

Phase Transformation and Densification of hBN-TiN Composites Fabrication by Spark Plasma Sintering

Mettaya Kitiwan^{1,a}, Akihiko Ito^{1,b} and Takashi Goto^{1,c}

¹Institute for Materials Research, Tohoku University, Sendai 980-8577 Japan

^amettaya@imr.tohoku.ac.jp, ^bitonium@imr.tohoku.ac.jp, ^cgoto@imr.tohoku.ac.jp

Keywords: hexagonal boron nitride, titanium nitride, spark plasma sintering

Abstract. hBN-TiN binary composite was fabricated using spark plasma sintering (SPS) at temperatures between 1973 and 2273 K. With increasing TiN content from 10 to 90 vol%, the relative density increased from 75.7 to 96.4%. The maximum relative density of 96.4% was achieved in the hBN-TiN containing 90 vol% TiN sintered at 2273 K. hBN and TiN was stably coexisted at 1973 K without TiB₂ formation.

Introduction

Hexagonal boron nitride (hBN), having analogous crystal structure of graphite, has attractive as a structural material. The structure of hBN consists of strong covalent bond of B and N in hexagonal ring, whereas their interlayers are bonded by weak van der Waals force which make each planar of hexagonal network slides easily [1-3]. Because of this morphology, hBN is widely employed as a lubricant powder; besides, it has excellent chemical inertness, and hBN is therefore suitable to use as crucible for molten steel. hBN was utilized as an additive in many composite systems such as Si₃N₄-hBN [4-7], AlN-hBN [8], TiB₂-hBN [9] and Al₂O₃-hBN [10]. These systems were investigated in an attempt to improve both densification and mechanical properties.

Titanium nitride (TiN) exhibits excellent tribology properties and high chemical stability, and thus TiN is widely used as protective coating. The sintering of bulk TiN is restricted due to low sinterability and decomposition at high temperature. A composite system would promote the densification in sintering. The combination of TiN and cubic BN (cBN) had been examined whereas TiN exhibits high chemical activity with cBN [11]. According to the thermodynamic calculation, the BN-TiN mixture can be decomposed and form new phase of TiB₂ at high temperature. The reaction can be expressed as follow [12]:



Since hBN can hardly sinter and easily reacted with TiN, the hBN-TiN system particularly at high hBN content more than 40 vol% has not been reported. In this study, hBN-TiN composites were prepared by spark plasma sintering (SPS) at TiN content from the 10 to 90 vol%. The effects of sintering temperature and pressure on densification, phase transformation and morphology were investigated.

Experimental Procedure

hBN (10 μm, Kojundo Chemical Laboratory, Sakado, Japan) and TiN (1.2–1.8 μm, Wako Pure Chemical, Osaka, Japan) powders were used as starting materials. The powders were mixed in an agate mortar then passed through a 200 mesh sieve. The powder was filled in a graphite die (inner diameter of 10 mm) with an appropriate amount to obtain a pellet thickness around 3 mm. The sintering was conducted in SPS apparatus (SPS-210LX, Fuji Electronic Industrial, Kawasaki, Japan). The sintering temperatures increased from 1973 to 2273 K at the heating rate 1.67 K s⁻¹ under uniaxial pressure of 10 – 100 MPa and then remained for 300 s. The SPS chamber was kept in a vacuum.

Bulk densities of hBN-TiN composites were measured by Archimedes method then calculated relative density from theoretical densities of hBN (2.27 Mg m⁻³) and TiN (5.39 Mg m⁻³). The phase

was examined by X-ray diffractometry (XRD; RAD-2C, Rigaku) in the 2θ range of $20\text{--}90^\circ$ with $\text{CuK}\alpha$ radiation. Microstructure was observed by a scanning electron microscope (SEM; Hitachi S-3100).

Results and Discussion

Figure 1 shows the XRD pattern of hBN-TiN composite (60 vol%TiN) sintered at various temperature. At 1973 K, there was no TiB_2 formation (Fig. 1(a)). The tiny peak of TiB_2 was found at 2073 K in the hBN-TiN composites at 60 and 70 vol%TiN (Fig. 1(b)). At 2173 K, the reaction between hBN and TiN formed in a wide range between 20 and 80 vol%TiN while the TiB_2 could be formed in all composition at 2273 K. With increasing temperature, peak intensity of TiB_2 increased while those of hBN and TiN decreased consistently. The reaction of BN and TiN to form TiB_2 was reported to initiate around 1900 K [13]. In present study, the hBN-TiN binary compound could be maintained almost up to 2073 K. This was higher than that of the literature [13]. Due to the rapid sintering characteristic of SPS, the TiB_2 formation could be retarded.

