

MICROSTRUCTURAL EVOLUTION DURING COMBUSTION SYNTHESIS OF TiC-Fe CERMET^①

Fan Quncheng, Chai Huifen and Jin Zhihao

*State Key Laboratory for Mechanical Behavior of Materials,
Xi'an Jiaotong University, Xi'an 710049, P. R. China*

ABSTRACT (Ti + C) + 30 % Fe powder mixture was used for a combustion front quenching test, and the quenched sample was analysed by scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis to study the microstructural evolution during the combustion synthesis, meanwhile, the combustion temperature was measured. The results showed that the reaction of Ti + C takes place in Ti and Fe particles, respectively, and it is earlier in the Ti particle than that in the Fe particle. The reaction in the Ti particle can be described with a ternary reaction-diffusion model, while the reaction in the Fe particle can be described with a solution-precipitation model. The molten Ti and Fe particles fuse together subsequently accelerating the formation of the final product, TiC particles and α -Fe binder.

Key words microstructural evolution TiC-Fe cermet combustion synthesis

1 INTRODUCTION

Since it was discovered in 1967, the combustion synthesis has been used for synthesizing a variety of compounds and composites, e.g. TiC^[1], TiC-Al^[2-4], TiC-Ti^[5], TiC-Al-Cu^[6] and TiC-Fe^[7-10] etc. However, the mechanisms of the combustion syntheses have not been well understood because both the high combustion temperature and rate make the microstructural evolution during the combustion syntheses very difficult to be observed. If the combustion front which was self-propagating in a combusting sample was quenched, the initial, intermediate, and final products would be frozen in the quenched sample. Thus, the microstructural evolution could be observed and analysed by SEM and EDX. With this combustion front quenching method, the microstructural evolution of TiC was observed^[11, 12], and role of iron addition in the combustion synthesis of TiC-Fe cermet was studied^[13, 14]. Up to the present, however, the microstructural evolution of any polynary system has not been observed successfully because of its complexity. The objective of the work is to

study the microstructural evolution of TiC-Fe system during the combustion synthesis using the coarse Ti and Fe powders.

2 EXPERIMENTAL

56 % titanium powder (135 ~ 154 μm), 14 % carbon black (0.033 ~ 0.079 μm) and 30 % iron powder (135 ~ 154 μm) were mixed thoroughly and were uniaxially pressed in a steel die forming a green compact (14 mm \times 18 mm) with a relative density of about 60 %, and part of the compact was pushed out of the die, with the remaining part being left in the die. The compact was then ignited in a reaction chamber with an incandescent graphite flat which was 2 mm above the top surface of the compact at a pressure of 0.1 MPa of argon. So, the combustion front self-propagated from the top toward the bottom of the compact but self-quenched before it reached the bottom because of the cooling effect of the steel die. The sample with the quenched combustion front was cut longitudinally and prepared as a metallographic specimen, and its microstructure was observed and analysed

① Project supported by the Doctorate Foundation of Xi'an Jiaotong University

Received Sep. 10, 1998; accepted Nov. 27, 1998

with SEM and EDX.

To measure the combustion temperature, a small hole (2 mm in diameter and 8 mm in deep) was drilled at the centre of bottom of the sample which was the same as that used in the quenching test but wholly pushed out of the die. A junction of W-3 %Re vs W-25 %Re thermocouple with a wire diameter of 0.1 mm was inserted into the hole, and the other end of the thermocouple was linked up with an X-Y recorder. The compact was ignited by use of the method identical with that in the quenching test, and the combustion wave self-propagated through the compact from above to below, thus, a temperature-time profile was drawn by the X-Y recorder.

3 RESULTS AND DISCUSSION

Fig.1 shows the measured temperature-time profile of the combustion synthesis at a point in the combusting compact. An exothermic peak, having a temperature of 1 926 K, is presented on the profile. This means the combustion temperature is above the melting point (1 811 K) of iron but below the melting point (1 945 K) of titanium.

