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FORMATION OF TiB₂/TiN NANOCOMPOSITE POWDER BY HIGH ENERGY BALL MILLING AND SUBSEQUENT HEAT TREATMENT

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ABSTRACT: TiB₂/TiN nanocomposite powder was fabricated by high energy ball milling and subsequent heat treatment. Microstructure development of the powder mixtures was monitored by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Ball milling BN and elemental Ti powder mixture at ambient temperature resulted in the formation of TiN. After 40 h of milling, the powder mixture was consisting of a small amount of nanosized TiN particles, nanocrystalline Ti and amorphous phase. The nanocrystalline Ti and amorphous phase converted to TiN and TiB₂ after subsequent heat treatment.

KEY WORDS: titanium nitride, titanium boride, milling, composite powder

1. INTRODUCTION

Researches have shown that fine-grained TiB₂ possesses extraordinary resistance to plastic deformation at high temperatures. Further more, the fracture toughness of 5 Mpa.m^{1/2} is also encouraging. The melting temperature of TiN, on the other hand, is even higher than that of TiB₂; however, its elastic modulus and hardness are lower and it can deform plastically at high temperatures. This combination of extreme resistance to plastic deformation of the TiB₂ and the high-temperature plasticity of the TiN phase suggests that a TiB₂-TiN composite should be attractive as a high-temperature structural ceramic [4-5]. It is believed that this composite approach might yield a unique combination of high-temperature hardness and stability with a adequate fracture toughness. In addition, the high electrical and thermal conductivities of both can make attractive for functional applications in high performance electrical systems [6]. Porous TiB₂/TiN composites were obtained by using the conventional SHS method using Ti, B and BN powders as raw materials [7]. In addition, Zhang also prepared TiB₂/TiN composites by reactive hot pressing from TiH₂ and BN in presence of Ni which acted as an effective additive [8].

Recently, a modified method of displacement reaction synthesis has been introduced by Olevsky et al.[9], namely, displacement reactions in fully dense, very fine elemental powder blends. Solid-state synthesis of TiB/TiN and TiB₂/TiN ceramics matrix in situ composites via displacement reactions in fully dense BN-Ti blends has been accomplished in their work. However, the evolution of microstructure in the processing is governed by the diffusion of nitrogen and boron into titanium, it usually takes a relative long time to accomplish the displacement reaction process. Therefore, using powder mixtures, which are high-energy ball milled for proper time, as raw materials to prepare bulk materials might be helpful. With fine

submicron/nanosized starting powders, the short diffusion distances allow the synthesis of new phases to be completed over relatively short time periods, thus preventing the undesirable coarsening of the microstructure.

In recent years, high energy ball milling (mechanical alloying) has been widely used to produce supersaturated crystalline solid solution, amorphous phases, nanocrystalline solids, and compounds through *in-situ* solid-solid, gas-solid, and liquid-solid reactions. Furthermore, high-energy milling can be designed as an intermediate step to promote reactions that can be complete at high temperatures. Munir *et al.* have investigated the synthesis of carbides, silicides, nitrides and borides by this processing [10-15]. TiB₂ powder has also been prepared via high energy ball milling [16]. Calka reported that TiN, AlN and WN powders were produced by milling the corresponding metal in nitrogen atmosphere [17]. Hence, considering that the specific properties and potential applications of TiB₂/TiN composites, it is meaningful to study if the TiB₂/TiN composite powder could be obtained by high-energy ball milling process.

Here we report on the reactions in the 3:2 Ti/BN starting composition in high energy ball milling processing and sequent heat treatment.

2. EXPERIMENTAL PROCEDURE

The raw materials used in this study were 99.9% pure Ti powder with a sieve size -400 mesh and 99.5% pure BN powder with an average particle size 4 μm .

