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Characterization of structure and properties of TiN–TiB_2 nano-composite prepared by ball milling and high pressure heat treatment

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Abstract

Synthesis of TiN–TiB_2 nano-composite was investigated by mechanical milling of mixture of Ti and hexagonal boron nitride (h-BN) and subsequent sintering under high pressure and high temperature (HPHT). A TiN–TiB_2 composite was fabricated by ball milling of the mixture for 70 h and then sintering at 5 GPa, 1300 °C. The composite has micro-hardness of 8.8 GPa and electrical resistivity of 2×10^{-4} Ω cm. The formation mechanism of the composite was discussed based on thermodynamics and kinetics.

Keywords: Nitride materials; Mechanical alloying; Mechanical properties; High pressure

1. Introduction

The design and manufacture of functional materials for applications at high stress and high temperatures is one of the most challenging tasks of modern engineering [1]. Refractory materials, such as borides, nitrides and carbides, and their combinations (ceramic matrix composites) are natural candidates for these demanding applications due to their exceptional hardness and stability at very high temperatures. Titanium diboride (TiB_2) is a refractory compound with a very high melting point, high elastic modulus, and high hardness. The melting temperature of titanium nitride (TiN) is even higher than that of TiB_2; however, both its elastic modulus and hardness are lower than those of TiB_2, and it plastically deforms at the high temperature. Therefore, it is believed that combining TiB_2 and TiN into composite material can yield unique ductility/fracture toughness. The potential application for such a material could be jet engine parts, armor plates, cutting tools, and dies, etc. The high electrical and thermal conductivities of both TiB_2 and TiN can make TiB_2–TiN composites attractive for functional applications in high stress and high temperatures electrical systems.

TiB_2 and TiN are generally prepared by different routes: TiN is often produced by the chemical or physical vapor deposition (CVD or PVD) method, while TiB_2 is usually sintered by hot pressing [2]. Therefore, it is difficult to formulate composites featuring both ceramics by conventional methods. Recently, self-propagating high temperature synthesis (SHS) technique has been employed to produce a variety of advanced materials, including borides, nitrides, carbides, intermetallics, etc. According to Zhang et al. [3], boride-containing ceramic composites can be produced by using boron carbide (B_4C) and nitride (BN) as reactants in a self-sustaining combustion process. Using of hexagonal BN (h-BN) as a reactant to synthesize TiN–TiB_2 composites not only leads to the formation of boride, but also provides a solid source of nitrogen to resolve the problem of infiltration-limited reactions with gaseous nitrogen.

In recent decades, high-energy ball milling has been recognized as an effective way to prepare nanocrystalline or amorphous materials. Metal nitride phases have been obtained by ball milling of elemental powders in nitrogen or dry ammonia atmosphere. [4–6] In particular, TiN has been already obtained

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by this kind of method [7,8]. However, there are few reports on fabricating nanocomposite materials by combing mechanical milling and HPHT technique.

Here we report the application of mechanical milling and HPHT to fabricate TiN–TiB_2 nano-composites from consolidated BN–Ti powder blends. Using the nano-size starting powders produced by ball milling decreases the reaction time due to the short diffusing distances of the consolidated powders under high pressures, thus prevents coarse microstructures. Consequently, this method could be a promising route to in situ prepares the composites containing TiN and TiB_2 phases.

2. Experimental methods of approach

The titanium (−200 mesh, 99% purity) and boron nitride (99% purity) powder were milled in high pure nitrogen atmosphere using a high-energy ball mill (GN-2, Shengyang, China). Stainless balls and vial were used. The ball-to-powder weight ratio was approximately 15:1. The molar ratio of Ti and BN was 3:2 according to the following reaction:

