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Microstructure of XD^{TM} Ti-6Al/TiC composites

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XD^{TM} method has been used to prepare TiC particles reinforced titanium composites. The phases constitute and microstructure of the Ti-6Al/TiC composites have been investigated by XRD and SEM. The lattice parameter value of TiC calculated from the XRD pattern has indicated that there exists carbon deficiency in TiC. The microstructure observed by SEM has shown that TiC is of dendritical and spherical morphology, which quite different from that of the TiC in Al/TiC master alloy. In macrostructure, the TiC particles homogeneously distribute in the matrix, but the spherical TiC mainly segregate at the grain boundary, especially at the triangle grain boundary. Microstructure of the interface has also been observed by TEM and HTEM. No reaction product has been found in the interface, but a C atom diffusion layer was determined by energy spectrum diffraction and observed by HREM image of interface microstructure. Although no definite crystallographic relationship can be defined, a orientation relationship of $[01\bar{1}0]_{Ti}//[011]_{TiC}$ has been obtained.

1. Introduction

Titanium-based alloys have received increasing attention due to their high strength-to-weight ratio and high-temperature properties, to extend the usefulness of these materials, composites with high strength and lightweight reinforcements have been extensively studied. Most of these investigations centred on consolidating the matrix material and the reinforcements together via various techniques, the most common of which are solid-state sintering, liquid infiltration and plasma spraying [1]. Recently, *in situ* has attracted more attention as a method to prepare titanium matrix composites [2, 3]. One advantage of *in situ* composites is their thermodynamic stability compared with those produced by conventional means. Another advantage is the fine scale of reinforcements possible with this technique. TiC as an alternative reinforcing phase has been tried because of its thermodynamic compatibility to titanium. Its Young's modulus of 420 GPa is almost 4 times that of Ti, and coefficients of expansion of Ti and TiC closely match. Several investigators have reported the Ti-TiC and Ti-6Al-4V/TiC bond to be fairly good [4, 5].

In this study, an *in situ* method, XD^{TM} method, was used to prepare Ti/TiC composites. The microstructure of the composites has also been observed.

2. Experimental procedure

High purity (99.7pct, 45 μm) titanium powder, 99.6 pct aluminum powder with 29 μm and black carbon (99.8pct, <0.05 μm) were used as raw materials. The Ti, Al and C powders (40at pct Al, 30at pct Ti, and 30at pct C) were ball milled for 24 hours. Then they were uniaxially pressed into green compacts with 50–60pct of theoretical density, named Al-Ti-C preform. Then the preform was heated in vacuum to reaction synthesized Al/TiC, also named as master alloy. And then the master alloy was melted with sponge titanium to prepare Ti/TiC composites according to expected TiC content. The melting was carried out by non-consumable vacuum arc melting furnace in a water-cooled copper crucible. To ensure the chemical homogeneity of the melted alloy, the ingots were melted at least three times. The composition of the composites determined by chemical analysis was listed in Table I. Assuming that C element has been converted completely into TiC, the TiC content is about 8.9 wt%. The X-ray diffraction (XRD) analyses were conducted in a Rikagu D/max-RB X-ray diffractometer. The microhardness was achieved by a XDS-III microhardness instrument and the result is a average of at least three dates. The microstructure of the composites was observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) with energy spectrum diffraction (ESD) analysis and high-resolution electron microscopy (HREM).

3. Results and analyses

3.1. X-ray diffraction analysis

The XRD result of the as-cast sample is given in the Fig. 1. It has been shown clearly that the phases present are titanium and TiC. Peak shift, as compared with standard data, was observed.

The lattice parameter value, a, associated with each peak position was calculated and plotted as a function