Powder mixtures consisting of a BN: Ti molar ratio of 2:3 were ball milled in a GN-2 High-energy Ball Milling Machine (Shengyang Science Equipment Factory, China). The milling was conducted using hardened steel balls with a diameter of 5 mm. The ball-to-powder weight ratio was 10:1, and the milling speed was 360 rpm. The hardened steel canister was evacuated to 0.2 Pa and flushed with Ar gas. The milling runs were suspended for 0.5 hr to cool the canister whenever the powder was milled for 5 hr. After milling for selected times, ball milled powder mixtures were taken out in Ar for analysis.

Heat treatment was carried out in vacuum at 400 °C and 700 °C, respectively, for 1 h. The heating rate was also 10 °C/min.

The powders were characterized by X-ray diffraction (XRD, Cu K α radiation: $\lambda = 0.154$ nm). In addition, as-milled powder was investigated by a transmission electron microscopy (TEM, Hitachi H800) with energy dispersive spectrometry (EDS). The operating electron voltage was 200 kV. As-milled powder was also investigated by a scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1. Reaction in ball milling process

X-ray diffraction (XRD) patterns of the powder mixtures after different milling times are shown in Figure 1. In current work, BN has a hexagonal crystal structure, $a=0.251$ nm, $c=0.666$ nm (as shown in Fig.1a). After 10 h of milling, the (002) reflection of BN disappeared completely while the (100) reflection is still visible. No TiN or TiB₂ is detected in the powder mixture (Fig 1b). The disappearance of the (002) reflection indicates that the correlation length of ordered stacking in the [002] direction is reduced dramatically in milling process, in agreement with the fact that BN tends to separate into very small slices.

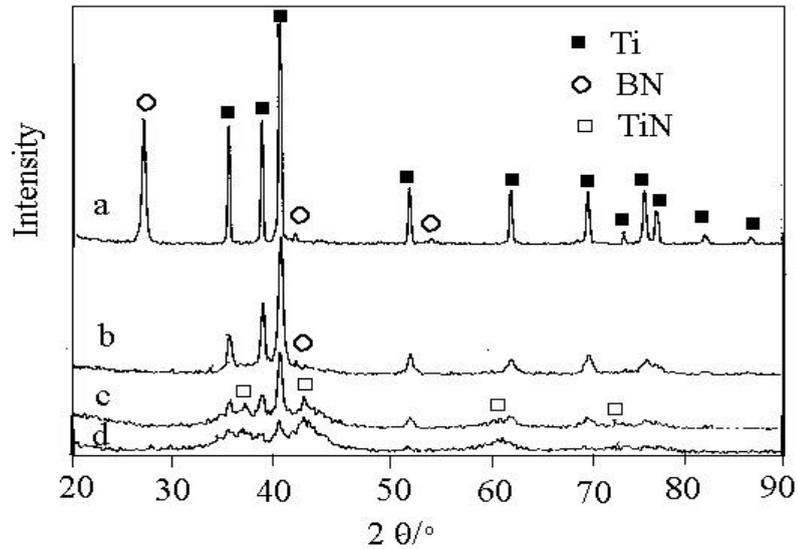


Figure 1 XRD patterns of the powder mixtures milled for different times, (a) before milling, (b) 10 h, (c) 30 h, and (d) 40 h

With increasing milling time, the diffraction peaks of crystalline Ti becomes broader and of less intensity, but their positions do not shift (Fig 1c). After 30hr of milling, the average diameter of Ti grains is around 20 nm by Scherrer formula. TiN peaks appeared at that time, but no TiB_2 was found (Fig. 1c). The lattice parameter of TiN is found to be 0.424 nm, which does not change during the subsequent milling process.

With further milling up to 40 hr, the decrease in the integral intensity of the Ti peaks is associated with the formation of amorphous phase (Fig. 1 d) . Fig.2 shows that mixed powders of Ti and BN formed spherical particles. Particles of powder mixture milled for 10 hr and 40 hr, respectively, all have an average size 120 nm. Namely, milling times do not affect the particle size. A similar phenomenon has been found that particle size maintains a steady level during ball milling of the powder mixture of elemental titanium and graphite [14]. Since hexagonal BN and graphite are excellent lubricate and tend to separate to slices, the formation of composite particles of Ti+C or Ti +BN is attribute to their excellent lubricate ability, which can abate the impact of balls. Hence, during ball milling process the repeated deformation may occur in these composite particles, however, the fracture and welding of the powders impossibly occur repeatedly.

