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Reaction sequences and influence factors during carbothermal synthesis of ultrafine TiN powders

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Abstract Ultrafine TiN powders were synthesized by Carbothermal Reduction-Nitridation (CRN) method using nano titania and nano carbon black as raw materials. Phase transition sequences during reaction and influence of main technological factors were investigated using X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The results indicate that phase transition sequences were $TiO_2 \rightarrow Ti_{10}O_{19} \rightarrow Ti_3O_5 \rightarrow TiO_xN_y \rightarrow TiN$. At the same time, CRN reaction consists of three continuous stages. In the first stage, nano TiO_2 powders were reduced to Ti_3O_5. In the second stage, Ti_3O_5 was totally converted into TiO_xN_y. TiN solid solution formed completely by the end of the third stage. The rapidest reaction rate was observed in the second stage and the lowest was in the third stage. Higher reaction temperature, longer isothermal time, or larger nitrogen pressure was in favor of synthesizing TiN powders.

Introduction

Titanium nitride (TiN) belongs to transition metal nitride, and it is a typical material with a wide range of stoichiometry (TiN_{1-x} $0 < x < 0.61$). Due to its excellent physical and chemical properties such as high melting temperature (2930 °C), high hardness, wear resistance, oxidation resistance, relatively low specific gravity, Titanium nitride is very attractive in various engineering technology fields such as cutting tools , hard coating on machining tools.

Many study results [1–6] show that properties of titanium nitride particle have significant effect on its advanced applications. The smaller the size of titanium nitride particle and the lower the sintering temperature is, the better the mechanical properties are, such as transverse rupture strength (*TRS*), wears resistance and fracture toughness. So in recent years, more and more studies have focused on the preparation of powders with high purity, ultrafine or nano particle size, narrow particle-size distribution, and minimum agglomeration. The present methods of preparing ultrafine or nano titanium nitride include microwave plasma chemical vapor deposition (MPCVD) [7], direct current arc plasma [8], microwave plasma [1], RF plasma [9], thermal nitridation synthesis [10, 11], mechanic alloying [12–15], mechanic alloying and subsequent heat treatment [16, 17], combustion-reduction [18], ammonia gas nitridation [19]. Carbothermal Reduction Nitridation (CRN) method is deemed as an economical method for production of non-oxide ceramic materials [20]. However, to our knowledge, nobody had synthesized ultrafine titanium nitride powders via CRN so far. In the study, we attempt to synthesize ultrafine titanium nitride powders via CRN, in which nano titania and nano carbon black are used as starting materials. Its phase transition and influence factors are investigated.

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Experimental procedure

Materials

The starting materials for the experiments are shown in Fig. 1. The mixtures of nano titania and nano carbon black were prepared with a C-to-Ti molar ratio of 2:1, hard alloy balls were used as the milling media, and the ball-to-powder weight ratio is 5:1 for all the tests conducted. The mixtures were put into polyurethane jar and roll milled for 10 h in absolute alcohol. Subsequently, the milled powder was transferred into oven for drying.

Heating experiments

A given weight of dried powder was put into the graphite crucible in a vacuum carbon tube furnace (model ZR-50-22Y, China), followed by evacuation to 1.0×10^{-2} MPa. Then the furnace was heated at the temperature increase rate of 20 °C/min. When the temperature was up to 900 °C, stopped evacuating and filled the furnace with nitrogen gas until pressure reached 0.02 or 0.05 Mpa. After that, the furnace was heated at 10°C/min rate continuously. When reaching the desired temperature (1200–1400 °C),the sample was isothermally treated for 1–3 h. Finally, the sample was taken out from the furnace and analyzed when the furnace was cooled down to room temperature.