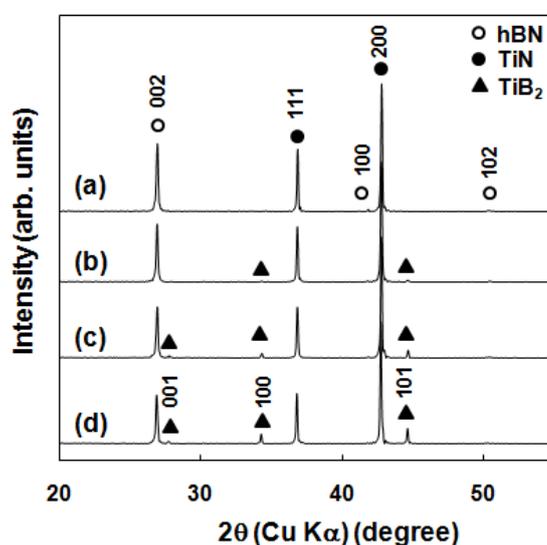


Fig.1. XRD patterns of hBN-60vol%TiN composites sintered at (a) 1973 K (b) 2073 K (c) 2173 K and (d) 2273 K.

The relative densities of composite as a function of TiN content at various temperatures are presented in Fig. 2. The hBN-TiN composite at 10 vol%TiN was broken after sintered; therefore, the density of this specimen could not be shown. The increasing in TiN amount from 10 to 50 vol% resulted in the increasing of relative density: for example, from 88.8 to 94.1% at 1973 K as shown as black triangle in Fig. 2(a). The composite sintered at lower temperature exhibited higher density because of high pressure during sintering at lower temperature, i.e., 100 MPa at 1973 K, 50MPa at 2073 K, 30 MPa at 2173 K and 10 MPa at 2273 K. This result suggested that pressure during SPS process plays an important role on densification of hBN-TiN composite. Figure 2(b) shows that the relative densities of composite at 60–90 vol%TiN increased from 85.0 to 96.4%. In this composition range, by applying same pressure, the relative density increased with increasing sintering temperature.

The increase in TiN content promoted the densification of composites. Although the increase in density might be slightly associated with TiB_2 formation (TiB_2 : 4.50 Mg m^{-3}) the content of TiB_2 was small even at 2273 K as shown in Fig. 1(d). The effect of the TiB_2 formation on the density of hBN-TiN composites could be minimal. The hBN-TiN composites composed of TiB_2 were indicated with star symbol (*) in Fig. 2(a) and (b).

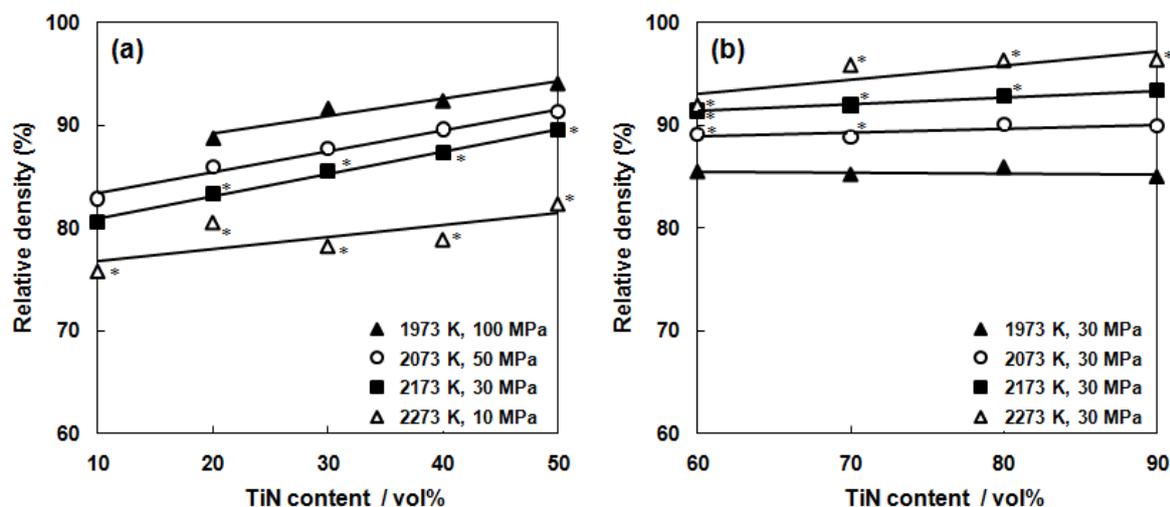


Fig.2. Effect of temperature and pressure on relative densities of hBN-TiN composites.

The microstructures of hBN-TiN composites sintered at 2273 K are depicted in Fig. 3. The composites containing 10–30 vol%TiN (Fig. 3(a)-(b)) show loose morphology because of the low densification of hBN powder. The progress of consolidation was remarkably observed in composite containing 50 vol%TiN (Fig.3 (c)). It is known that the sinterability of TiN is higher than that of hBN, and thus the densities of hBN-TiN composites in the high TiN composition was promoted by mainly densification of TiN phase. A small amount of TiB_2 formed during the sintering at more than 2073 K. This in-situ TiB_2 formation has been also beneficial to the densification.