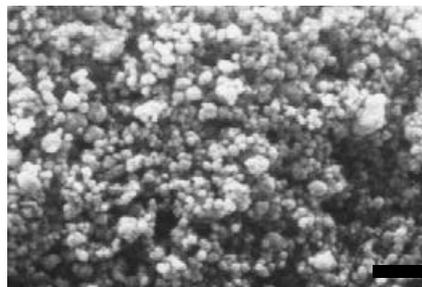


Figure 2 SEM micrograph of powders milled for 40 h (1 bar =500 nm)

Fig.3 shows the TEM image of powder mixture milled after 40 hr. The electron diffraction patterns demonstrated that the product is consisting of nanocrystalline Ti, amorphous B and BN.

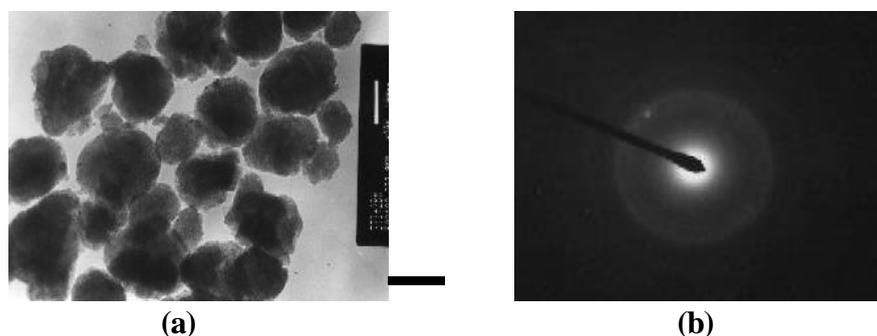


Figure 3 TEM image of the powder mixtures milled for 40h (a), (b) electron diffraction patterns of (a), showing nanocrystalline Ti in amorphous phase (1 bar =100 nm)

3.2. Reaction mechanism in ball milling process

It is believed that a high heat of formation serves as the driving force of the combustion reaction in milling process. This is in agreement with a conventional SHS reaction. For it to be selfsustaining, the process must be associated with high temperature reactions. Researchers have demonstrated that the value of $\ddot{A}H_{298}/Cp_{298}$ should be above 2000 in thermally ignited systems [10]. Thus, the value of $\ddot{A}H_{298}/Cp_{298}$ can be used as a rough guide to the existence of combustion in milling process[14, 18].

The value of $\ddot{A}H_{298}/Cp_{298}$ of reaction (1) in this work is about 4100K.



Therefore, it is possible that the formation of TiN and TiB₂ occurs by self-propagating reaction during ball milling using Ti and BN as raw materials.

Another factor relative with self-propagating reaction is the particle size of reactants. In general, the reaction rate in the powder system is dependent on particle size [10, 19]. In particular, it has been reported that propagation of combustion wave in selfpagating high temperature synthesis (SHS) is accelerated by the refinement of particle size, whereas combustion becomes difficult and even disappears as particle size increases [19]. Previous investigations show that ignition of the combustion reaction requires an initial premilling period (incubation) during which ball milling leads to a change in the factors determining the critical combustion condition. Hence, some researchers have proposed that there exist a critical particle size for ignition of the combustion reaction during the course of high energy ball milling[14, 20].

