

Journal of Alloys and Compounds 365 (2004) 149-156

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Influence of stearic acid on mechanochemical reaction between Ti and BN powders

Jung-Soo Byun, Jae-Hyeok Shim, Young Whan Cho*

Nano-Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea

Received 8 May 2003; received in revised form 2 June 2003; accepted 2 June 2003

Abstract

The influence of stearic acid as a process control agent on the mechanochemical reaction between Ti and BN to form TiN/TiB₂ nanocomposite powder by high energy ball milling has been investigated. A powder mixture of pure Ti and hexagonal BN powders with a molar ratio of 3:2 was milled for up to 40 h with up to 1.75 wt.% of stearic acid. The XRD analysis shows that an intimate mixture of TiN and TiB₂ crystalline powders was formed during milling by a displacement reaction. It has been observed by monitoring the temperature of the vial surface during the milling process that the addition of over 1.5 wt.% of stearic acid changed the reaction mode from a mechanically induced self-propagating reaction (MSR) to a gradual reaction. It has also been found by XRD and TEM analyses that the MSR produces TiN and TiB₂ particles initially of sub-micron size, which are reduced gradually by further milling. However, there still remain some coarse TiB₂ particles larger than a few hundred nanometers even after 16-h milling due to their extremely high hardness. On the other hand, the gradual reaction induced by stearic acid successfully inhibits the formation of coarse TiB₂ particles and eventually decreases the crystallite size of the products below 40 nm after 16 h of milling.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Transition metal alloy; Nanostructured materials; Mechanical alloying; Powder metallurgy; TEM

1. Introduction

There has been increasing interest in refractory materials such as carbides, nitrides, borides and silicides owing to their exceptional hardness and stability at high temperatures. However, single-phase refractory materials have reached their optimum stages and attention has now turned to composite refractory materials. On the other hand, nanocrystalline refractory materials have recently received much attention owing to their improved mechanical properties [1]. A variety of techniques for preparing nanocrystalline materials have been proposed over a decade. Among them, high energy ball milling has been recognized as an effective way of producing nanocrystalline, amorphous and other non-equilibrium structured powders mainly through a solid-state reaction [2]. Particularly, high energy ball milling accompanying chemical reactions, i.e. mechanochemical processing, is considered to be very effective for preparing nanocomposite powders including more than two phases.

E-mail address: oze@kist.re.kr (Y.W. Cho).

0925-8388/\$ - see front matter © 2003 Elsevier B.V. All rights reserved. doi:10.1016/S0925-8388(03)00638-8

Recently, it has been reported that nanocrystalline TiN/TiB₂ composite powder was synthesized from Ti and BN powders by high energy ball milling [3]. TiB₂ exhibits a high elastic modulus and high hardness. However, pure TiB₂ is not deformed plastically even at very high temperatures due to its intrinsically high Peierls barrier to the dislocation movement [4]. On the other hand, TiN has a relatively low elastic modulus and low hardness compared to TiB₂ and can be deformed at high temperatures. Therefore, it is expected that a nanocomposite of TiN and TiB₂ might provide a desired combination of high-temperature hardness and stability with adequate ductility and fracture toughness [5]. The mechanochemical synthesis from Ti and BN powders to form TiN/TiB2 nanocomposite powder is completed through a mechanically induced self-propagating reaction (MSR) [6,7] and a nanometer scale mix of the product powders by further milling. However, there still remains a significant portion of coarse TiB₂ particles because TiB₂ is much harder than TiN. Therefore, it is desirable to reduce coarse TiB₂ particles during the milling process.

The purpose of the present study is to mechanochemically synthesize nanocrystalline TiN/TiB₂ composite powder

^{*} Corresponding author. Fax: +82-2-958-5379.

using high-energy ball milling with the addition of stearic acid as a process control agent (PCA) to efficiently reduce the crystallite size by suppressing MSR. The effect of stearic acid on the ignition of MSR is investigated and the structures of TiN/TiB_2 powder by both MSR and gradual reactions are compared.

