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Preparation of TiB_2–$TiC_{0.5}N_{0.5}$ Ceramic Composite by Reactive Hot-Pressing and its Microstructure

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Abstract: In this paper, using TiH_2, BN and B_4C as raw materials, reactive hot-pressing method is proposed to produce TiB_2–$TiC_{0.5}N_{0.5}$ ceramic composite. In the produced TiB_2–$TiC_{0.5}N_{0.5}$ composite, very fine (in general, 10 nm) $TiC_{0.5}N_{0.5}$ precipitates are found dispersed in TiB_2 grains by using SEM and TEM. The mechanism of the formation of this kind of structure and how to control it by processing design and its influence on the properties of the material are worth further study.

1 INTRODUCTION

With good properties, such as high melting point, superhardness, good stability and good electrical conductivity, TiB_2 and Ti(C,N) ceramics are candidates for cutting tools, wear resistance materials and electrode materials.[1,2]

Being used as cutting tools, the hardness of TiB_2 is higher than that of Ti(C,N), but on the other hand the friction factor of Ti(C,N) to the material to be cut, such as steel, is greatly reduced by containing nitrogen, which is good for cutting. By combining TiB_2 and Ti(C,N) as composite materials, the advantages of the two can be adopted. Having studied it for years, Watanabe *et al.* achieved good results and considered it as a prospective cutting tool material.[3–5] They used a two-step process, i.e. produced TiB_2 and Ti(C,N) powders first, mixed them in a composition and then hot-pressed[3,5] or pressureless sintered them.[4] Pressureless sintering reduces the manufacturing cost. In this paper, a one-step process, or reactive hot-pressing method was used. The reaction is as follows:[6,7]

$$9Ti+2BN+2B_4C \rightarrow 5TiB_2+4TiC_{0.5}N_{0.5} \quad (1)$$

In the composite ceramics prepared according to this reaction, the volume content of TiB_2 is 62 vol% and that of $TiC_{0.5}N_{0.5}$ is 38 vol.%. Using this method, the step of composing raw materials was omitted and the processing was simplified, resulting in a greatly reduced cost. This paper focuses on the preparation of the material and its microstructural characteristics.

2 EXPERIMENTAL PROCESS

Using powders of TiH_2 (99·5% pure, particle size <45 μm), BN (99·3% pure, B_2O_3 0·44%, Na_2O 0·14%, average particle size 1 μm) and B_4C (99·8% pure, particle size 5–8 μm) as raw materials, the burden calculation was in accordance with reaction (1). 2 wt% Ni powder (<0·1 μm) was added to improve sintering. Ball milled by Al_2O_3 balls in alcohol for 12 h, the mixed powder was dried and hot pressed at 1850 °C, 25 MPa in vacuum for 30 min. A disc with a diameter of 70 mm and thickness of 5 mm was finally obtained.

The disc was cut into specimens by electrical discharge machining (EDM). After grinding and polishing, the final size was 2·7 × 4·7 × 35 mm. The density was obtained by liquid displacement. The phase composition was analysed by XRD. The Vickers hardness was tested with a load of 20 kg. The flexural strength was tested by three-point bending method (the span was 20 mm and the

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Table 1. Properties of TiB_2–$Ti_{0.5}N_{0.5}$ ceramic composite produced by hot pressing

	Relative density (%)	Vickers hardness (GPa)	Bending strength (MPa)	Fracture toughness (MPa · $m^{1/2}$)	Electrical resistance ($\mu\Omega$ · cm)	Phase composition
This study	97·0	25	435 ± 66·8	6·44 ± 0·51	15·9	TiB_2,$TiC_{0.5}N_{0.5}$
Watanabe *et al.* ($TiC_{0.5}N_{0.5}$–30 wt% TiB_2)	>99	20·5	800	4	—	TiB_2,$TiC_{0.5}N_{0.5}$

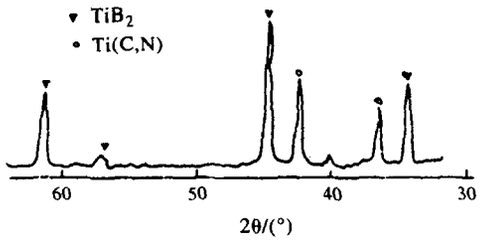

Fig. 1. XRD pattern of TiB_2–$TiC_{0.5}N_{0.5}$ ceramic composite produced by reactive hot pressing.

loading speed was 0·5 mm/min). The fracture toughness K_{IC} was tested by SENB method (2 × 4 × 20 mm, notch width < 0·2 mm, depth about 1·6 mm, load speed 0·5 mm/min). The electrical resistivity was also measured. The value for each of the properties was the average of five figures and is listed in Table 1. For comparison, the results obtained by Watanabe *et al.*[3] are also listed. To analyse the microstructure, SEM, TEM and HREM were used.

