[Article ID] 1003－6326(2002)06－1158－06

Formation and growth mechanism of TiC crystal in TiC_p/Ti composites①

JIN Yun-xue(金云学), WANG Hong-wei(王宏伟), ZENG Song-yan(曾松岩), ZHANG Er-lin(张二林)
(National Key Laboratory for Precision Hot Processing of Metal, Harbin Institute of Technology, Harbin 150001, China)

[Abstract] Ti-C and Ti-Al-C alloys were prepared using gravity and directional solidification processes. Morphologies of TiC crystal were investigated by using SEM, XRD and EDX. Also, the formation and growth mechanism of TiC crystal have been analyzed on the basis of coordination polyhedron growth unit theory. During solidification of titanium alloys, the coordination polyhedron growth unit is TiC_6. TiC_6 growth units stack in a linking mode of edge to edge and form octahedral TiC crystal with {111} planes as present faces. Although the growing geometry of TiC crystal is decided by its lattice structure, the final morphology of TiC crystal depends on the effects of its growth environment. In solute concentration distribution, the super-saturation of C or TiC_6 at the corners of octahedral TiC crystal is much higher than that of edges and faces of octahedral TiC crystal. At these corners the driving force for crystal growth is greater and the interface is instable which contribute to quick stacking rate of growth units at these corners and result in secondary dendrite arms along TiC crystallographic 〈100〉 directions. TiC crystal finally grows to be dendrites.

[Key words] titanium alloys; composites; TiC; morphology; growth mechanism
[CLC number] TB 331 [Document code] A

1 INTRODUCTION

Particles reinforced titanium alloy matrix composites (TMC_p) have wide application fields for their attractive high specific strength, specific modulus and elevated temperature properties. Unlike other processes for fabrication of TiC particles reinforced TMC_p, casting process is utilized by many researches in China owing to the simplicity in fabrication, the cost-effectiveness, and the possibility of near-net shape processing. However, TiC in as cast composites has two types of morphologies, the eutectic TiC with particle-shape or bar-like and the primary TiC with large size of dendrites. The primary TiC will degrade composite's properties[1~3]. Thereby the controlling of morphology and size of primary TiC has become key functions for further improving the properties of alloy. Tsang et al[4] try to break up TiC dendrites to promote the properties of alloy by using forging process. But this process also give rise to pre-crack in TiC particles and the pre-crack becomes crack initiation leading to the fracture of alloys, indicating that it is not the optimum process for the controlling of morphology of TiC crystal in alloy. Heat treatment process can change the morphology and size of TiC and prevent the occurrence of pre-crack in particles[5]. It becomes one of the effective ways to control the morphology of TiC. If the growth of TiC crystal can be controlled or suppressed during the composite fabricating processing and make it form needed morphology, the properties of composites can be improved significantly. Many works have been done to investigate the morphology and size of TiC in super-alloys and its formation mechanism[6,7]. Up to now, despite primary TiC in Ti alloys is large dendrite and it significantly influence the properties of alloy, the researches on the morphology and size of TiC crystal in Ti matrix composites are few. Thus, the goals of this paper are to investigate the formation and growth of dendritic primary TiC in Ti-xAl-yC alloys and to analyze the formation mechanism of morphology of TiC on the basis of coordination polyhedron growth unit theory.

2 EXPERIMENTAL

In this experiment, two kinds of fabrication processes were used to prepare specimens. One is gravity solidification, the other is directional solidification.

Alloys of button ingots of about 50 g each one were melted using an arc furnace with non-consumable tungsten electrode under argon atmosphere from sponge titanium, 99.99% (mass fraction) purity aluminum, 45 μm and 99.2% purity titanium powders, and 5~15 μm pure TiC powders. Each button ingot was melted at least

① [Foundation item] Project(99JS61.5.1.ZS6102.) supported by the Foundation of National Key Laboratory of Precision Hot Processing of Metal
[Received date] 2001－11－21; [Accepted date] 2002－01－09

