Effect of TiN addition on the properties of spark plasma sintered TiB$_2$

Manabu KOIDE†, Khaled JABRI‡, Atsushi SAITO, Masakazu IMORI and Tomohiro SATO‡

National Institute of Technology, Nagaoka College, 888 Nishikatakai, Nagaoka, Niigata 940–8532, Japan
‡SINTER LAND Inc, 123 Ameike, Nagaoka, Niigata 940–2055, Japan

The sintering of hardly sintered TiB$_2$ powder has been investigated using the spark plasma sintering (SPS) technique. The investigation revealed that TiB$_2$ powder can be sintered to highly dense bulk samples using SPS technique. However optimization of the sintering condition could not generate bulk samples with a fine microstructure. The addition of TiN was found to be effective in obtaining bulk samples with fine structure. Sample bending strength largely improved from 120 MPa for TiN free samples to more than 373 MPa, much higher than that of graphite, for TiN containing samples. The improvement in bending strength is attributed to the fine structure formed and to the strong bonding between TiB$_2$ and TiN particles.

Key-words : TiB$_2$, Sintering, Spark plasma, Fine structure, High mechanical properties, Mold

1. Introduction

Graphite molds are widely used for spark plasma sintering (SPS) technique, because graphite has high melting temperature of 3500°C, high thermal conductivity of 120 W/m·K, excellent electrical resistivity of 1500 μΩ·cm and low thermal expansion coefficient of $50 \times 10^{-6}$ K$^{-1}$. In contrast to the excellent thermal and electrical properties, graphite has weak mechanical properties represented by a bending strength that does not exceed 100 MPa. molds made of graphite do not hence withstand higher sintering pressure. The development of new materials with excellent mechanical as well as thermal and electrical properties are desired.

Pure TiB$_2$ has been reported$^{1,2}$ to have a melting temperature of 3200°C, an electrical resistivity of 9 Ω cm, a thermal conductivity of 100 W/m·K at room temperature and a thermal expansion coefficient of $70 \times 10^{-7}$ K$^{-1}$ close to that of graphite. Also, pure TiB$_2$ has been reported$^{4,5}$ to have a hardness of around 3000 Vickers, a bending strength of around 400 MPa, an elastic modulus of 520 GPa much higher than that of graphite.$^6$

M. Kitiwan et al.$^7$ have reported that TiB$_2$ is hardly sintered using conventional sintering techniques such as hot press and hot isostatic press techniques. And, they claim in their report that SPS technique is useful for sintering TiB$_2$ powder at temperatures as high as 2300°C. The sintering of TiB$_2$ at lower temperatures is desired for its application in different fields including molds for SPS technique, glass lens, etc.

In the present study, the sintering conditions of pure TiB$_2$ using SPS technique have been investigated at temperatures lower than those reported in Ref. 7 as well as the effect of Titanium nitride (TiN) addition on TiB$_2$ microstructure and mechanical properties. TiN which has inferior mechanical properties to TiB$_2$ but much superior to graphite has been selected as an additive to control TiB$_2$ particle growth in case of the sintering conditions cannot be effective to achieve TiB$_2$ bulk sample with a fine microstructure.$^8$-$^9$

2. Experimental procedures

TiB$_2$ powder of purity of 99.8% and particle distribution of 2–3 and 63 μm passing sieve particles has been used. TiN used has a purity of 99.8% and particle distribution of 53 μm passing sieve particles. Samples with desired composition of TiB$_2$–TiN are weighed from TiB$_2$ and TiN powders and hand mixed in a alumina mortar. Pellet samples with a diameter of 20 mm and a thickness of 5 mm has been sintered in graphite molds using the sintering machine LABOX-650F of SINTER LAND Inc of Japan.

The heating rate is fixed to 30 K/min from room temperature to 1500°C, to 20 K/min from 1500 to 1700°C and to 15 K/min from 1700 to 1900°C. The holding time at 1900°C was 60 min. The sintering pressure was 60 MPa and the atmosphere was vacuum.

The temperature is measured at the mold surface using a radiation thermometer. The holding temperature and pressure are selected to be high as possible for fast sintering and thus preventing particle growth. But they are fixed to values so that the physical and mechanical properties of graphite mold used are not affected.