2. Experimental procedure

The starting powders used in this study were 99% pure Ti with a particle size of less than 45 µm and 99% pure hexagonal BN of average 4 µm. A mixture of Ti and BN was prepared with a molar ratio of 3:2. The Ti/BN mixture was charged together with stearic acid and Cr-steel balls (two 12.7 mm and four 6.35 mm in diameter) into a tool steel vial with an O-ring seal under Ar atmosphere. The amount of stearic acid was controlled from zero up to 1.75 wt.%. The ball-to-powder weight ratio (BPR) was fixed at 5:1. The high-energy ball milling was carried out for up to 40 h using a SPEX 8000 mixer/mill. During the milling process, the temperature of the vial surface was monitored using a non-contact infrared thermometer. The as-milled powders were investigated by X-ray diffraction (XRD) using Cu Ka radiation, and transmission electron microscopy (TEM) using Philips CM30 operating at 200 kV.

3. Results

3.1. MSR without stearic acid

Fig. 1, reproduced from our previous article [3] where all experimental procedures were the same except that the BPR was 10:1, shows XRD patterns of Ti/BN mixtures milled without stearic acid for different milling times. After some incubation time, the Ti/BN mixture abruptly reacted to form TiN/TiB₂ powder, which resulted in a sudden increase in the









Fig. 2. (a,b) Bright field images of the powder milled without stearic acid for 105 min, (c) micro diffraction pattern of TiN [112] zone axis obtained from crystallite A and (d) micro diffraction pattern of TiB₂ [$1\overline{100}$] zone axis obtained from crystallite B in (b).

vial surface temperature. Fig. 2 shows bright field (BF) images of the powder whose milling was interrupted 1 min after the MSR. The crystallites just after MSR are very coarse and the size is in the order of 100 nm. Using micro diffraction as shown in Fig. 2c,d, the products could be indexed as TiN and TiB₂. The displacement reaction during milling could be represented as:

$$3\mathrm{Ti} + 2\mathrm{BN} = 2\mathrm{TiN} + \mathrm{TiB}_2 \tag{1}$$

Munir [8] proposed a simple guideline to decide whether or not a self-propagating reaction might occur for a certain



Fig. 3. TEM micrographs of the powder milled without stearic acid for 16 h: (a) dark field image and (b) high resolution image.

system. According to his proposal, the reaction can start without additional energy from an exterior source when $-\Delta H/C_p$ is above 2000 K. The $-\Delta H/C_p$ value of reaction (1) calculated by Thermo-Calc [9] is ~3800 K, which indicates that reaction (1) can progress via MSR.

With further milling, the peaks of the products in the XRD patterns broaden while no other phases are observed. Fig. 3 shows TEM images of the powder milled for 16 h. The dark field (DF) image shows that the crystallite size is below 10 nm. In this article, all DF images are obtained from the diffraction rings of TiN {111} and {200}, and TiB₂ {1010} and {1011}. As shown in Fig. 3b, however, there still remains a significant portion of coarse TiB₂ crystallites, probably because of its very high hardness.



Fig. 4. Variation in vial surface temperature with milling time.

3.2. Gradual reaction

In order to control MSR, stearic acid was added as a PCA and in order to detect MSR the vial surface temperature during milling was measured as shown in Fig. 4. Fig. 5 shows that the incubation time for the MSR depends on the concentration of stearic acid. The incubation time is \sim 200 min without stearic acid and there is little change up to 1 wt.% of stearic acid. The incubation time is rather longer than that in the previous article [3] because the BPR is reduced from 10:1 to 5:1. The addition of stearic acid of between 1 and 1.5 wt.% slightly increases the incubation time, but the MSR still occurred. When 1.5 wt.% of stearic acid is added, however, the MSR was suppressed in one experiment while it occurred in another one. With over 1.5 wt.% of stearic acid, reaction (1) always proceeded gradually. Therefore, the critical concentration of stearic acid to inhibit the MSR of reaction (1) is ~ 1.5 wt.%. Fig. 6 shows the XRD patterns of the powders with different amounts of stearic acid after 16-h milling. Up to 1.375 wt.% of stearic acid, there is



Fig. 5. Incubation time for MSR with different amount of stearic acid.



Fig. 6. XRD patterns of the powders milled for 16 h with (a) 0, (b) 0.5, (c) 1, (d) 1.25, (e) 1.375, (f) 1.5 and (g) 1.75 wt.% stearic acid.

no distinct difference in the XRD patterns of the powders. However, with over 1.5 wt.% of stearic acid, both TiN and TiB₂ peaks broaden much more, which means that the suppression of the MSR resulted in the reduction of the average



Fig. 7. XRD patterns of the powders milled with 1.75 wt.% stearic acid for (a) 4, (b) 6, (c) 8, (d) 16 and (e) 40 h.

crystallite sizes. The crystallite sizes of TiN and TiB_2 , estimated by Scherrer's formula [10], are 9 and 19 nm without stearic acid, and 5 and 8 nm with 1.75 wt.% of stearic acid, respectively.