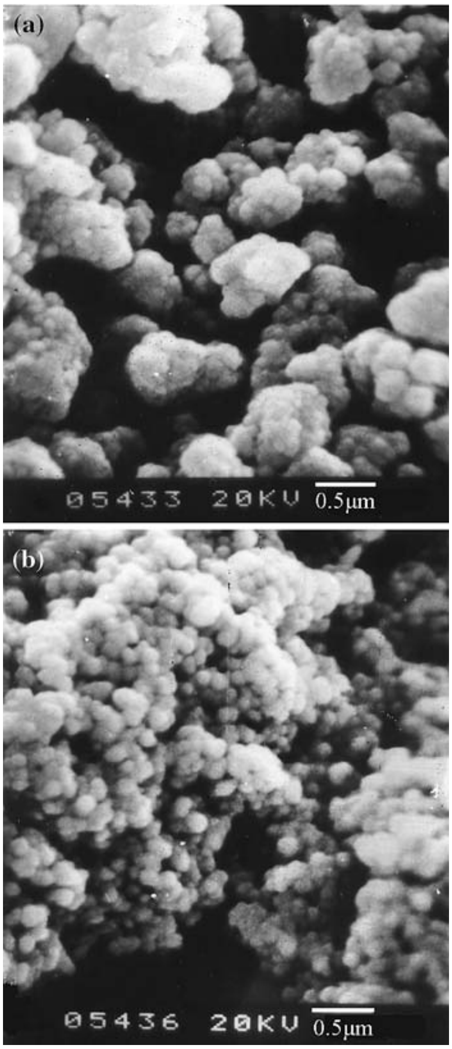

Fig. 1 SEM micrographs of nano TiO_2 (**a**) and nano carbon black (**b**)

Products characterization

A multifunctional thermal analyzer (model NETZSCH STA 449 C, Germany) was used to investigate the TGA of TiO_2 CRN process under a flowing nitrogen atmosphere with the temperature increase rate of 5°C /min. The phase composition analysis of reaction products was carried out by X-ray diffraction (model DX-2000, China). The experimental parameters were as follows: tube voltage was 40 KV, current was 30 mA, CuKα, $\lambda = 1.54056$Å, scanning speed was 0.05°/s. The shape, particle size, particle size distribution and agglomeration of reaction products were observed with scanning electron microscopy (SEM) (model S-450, Japan).

Results and Discussion

Reaction sequences analysis

Generally speaking, the overall reaction equation of synthesizing titanium nitride by carbothermal reduction of titania can be expressed as follows:

$$TiO_2 + 2C + \frac{1}{2}N_2 \rightarrow TiN + 2CO \quad (1)$$

In fact, reaction (1) should include a series of complicated intermediate reactions. For years, researchers have different views on which kind of intermediate products occur in this reaction. According to White [21], the reaction sequences were $TiO_2 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiN$; While Soey [22] consider the phase transformation of reaction process is: $TiO_2 \rightarrow Ti_3O_5 \rightarrow TiN_xC_yO_z \rightarrow TiN_x$ $(x \leq 1)$.

In order to study phase transition sequences of reaction (1), three different temperatures (1200, 1250, 1300 °C) were chosen in our experiments. Figure 2 shows the XRD patterns of reaction products