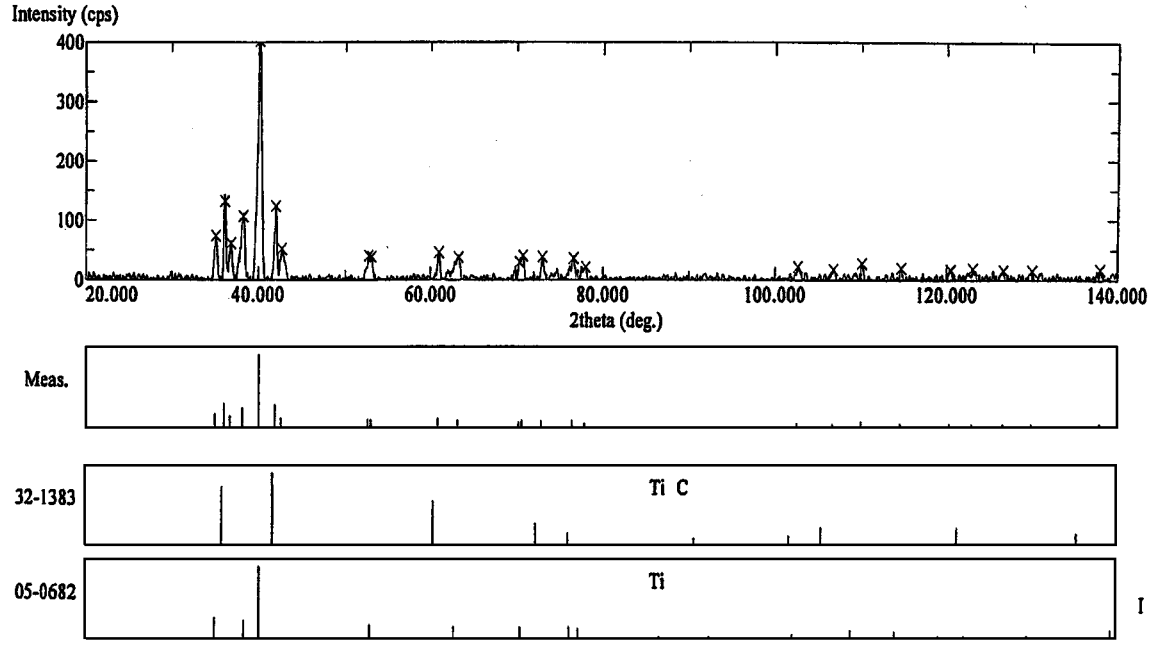

Figure 1 XRD pattern of Ti/TiC composites.

of $1/2(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ in order to determine the least line as in the following equation:

$$\alpha = \alpha_0 + K \cdot \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \qquad (1)$$

Where α_0 is the extrapolated true value of α when θ approaches 90 degrees and K is the slope of the least lines.

The lattice parameter of TiC is 0.43149 nm, less than the standard values, 0.43283 nm. According to the Ti-C phase diagram (Fig. 2), TiC exists over a large range of stoichiometry from $TiC_{0.48}$ to TiC. From the study of Kerans *et al.* [6], TiC_{1-x} varies in composition from 33 to 49 at% C at room temperature. Previous studies have suggested that in this carbon-deficient structure, the titanium sublattice is relatively perfect, whereas the carbon sublattice is only partially filled [7]. The basic calculation displays that there exist vacancies.

TABLE I Compositions of the composites (wt pct)

Element	Al	C	O	Ti
wt.pct	5.22	1.78	0.32	balance

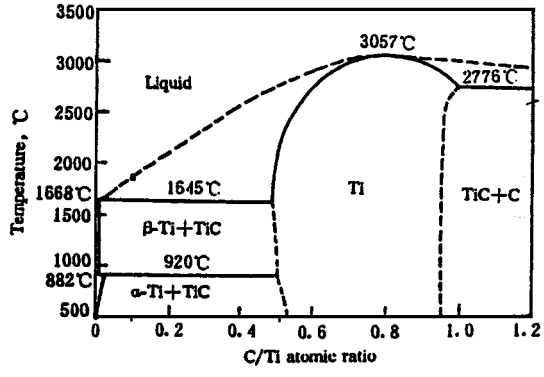

Figure 2 Phase diagram of Ti-C system.

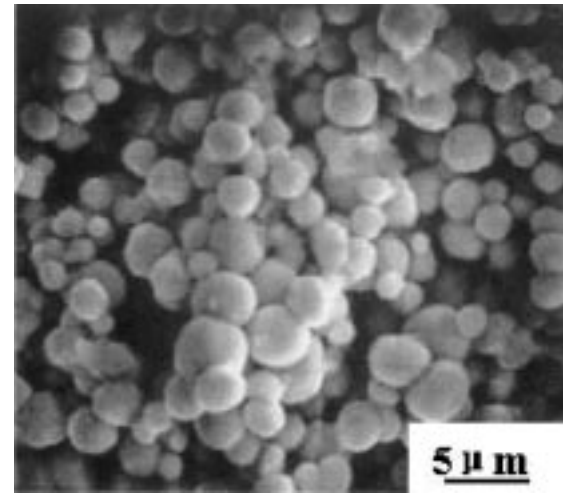

Figure 3 Microstructure of TiC extracted from Al/TiC master alloy obtained by reaction synthesis.