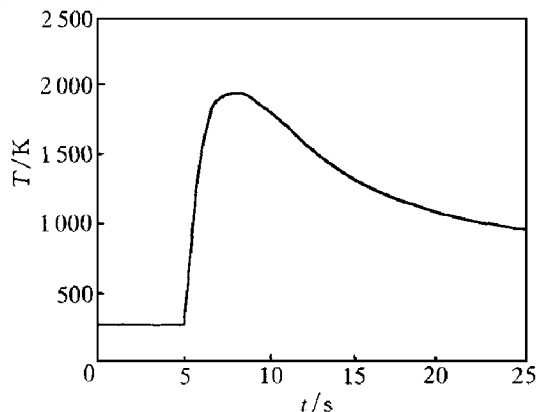


Fig.1 Temperature-time profile of combustion reaction

The SEM results showed that the combustion reaction of Ti + C occurs in the Ti particle and Fe particle, respectively, and it is earlier in the Ti particle than it in the Fe particle.

Fig.2 shows the reaction in the Ti particle. It can be seen that the reaction started from the

surface layer "A" of the Ti particle, as shown in Fig.2(a), and propagated continuously toward the central region "B", as shown in Fig.2(b). The microstructure of the reacted region "C" is shown in Fig.2(c) in which many particles, with an average diameter of about 1.0 μm , have been formed and separated by a binder phase. EDX results showed that these particles are TiC in which a small amount of Fe atoms were dissolved with Fe/Ti mole ratio of 6.50/93.50, and the binder phase was a Ti-rich solid solution with Fe/Ti mole ratio of 18.90/81.10. Although the central region "B" was also a Ti-rich solid solution, the Fe content in it (Fe/Ti mole ratio of 4.50/95.50) was lower than that in the binder phase. Of course, there must be carbon atoms in these phases. It should be noted that the shape and size of the initial titanium particle are still retained by the Ti particle having begun to react, as shown in Fig.2(a) and 2(b). In consideration of the combustion temperature below the melting point of Ti, the temperature at which the reaction of Ti + C began to take place in the Ti particle would be much lower than the melting point of Ti. Deevi^[15] measured ignition temperature, T_{ig} , of Ti + C \rightarrow TiC reaction as 1 300 K. In addition, the result of Saidi *et al*^[8] showed that as the iron content increases, the T_{ig} of Ti-C-Fe system decreases and reaches a minimum of 1 333 K at 60 % Fe. These experimental results indicate that the reaction of Ti + C starts at a temperature much lower than the melting point of Ti. In this paper, in view of the presence of distinct reaction-diffusion layer in the surface layer of Ti particles having begun to react, it should be suggested that the reaction of Ti + C in the Ti particle resulted from a solid-state ternary reaction-diffusion. In other words, as diffusion of C and Fe into the Ti particle, TiC particles as well as a Ti-rich binder phase simultaneously formed within the ternary reaction-diffusion layer when the concentration of C was saturated. As the reaction-diffusion layer extended toward the centre of the Ti particle, accumulation of the released heat made the temperature in the reaction zone to increase, leading the Ti-rich binder phase in the reaction-diffusion layer to melt and flow with TiC particles (from Ti-Fe