$$3Ti + 2BN \rightarrow TiB_2 + 2TiN \qquad (1)$$

In order to investigate the reaction during the milling process, the samples were checked every 10 h. The 70 h milled blends were compacted to the Ø 8 mm × 6 mm pellets under a shaping pressure 40 MPa. The pellets were loaded into a cubic anvil high-pressure apparatus (DS-029a-type). 5 GPa were applied, then heated to different temperature for 5 min, finally the samples were quenched to room temperature. The pressure was given by a calibration curve that was established by determining the applied loads corresponding to the phase transformation pressures of bismuth, thallium and barium. Final dimension of the obtained samples were: Ø 6 mm × 4 mm. The sample A, B, C and D were synthesized at 25, 1100, 1200 and 1300 °C, respectively. The crystalline phases and structures of the samples were characterized by X-ray diffract meter (XRD) with Cu Kα radiation. The hardnesses of the samples were examined using a HXD-1000 microhardness tester with Vickers indenter, with a load of 9.8 N and duration of 30 s. The electrical resistivity (ρ) measurement was performed by Van de pauw method. The samples were in contact with two double silver electrodes oriented at 90° to each other. Silver paste (DAD-87 type) was painted onto both sides of the pellet, and baked at 300 °C for 1 h to burn out organic binder and formed Ag electrodes. Ag leads were attached to the electrodes using silver paste and were sintered again.

3. Results and discussion

3.1. Ball milling processing features

XRD patterns were generated for all powders milled with different time intervals. Fig. 1(a) showed the pattern of the initial powder. In Fig. 1(b), the h-BN peaks disappeared and those of Ti became significantly weak and wide. An amorphous peak was observed in the diffraction angle (2θ) ranging from about 10° to 30°, which indicated that h-BN was transformed into amorphous BN (a-BN) after 50 h of milling.

The intensity of Ti peaks continued decrease from Fig. 1(b–e). A weak diffraction peak was observed at $2\theta = 42.1°$ in Fig. 1(c), which was the strongest diffraction peak (2 0 0) of δ-TiN_x. Therefore, it was believed that δ-TiN_x emerged after milled for 70 h. As discussed in our previous paper, this is due to crystallization of the amorphous Ti–N alloy driven by mechanical milling. [9] The intensities of δ-TiN_x peaks significantly increased, and became more narrow, as shown in Fig. 1(c–e), which implied that more Ti reacted with N to form δ-TiN_x and the grain size of the δ-TiN_x increased with milling time.

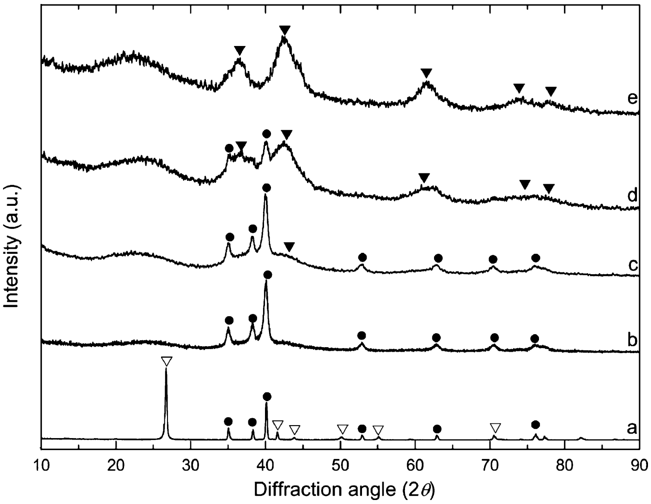

Fig. 1. XRD patterns for the titanium and boron nitride powder mixture milled for different time. (a) 0 h; (b) 50 h; (c) 70 h; (d) 120 h; (e) 160 h. (▽) h-BN; (●) Ti; (▼) δ-TiN_x.

XRD pattern of the sample after milled for 160 h, as shown in Fig. 1(e), consisted of a-BN and δ-TiN_x peaks, which indicated that Ti have been completely reacted with N and formed δ-TiN_x. It is deduced that N atoms from a-BN gradually diffuse into Ti lattice and form amorphous Ti–N alloy, then it crystallized to δ-TiN_x in ball milling process [10]. And these result in that the remaining a-BN became B-rich amorphous BN, which was confirmed by DSC measurement. Fig. 2 showed DSC curves of amorphous-BN produced by ball milling h-BN. The crystallization temperature of the a-BN at atmospheric pressure was about 630 °C, but above 900 °C for the B-rich amorphous BN [10]. This identified that the remained a-BN is not a-BN but a B-rich amorphous BN.

