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Densification and Microstructure of Monolithic TiN and TiB_2 Fabricated by Spark Plasma Sintering

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Abstract. Sintering behavior of monolithic TiN and TiB_2 was investigated using spark plasma sintering (SPS) at temperatures between 1673 and 2573 K. Relative density of TiN was increased from 82.3 to 96.7% while that of TiB_2 increased from 70.1 to 92.8% with increasing temperature. At temperatures between 1673 and 2273 K, TiB_2 was more difficult to consolidate compare to TiN. At 2473 K, TiB_2 densified rapidly to 92.8%.

Introduction

Titanium nitride (TiN) and titanium diboride (TiB_2) are promising materials for structural ceramic applications due to their superior properties at high temperature. They have high melting points with relative low density and high strength. TiN have unique combination of physical and chemical properties such as high hardness, high thermal conductivity and high corrosive resistant [1]. TiN is widely employed as wear resistant surface coating for cutting tools. TiB_2 possesses high thermal conductivity, high electrical conductivity and excellent chemical stability [2]. These properties are suitable for high temperature and wear resistant applications such as cutting tools, evaporation crucible and armor plate. However, the sintering of these monolithic ceramics is restricted because very high temperature is required for accomplishing fully densification.

Various sintering methods such as pressureless sintering, hot-pressing (HP), hot-isostatic pressing (HIP) and spark plasma sintering (SPS) have been attempted to achieve high density of hard materials. Among these processes, SPS is known as rapid consolidation technique. It provides many advantages over conventional techniques and becomes extensively utilized. In SPS process, direct electric current pulse is supplied to graphite die and is passed through sample if it is conductive. The conductive die is consequently generated heat and acts as the heating source then sample is heated from both outside and inside itself. Due to this heating mechanism, SPS is possible to produce dense ceramic at a lower temperature in a shorter time [3-5].

This research aims to consolidate TiN and TiB_2 by SPS without any sintering additive. The effects of SPS condition on the density and microstructure of these monolithic TiN and TiB_2 were studied.

Experimental Procedures

TiN (1.2 – 1.8 μm, Wako Chemical) and TiB_2 (2 – 3 μm, Kojundo Chemical) were used as starting materials. The powder was filled in a graphite die (inner diameter of 10 mm) with an appropriate amount to obtain a sample thickness about 3 mm. The sintering was performed in SPS apparatus (SPS-210LX, Fuji Electronic Industrials) at temperatures between 1673 and 2573 K for a dwelling time of 1 to 5 min with the heating rate of 1.67 K s^{-1}. The SPS chamber was kept in a vacuum, then uni-axial pressure of 10 – 100 MPa were applied to the sample through graphite punch rods. The pressure applied on specimens was varied with the sintering temperature depending on the strength of graphite mold.

After sintering, specimens were removed from the die and ground the outer surface to remove carbon contamination then polished to mirror surface. The bulk densities of specimens were measured by Archimedes method then calculated relative density using the theoretical density of

TiN (5.4 Mg m^{-3}) and TiB_2 (4.5 Mg m^{-3}). The microstructures of polished surface of sintered specimens were observed using scanning electron microscope (SEM; S-3100H, Hitachi).

Results and Discussions

The effect of sintering temperature and pressure on relative density of TiN and TiB_2 was showed in Fig. 1. The relative density of TiN increased from 82.3 to 96.7% with increasing sintering temperature from 1673 to 2173 K. However, it was slightly decreased to 92.4% after further increased temperature from 2273 to 2573 K. The relative density of TiB_2 increased from 70.1 to 81.0% with increasing temperature from 1673 to 1973 K, then it decreased to 76.9% at 2273 K. The density of TiB_2 rapidly increased to 92.8% at 2473 K. The densification of TiB_2 was more difficult compare to that of TiN in the temperature range between 1673 and 2273 K.

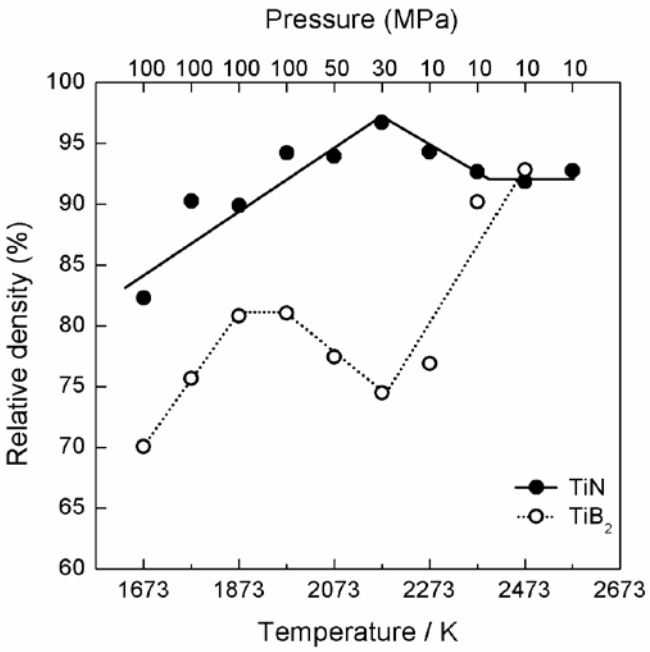

Fig.1. Effect of sintering temperature and pressure on relative densities of TiN and TiB_2.