3 RESULTS AND DISCUSSION

Figure 1 is the XRD pattern of the composite ceramics. It can be seen that there are only TiB_2 and $TiC_{0.5}N_{0.5}$ and no other phases, indicating the high temperature reaction was in accordance with reaction (1).

Fig. 3. TEM photograph of a TiB_2 grain, showing platelet precipitates of $TiC_{0.5}N_{0.5}$.

Figure 2 is the SEM photograph of the polished surface, in which the heavy grey phase is TiB_2, the light grey phase is $TiC_{0.5}N_{0.5}$, the bright phase is Ni and the dark region corresponds to the pores. It can be seen that the size of TiB_2 grains are generally larger than those of $TiC_{0.5}N_{0.5}$ and the additive Ni is distributed in the triple junctions. Moreover, inside the TiB_2 grains, many very fine $TiC_{0.5}N_{0.5}$ particles are distributed. It is clearer in the TEM photograph that platelets of $TiC_{0.5}N_{0.5}$ precipitated in TiB_2 grains (Fig. 3). The sizes of the $TiC_{0.5}N_{0.5}$ precipitates are of the order of some 10 nm. Williams *et al.*[8,9] have always found the platelet precipitates of TiC of some nanometers in TiB_2 and ZrB_2 single crystals caused by the addi-

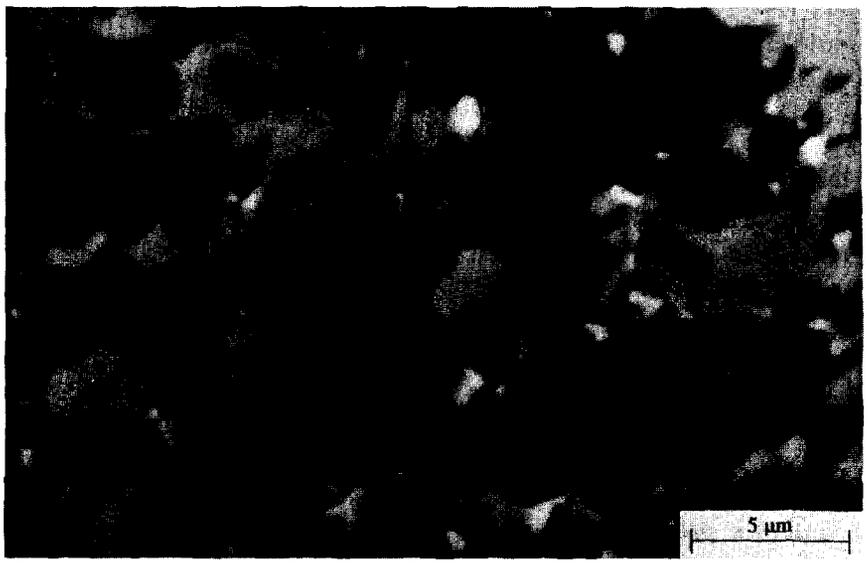

Fig. 2. SEM photograph of polished surface of the TiB_2-$TiC_{0.5}N_{0.5}$ composite, heavy grey phase is TiB_2, light grey phase is $TiC_{0.5}N_{0.5}$, bright phase is Ni and the dark region is pores.

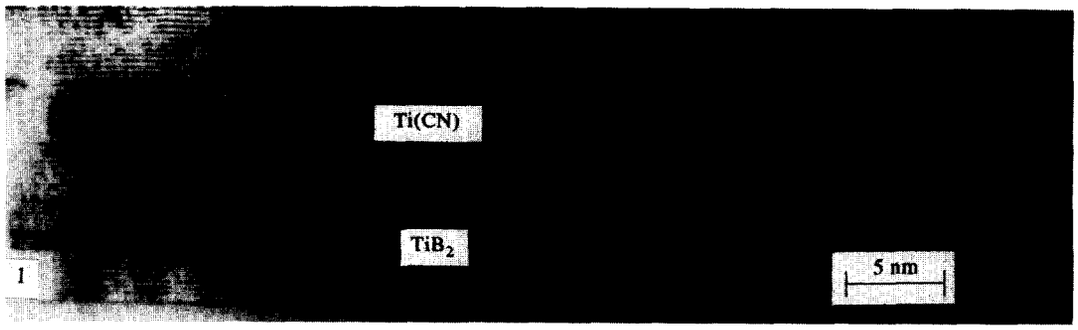

Fig. 4. HREM picture of a $TiC_{0.5}N_{0.5}$ precipitate in TiB_2 grain.