The density of sintered samples is measured by Archimedes technique. Samples hardness is measured using MATSUZAWA VMT-7S hardness tester. Bending strength is measured using Shimadzu universal testing machine UH-F500kNC with the distance between fulcrums of 20 mm. The microstructure is observed using scanning electron microscope JEOL JSM-6060A and the chemical composition are analyzed by EDS spectra.

3. Results and discussion

Figure 1 shows the density of the sintered samples with TiN content. The density of sintered samples increased almost linearly with TiN content from 4.46 to 5.38 g/cm$^3$. The relative density for all samples was almost constant and between 98.7–98.8%.

Figure 2 shows X-ray diffraction pattern of the samples. Only TiB$_2$ and TiN crystals were detected. The relative intensity of peaks attributed to TiN relative to those of TiB$_2$ increased with...
increasing TiN content. This points to the fact that TiB2 and TiN did not react between each other and are held in a matrix structure.

Table 1 shows samples hardness and fracture toughness. Fracture toughness was measured based on JISR1607 by IF (Indentation Fracture) and calculated using the following equation:

\[
K_{IC} = \frac{E^2 P a}{C^3} \quad [\text{MPa m}^{1/2}]
\]

where \(E\) is Young’s modulus providing that TiB2 and TiN have almost same Young modulus of 520 GPa, \(P\) is half of crack average length in mm, \(a\) is indentation area in mm². 

Hardness values decreased with increasing TiN content. The hardness decreasing rate was almost proportional to TiN increasing content which is in agreement with density and X-ray results. However fracture toughness did not show significant change up 75 mol% of TiN content. But above this value, it sharply decreased. Fracture toughness change was not proportional to TiN content as in the hardness.

Figure 3 shows SEM micrograph of the sintered samples. And, Fig. 4 shows the dependence of TiB2 particle size average, estimated from SEM micrographs, on TiN content. The average size is determined by estimating the size of each grain from the backscattered electron image on the SEM micrograph and taking the average of counted particles total size. Sample containing TiB2 and TiN have small grain size compared to pure TiB2 and pure TiN. The grain size are 60 and 55 \(\mu\)m, respectively. Particle size and morphology in TiB2–TiN containing samples were not clearly affected by the content of TiB2 or TiN.

The non-growth in grains of samples containing TiB2–TiN is attributed to the non-reaction between TiB2 and TiN and to the effect of each element on the diffusion of the other. The large decrease in fracture toughness of TiN samples is attributed to the large grain growth.

Figure 5 shows bending strength of the sintered samples. The bending strength largely improved with the addition of TiN, which is in consistence with particle size variation and morphology.
Figure 6 shows SEM-EDS mapping for Ti, B and N elements in 50TiB₂–50TiN (mol %) sample.

4. Conclusion

The properties of TiN added TiB₂ are investigated. TiN added TiB₂ has higher mechanical strength than graphite. Also, the presence of TiB₂ with TiN was found to be very effective on controlling grain growth.

References

1) M. Ishihara, J. Sumita, T. Shibata, T. Iyoku and T. Oku, Nucl. Eng. Des., 223, 251–260 (2004).
2) A. E. McHale, ed., Phase Equilibria Diagrams, Vol. X, Borides, Carbides, and Nitrides, American Ceramic Society (1994) pp. 140–141.
3) R. Telle and G. Tetzow, Mater. Sci. Eng., A, 105/106, 97–104 (1988).
4) L.-H. Li, H.-E. Kim and E. S. Kang, J. Eur. Ceram. Soc., 22, 973–977 (2002).
5) T. S. R. Ch. Murthy, B. Basu, R. Balasubramaniam, A. K. Suri, C. Subramanian and R. K. Fotebar, J. Am. Ceram. Soc., 89, 131–138 (2006).
6) M. Moriyama, J. Ceram. Soc. Japan, 109, 550–556 (2001).
7) M. Kitiwan, A. Ito and T. Goto, J. Eur. Ceram. Soc., 34, 197–203 (2014).
8) K. Shobu and T. Watanabe, Journal of the Japan Society of Powder and Powder Metallurgy, 32, 215–218 (1985).
9) T. Yamada, M. Shimada and M. Koizumi, Journal of the Ceramic Association, Japan, 89, 621–623 (1981).