The microstructures of polished surface of TiN after sintering at different temperatures were depicted in Fig. 2. At 1673-1873 K (Fig. 2(a)-(b)), the connected pores were observed in sintered specimen. The isolated pore formed at 1973 K (Fig. 2(c)). The maximum relative density was achieved at 2173 K which was in good agreement with the microstructure (Fig. 2(d)). Although the high densification was reached at 2173 K, pore growth was incipient at this temperature. The pore size increased with increasing temperature from 2273 to 2573 K. This behavior was responsible for the slightly declined in density of TiN specimens at above 2173 K.

The microstructures of TiB_2 specimens sintered at various temperatures were depicted in Fig. 3. At 1673 K (Fig. 3(a)), almost no densification and no grain growth were observed. From 1773 to 2273 K (Fig. 3(b)-(d), the neck growth progressed but the relative density of this range was far lower than that of TiN. At 2373 to 2473 K, the densification of TiB_2 progressed and the microstructure of TiB_2 (Fig. 3(e)-(f)) exhibited round shape pores. Those spherical pores might be formed by the evolution of small pores at the triple boundary. CO or CO_2 gas might have trapped and volume of gas might be expanded with increasing temperature.

According to relative density and morphology, the sintering of TiB_2 by SPS seemed to be more difficult compare to that of TiN at less than 2273 K. The densification mechanism of TiN and TiB_2 by SPS is not well understood; however, the activation energy of B diffusion in TiB_2 could be higher than that of N diffusion in TiN. Then, the B diffusion in TiB_2 might become almost the same as the N diffusion in TiN at around 2473K.

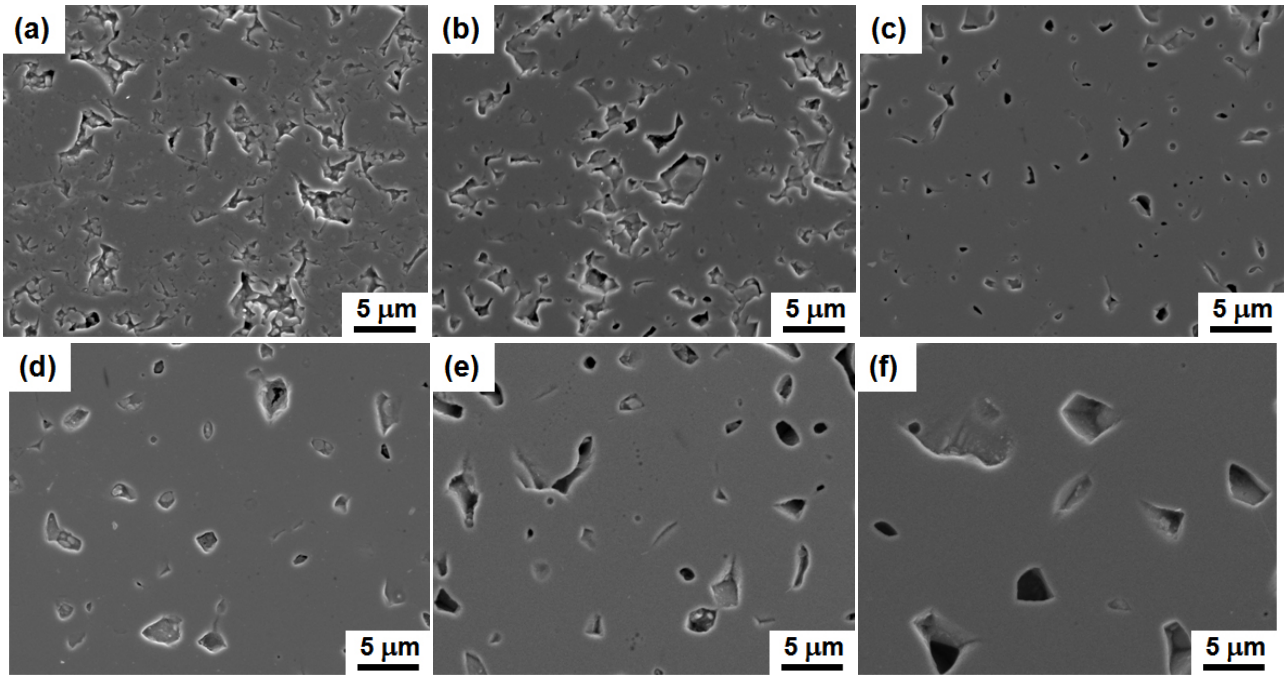

Fig.2. SEM microstructure of polished surface of TiN specimens sintered at different temperature (a) 1673 K (b) 1873 K (c) 1973 K (d) 2173 K (e) 2273 K and (f) 2473 K.