three times to promote homogeneity of the as-cast structure. In addition, in order to prevent the loss of powders from mixing and melting processes, the pure Ti powders and TiC powders were uniformly mixed and then they were pressed into compacts with size of d15 mm × 10 mm using 100 ton hydraulic pressure machine. 3 kg master ingots for directional solidification have the same compositions and fabrication process, and were prepared by induction skull furnace melting. The size of as-grown ingots was typically 8 mm in diameter and 100mm in length. Directional solidification was performed in a floating zone furnace at growth rate 15 mm·h^{-1} and thermal gradient 100 ℃·mm^{-1} under argon gas flow. Microstructures of growing and quenched zone of specimens quenched entirely in Ga-In alloy during solidification were observed. Samples with dimensions of 10 mm × 10 mm × 5 mm cut from button ingots and directional solidification specimens were polished and then they were etched to make TiC exposed. Etching was done using a solution of 4% HF-12% HNO_3-84% H_2O by volume. A Rigaku X-ray diffractometer(XRD) was used to determine phase constitution of samples. JEOL and JSM-5600LV scanning electron microscopes(SEM) equipped with an energy-dispersive X-ray spectrometer(EDX) was used to characterize the microstructures and test the micro-zone compositions. Table 1 lists the chemical compositions of the samples.

Table 1 Chemical composition of specimens(%)

Specimen	Nominal composition	C	Al	Ti
1*	Ti-0.4C	0.38	0	Bal.
2	Ti-0.8C	0.76	0	Bal.
3	Ti-2.0C	1.96	0	Bal.
4*	Ti-6Al-2.0C	1.98	6.20	Bal.
5	Ti-6Al-1.2C	1.20	5.93	Bal.
6	Ti-10Al-2C	1.96	9.80	Bal.

* —Directional solidification

3 RESULTS AND DISCUSSION

3.1 Morphology of primary TiC in Ti alloys

SEM photograph of Ti-2C alloy in Fig. 1 shows that there are two types of morphologies in titanium matrix; one is dendritic and another is rod-like. The XRD and EDX results indicate that both of them are TiC phase and dendrites are primary TiC[8].

TiC has a NaCl-type crystal structure and is face center cubic crystal. In TiC, carbon atoms fill in octahedral interstitials. Under ideal conditions, TiC is stoichiometric. However, on the condition of cast, the TiC

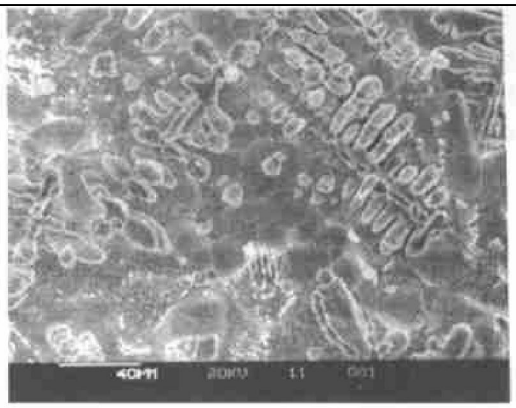

Fig. 1 SEM photograph of Ti-2.0C alloy

is highly substoichiometric TiC_{1-x} owing to non-equilibrium solidification. Fig. 2 is the XRD result of extracted TiC powders from Ti-10Al-2C alloy. X-ray diffractometry pattern indicates that each diffraction peak drifts to right to some extent and the lattice parameter of reference TiC powders, a= 0.431 0 nm, is lower than that of standard TiC. According to Ref. [9], TiC in alloy should be substoichiometric $TiC_{0.82}$ corresponding to this lattice parameter. In light of Ti-C equilibrium phase diagram, even though under the condition of equilibrium solidification, TiC formed in eutectic reaction is substoichiometric $TiC_{0.68}$[10]. With continuous cooling, C content in TiC increases and TiC is also substoichiometric even at ambient temperature. Under casting condition, diffusion of solute in the solid is neglected due to quick cooling rate which leads to TiC in alloy is non-stoichiometric. Thus, TiC in titanium matrix composites prepared using casting process is C deficient and substoichiometric TiC_{1-x}.

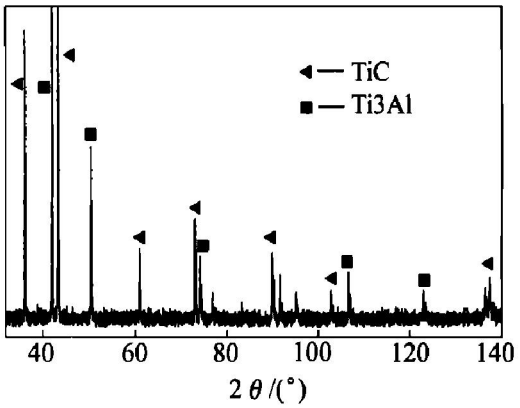

Fig. 2 XRD pattern of extracted TiC powders in Ti-10Al-2C alloy

3.2 Formation of TiC crystal cell

For Ti-C binary eutectic alloy as shown in Fig. 3, the C composition at eutectic point is 0.8%. A hypereutectic alloy is solidifying as: $L \rightarrow L_1$ + TiC, $L_1 \rightarrow (\beta)$ Ti+ TiC. TiC crystal cell freely nucleates and grows in