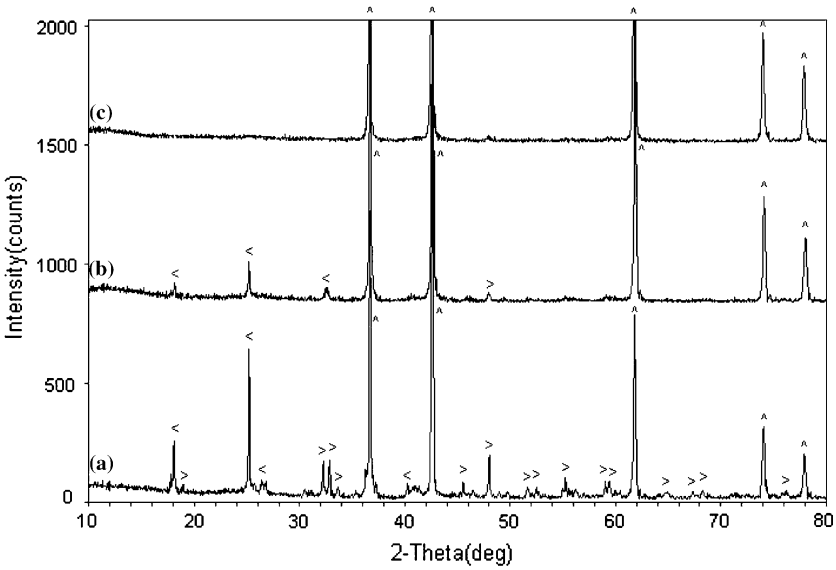

Fig. 2 XRD patterns of synthesized products in the temperature range 1200–1300 °C. (**a**) 1200 °C; (**b**) 1250 °C; (**c**) 1300 °C. (>): Ti_3O_5; (<): $TiO_{0.34}N_{0.74}$; (^): TiN

at 1200–1300 °C with isothermal treatment for 2 h when nitrogen pressure was 0.05 MPa.

From Fig. 2, it was known that the phase compositions of products consisted of cubic TiN, $TiO_{0.34}N_{0.74}$, and a little Ti_3O_5 when reaction temperature was 1200 °C (Fig. 2a). When temperature increased to 1250 °C (Fig. 2b), most diffraction peak of Ti_3O_5 disappeared, intensity of characteristic peak of cubic $TiO_{0.34}N_{0.74}$ weakened enormously, while intensity of characteristic peak of TiN enhanced greatly. The temperature was elevated to 1300 °C (Fig. 2c), there was only characteristic peak of cubic TiN with enhanced intensity, which indicated nano titania had been transformed into cubic titanium nitride entirely.

Based on above analysis, the phase transition sequences of carbothermal synthesis of titanium nitride from titania and carbon black were:$TiO_2 \rightarrow Ti_nO_{2n-1}$ $(4 \leq n < 10)$ $\rightarrow Ti_3O_5 \rightarrow TiO_xN_y \rightarrow TiN$. Because reaction temperature of TiO_2 being reduced to intermediate oxide Ti_nO_{2n-1} $(4 \leq n < 10)$ [21] is lower than the lowest experimental temperature of 1200 °C, thus no diffraction peak of Ti_nO_{2n-1} $(4 \leq n < 10)$ appeared.

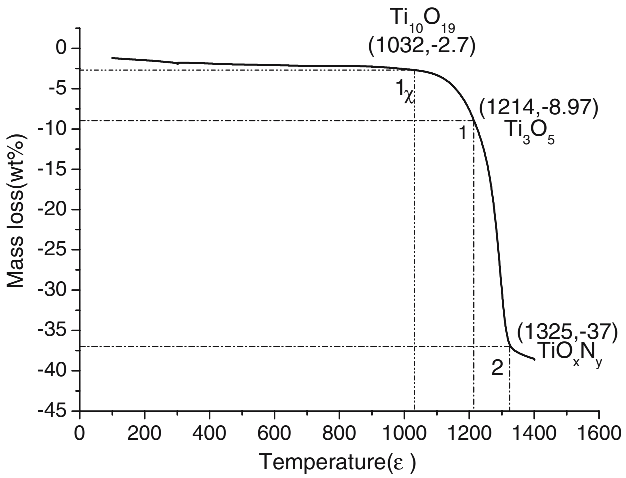

Fig. 3 TG curve of TiO_2 CRN reaction

From the phase transition sequences, the reaction equations included in overall reaction (1) were as follows:

$$TiO_2 + \frac{1}{n}C \rightarrow \frac{1}{n}Ti_nO_{2n-1} + \frac{1}{n}CO(4 \leq n < 10) \tag{2}$$

$$Ti_nO_{2n-1} + \frac{n-3}{3}C \rightarrow \frac{n}{3}Ti_3O_5 + \frac{n-3}{3}CO(4 \leq n < 10) \tag{3}$$