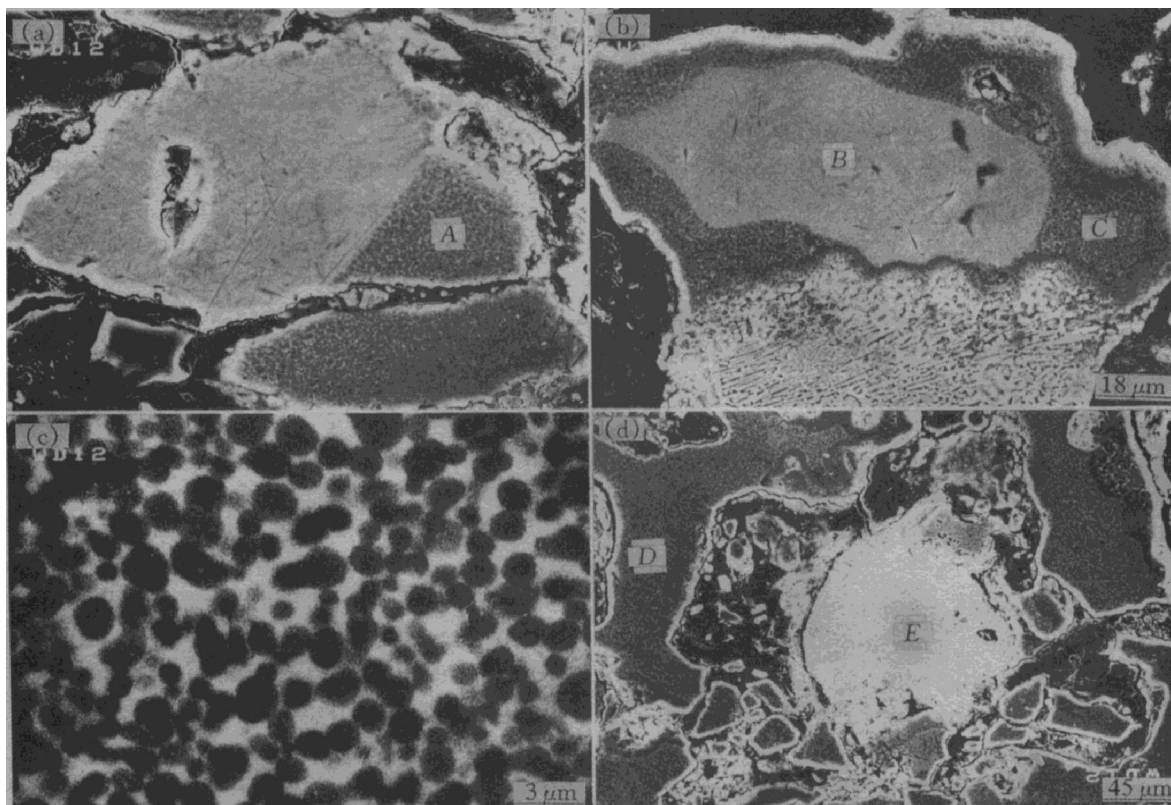


Fig.2 SEM micrographs showing reaction in Ti particle

(a) —Starting from surface layer “A” ; (b) —Propagating toward centre “B” ;

(c) — Microstructure of reacted region “C” ;

(d) — Melting and flowing of reacted Ti particle “D” beside unreacted Fe particle “E”

phase diagram, as the Fe content increases, the melting point of Ti decreases and reaches a eutectic temperature of 1 359 K), as shown in the region “D” in Fig.2(d). It is interesting to note that in Fig.2(d), no indication of a change is observed in the Fe particle indicated by letter “E”. This implies that the reaction of Ti + C in the Fe particle is latter than that in the Ti particle.

Fig.3 shows the combustion reaction in Fe particles. In Fig.3(a), there is a structural difference between the surface region “F” and the central region “G” of the Fe particle. The EDX results showed that the C and Ti content in the region “F” (12.18 % (mole fraction) C, 1.31 % (mole fraction) Ti and 86.51 % (mole fraction) Fe) are higher than those in the region “G” (4.34 % (mole fraction) C, 0.24 % (mole fraction) Ti and 95.42 % (mole fraction) Fe). Fig.3

(b) shows the microstructure of the region “F”, and the composition of the matrix is similar to that of the region “G”, while a relatively large amount of C and a few Ti atoms (45.35 % (mole fraction) C, 0.38 % (mole fraction) Ti and 54.27 % (mole fraction) Fe) are contained in the rod-shaped phase, which would be an (Fe, Ti) C phase. Apparently, the changes mentioned above mainly result from diffusion of Ti, particularly C into the Fe particle. The diffusion brought down the melting point of the Fe particle and led the Fe particle “H” to melt, as shown in Fig.3(c), at a lower temperature than the melting point of Fe, since it became ledeburite when it was cooled, as shown in Fig.3(d). The melting of the Fe particle accelerated the dissolving of C and Ti into the molten Fe droplet, and when C and Ti concentrations were saturated, as shown in Fig.3(e), the TiC parti-

cles got to precipitate out, as shown in Fig. 3 (f). The above results indicate that the reaction of Ti + C in Fe particles undergoes two processes, i. e. a process of C and Ti dissolving into Fe particles and a process of TiC particles precipitating out of the saturated droplets. Consequently, the reaction can be described with a solution-precipitation model.