Fig. 8. (a) Bright and (b) dark field image of the powder milled with 1.75 wt.% stearic acid for 6 h, and (c,d) selected area diffraction patterns (SADPs), respectively, of particles A and B in (b).

Fig. 7 shows the XRD patterns of Ti/BN powders with 1.75 wt.% of stearic acid milled for different times. After milling for 6 h, TiN peaks appears with broadened Ti peaks. Further milling increases the intensities of TiN and TiB₂. After milling for 16 h, the displacement reaction (1) seems to be almost completed judging from the XRD data.

3.3. Microstructure

Fig. 8 shows images and selected area diffraction patterns (SADPs) of the powder milled with 1.75 wt.% of stearic acid for 6 h. Particle A in Fig. 8b represents the products of reaction (1), which consist of TiN and TiB₂ as can be seen from SADP, while particle B seems to be unreacted. It may



Fig. 9. (a,d) Bright field image and (b,e) dark field image of the area marked by rectangle in (a) and (d), and (c,f) SADPs, respectively, of the powder milled for 16 h without and with 1.75 wt.% stearic acid.



Fig. 10. (a,c) Dark field image and (b,d) SADP of the powder milled for 8 h with 1.25 and 1.75 wt.% stearic acid, respectively.

also be inferred from Fig. 8 that reaction (1) is completed as a whole within a particle triggered by the impacts during milling even though the transfer of the reaction between particles by exothermic heat is difficult. The crystallite size of the TiN/TiB₂ products is ~ 20 nm as shown in Fig. 8b, which seems to be typical among several DF images, even though there are a few particles whose crystallite size is above 40 nm. Compared with the results right after the MSR as shown in Fig. 2, the gradual reaction results in much smaller crystallites.

Fig. 9 shows TEM micrographs and SADPs of the powders milled for 16 h without and with 1.75 wt.% stearic acid. The DF image of the as-milled powder without stearic acid shows that the crystallite size is \sim 10 nm. However, the SADP shows the spots diffracted from coarse TiB₂ particles besides the rings diffracted from the fine particles. It could be observed by tilting the specimen that there are some coarse TiB₂ particles of over 100-nm diameter, two of which are indicated by the arrows in Fig. 9a. On the other hand, there are no such coarse TiB₂ particles when milled with 1.75 wt.% stearic acid as shown in Fig. 9d,f. Furthermore, the size of the fine TiN and TiB₂ crystallites is even smaller than that without stearic acid as compared in Fig. 9b,e. The reduction in crystallite size observed by TEM is in agreement with the X-ray result as shown in Fig. 6.

There is no effect of stearic acid on the crystallite size unless the amount of stearic acid is enough to result in a gradual reaction. Fig. 10 shows TEM micrographs and SADPs of the powders milled for 8 h with 1.25 or 1.75 wt.% of stearic acid. While the powder with 1.25 wt.% stearic acid shows still coarse crystallites together with fine crystallites, the powder with 1.75 wt.% of stearic acid induced a gradual reaction which results in a fine mixture of nanocrystalline TiN/TiB₂ and unreacted Ti/BN.

4. Discussion

The structural evolution from a Ti and BN mixture to TiN/TiB_2 nanocomposite powders can be divided into three stages when the MSR occurs. At the first stage, crystallite sizes decrease, reactants mix on a fine scale, and chemically active defect sites form during the incubation time. The MSR abruptly occurs to produce TiN and TiB₂ of sub-micron sizes. Finally, further milling reduces the crystallite size and mixes the products on a nanometer scale. The milling mode





Fig. 11. Dark field images obtained from the TiN/TiSi₂ nanocomposite powders milled for 16 h (a) without and (b) with 1.5 wt.% stearic acid. The arrows in (b) indicate some unreacted Si₃N₄.