Shim et al. reported that reaction progress between Ti and BN during mechanical milling process was in a self-sustaining reaction form [11], while our result did not show that δ-TiN_x

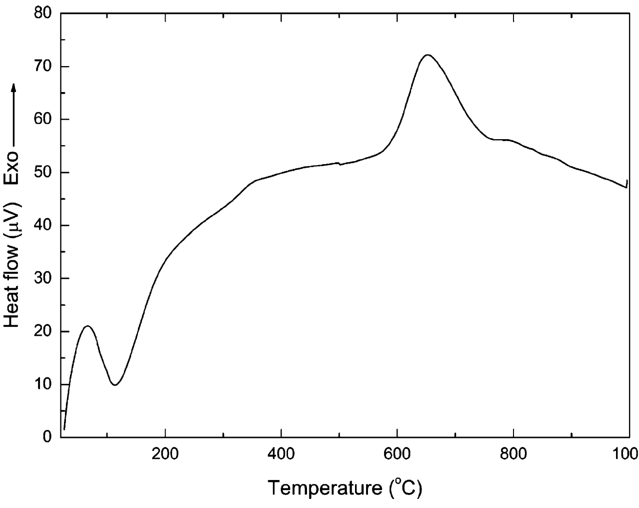

Fig. 2. DSC curves of h-BN milled for 35 h.

was formed by a self-sustaining reaction. Furthermore, no TiB_2 was observed during mechanical milling process.

3.2. High-temperature high-pressure treatments

XRD patterns of the sample A, B, C and D were shown in Fig. 3(a–d). The XRD results showed that sample A was composed of Ti and a small amount of δ-TiN_x, no TiB_2 diffraction peak was observed in Fig. 3(a). When the temperature reached 1100 °C, the peak of h-BN (2 0 0) appeared and the peaks of δ-TiN_x were stronger in Fig. 3(b), which meant that a-BN crystallized and the content of δ-TiN_x increased in the sample B. TiB_2 was still not synthesized. Since the formation heat of TiN is −340.2 kJ/mol, more negative than that of TiB_2 (−281.4 kJ/mol) [12], Ti prefers to react with N than B from the point of view of thermodynamics. On the other hand, B atom radius (1.17 Å) is larger than that of N atom (0.75 Å), so formation of Ti (B) solid solution is much more difficult than formation of Ti (N) solid solution from the point of view of kinetics. This conclusion can be further affirmed by the Ti–B and Ti–N phase diagrams, which shows that the solubility of B atoms in α-Ti (<1 at%) much less than that of N atoms in α-Ti below 1000 °C [13]. Hence, Ti atoms react more easily with N than B atoms. Similar result was found in preparation of Fe–N alloy by mechanical milling or annealing of the mixture of Fe and BN [14]. The emergence and intensification of the peaks of TiB_2 as shown in Fig. 3(c and d) indicated that Ti began to react with B to form TiB_2 at 1200 °C and reacted completely at 1300 °C. The sample D was only composed of TiN and TiB_2, which meant TiN–TiB_2 composites had been obtained. According to the thermodynamic data reported by Zhang et al. [3], the enthalpy of reaction (1) at standard condition is $\Delta H^\circ_{298} = -452$ kJ/mol, and the free enthalpy is $\Delta G^\circ = -407$ kJ/mol at 1227 °C. It can be seen that the reactions are highly exothermic and satisfy the thermodynamic conditions for self-sustaining combustion process. It means that TiN–TiB_2 composites can be produced by self-propagating high-temperature synthesis above 1200 °C.

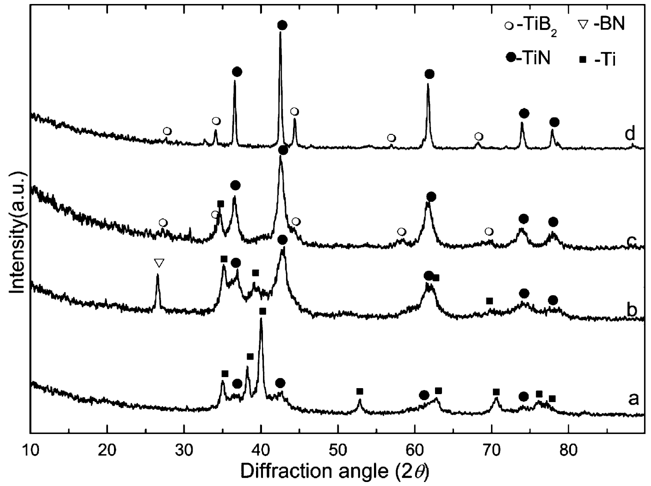

Fig. 3. XRD patterns for milled 70 h sample high pressure (5 GPa) and different temperature treatment. (a) 25 °C; (b) 1100 °C; (c) 1200 °C; (d) 1300 °C.

