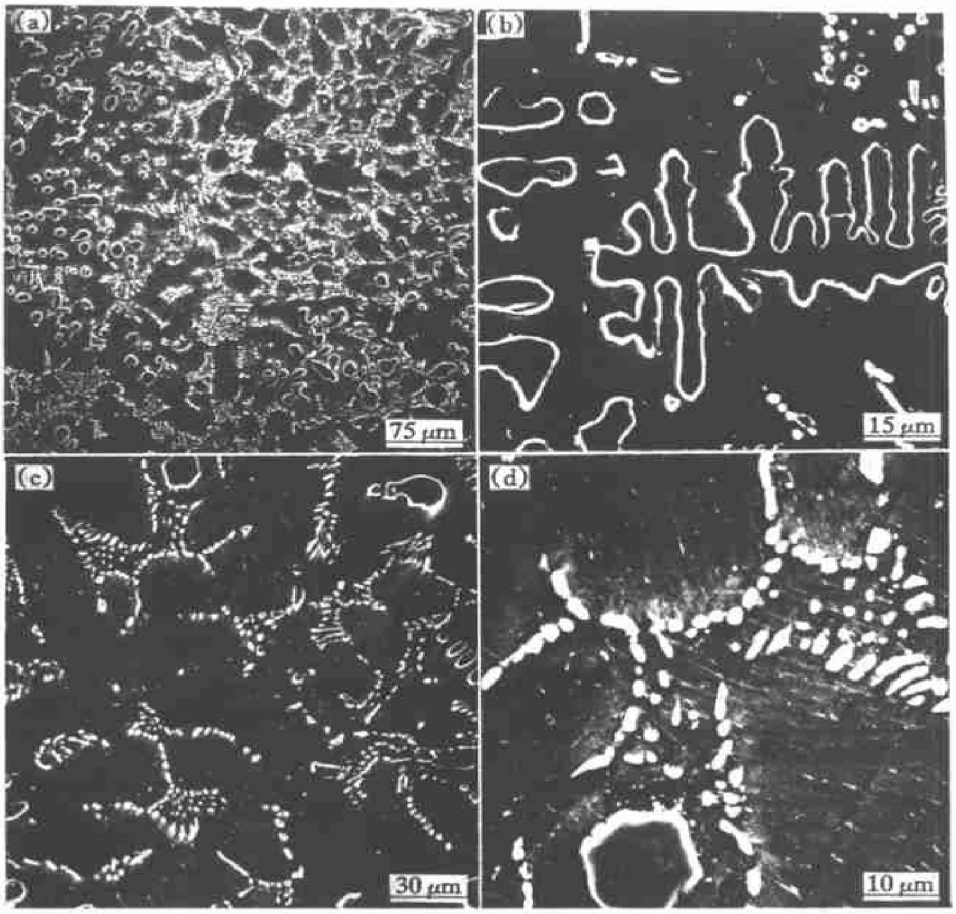

Fig.3 Microstructures of Ti-6Al/10TiC composites

(a) —Low magnification microstructure, showing two different TiC morphologies; (b) —Morphology of dendritic TiC; (c) and (d) —Distribution of spherical TiC, which mainly segregate at grain boundary, especially at triple-point grain boundary