Saidi *et al.*^[8] developed a combustion model for the Ti-C-Fe system under a thermal explosion mode, and they proposed that during the heating period Ti and Fe particles reacted in the solid state to produce FeTi_2 which was a eutectic compound having a melting point of 1085 °C. At the ignition temperature, which

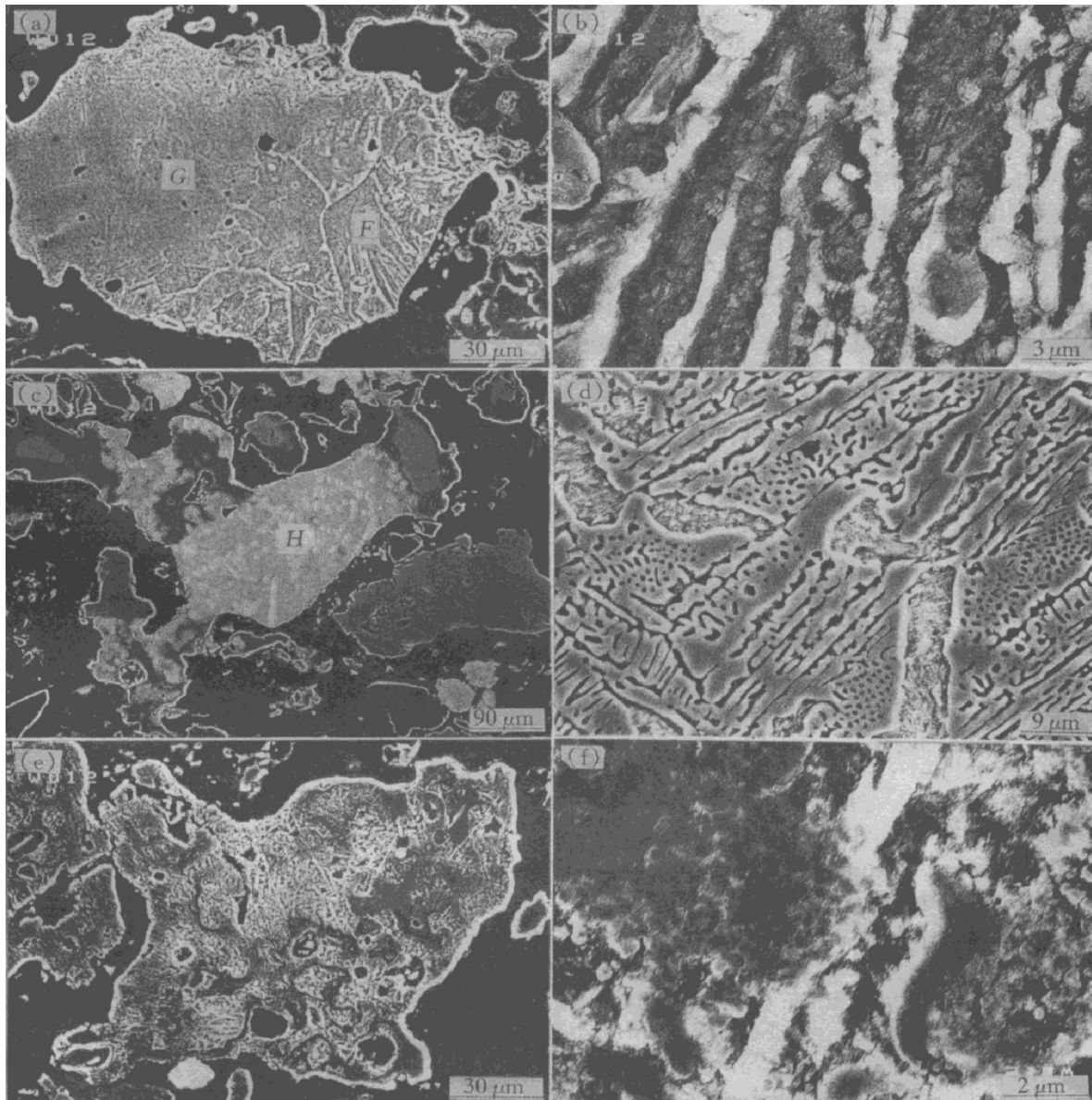


Fig.3 SEM micrographs showing reaction in Fe particle

- (a) —Structural difference between surface region “F” and central region “G”;
- (b) — Microstructure in region “F”;
- (c) — Melting of Fe particle “H”;
- (d) —Ledeburite in molten Fe particle “H”;
- (e) —Saturated Fe droplet;
- (f) —Precipitating of TiC particles