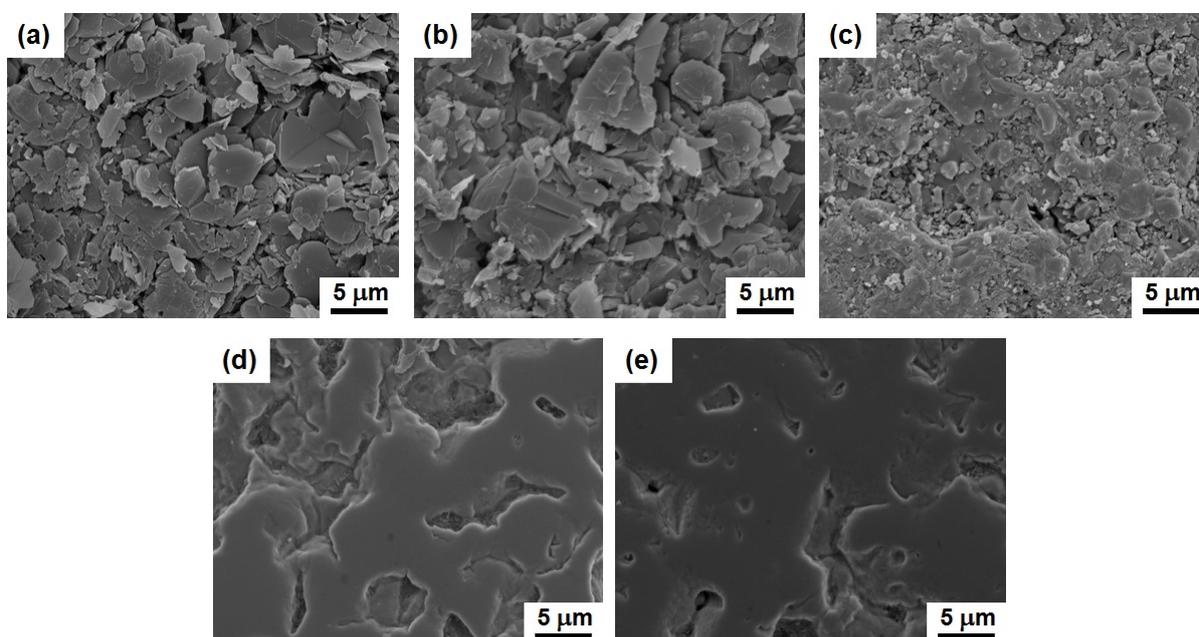


Fig.3. SEM surface microstructure of hBN-TiN composites with the TiN content of (a) 10 vol% (b) 30 vol% (c) 50 vol% (d) 70 vol% and (e) 90vol%.

Summary

hBN-TiN composites were consolidated by SPS. With increasing TiN content from 10 to 90 vol%, the relative density increased from 75.7 to 96.4%. The maximum relative density of 96.4% was achieved in the hBN-TiN composites at 90 vol%TiN sintered at 2273 K. hBN and TiN was stably coexisted at 1973 K without TiB_2 formation. The densification could have been enhanced by in-situ TiB_2 formation.

Acknowledgements

This research was supported in part by the Global COE Program of Materials Integration, Tohoku University.

References

- [1] A. Lipp, K.A. Schwetz and K. Hunold: *J. Eur. Ceram. Soc.* Vol. 5 (1989), p. 3
- [2] M. T. Hagio, K. Kobayashi, H. Yoshida, H. Yasunaga and H. Nishikawa: *J. Am. Ceram. Soc.* Vol. 72 (1989), p. 1482
- [3] J. Eichler and C. Lesniak: *J. Eur. Ceram. Soc.* Vol. 28 (2008), p. 1105
- [4] T. Kusunose, T. Sekino, Y.H. Choa and K. Niihara: *J. Am. Ceram. Soc.* Vol. 85 (2002), p. 2689
- [5] W. Ruigang, P. Wei, J. Menging, C. Jian and L. Yongming: *Mater. Sci. Eng. B* Vol. 90 (2002), p. 261
- [6] Y. Sun, Q. Meng, D. Jia and C. Guan: *J. Mater. Process. Tech.* Vol. 182 (2007), p. 134
- [7] Y.L. Li, R.X. Li and J.X. Zhang: *Mater. Sci. Eng. A* Vol.483–484 (2008), p. 207
- [8] W.S. Choa, Z.H. Piao, K.J. Lee, Y.C. Yoo, J.H. Lee, M.W. Cho, Y.C. Hong, K. Park, W.S. Hwang: *J. Eur. Ceram. Soc.* Vol. 27 (2007), p. 1425
- [9] M. Herrmann, J. Räthel, S. Höhna, J. Eichler and A. Michaelis: *J. Eur. Ceram. Soc.* Vol. 31 (2011), p. 2401
- [10] A. Abreal, D. Goeriot, F. Thevenot, M. Lagace, B. Gueroul and M. Rigaud: *J. Eur. Ceram. Soc.* Vol. 15 (1995), p. 841
- [11] E. Benko, J. S. Stanisław, B. Krolicka, A. Wyczesany, T. L. Barr: *Diam. Relat Mater.* Vol. 8 (1999), p. 1838
- [12] P. Rogl and J.C. Schuster: *Phase Diagrams of Ternary Boron Nitride and Silicon Nitride System* (ASM International, United States of America 1992)
- [13] L. Brewer and H. Haraldsen: *J. Electrochem. Soc.* Vol. 102 (1955), p. 399