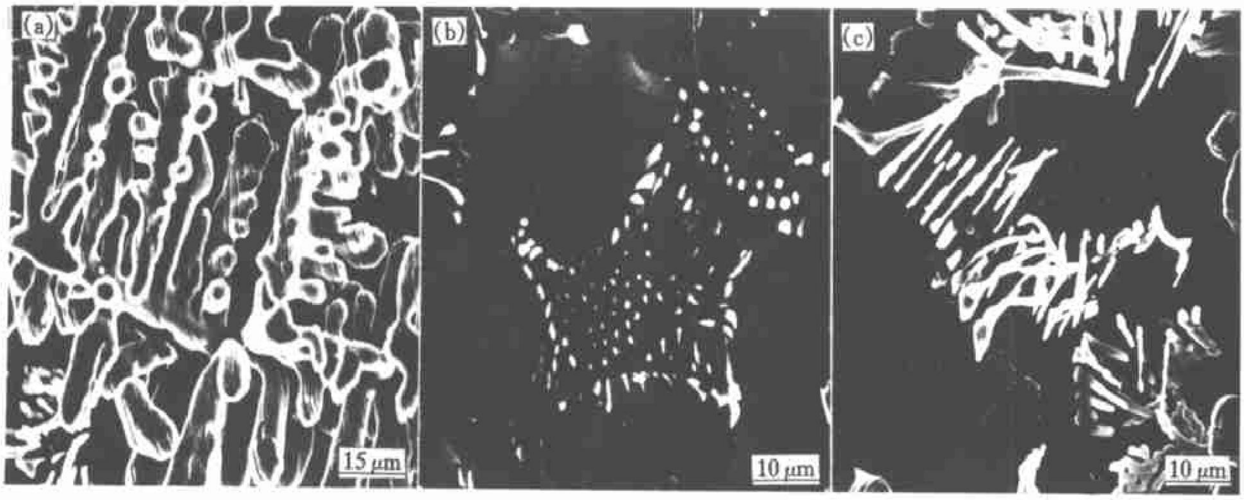

Fig.4 Microstructures of deeply etched Ti-6Al/10TiC

(a) — Morphology of dendritic TiC; (b) and (c) — Morphology of "spherical" TiC, showing that the "spherical" TiC is in short round bar-shape

3.3 Effects of Al on morphology of TiC

The effects of Al content on the microstructure of titanium matrix composites and the morphology of TiC reinforcement are shown in Fig.5. In the microstructure of Ti-10Al/10TiC composites (Fig.5 (a)), TiC still possesses two kinds of morphologies, dendritic primary TiC and short bar-shape eutectic TiC, which is the same as that in Ti-6Al/10TiC (Fig.3). Although the morphology of primary TiC, shown in Fig.5(b), does not change, the size is smaller than that in Ti-6Al/10TiC (Fig.3). When the aluminum content is increased to 25 % (Fig.5(c) and (d)), a little of the short bar-shape TiC can be found and its size becomes much smaller than that formed in Ti-6Al/10TiC (Fig.3) and Ti-10Al/10TiC (Fig.5(a), (b)). Although the dendritic TiC can still be observed, the dendritic arms become shorter in length and smaller in diameter. Great changes in the microstructure and the morphology of the TiC are observed when the aluminum content is increased to 35 % (Fig.5(e), (f)). Only one kind of TiC exists, and it is in thin plate or spherical shape and the diameter is about 2 ~ 5 μm.

4 ANALYSES AND DISCUSSION

From the Ti-C phase diagram (Fig.2), there is eutectic reaction in the Ti-rich corner at 1 650 ℃ for a carbon content of about 1.14 %. From the Ti-Al phase diagram, there exists a peritectic reaction in the Ti-rich side[13]. Therefore, it is an eutectic-peritectic ternary phase diagram for Ti-Al-C system, whose liquidus surface and isothermal section at 1 000 ℃ are shown in Fig.6. The constitution points of Ti-6Al/10TiC and the other composites have been shown in Fig.6. From Fig.6(a) and (b), the solidification process of Ti-6Al/10TiC can be described as follows:

$$L \rightarrow L + TiC_{primary}$$
$$L \rightarrow TiC_{eutectic} + \beta(Ti)$$
$$\beta(Ti) \rightarrow \alpha(Ti) \qquad (2)$$

Thus during the solidification, primary TiC will first precipitate in dendritic shape from the melt with decreasing temperature. When the temperature is decreased to the eutectic temperature, an eutectic reaction will happen and the new TiC will form in short bar-shapes.

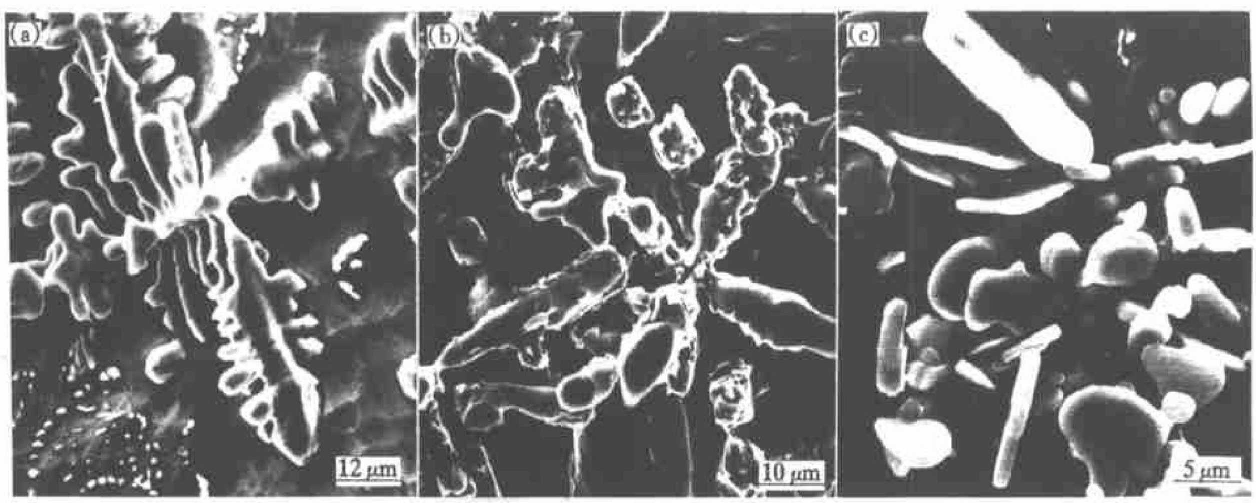

Fig.5 Microstructures of TiC reinforced titanium composites with different aluminum contents
(a) —Ti-10Al/10TiC; (b) —Ti-25Al/10TiC; (c) —Ti-35Al/10TiC