$$Ti_3O_5 + (5-3x)C + \frac{3y}{2}N_2 \rightarrow 3TiO_xN_y + (5-3x)CO \tag{4}$$

$$TiO_xN_y + xC + \frac{1-y}{2}N_2 \rightarrow TiN + xCO \tag{5}$$

However, Boudeward gas–solid reaction existed in this system,

$$2C + CO_2 \rightarrow 2CO \tag{6}$$

and when temperature is above 800 °C, the reaction will tend to produce CO. So intermediate oxide Ti_3O_5 was generated actually via,

$$Ti_nO_{2n-1} + \frac{n-3}{3}CO \rightarrow \frac{n}{3}Ti_3O_5 + \frac{n-3}{3}CO_2 \tag{7}$$

Figure 3 shows the TGA results of reaction process for synthesizing titanium nitride through nano titania CRN under flowing nitrogen atmosphere. From the weight loss curve of reactant in Fig. 3, it is obviously known that the reaction process can be divided into three stages with point 1, 2 as the dividing points. The first stage ended when nano TiO_2 had been reduced to intermediate oxide Ti_3O_5 fully (weight loss is 8.97%). If titanium oxide $Ti_{10}O_{19}$ (weight loss is 2.7%) appeared in reaction process, it was considered as the dividing point 1′. Before the appearance of $Ti_{10}O_{19}$, weight loss rate of reactants was very slow, which means the reaction progressed slowly; whereas after that, weight loss of reactants became quicker and quicker with synthesis of lower titanium oxide until terminate of stage I. This can be explained with Boudeward gas–solid reaction (9). Because solid–solid reaction between titania and carbon black occurred at the beginning of reaction, its rate was very slow; but with resultant CO participating in reducing reaction, the reaction was accelerated. Owing to existence of Boudeward gas-solid reaction, content of CO was kept at a highest level in system, which ensured reaction (7) progressed continuously.

The second stage ended as Ti_3O_5 had been converted into cubic TiO_xN_y fully. With Ti_3O_5 being converted into cubic TiO_xN_y gradually, the amount of CO produced raised rapidly, which was indicated by the sudden accelerate of weight loss from Fig. 3. Until the weight loss rose to 37% caused by reaction, an inflexion appeared in TG curve. The weight loss was close to theory value (38.65%) according to reaction:

$$TiO_2 + 1.66C + 0.37N_2 \rightarrow TiO_{0.34}N_{0.74} + 1.66CO \qquad (8)$$

Inhomogeneous mixing of raw materials and the error of TG experiment were taken into accounted, it could be judged that the cubic phase in the second stage was $TiO_{0.34}N_{0.74}$, which agreed with XRD phase compositions analysis result of reaction process completely.

The third stage ended with the formation of titanium nitride. The main reaction was Eq. 5. It was seen from TG curve that reaction rate in this stage was much lower than that of the second stage. Because substitution reaction among C, N atoms and O atoms occurred in the third stage was completed through diffusion, its rate was awfully slow.

The end temperature of every stages observed by TG analysis lag for some time accordingly, compared with the results showed in Fig. 2, because of difference of open experimental system, rate of temperature increase, quantity of N_2, isothermal treatment time and so on.

Influence of main technological factors

Reaction temperature

Figure 4 shows the XRD patterns of reaction products at 1300 and 1400 °C. TiN was prepared successfully at these temperatures. Compared with that of products at 1300 °C, the characteristic diffraction peak intensity of products at 1400 °C increased, which suggests TiO_2 CRN reacts more thoroughly and gets titanium nitride with higher purity at higher reaction temperature.

Figure 5a, b are SEM micrographs of TiN products. In theory, specific surface area of ultrafine TiN particles prepared was big with high surface energy. However, absolute alcohol was used as dispersant because no special dispersant was available for SEM test, so agglomeration was observed in TiN particles. The products prepared at different temperatures had no pronounced particle change showed in Fig. 5 (a) and (b), the main reason is that actual reaction temperature (1300 and 1400 °C) is much lower than its melting point.