super-cooling molten. Geometry of TiC crystal cell in molten during nucleation is not influenced by the kinetic conditions, such as heat transfer, solute transfer, and the geometry of TiC crystal cell depends on its crystal lattice. Octahedral TiC crystal cells, as shown in Fig. 4, were observed in quenched zone of directionally solidified Ti-2.0C specimens. The ideal geometry of TiC crystal in Ni-based alloys is octahedron[6]. Octahedral TiC is a balance geometry deceived by its crystal lattice in terms of the growth process and the morphology of primary TiC in Ti alloys.

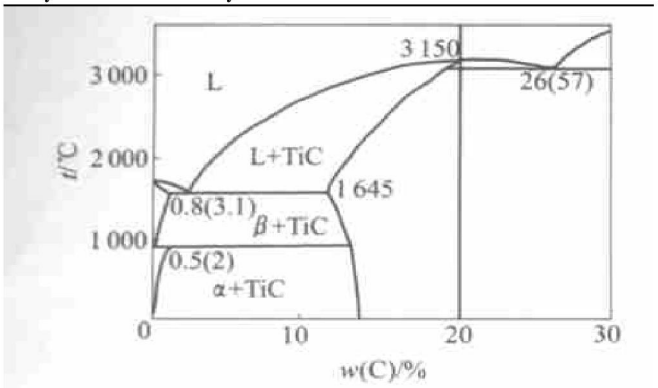

Fig. 3 Ti-C binary diagram[11]

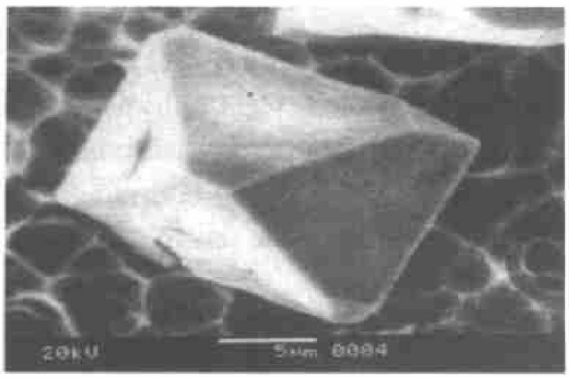

Fig. 4 Ideal geometry of TiC crystal

The researches on crystal growth indicated that during crystal growth, groups consisted of the strong binding-forces growth unit enter growth facet instead single atom entering growth facet. In TiC crystal, the strongest binding is Ti-C binding and the most possible growth unit is TiC_6 or Ti_6C. The formation energies of TiC_6 and Ti_6C are 3.9 MJ/mol and 7.1 MJ/mol, respectively[11]. The formation energy of TiC_6 is lower than that of Ti_6C, so it is easy for the formation of TiC_6 comparing to the formation of Ti_6C and the growth unit should be TiC_6 during TiC crystal growth. On the basis of coordination polyhedron growth law, growth unit of TiC coordination polyhedron also should be TiC_6[12].

Considering the coordination polyhedron growth unit theory[12], the most stable mode for linking a six-coordination TiC_6 octahedron growth unit is edge with edge linking. When the linking of octahedra is edges, the existence of tetrahedral cone terrace, as sketched in Fig. 5, can contain a half of TiC_6 growth unit and four edges of TiC_6 growth unit link simultaneously giving rise to new terrace. Thus, the growth mode of {100} planes is continuous growth and its growth is much more easily than other planes, which make {100} planes non-present faces. On {111} planes, the linking mode for TiC_6 growth unit is face to face, and there are no terraces.

Fig. 6 is the schematic illustration of mechanism for octahedron growth units entering {111} planes. The growth course is analogous to two-dimensional nucleation, that is when one or more TiC_6 growth unit links with {111} planes, the terraces can occur. Other octahedra can only enter {111} planes by means of these terraces, therefore {111} planes have slowest growth rate and become present faces. Once TiC_6 octahedron growth units stack on the basis of entering {111} planes mechanism, the geometry of TiC is octahedron with {111} present faces, as shown in Fig. 7.