3.2. Microstructure

The microstructure of TiC extracted from Al/TiC master alloy synthesized by reaction has been shown in the Fig. 3. The TiC particles are of smooth surface and spherical shape. The size is less than 1 μm.

Fig. 4a–d show the microstructure of Ti-6Al/TiC composites. In the macrostructure of Ti/TiC composites, Fig. 4a, there exist two kinds of phases with different morphology in the matrix: dendritical phase (Fig. 4b) and spherical phase (Fig. 4c). The microhardness results have been shown in Table II. The spherical phases are too small to be measured, so microhardness value has not been obtained. To be compared, the microhardness of Ti alloy and TiC ceramic particle obtained from Metal Handbook has also been shown in the Table II. From the microhardness value, it can be

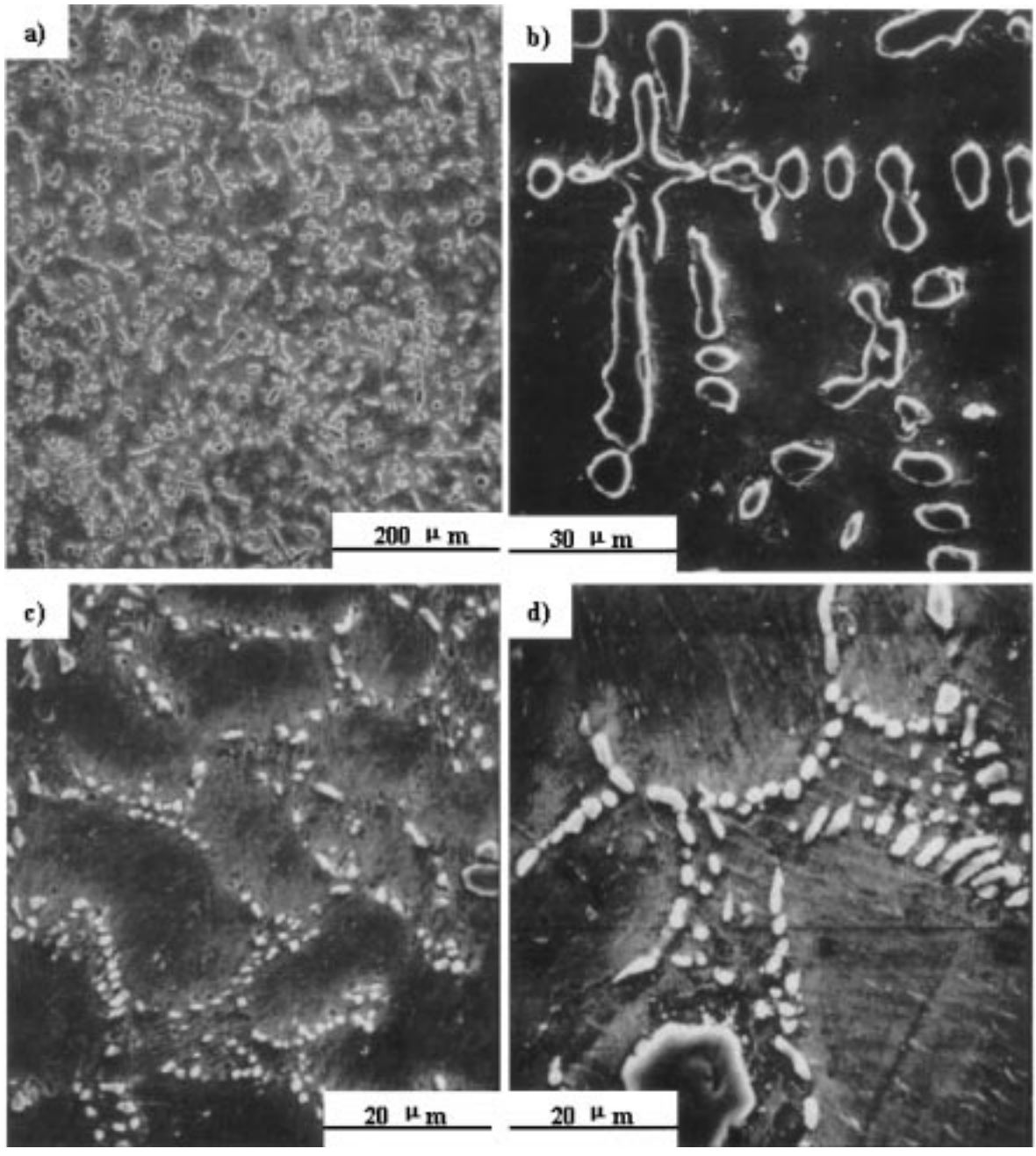

Figure 4 Microstructure of Ti-6Al/TiC composites.

identified that the dendritical phases are TiC. Combined with the morphology of the extracted TiC (Fig. 3) and XRD results of Ti/TiC, it can also be confirmed that the spherical phases are also TiC.

Although the presence of TiC particles make it difficult to measure the grain size accurately, it can assessed from some area, shown in Fig. 4c, that the grain size is about 30 μm.

In the macrostructure, TiC particles homogeneously distribute in the matrix, but in microstructure (Fig. 4c)

TABLE II Microhardness of matrix, dendritical phases, Ti alloy and TiC ceramic

Materials	Ti matrix	Dendritical phases	Ti alloy	TiC
Microhardness (kg/mm^2)	274	881.8–1287.5	200–280	880–1600