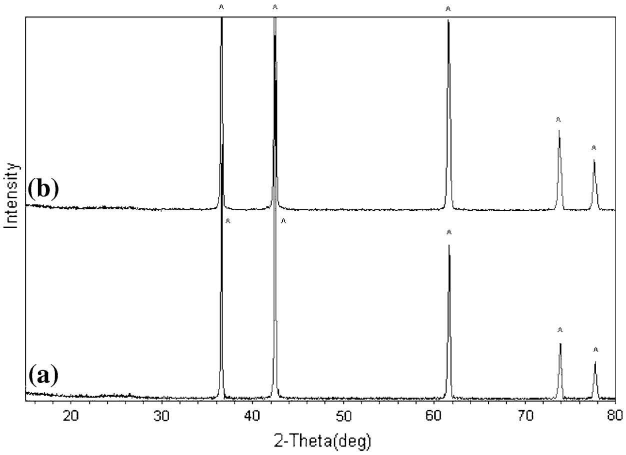

Fig. 4 XRD patterns of synthesized products at different reaction temperature. (**a**) 1300 °C; (**b**) 1400 °C. (^): TiN

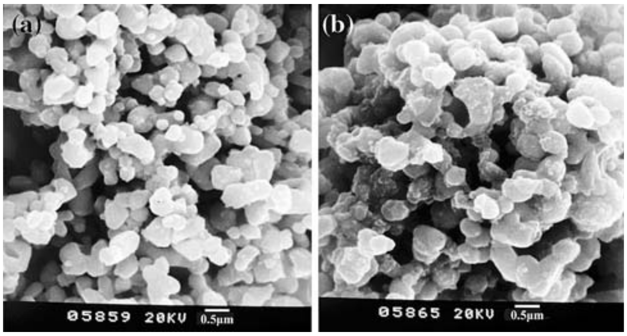

Fig. 5 SEM micrographs of synthesized products at different reaction temperature. (**a**) 1300 °C; (**b**) 1400 °C

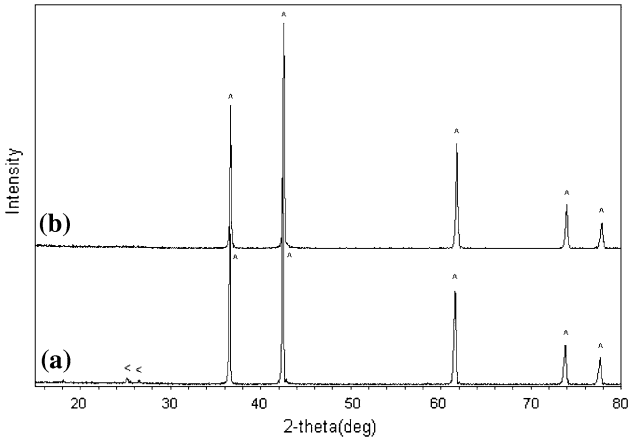

Fig. 6 XRD patterns of synthesized products at different isothermal time. (**a**) 1 h; (**b**) 3 h. (<): $TiO_{0.34}N_{0.74}$; (^): TiN

Isothermal treatment time

Figure 6 shows XRD patterns of products with different isothermal treatment time of 1 h and 3 h, respectively. There is also little amount of $TiO_{0.34}N_{0.74}$ in products except for TiN, when nitridation time was 1 h. This implies that most of nano TiO_2 have been transformed into TiN, the rest into $TiO_{0.34}N_{0.74}$, but nano TiO_2 CRN didn't react entirely. As nitridation time was extended to 3 h, the characteristic diffraction peak of $TiO_{0.34}N_{0.74}$ had disappeared completely, just that of cubic TiN existed and its intensity enhanced further, which indicated that O atoms in $TiO_{0.34}N_{0.74}$ crystal lattice had been substituted fully by C and N atoms.