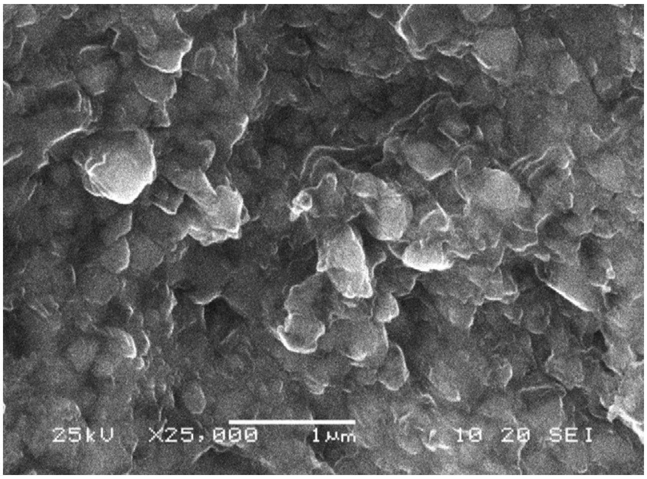

Fig. 4. HRSEM photography of TiN–TiB_2 composites synthesized at 5 GPa, 1300 °C.

Fig. 4 showed the SEM photograph of the sample D. The result indicated that this composite was high dense and its grain size was fine and uniform. Fig. 5 showed TEM image and selected area diffraction pattern (SADP) of the sample D. (2 0 0) and (3 1 1) diffraction rings of TiN and (1 1 2) ring of TiB_2 were observed clearly in the SADP of Fig. 5(b), which confirmed that the sample D consists of TiN and TiB_2. From the bright field image (Fig. 5(a)) the grain sizes of TiN and TiB_2 can be estimated to be in the range between 20 and 40 nm.

Olevsky et al. synthesized TiB_2–TiN ceramics composites via displacement reactions in fully dense BN–Ti blends at 1600 °C [1]. The evolution of microstructure in their process is dominated by the diffusion of nitrogen and boron into titanium, so that it usually takes a relative long time (∼20 h) to accomplish this diffusion. While in our experiments, it needed only 5 min to prepare TiN–TiB_2 composites at 5 GPa and 1300 °C. Ball mill drops synthesis temperature of TiN–TiB_2 composite and shortens the synthesis time due to the increase of specific surface area. High pressure may reduce activation energy of reaction of B (and N) with Ti and promotes the crystallite nucleation velocity. High pressure can also restrain long-range diffusion of atom in crystal growth and densify the product; which is benefit to in situ synthesize high dense nano-composites.

3.3. Mechanical and electrical properties of composites

The Vicker hardness (HV) and resistivity of the sample A, C and D were listed in Table 1. The microhardness of the samples increased with increasing sintering temperature. The sample D has the lowest resistivity ($2 \times 10^{-4}\,\Omega$ cm), indicating that the TiN–TiB_2 composite is of very good conductor. The increase of TiB_2 content improves the hardness and toughness of the TiN–TiB_2 composites. Moreover, the conductivity of the TiN–TiB_2 composites increases with TiN content [15]. As mentioned above, when the sintering temperature is higher than 1200 °C, TiB_2 and TiN contents in the composites increase obviously, so that the sample D has higher hardness and good conductivity.

Table 1
HV and electrical resistivity of TiN–TiB_2 composites

	Sample name		
	A	C	D
Synthesized conditions	5 GPa, 20 °C, 5 min	5 GPa, 1200 °C, 5 min	5 GPa, 1300 °C, 5 min
HV (GPa)	1.76	7.35	8.84
Resistivity (Ω cm)	5.74×10^{-2}	3.43×10^{-4}	2.0×10^{-4}

Fabrication and properties of TiN–TiB_2 composites are also reported in many literatures [16–18], where the composites are prepared at 1600–1850 °C and the hardness is 14.8–24.5 GPa. The reported hardness is higher than 8.8 GPa of our product that is attributed to that their sintering temperature is much higher than present work. Higher sintering temperature can eliminate the pores in the composite during the solid-state diffusion reaction and improve the hardness.