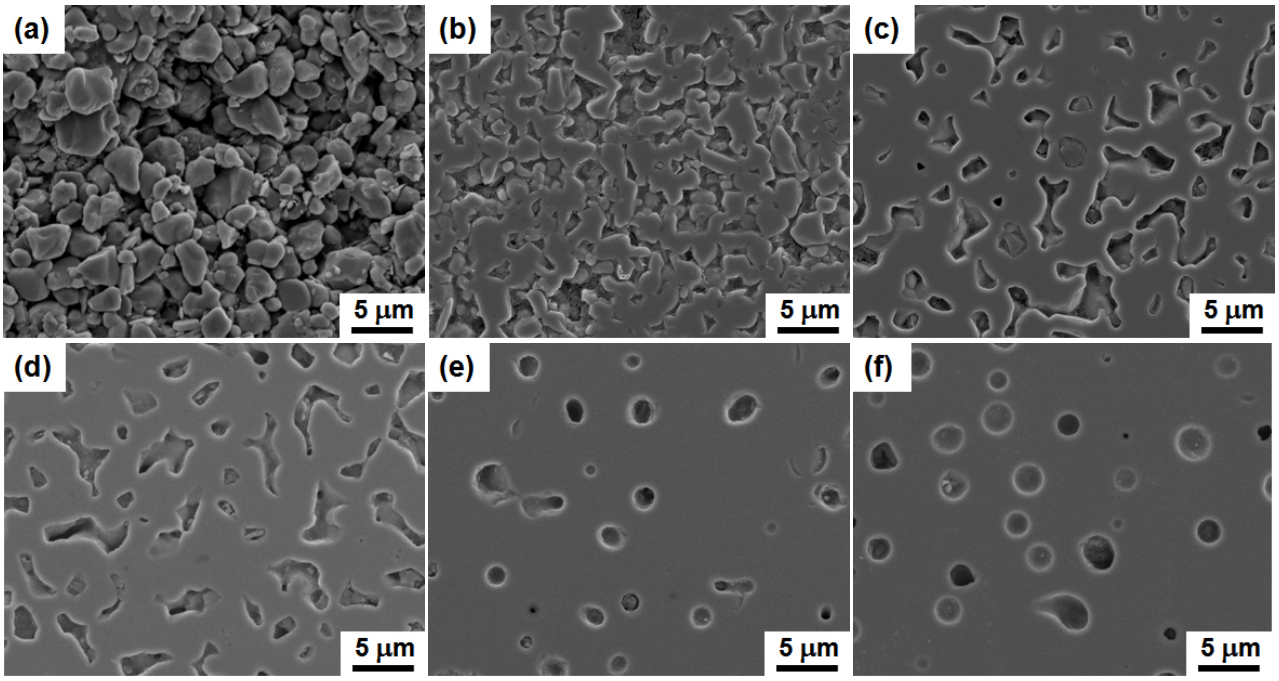

Fig.3. SEM microstructure of polished surface of TiB_2 specimens sintered at different temperature (a) 1673 K (b) 1773 K (c) 1973 K (d) 2273 K (e) 2373 K and (f) 2473 K.

Summary

The SPS was successfully utilized to prepared high density of monolithic TiN and TiB_2.The maximum density of TiN was 96.7% at 2173 K while that of TiB_2 was 92.8% at 2473 K. At less than 2373 K, TiB_2 was more difficult to consolidate by SPS compare to TiN and almost the same of density as that of TiN at 2473 K.

Acknowledgements

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References

[1] H. Kuwahara, N. Mazaki, M. Takahashi, T. Watanabe, X. Yang, T. Aizawa: Mater. Sci. Eng. A Vol. 319–321 (2001), p. 687

[2] R.G. Munro: J. Res. Natl. Inst. Stand. Technol. Vol. 105 (2000), p. 709

[3] M. Omori: Mater. Sci. Eng. A Vol. 287 (2000), p. 183

[4] W. Chen, U. Anselmi-Tamburini, J.E. Garay, J.R. Groza, Z.A. Munir: Mater. Sci. Eng. A Vol. 394 (2005), p. 132

[5] Z. A. Munair, U. Anselmi-Tamburin, M. Ohyanagi: J. Mater. Sci. Vol. 41 (2006), p. 763