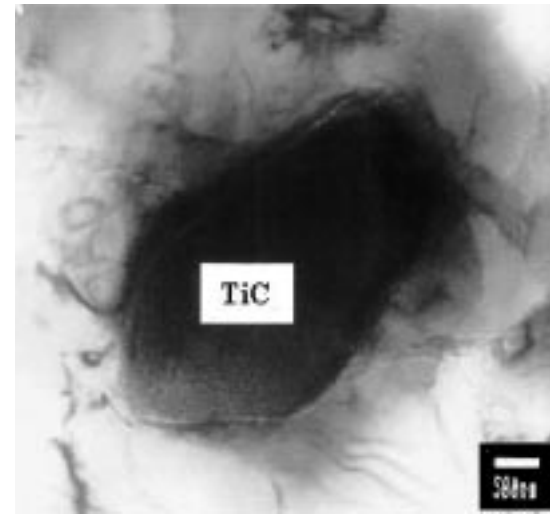

Figure 5 Morphology of spherical TiC particle observed by TEM, showing that TiC particle is of smooth outline.

the spherical TiC particles mainly segregate at the grain boundary, especially at the triangular grain boundary (Fig. 4d), which show that TiC particles can hardly be a nucleation site for the nucleating of Ti during solidification process.

In the case of change of shape of TiC from sphere to dendrite during the process, it is due to that: From the Ti-C binary alloy phase diagram, shown in Fig. 2, the liquidus temperature and the solidus temperature for Ti-1.78wt%C are about 1973 K and 1918 K, respectively. In general, the melting temperature of titanium alloy is about 1973 K–2173 K, so it is possible in the melting process for TiC particles to partially dissolve into the titanium alloy and precipitate from titanium melt to form dendritical shape during the solidification process. As a result, the dendritical and spherical TiC particles are obtained in this work.

It can also be concluded that it is necessary to study the effects of alloying elements on the shape of TiC and to control the melting and solidifying technology in order to control the shape and size of TiC.

The morphology of spherical TiC particle observed by TEM has been shown in Fig. 5. TiC particle is of smooth outline, and no sharp angle exists, which quite different from that of SiC in Ti/SiC composites prepared by adding SiC particle into titanium in which SiC usually has sharp angle. Some dislocations have also been observed in the matrix due to the addition of TiC.