Fig.2 and Fig.3 indicate that the mixing of the reactants of Ti and BN on a nanometre scale which favors mass transfer, and the diffusion path length is considerably reduced. Thus, it is possible for TiN and TiB₂ to form by self-propagating in the milling process. Previous study on displacement reaction of Ti and BN shows that when Ti reacted with BN at elevated temperatures, TiN formed at about 1000°C while TiB₂ occurred above 1200°C [8, 9]. Namely, that N atoms diffused and reacted with Ti was prior to B. Therefore, TiN is relatively easier to form in current work. On the other hand, the formation of TiN also shows that the mixing of the reactants on a nanometre scale and the diffusion path length is considerably reduced.

In current work, it was found that when a steel flake was used to clean the powder

mixture in Ar, milled for 40 hr and attached on the milling balls, the powder mixture began to combust. The final product, showing golden-yellow color, is consisting of TiB_2 and TiN . The result indicates that the reactants have been mixed on a nanometre scale and a sparkle, generated by the friction of steel flake and balls, triggered the combustion reaction. According to the conventional analysis above, the formation of TiN and TiB_2 should occur by self-propagating reaction, however, there is no extra heat to trigger the reaction during milling process. It is not surprising that the kinetic energy of milling balls cannot trigger the combustion reaction in this work. Carslaw and Jaeger demonstrated that the majority of heat generated by the impact in balling milling processing is direct proportional to friction coefficient [21]. Considering that BN is an excellent lubricate and the powder particles are spherical, the heat generated is small and can not result in a rapid temperature increment in a small area to ignite the combustion. The heat generated by the impact of milling balls distributes in a relatively large area and finally diffuses through the canister to outer space.

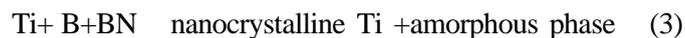
In summary, the evolution of the powder mixture during milling processing is as follows:

During 0-10 hr, BN are separated into BN slices.

During 10-30 hr, reaction (2) takes place,



During 30-40 hr, reaction (3) takes place



3.3 Effect of subsequent heat treatment on microstructure of powder mixture

In order to further study the structure evolution of the powder at elevated temperature, the annealing experiments were performed. Fig. 4 shows the XRD patterns of powder mixture milled for 40 hr followed by heat treatment in Ar. Compared with powder mixture before heat treatment, the amount of TiN increased when the powder mixture was annealed at $400^\circ C$ for 1 h (Fig.1d), and a trace of Ti are detected in the powder mixture (see Fig. 4c), but no TiB_2 or TiB were found.

When the powder milled for 40 h was annealed at $700^\circ C$ for 1h, TiB_2 and TiB peaks appeared beside TiN peaks (Fig.4b). The result shows that TiB is a intermediate phase. Previous work [9] demonstrated that when the mixed powders of Ti/BN in the 3:2 starting composition were annealed at $1000^\circ C$ for 20 hr, the reaction (4) took place:



Namely, the milling technique can dramatically promote the reaction. The broader and less intensity TiB_2 peaks indicates the TiB_2 is a nanostructural phase.

When the powder mixture milled for 40 h was heated to $1300^\circ C$, only TiB_2 and TiN were detected (Fig.4a). The XRD result indicates that the ball milled powder mixture converted to TiB_2 and TiN after this heat treatment. Reaction (1) is accomplished up to now. In addition, the TiB_2 and TiN peaks become of sharper and intensity. Hence, the nanocrystalline TiB_2 and TiN condensed to submicron/micron-crystalline TiB_2 and TiN .

TEM images of powder mixture milled for 40 h and heated to $1300^\circ C$ are shown in Fig.5. TiN grains are about 180 nm in size, bigger than the original particles before heat treatment. This result suggests the growth of nanosized TiN grains, in agreement with the XRD (Fig.1, Fig4). The powder shows golden-yellow color while powder mixtures before this heat treatment, or annealed at $400^\circ C$ or annealed at $700^\circ C$ for 1 h all are black presumably as a

result of very small TiN grain size. Fig.5a shows conglomerations of sintered TiN grains. Fig.5b shows small particles are located in TiN grains. These particles are determined to be TiB₂ grains by EDS analysis. These TiB₂ particles are about 70 nm in size.