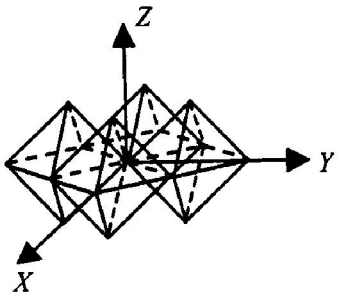

Fig. 5 Schematic illustration for edges linking of TiC_6 growth units

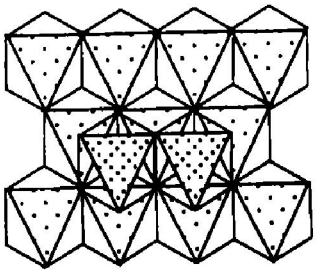

Fig. 6 Mode for TiC_6 growth units entering [111] plane

These results are identical to experimental results presented in Fig. 4. Each present face in ideal geometry of TiC also conforms with Bravais law which indicates that the present face would be a face having higher atom array density and larger plane spacing after crystal growth. TiC is face center cubic structure and the dense planes are {111} planes, thereby the {111} planes are present faces. The present faces of octahedral TiC are {111} planes by TEM investigation[6].

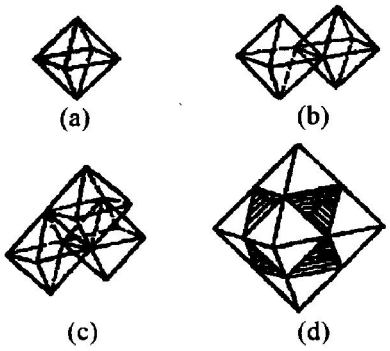

Fig. 7 Scheme for TiC_6 growth units stack and form octahedron
(a) —Single TiC_6 growth unit;
(b) —Linking of two TiC_6 growth units;
(c) —Stacking of TiC_6 growth units;
(d) —Final octahedron

3.3 Growth of TiC crystal

On the condition of non-equilibrium solidification, the growth kinetics and solute transfer play a deceive role on the final morphology of crystal. For octahedral TiC cell, its growth in molten has two types of transfer courses, the mass transfer and heat transfer. In this experiment, the water cooled copper furnace has strong chill capability and can make the whole molten supercooled that provides kinetic conditions for faster growth and induces to interface instability of TiC crystal cell. During the growth of TiC crystal, Ti and Al atoms diffuse into molten from crystal, and vice versa, TiC_6 growth units in molten stack on TiC crystal in three-dimensional directions. On the assumption that: 1) TiC crystal precipitating from molten is spheroidal; 2) Solute transfer is the controlling factor of TiC crystal growth and the influence of convection on solute transfer is negligible; 3) The solute transfer capability is the same in three-dimensional directions, for spheroidal crystal cell with radius R_0, under quasi-steady state condition the diffusion distribution of C solute should satisfy the Laplacian equation:

$$\nabla^2 c(r) = 0 \tag{1}$$

Boundary conditions for Eqn. (1) are

$$c(r)_{r=\infty} = c_0$$

$$c(r)_{r=R_0} = c_e$$

So the equation to be solved is

$$c(r) = c_0 + (c_e - c_0)\frac{R_0}{r} \quad (r \geqslant R_0) \tag{2}$$

where $c_0 = c$, solute concentration in alloy, %; $c_e = c$, solute concentration at matrix interface, %.

From Eqn. (2) we can predict that the solute distribution surrounding TiC polyhedral crystal has gradient changing tendency, as illustrated in Fig. 8. Carbon or TiC_6 super-saturation at corners and edges of TiC polyhedron is greater than at faces of TiC polyhedron causing non-uniform solute super-saturation and concentration gradient at each position of TiC crystal. Corners and edges with greater super-saturation have faster growth rate and make crystal geometry non-stable. Corners having faster growth rate grow into the molten with greater super-cooling and solute concentration. The above results make phase transformation driving force and growth rate further increase. As a result, TiC crystal becomes dendritic morphology. TiC is face center cubic structure and its characteristic growth direction is in ⟨100⟩ directions. TiC crystal branches along six corners of octahedral TiC accompanied by occurrence of dendrite arms in the ⟨100⟩ directions. At initial branching stage, the six ⟨100⟩ directions have the same growth kinetic and polyhedral TiC uniformly branches in these directions as shown in Fig. 9. Fig. 9(a) and Fig. 9(b) are the morphologies of initial branching TiC.