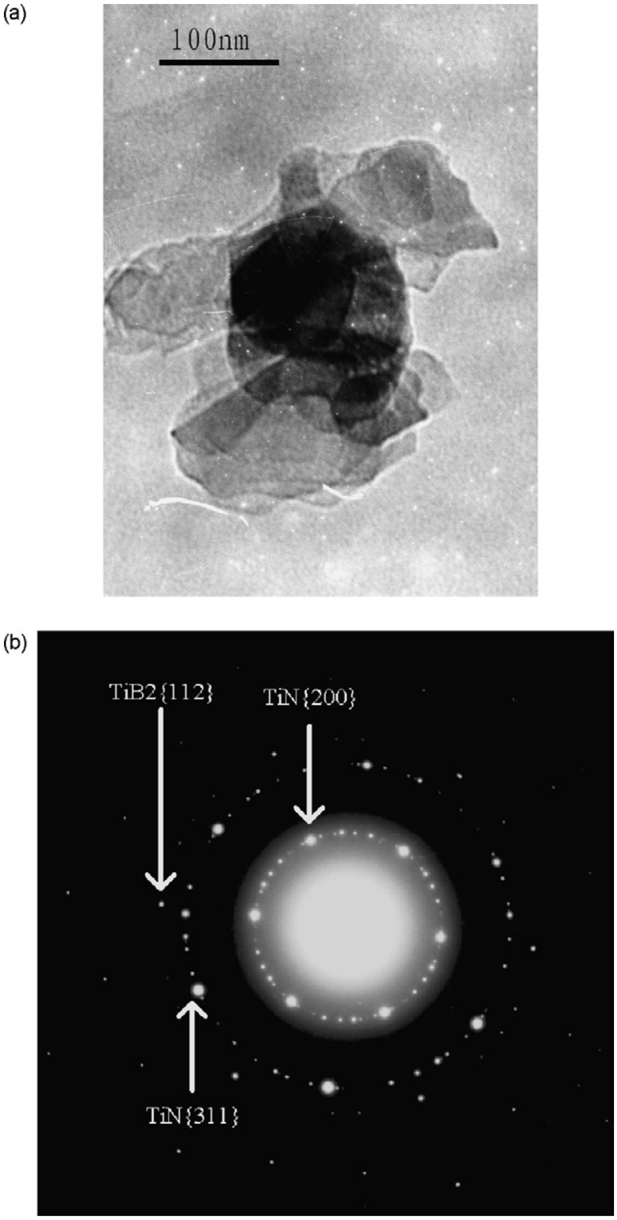

Fig. 5. TEM photography of TiN–TiB_2 composites synthesized at 5 GPa, 1300 °C. (a) Bright field image; (b) selected area diffraction pattern (SADP).

4. Conclusions

TiN–TiB_2 composites were in situ synthesized by sintering 70 h-milled mixture of Ti and a-BN powders with nanometer size at 5 GPa and 1300 °C. The nanostructure powders prepared by ball milling are benefit for increasing solid-state reaction activity between Ti and a-BN and decreasing synthesis temperature and time.

Higher temperature and longer time of sintering can increase the content of TiB_2 and TiN in the composites, and employment of high-pressure can restrict the grains to grow quickly and irregularly. The sample synthesized at 5 GPa and 1300 °C had the highest HV and the lowest resistivity, which is 8.8 GPa and 2×10^{-4} Ω cm, respectively.

5. Summary

Thermodynamics, kinetics, and transformation between BN and Ti, and the microstructural features of high dense TiN–TiB_2 nano-composites were discussed. An explanation based on diffusion process between a-BN and Ti was proposed during ball milling process. The HPHT product with fine and homogeneous microstructure should be produced using nanometer precursor as starting materials. Ball mill drops synthesis temperature and shortens the synthesis time. High-pressure technique is benefit to in situ synthesize high dense nano-composites. TiN–TiB_2 nano-composites show high hardness and low electrical resistivity. Similar properties may exist in ZrB_2–ZrN, HfB_2–HfN, etc. composites.

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