Figure 7a, b are SEM micrographs of products. Since isothermal treatment time was 1 h, the whole reaction didn't finish from the XRD compositions analysis and some carbon black unreacted were found in Fig. 7a. Isothermal time was extended to 3 h, TiO_2 CRN progressed thoroughly. No small particles of carbon black were found from Fig. 7(b) because almost all carbon black were used up for substituting O atoms in $TiO_{0.34}N_{0.74}$. Besides, compared with Fig. 7(a), pronounced grain growth and shape change of TiN were not observed from Fig. 7(b).

Nitrogen pressure

The XRD patterns of products synthesized under nitrogen pressure of 0.02 and 0.05 MPa were shown in Fig. 8.There were some differences between the phase compositions at different nitrogen pressures, which were concluded from Fig. 8. When nitrogen pressure was 0.02 MPa, there was also small amount of cubic $TiO_{0.34}N_{0.7}$ except for TiN for no enough nitrogen was available in system. While nitrogen pressure rose to 0.05 MPa, products were cubic TiN for there were enough N atoms substituting O atoms in $TiO_{0.34}N_{0.7}$. This indicated that nano TiO_2 CRN could react thoroughly as long as reaction temperature and

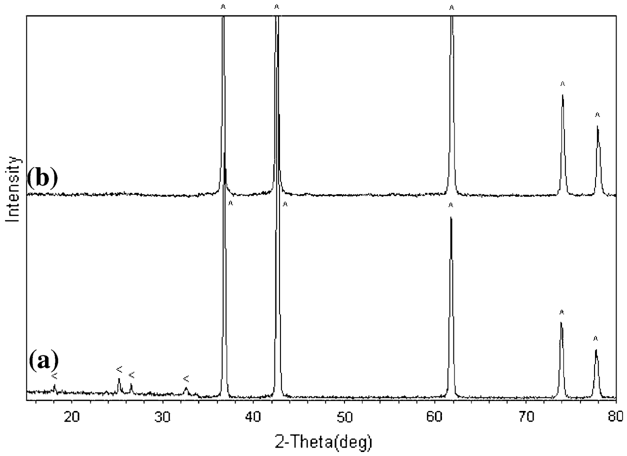

Fig. 8 XRD patterns of synthesized products at different nitrogen pressure. (**a**) 0.02 MPa; (**b**) 0.05 Mpa. (<): $TiO_{0.34}N_{0.74}$; (^): TiN

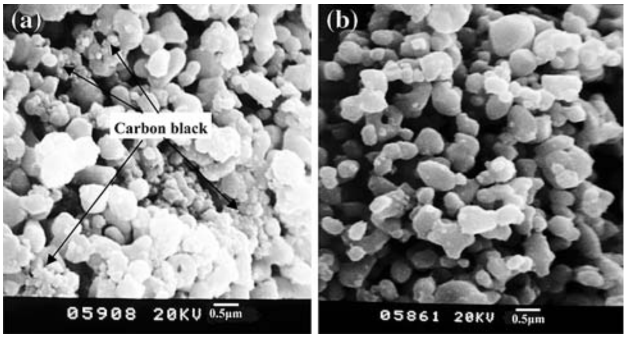

Fig. 7 SEM micrographs of synthesized products at different isothermal time. (**a**)1 h; (**b**)3 h

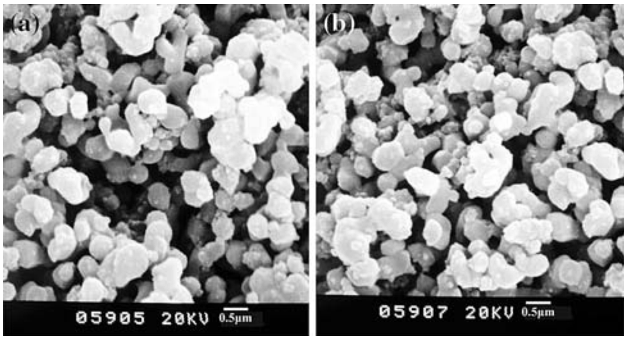

Fig. 9 SEM micrographs of synthesized products at different nitrogen pressure. (**a**) 0.02 MPa; (**b**) 0.05 Mpa

isothermal treatment time are proper and enough nitrogen is available for reaction.