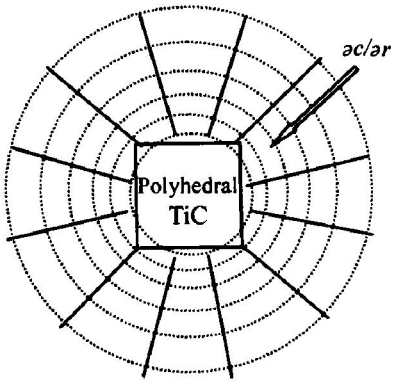

Fig. 8 Concentration distribution surrounding TiC crystal

TiC crystal in molten has different growth environments owing to the functions of influence factors such as heat flow, and these influence factors contribute to the growth rate of crystal cell at one direction faster than other directions resulting in the occurrence of first dendrite arms and secondary dendrite arms, as shown in Fig. 9(c). Because the growth driving force and supersaturation at different directions of crystal during TiC growth are different, the growth rates at different directions are different leading to various sizes dendrites in different directions as shown in Fig. 9(d).

Fig. 10 is the model for the nucleation and growth of dendrite TiC. The mode illustrates that in molten octahedral TiC crystal cell was firstly formed(Fig. 10(a)). Then, it protrudes in the ⟨100⟩ directions due to the effects of concentration and temperature distribution and branches into secondary dendrite arms, as described in Fig. 10(b) and Fig. 10(c), respectively. Finally, TiC crystal cell develops into larger size of dendrite TiC, as shown in Fig. 10(d).

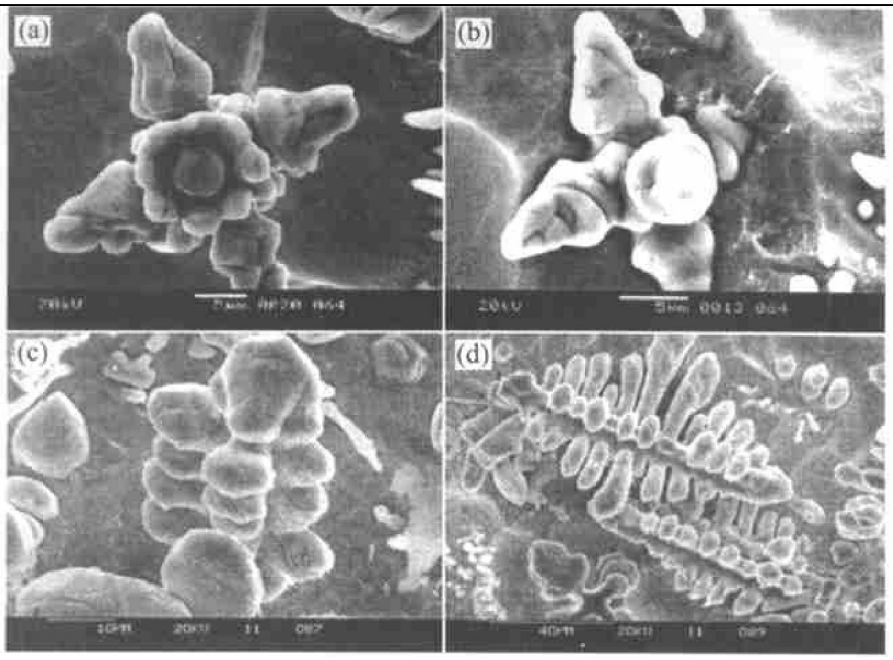

Fig. 9 Branching and growing course of TiC crystal in ⟨100⟩ direction
(a), (b) —TiC in initial branching; (c) —TiC branching into secondary dendrite arms;
(d) —Developed TiC dendrite