almost matched the melting point of the Fe-Ti alloy, C dissolved in the droplets of FeTi₂ and the subsequent production of TiC released enough heat to initiate a self-sustaining reaction. Also, they examined this model by heating a pre-compacted mixture of Ti-C-Fe to 1 100 °C and quenching the sample just before ignition, and SEM inspection of this sample showed that some liquid droplets around the Fe particles. However, the results of Choi and Rhee^[7] showed that X-ray diffraction pattern for the sample of mixture of Ti and Fe powders heated up to 1 200 °C at rate of 8 °C/min is composed of TiFe, TiFe₂, Ti, and Fe rather than FeTi₂. In the present work, the melting of Fe particles mainly results from the diffusion of C into the Fe particles bringing the melting point of the Fe-C alloy down to 1 148 °C (eutectic point). It is well known that the interstitial diffusion rate is higher than the substitutional diffusion one^[16], so it is impossible that FeTi₂ is formed by reaction between Ti and Fe in the solid state before the diffusion of C into Fe. In addition, the diffusion rate of atoms in BCC is higher than that in FCC crystal^[17], and Ti is BCC at 882 ~ 1 672 °C, while Fe is FCC at 912 ~ 1 394 °C, therefore, the reaction of Ti + C in Ti particles is earlier than that in Fe particles. With temperature increasing, reacted Ti droplets fused together with the reacting Fe droplets, as shown in Fig. 4(a). Fig. 4(b) shows the microstructure of reacted region "I", which is composed of TiC particles and the Ti-rich binder. The fusing of reacted Ti and reacting Fe droplets accelerated the interdiffusion between Ti and Fe, benefiting the reaction in the reacting region "J" and the formation of α Fe binder in the reacted region "I".

The combustion-synthesized product, as shown in Fig. 5(a), is composed of TiC-Fe cermet and many pores, and these pores are present in an arbitrary shape and random distribution. Fig. 5(b) shows the microstructure of the TiC-Fe cermet, and the TiC particles have an average diameter of about 3.0 μ m.

4 CONCLUSIONS

The combustion reaction of Ti-C-Fe system

produces TiC-Fe cermet. The reaction of Ti + C takes place in Ti particles and in Fe particles, respectively, and the reaction in Ti particles is earlier than that in Fe particles. The reaction in Ti particles can be described with a ternary reaction-diffusion model, namely, the simultaneous diffusion of C and Fe into Ti particles leads the reaction to occur within the saturated layer and to propagate toward the centre forming TiC particles and a Ti-rich binder. While the reaction in Fe particles can be described with a solution-precipitation model. Namely, a diffusion of C and Ti into the Fe particle leads the melting point of the Fe particle to decrease, and subsequent melting of the Fe particle improves dissolving of C and Ti atoms into the Fe droplet. As the concentration of C and Ti is saturated in the Fe droplet, TiC particles precipitate, with α Fe binder separating the TiC particles. Afterwards,

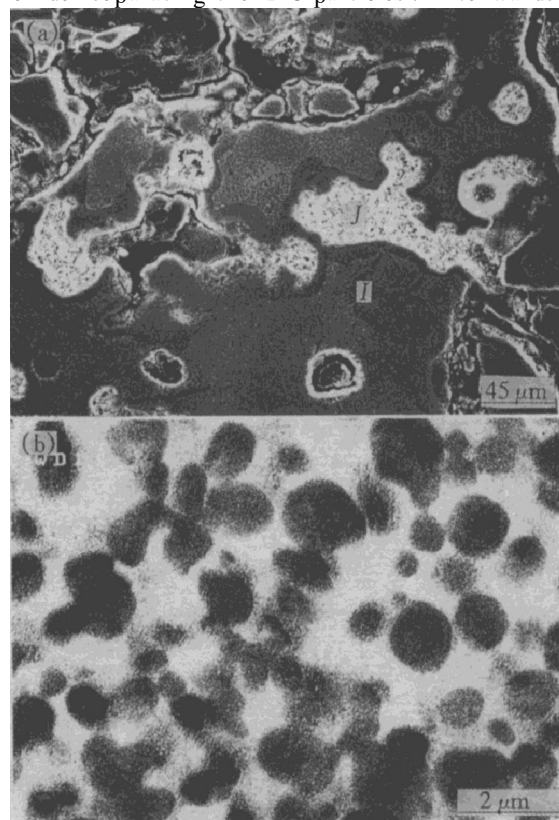


Fig. 4 SEM micrographs showing fusion of Ti with Fe droplets

(a) — Macrostructure;