Fig. 6 shows the microstructure of interface between TiC reinforcement and Ti-6Al matrix. The selecte

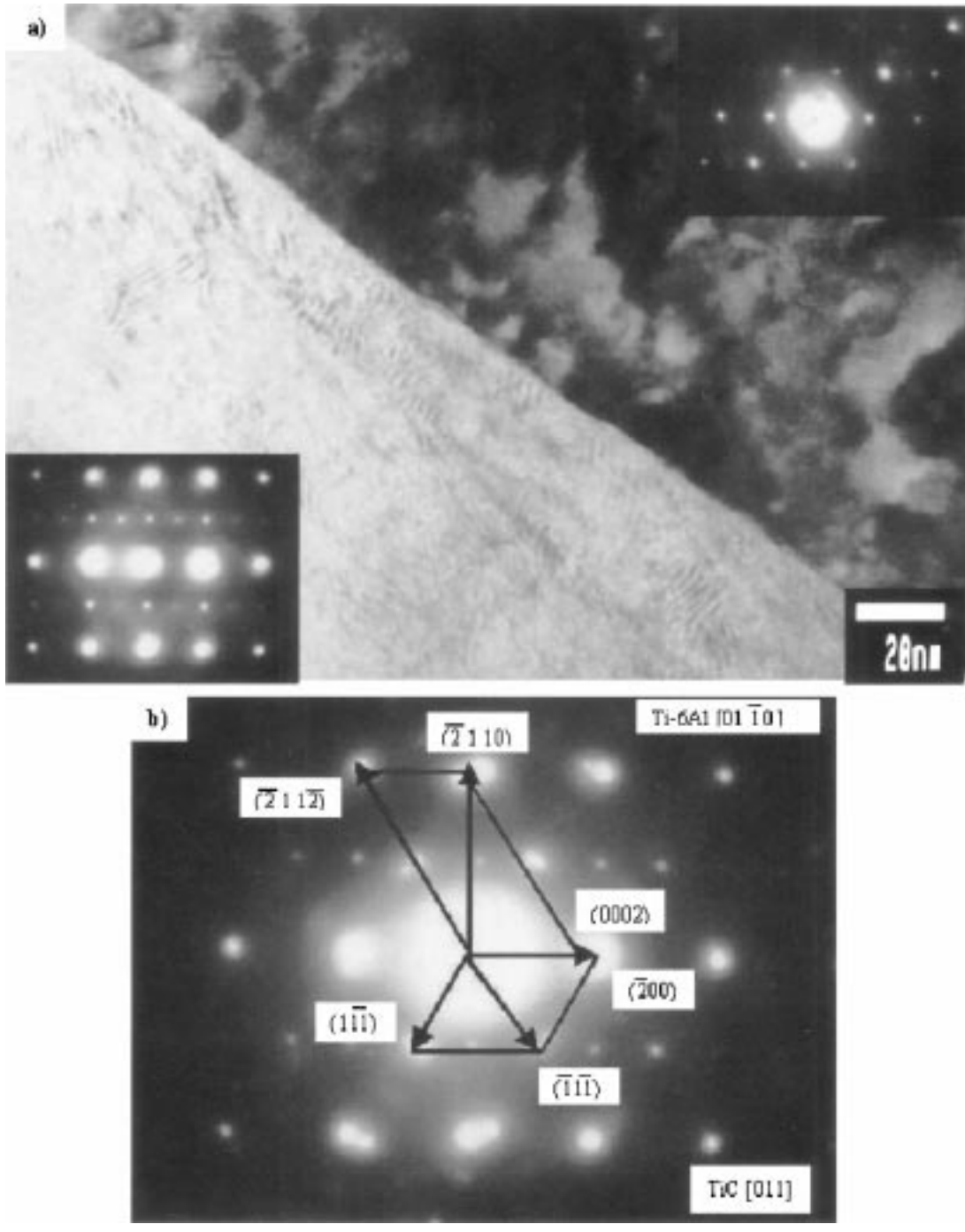

Figure 6 Interfacial microstructure and selected electron diffraction pattern. (a) interfacial microstructure (b) electron diffraction pattern along $[01\bar{1}0]//[011]$.