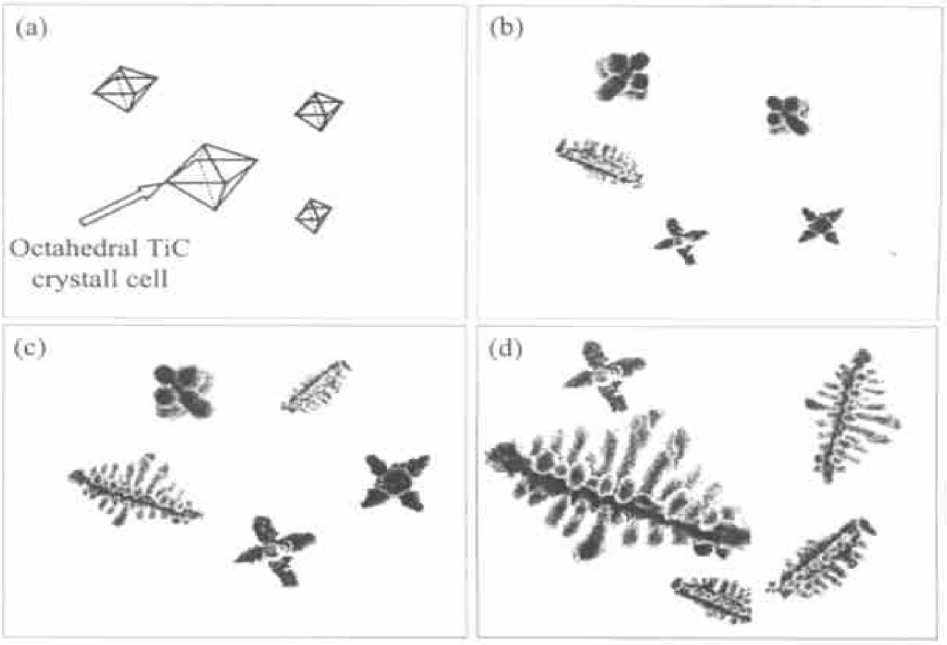

Fig. 10 Model for nucleation and growth of dendrite TiC
(a) —Octahedral TiC crystal cells; (b) —crystal cell branching into fine secondary dendrite arms;
(c) —Further growth of secondary dendrite arms; (d) —Developed TiC dendrite

4 CONCLUSION

The geometry of primary TiC in Ti alloys is octahedral crystal. The octahedron is ideal geometry of initial TiC crystal because at the initial stage of TiC crystal growth the influence of solute diffusion is negligible. When TiC crystal further grows, octahedral TiC crystal branches in the ⟨100⟩ directions and forms TiC dendrite owing to the effects of temperature distribution and concentration distribution which lead to the corners of octahedral TiC have faster growth rate than other positions.

[REFERENCES]

[1] ZHANG Er-lin, ZHU Zao-jun, ZENG Song-yan. Review on in-situ particulate reinforced titanium matrix composites (TMCS) [J]. Chinese Journal of Rare Metals, 1999, 23 (6): 436-442.

[2] Ranganath S. A review on particulate-reinforced titanium matrix composites[J]. Journal of Materials Science, 1997, 32: 1-16.

[3] ZHANG Er-lin, JIN Yun-xue, ZENG Song-yan. Microstructure of in-situ TiC particle reinforced titanium alloy matrix composites[J]. Trans Nonferrous Met Soc China, 2000, 10(6): 764-768.

[4] Tsang H T, Chao C G, Ma C Y. In situ fracture observation of a TiC/Ti MMC produced by combustion synthesis [J]. Scripta Materialia, 1996, 35(8): 1007-1012.

[5] ZHANG Er-lin, JIN Yun-xue, ZENG Song-yan, et al. Temperature dependence of morphology of TiC reinforcement in in-situ Ti-6Al/TiC composites[J]. Journal of Materials Science Letters, 2001, 20: 1063-1065.

[6] LIU Lin. Study on Crystal Growth Characteristics of MC Carbides in Super-Alloys and Function Mechanism of Refractory Elements[D]. Xi'an: Northwestern Polytechnical University, 1988, 9-30.

[7] XING Zhang-ping. Dissertation for the Degree of Doctor of Engineering[D]. Harbin: Harbin Institute of Technology, 1995. 30-60.

[8] JIN Yun-xue, ZHANG Er-lin, ZENG Song-yan, et al. Fabrication and microstructure of TiCP/Ti composites in melting-casting[J]. Foundry, 2001, 50(2): 70-73.

[9] Zueva L P(П. В. зуева), Gusev A Y(А. И. Гусев). Influence of non-stoichiometry and order on lattice parameters of TiC. Physics of the Solid State, 1999, 41(7): 1134-1141.

[10] Yamaguchi S, Umakoshi Y. Intermetallics[M]. Tokyo: Japanese Industrial Press, 1987: 79.

[11] LIU Lin, FU Heng-zhi, SHI Zheng-xing. Relationship between primary morphology and crystal structure of MC carbides precipitated in superalloys[J]. Acta Metallurgica Sinica, 1989, 25(4): A282-A287.

[12] ZHONG Wei-zuo, HUA Su-kun. Geometry of Crystal Growth[M]. Beijing: Science Press, 1999. 205-208.

(Edited by LONG Huai-zhong)