tive (C, for example). They suggested that the precipitates can improve the property of creep resistance of a single crystal of TiB_2 or ZrB_2. However, in composite ceramics, the precipitates of $TiC_{0.5}N_{0.5}$ in TiB_2 grains are obviously coarser. The influence of this kind of precipitate structure on the properties of the composite requires further study.

Figure 4 is the HREM picture of a $TiC_{0.5}N_{0.5}$ precipitate, which shows the co-growth phenomenon of $TiC_{0.5}N_{0.5}$ precipitate and TiB_2 matrix. It then can be suggested that the mechanisms of the formation of the composite microstructure are as follows.

At high temperatures, B, C and N are dissolved in Ti melt. When their respective solubilities come up to saturation level, the corresponding phase begins to be crystallized:

$$\mathrm{Ti(l)+2B} \longrightarrow \mathrm{TiB_2(s)}$$

$$\mathrm{Ti(l)} + \tfrac{1}{2}\mathrm{C} + \tfrac{1}{2}\mathrm{N} \longrightarrow \mathrm{TiC_{0.5}N_{0.5}(s)}$$

It is estimated that $TiC_{0.5}N_{0.5}$ precipitated from TiB_2 grains may be the result of the crystallization of the two phases in Ti melt at the mean time. However, the detailed mechanism of the formation of this structure and how to control it need further study.

4 CONCLUSIONS

Using TiH_2, B_4C and BN as raw materials, TiB_2–$TiC_{0.5}N_{0.5}$ composite ceramics can be fabricated by reactive hot pressing. Additionally, by properly adding C and B the ratio of the content of the two phases and that of C/N in Ti(C,N) can be adjusted.[7] By microstructure analysis, it is found that platelet $TiC_{0.5}N_{0.5}$ crystals on the scale of 10 nm precipitated in TiB_2 grains. The mechanism of the formation of this kind of structure and its influence on the properties of the material are worth further study.

REFERENCES

1. WATANABE, T. & TOKUNAGA, Y., Recent studies on the metal diboride. *J. Met. Soc. Jap.*, **25**(12) (1986) 1018–25.
2. SHOBU, K., WATANABE, T., ENOMOTO, Y., UMEDA, K. & TSUYA, Y., Frictional properties of sintered TiN–TiB_2 and Ti(CN)–TiB_2 ceramics at high temperature. *J. Amer. Ceram. Soc.*, **70**(5) (1987) C-103-C-104.
3. SHOBU, K., WATANABE, T. & YAMAMOTO, H., Hot pressing of Ti(CN)–TiB_2 system. *Yogyo-Kyokai Shi*, **93**(5) (1985) 46–50.
4. WATANABE, T., YAMAMOTO, H., SHOBU, K. & SAKAMOTO, T., Factors affecting the porosity and bending strength of Ti(CN)–TiB_2 materials. *J. Am. Ceram. Soc.*, **71**(4) (1988) C-202-C-204.
5. WATANABE, T., Effects of carbide addition on the mechanical properties of the $TiC_{0.5}N_{0.5}$–30 wt% TiB_2-carbide sintered compacts. *J. Ceram. Soc. Jap.*, **99**(2) (1991) 146–9.
6. ZHANG, G., Preparation of TiB_2–Ti(C,N) ceramics by reactive hot-pressing. Chinese patent, CN1056859A, C04B35/58, 1991-12-11.
7. ZHANG, G., Study on TiB_2-Ti(C,N) ceramic composites prepared by reactive hot-pressing. *J. Chinese Ceram. Soc.*, **21**(2) (1993) 182–7.
8. HAGGERTY, J. S. & LEE, D. W., Plastic deformation of ZrB_2 single crystals. *J. Am. Ceram. Soc.*, **54**(11) (1971) 572–6.
9. MOCHEL, P., ALLISON, C. & WILLIAMS, W. S., Study of titanium carbide precipitates in titanium diboride by electron energy loss spectroscopy. *J. Am. Ceram. Soc.*, **64**(4) (1981) 185–7.