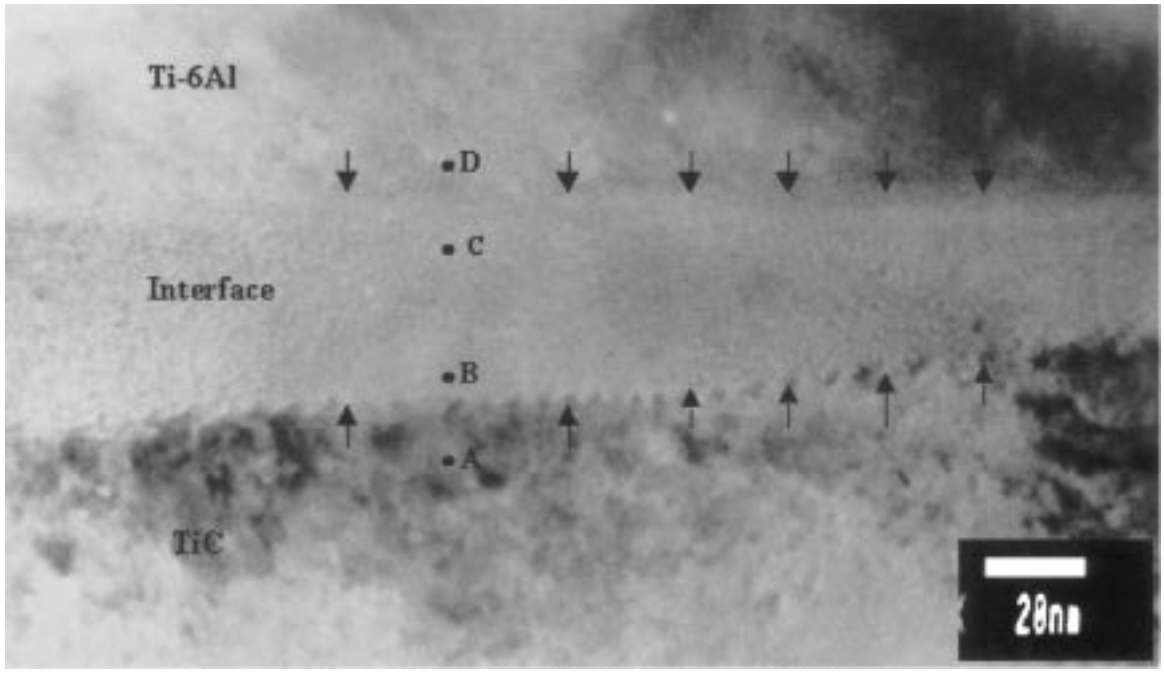

Figure 7 Interface Microstructure of Ti/TiC and ESD results, showing a diffusion layer was formed between the Ti-6Al matrix and TiC particle.

electron diffraction patterns have also been shown. A clean and smooth interface without reaction product is clearly observed. But, in some place of interface, diffusion layer can be observed which has been shown in Fig. 7. The energy spectrum diffraction results at different position have also been shown in Fig. 7 and Table III. C element diffraction peaks have been found in both Ti-6Al matrix and interface. The CPS value of C element decreases and the CPS value of Al element increases with the increasing of distance from the TiC particle. All of these show that: firstly, the reaction between Ti and C dose not happen completely and a little C atom remain in the titanium alloy; secondly, C atom diffuses through the interface into Ti-6Al matrix and forms a diffusion layer between the matrix and TiC particle because of its small size and fast diffusion rate in titanium. Hence, the solubility of carbon in β - titanium for Ti-TiC system was suspected to be higher than 0.55 at%. The diameter ratio of carbon to titanium, 0.58, is lightly less than the upper limit of 0.59 suggested by Hagg [8]. This suggests that carbon atom can form an interstitial solid solution with titanium. The maximum radio of interstitial space for octahedral body in titanium crystal is about $r_B = 0.54$ A, and the radius of carbon is about 0.77 A, so the solute C atoms expand the unit cell of titanium and produce stress