Figure 9a, b are SEM micrographs of products at 1330 °C with 3 h isothermal treatment, when nitrogen pressure was 0.02 and 0.05 MPa, respectively. From Fig. 9, it is known that change of nitrogen pressure has little effect on the shape, grain size and distribution, agglomeration of TiN powders.

Conclusions

The reaction of synthesizing TiN by CRN of nano TiO_2/carbon black mixture consists of three continuous stages: the first stage ends with all TiO_2 being reduced to Ti_3O_5. Reaction rate increased more and more quickly as the reaction progressed in this stage. The second stage ends with all Ti_3O_5 were converted into TiO_xN_y. Reaction rate was the rapidest in second stage. The third stage ends with the formation of all cubic TiN. Reaction rate of this stage was the lowest in three stages. The phase transition sequences were: $TiO_2 \rightarrow Ti_{10}O_{19} \rightarrow Ti_3O_5 \rightarrow TiO_xN_y \rightarrow TiN$. TiN powders can be synthesized with elevated reaction temperature or prolonged isothermal thermal treatment time, or increased nitrogen pressure, when other technological factors keep constant.

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References

1. Castro DT, Ying JY (1997) NanoStruct Mater 9:67
2. Liu L, Xu YD, Li H, Li GH, Zhang LD (2002) J Eur Ceram Soc 22:2409
3. Wexler D, Parker D, Palm V, Calka A (2004) Mater Sci Eng A375–377:905
4. Liu L, Han CL, Xu YD, Chao S, Shi M, Feng JP (2004) Mater Sci Eng A382:122
5. Andrievski RA (1997) NanoStruct Mater 9:607
6. Andrievski RA (1999) Int J Refract Met Hard Mater 17:153
7. Gu HC, Hu LM (1994) J East China Uiniversity of Sci Tech 20(2):141 (in Chinese)
8. Cao LH, Fu L, Fan YS (1997) Chinese J Ceram Soc 25(1):106 (in Chinese)
9. Sakka Y, Okuyama H, Uchikoshi T, Ohno S (1997) NanoStruct Mater 8(4):465
10. Yang XG, Li C, Yang BJ, Wang W, Qian YT (2004) Chem Phys Lett 383:502
11. Yang XG, Li C, Yang BJ, Wang W, Qian YT (2004) Mater Res Bull 39:957
12. Yamasaki T, Zheng YJ, Ogino Y, Terasawa M, Mitamura T, Fukami T (2003) Mater Sci Eng A350:168
13. Welham NJ, Llewellyn DJ (1999) J Eur Ceram Soc 19:2833
14. Zhang S, Tam SC (1997) J Mater Process Tech 67:112
15. Wexler D, Parker D, Palm V, Calka A (2004) Mater Sci Eng A 375–377:905
16. Ren RM, Yang ZG, Shaw LL (2000) Mater Sci Eng A286:65
17. Li JL, Li F, Hu KA, Zhou Y (2002) J Alloys Comp 334:253
18. Lin L (2000) Dev Appl Mater 15(5):6 (in Chinese)
19. Li JG, Gao L, Zhang QH, Sun J, Li W (2003) Chinese J Inorg Mater 18(4):765 (in Chinese)
20. Berger LM, Gruner W, Langholf E, et al (1999) Int J Refract Met Hard Mater 17:235
21. White GV, Mackenzie KJD, Brown IWM, et al (1992) J Mater Sci 27:4294
22. Shaviv R (1996) Mater Sci Eng A209:345