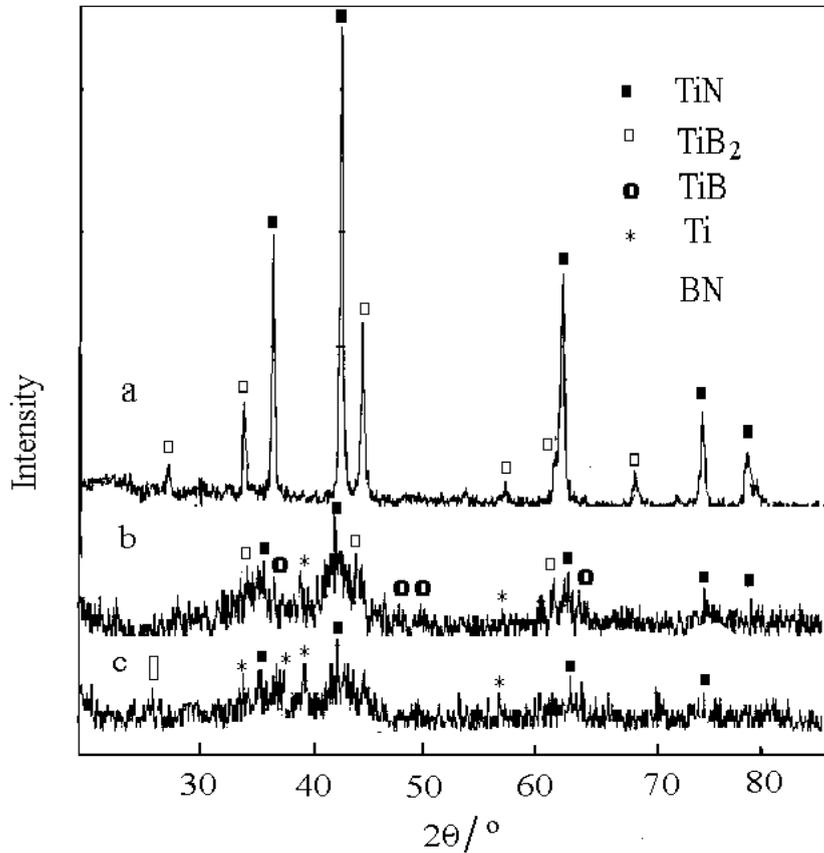


Figure 4 XRD patterns of powder mixtures, (a) heated to 1300°C at a heating rate 10°C/min and cooled, (b) annealed at 700°C for 1 hr, and (c) annealed at 400°C for 1 hr,

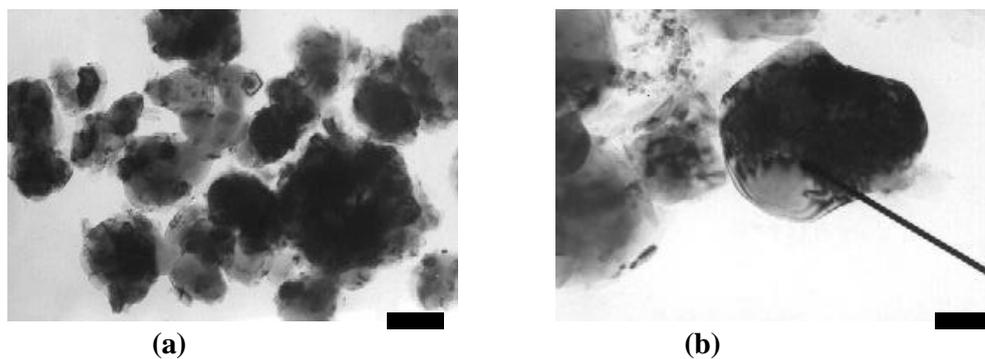


Figure 5 TEM images of powders milled for 40 hr and heated to 1300°C, showing conglomerations of sintered TiN grains (a), and nanosized TiB₂ grains in TiN grains (b) (1 bar =100 nm).