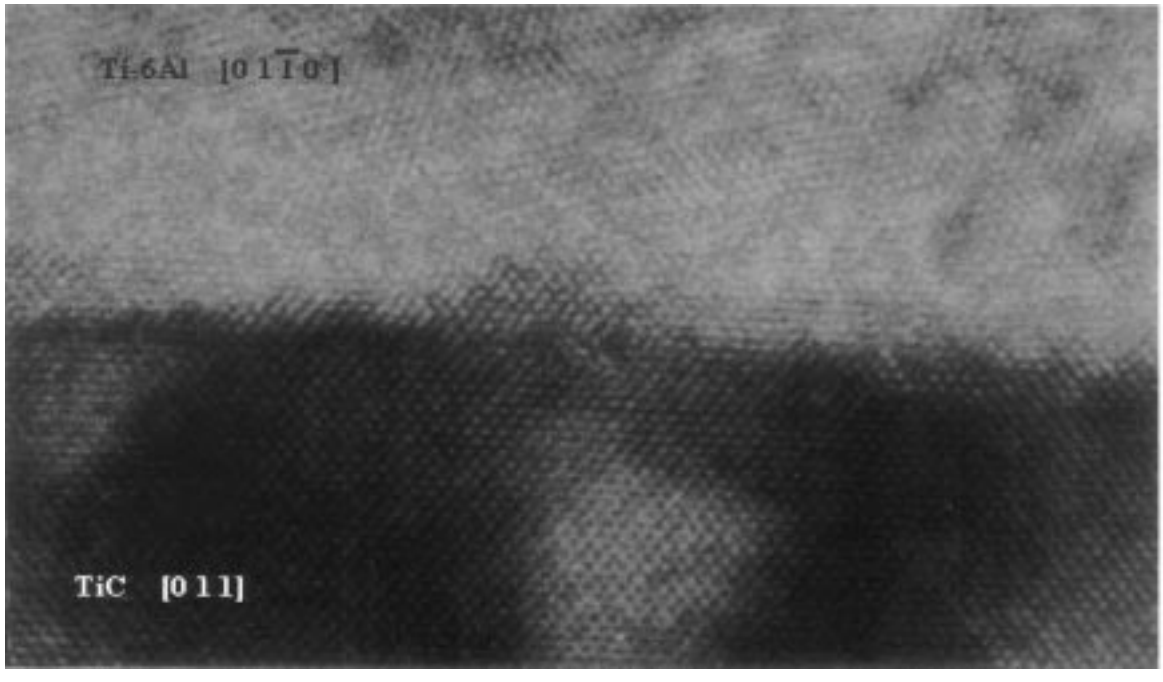

Figure 8 HREM image of TiC/Ti interface along $[01\bar{1}0]_{Ti}//[011]_{TiC}$.

TABLE III ESD analysis results at different determining position

	CPS value at different determining position of EXD			
	TiC	Interface		Ti(Al)
Element	A	B	C	D
Ti	101.1	89.1	72	79.2
Al	2.13	9.78	15	16.2
C	12.76	2.73	2.25	2.26
Al/(Ti + Al + C)	0.018	0.096	0.168	0.0168
C/(Ti + Al + C)	0.11	0.027	0.025	0.023

fields around these atoms which strength the titanium matrix.

However, in SiC particle reinforced titanium composites prepared by PM technology, heavy reaction which markedly affect the mechanical property of composites happens and Ti_5Si_3 was observed at the interface between SiC particle and titanium matrix [6]. It can also be predicted that TiC has better thermodynamic stability in the composites.

Although no definite crystallography relationship can be defined, a clean and smooth interface is observed and the orientation relationship of $[011]_{TiC}//[0\bar{1}10]_{Ti}$ could be obtained in present sample, shown in Fig. 6b. The mismatching degree (δ) between two planes and the distance between mismatching dislocation (D) can be described as following, respectively

$$\delta = \frac{d_1 - d_2}{\frac{1}{2}(d_1 + d_2)} \tag{2}$$

$$D = \frac{(d_1 + d_2)^2}{4(d_1 - d_2)} \tag{3}$$

where, d is a distance between planes. For $d_{(200),TiC} = 0.2164$ nm and $d_{(002),Ti} = 0.2342$ nm, $\delta = 7.9\%$ and $D = 2.8517$ nm, which indicating that the elastic strain caused by mismatching dislocation is relative small.

The high resolution electron microscope (HREM) image of interface between TiC and Ti matrix along $[011]_{TiC}//[0\bar{1}10]_{Ti}$ has been shown in Fig. 8. Because of the presence of C atom as a solid solution atom, the crystal lattice of titanium unit cell has been changed, so it is difficult in the HREM image of interface to observe the crystal lattice of titanium, especially at the interface beside TiC particle.

4. Conclusion

(1) TiC reinforced titanium matrix composites has been produced by XD^{TM} technology, in which TiC particles are of dendritical and spherical morphology due to the melting temperature of composites.

(2) TiC distributes homogeneously in the matrix in macrostructure, but the spherical TiC has a tendency to segregate at the grain boundary in microstructure.

(3) No reaction product has been observed at the TiC/Ti-6Al interface, but a C diffusion layer was determined by ESD and observed by HREM.

(4) Although no definite crystallography relationship has been found between TiC and Ti, a orientation relationship of $[011]_{TiC}//[0\bar{1}10]_{Ti}$ has been obtained.

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