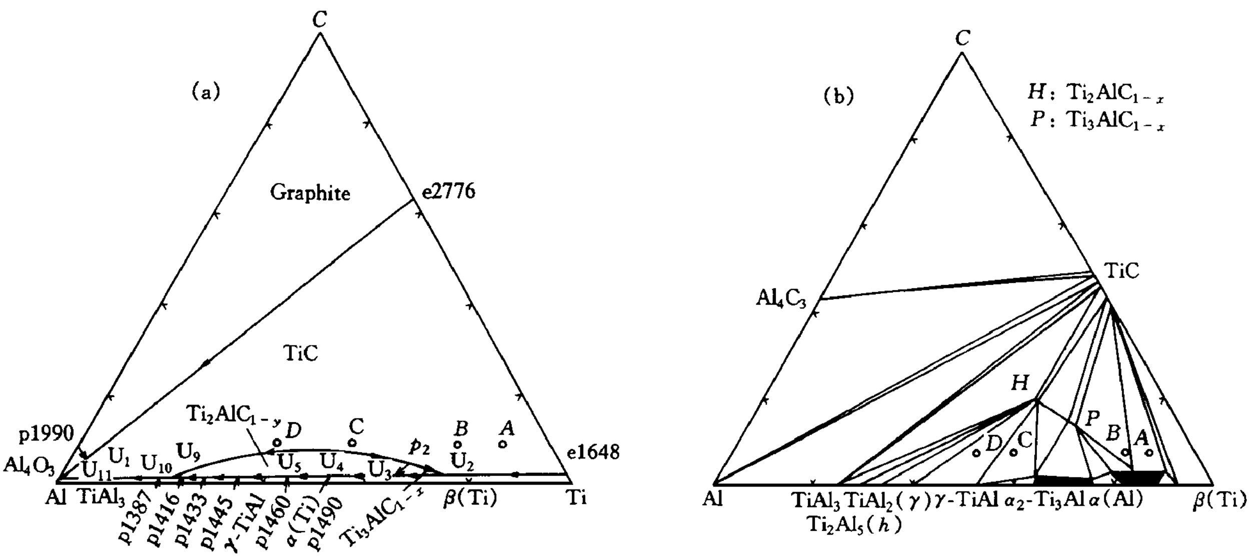

Fig.6 Liquidus surface (a) and isothermal section at 1 000 ℃ (b) of Ti-Al-C ternary phase diagram[16]

Although the aluminum is increased up to 35 %, the constitution points are still in the TiC single-phase zone at liquidus surface (Fig.6(a)). So the primary TiC with dendritic shape will first form during the solidification process. However, with decreasing temperature, the constitution points with different Al contents were in different phase zones. For example, the constitution points of Ti-35Al/10TiC and Ti-25Al/10TiC are in TiAl and $H(Ti_2AlC_{1-x(x=0.2)})$ binary phase zone, and TiAl, H and Ti_3Al ternary phase zone, respectively. As a result, intermetallic such as Ti_3Al, TiAl and eutectic TiC will precipitate during the following process, which are in good agreement with the XRD results.

During the growth process of primary TiC, there will be rich in Al element at the solidification interface of primary TiC with increasing Al content, which results in a constitutional supercooling and formation of new second phase, such as Ti_3Al and TiAl, at the solidification front of primary TiC. All of these restrain the growth of primary TiC, so the increasing of aluminum content makes the primary dendritic TiC smaller and shorter (Fig.5).

5 CONCLUSIONS

1) Two TiC morphologies have been observed in Ti-6Al/TiC composites: dendritic TiC and short bar-shape TiC, corresponding to primary and eutectic TiC, respectively. The eutectic TiC mainly distributes at the grain boundary, especially at the triple-point grain boundary, which indicates that TiC particles can not be a site for the nucleation of Ti during solidification process.

2) The addition of aluminum has a great influence on the size and the morphology of TiC. With increasing aluminum content up to 25 %, the TiC becomes smaller although it is still in dendrite or short bar-shape. However, when the aluminum content is more than 35 %, the morphology of TiC changes from dendrite to thin plate or particle.

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