According to reaction (1), the volume of TiN is about 1.5 times larger than that of TiB₂. In

addition, TiN/TiB₂ *in situ* formed during heat treatment. Therefore, during the growth of TiN grains, TiB₂ particles are possibly wrapped in TiN grains. In fact, almost TiB₂ grains found by TEM observation are nanosized and located in TiN grains.

The TiB₂/TiN nanocomposite powder prepared in this work is micro-scale TiN particles incorporated with nanosized TiB₂ particles. In conventional hot pressing process using Ti and BN as starting materials, TiB₂ and TiN tend to form large grains separately [8, 9]. If the powder mixture were impacted and sintered, the TiB₂/TiN nanocomposite was expected to obtain at a relatively low temperature. The TiB₂/TiN nanocomposite powder prepared in this work is relatively an ideal composite powder, further research is being carried out.

4. CONCLUSION

TiB₂/TiN nanocomposite powder has been prepared by high energy ball milling and subsequent heat treatment. The formation of TiN occurs after 30 hr of milling. After heat treatment, the final product is consisting of nanosized TiB₂ and micro-sized TiN particles. Nanosized TiB₂ particles are located in TiN grains. High energy ball milling can dramatically promote the reaction between Ti and BN.

REFERENCES

1. Ramberg, J., Woolfe, C. and Williams, W., *J. Amer. Ceram Soc.*, **68** (1985), C-78- C-79
2. Williams, W. S., *J. Appl.Phys.*, **35** (1964), 1329
3. Mestral, F. de. and Thevnot, F., *J. Mater.Sci.*, **26** [20] (1991), 5547
4. Barsoum, M. W. and Houng, B., *J. Amer. Ceram. Soc.*, **76** [6] (1993), 1445
5. Brodtkin, D., Kalidindi, S. R., Barsoum, M. W. And Zavaliangos, A., *J. Amer. Ceram. Soc.*, **79** [7] (1996), 1945
6. Lux, F., *J. Mater. Sci.*, **28** (1993),1285
7. Tomoshige, R., Muryama, A., and Matsushita, T., *J Amer. Ceram Soc.* **80**(3) (1997): 761
8. Zhang, G., Jin, Z., and Yue, x. G., *J Amer. Ceram Soc.* **78** (1995): 2831
9. Olevsky, F., Mogilevsky, P., et al., *Metall. Mater. Trans.*, **27A** (1996), 2071
10. Munir, Z. A., *Am. Ceram. Soc. Bull.*, **67**(2) (1988,), 342
11. Liu, K. W, Zhang, J. S., Wang, J. G., *J. Mater. Res.*, **13**[5] (1998),1198
12. Caer, G L., Bauer-Gross, E., and Pianelli, A., *J. Mat.Sci.*, **29** (1994) , 614
13. Yen, B. K., Aizawa, T. and Kihara, J., *J Amer. Ceram Soc.*, **79** [8] (1996), 2221
14. Wu, N. Q., *Mater. Sci. Tech.*, 1997, **14**[4], 287
15. Shaw, L. L., Yang, Z., and Ren, R., *J Amer. Ceram Soc.*,1998, **81** [3], 760
16. Andrievski, R. A., *J. Mat.Sci.*,**29**, 614
17. Calka, A., and Williams, J. S, *Mater. Sci.Foru.*, 1992, **88-90**, 787
18. Barin, I.,and Knacke, O., *Thermochemical Properties of Inorganic Substances*, 1973, p674, 749, 754, 790, Spring Verlag, New York
19. Deevi, S. C., *J. Mat.Sci.*, 1991, **26**:3685.
20. Chakurov, C., Rusanov, V., AND Koichec, J., *J. Solid State Chem.* , 1987, 71, 522
21. Carselaw, H. S., and Jaeger, J. C., *Heat conduction in solids*, 1959, New York, Oxford University Press, p255
22. Tonej, A., Tonej, A. M., and Duzevic, D., *Scripta Metall. Mater.* , 1991, **25**, 111