of TiN and TiB₂ products can be classified as a brittle-brittle system. It is known that TiB₂ is much harder than TiN. Therefore, coarse TiB₂ crystallites are difficult to reduce in size compared with TiN, which causes a portion of coarse TiB₂ particles to remain as shown in Figs. 2 and 9a. Therefore, it is necessary to control the crystallite size of TiB₂ during milling by suppressing the MSR and subsequently preventing the formation of coarse TiB₂ particles. It is worth comparing the aforementioned results with the structure of TiN/TiSi₂ nanocomposite mechanochemically synthesized from Ti and Si₃N₄ mixture [11]. This displacement reaction which can be expressed as

$$11\text{Ti} + 2\text{Si}_3\text{N}_4 = 8\text{Ti}\text{N} + 3\text{Ti}\text{Si}_2(\text{C54})$$
(2)

also progresses as a kind of MSR but $TiSi_2$ is softer than TiN. As milling progresses, the TiN and $TiSi_2$ products successfully form nanocomposite powder without coarse particles, where the crystallite size of TiN is ~10 nm and $TiSi_2$ seems to be amorphous. In such a system, there seems to be no big advantage in a gradual reaction against MSR compared with that in the TiN/TiB₂ system, even though the crystallite size of TiN is more reduced as shown in Fig. 11.

As shown in Section 3, ~0.2 mol.% (1.5 wt.%) of stearic acid successfully changed reaction (1) from MSR to a gradual reaction type. Such an amount is too small to consider the possibility that the change of reaction mode could be induced by other reactions such as that between Ti and C from the stearic acid. In general, the change of reaction mode by an inert additive is attributed primarily to two mechanisms, i.e. increasing the heat capacity and decreasing the contact area between the reactants [6,7]. The adiabatic temperature rise $(-\Delta H/C_p)$ of reaction (1) will decrease from ~3800 to ~3650 K due to the increase in specific heat by adding 1.5 wt.% of stearic acid. Therefore, it seems that the suppression of the MSR by stearic acid is primarily due to the decrease in contact area between the reactants.

Gradual reaction results in a fine crystallite size of TiN and TiB₂, which can be easily understood because there is no large temperature increase as the reaction proceeds. In addition, the TiN and TiB₂ products formed in a gradual reaction seem to be present as a composite as shown in Fig. 8. Further, it can be inferred from Figs. 8 and 10b that reaction (1) and mixing the products with unreacted amorphous Ti/BN occur simultaneously, which is advantageous for forming nanocomposite powders compared with simply milling two brittle phases of TiN and TiB₂ together.

5. Conclusion

Nanocrystalline TiN/TiB2 powders are synthesized from a mixture of Ti and BN powders by high-energy ball milling with the addition of stearic acid as a process control agent (PCA). The XRD analysis shows that Ti and BN powders form TiN and TiB₂ powders at the early stage of milling by a displacement reaction. Up to 1.5 wt.% of stearic acid, an abrupt increase in the temperature of the vial surface is detected, which indicates that the reaction progresses in an MSR form. Over 1.5 wt.% of stearic acid, MSR is suppressed and a gradual reaction occurs. It is found by XRD and TEM analyses that the MSR produces TiN and TiB₂ particles of sub-micron size while the gradual reaction produces nanocrystalline TiN and TiB₂ composite powders. Therefore, coarse TiB₂ particles which still remain even after 16 h when milling without stearic acid could be successfully inhibited by inducing a gradual reaction with stearic acid.

References

- [1] K. Niihara, J. Ceram. Soc. Jpn. 99 (1991) 974.
- [2] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.
- [3] J.-H. Shim, J.-S. Byun, Y.W. Cho, Scripta Mater. 47 (2002) 493.

- [4] J. Ramberg, C. Woolfe, W. Williams, J. Am. Ceram. Soc. 68 (1985) C78.
- [5] F. Olevsky, P. Mogilevsky, E.Y. Gutmanas, I. Gotman, Metall. Mater. Trans. A 27 (1996) 2071.
- [6] L. Takacs, Prog. Mater. Sci. 47 (2002) 355.
- [7] C. Chakurov, V. Rusanov, J. Koichev, J. Solid State Chem. 71 (1987) 522.
- [8] Z.A. Munir, Am. Ceram. Soc. Bull. 67 (1988) 342.
- [9] B. Sundman, B. Jansson, J.-O. Andersson, CALPHAD 9 (1985) 153.
- [10] B.D. Cullity, S.R. Stock, in: , Elements of X-Ray Diffraction, Prentice Hall, London, 2001, p 170.
- [11] J.-H. Shim, J.-S. Byun, Y.W. Cho, J. Metastable Nanocrystalline Mater. 15–16 (2003) 557.