(b) — Microstructure in reacted region "I"

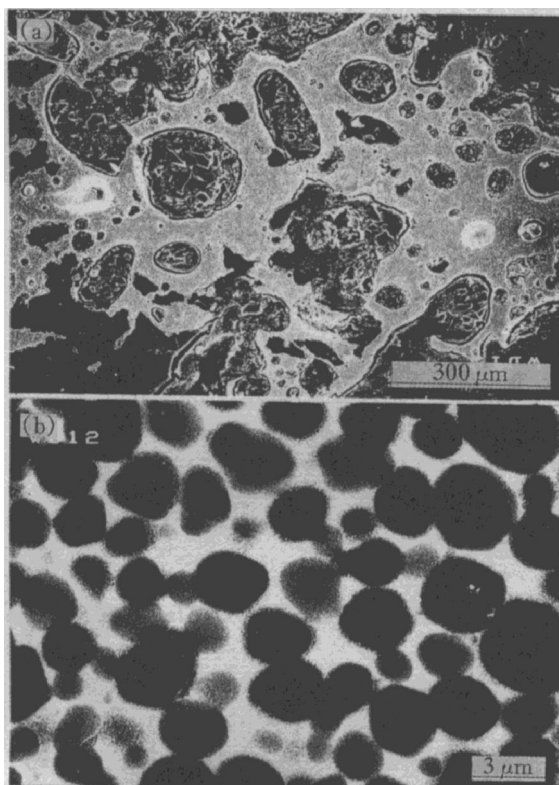


Fig.5 SEM micrographs showing combustion-synthesized product
(a) — Macrostructure ; (b) — Microstructure

the fusion of the reacted Ti droplets with the reacting Fe droplets accelerates the interdiffusion of Ti and Fe, and this leads the formation of the final product, TiC particles and α Fe binder.

REFERENCES

- 1 Holt J B and Munir Z A. J Mater Sci, 1986, 21 : 251 .
- 2 Zhang Erlin, Zeng Xiaochun, Zeng Songyan *et al.* Trans Nonferrous Met Soc China, 1996, 6(1) : 114 .
- 3 Zhang Erlin, Yang Bo, Zeng Songyan *et al.* Trans Nonferrous Met Soc China, 1998, 8(1) : 92 .
- 4 Long Chunguang, Xu Yiheng, Li Songrui *et al.* The Chinese Journal of Nonferrous Metals, (in Chinese), 1997, 7(1) : 162 .
- 5 Luo Xuming, Lu Haibo and Ma Fukang. The Chinese Journal of Nonferrous Metals, (in Chinese), 1995, 5 (4) : 141 .
- 6 Liu Jinshui, Xiao Hanning, Shu Zhen *et al.* The Chinese Journal of Nonferrous Metals, (in Chinese), 1998, 8(2) : 259 .
- 7 Choi Y and Rhee S W. J Mater Res, 1993, 8 : 3202 .
- 8 Saidi A, Chrysanthou A, Wood J V *et al.* J Mater Sci, 1994, 29 : 4993 .
- 9 Fan Quncheng, Chai Huifen and Jin Zhihao. J Mater Process Tech, (accepted) .
- 10 Fan Quncheng, Chai Huifen, Fang Xuehua *et al.* J Xi'an Jiaotong University, (in Chinese), 1994, 28 (7) : 123 .
- 11 Rogachev A S, Mukus'yan A S and Merzhanov A G. Dokl Phys Chem (Engl transl), 1987, 297 : 1240 .
- 12 Fan Quncheng, Chai Huifen and Jin Zhihao. J Mater Sci, 1996, 31 : 2573 .
- 13 Fan Quncheng, Chai Huifen and Jin Zhihao. J Mater Sci, 1997, 32 : 4319 .
- 14 Fan Quncheng, Fang Xuehua and Chai Huifen. Acta Metall Sinica, (in Chinese), 1994, 30(11) : B513 .
- 15 Deevi S C. J Mater Sci, 1991, 26 : 2662 .
- 16 Verhoeven J D. Fundamentals of Physical Metallurgy. New York: John Wiley & Sons, 1975 : 154 .
- 17 Guy A G and Hren J J. Elements of Physical Metallurgy. California: Addison Wesley, 1974 : 388 .

(Edited by Huang Jinsong)