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Influence of hot pressing sintering temperature and time on microstructure and mechanical properties of TiB_2 ceramics

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Abstract

In this paper, a titanium diboride ceramic was produced by the hot pressing sintering method. The effects of hot pressing parameters on the TiB_2 ceramic microstructure and mechanical properties were studied. The bending strength and fracture toughness were measured by three point bending testing and single edge notched bending tests (SENB), respectively. The microstructure features of the TiB_2 sintered material were revealed by means of SEM and TEM. The results show that the TiB_2 grain size increases quickly with the increasing temperature and time during hot pressing sintering. The density and the TiB_2 grain size have a great influence on the mechanical properties. The bending strength decreases with increasing TiB_2 grain size, whilst the fracture toughness increases. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hot pressing; Mechanical properties; Microstructure-final; Sintering; TiB_2

1. Introduction

TiB_2 ceramics have excellent physical and chemical properties such as high melting point, high hardness, and good corrosion resistance; moreover, TiB_2 ceramics have also an excellent electric conductivity. Such unique properties give to TiB_2 materials a wide application area such as advanced engineering ceramics (cutting tools, wear-resistant parts, armour materials, and cathode materials for Hall–Heroult cells).[1,2] However, up to now, the applications of TiB_2 ceramics are rather limited due to the difficulties that exist in producing fully dense materials. In the fabrication of TiB_2 ceramics, the key process is high temperature sintering. Literature[3] showed that sintering densification of TiB_2 is very difficult. One of the possible reasons is that TiB_2 is a compound with both ionic bond and covalent bonds, which demand very high sintering temperature for its densification. TiB_2 has a low crystalline boundary diffusion coefficient, which causes the slow densification speed and long sintering time. Additionally, a thin, oxygen rich layer (mainly TiO_2 and B_2O_3) that is on the surface of TiB_2 powder is found to be very detrimental to densification.[4] In the pressureless sintering processing, the sintering temperature of TiB_2 is higher than 2200 °C and the density of sintered materials is not more than 95% T.D (theoretical density).[5] The hot pressing sintering processing has been considered as an effective candidate sintering processing for TiB_2 ceramics. The main features of hot pressing sintering include lower sintering temperature, high sintering speed, and a uniform microstructure of sintered materials. Studies showed that hot pressing increased the density of TiB_2 ceramics significantly.[6]

In this study, hot pressing sintering was used to produce TiB_2 ceramics. Results about sintering processing features, microstructure and mechanical properties are reported.

2. Experimental

The main experimental material is TiB_2 powder, which was synthesized by the self-propagating high-temperature synthesis (SHS) method.[7,8] The average particle size is about 1.5 μm, and the chemical composition of TiB_2 powder is shown in Table 1.

In order to reduce the agglomerated TiB_2 powder to single particles, TiB_2 starting powder was milled by the wet-milling method for 2 h in a plastic bottle with agate

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Table 1
Chemical composition of TiB_2 starting powder materials

Experimental material	Content of boride	Main impurity
TiB_2	>98%	O (0.94%), N(0.077%), Mg (0.113%)

balls and acetone as media. The resultant slurry was dried in vacuum evaporator. The dried powder was screened through 80-mesh screen. After that, TiB_2 powder was put into a graphite die for hot pressing sintering. Hot pressing sintering was conducted in a hot pressing furnace with a flowing argon atmosphere, hot pressing temperature: 1773–2173 K, applied pressure: 30 MPa, sintering time: 30–120 min.

Scanning electronic microscopy (SEM), transmission electronic microscopy (TEM) and X-ray diffraction were used to evaluate microstructure of sintered materials. Density was inspected by Archimedes' method. Image analysis method was used to measure the grain size; the specimens were polished and etched with a dilute solution of hydrochloric and nitric acids ($HCl–HNO_3$ solution). The average grain size is the average value of 500 TiB_2 grains.

The hot pressed samples were cut into mechanical property testing specimens by spark cutting method, and the surface of the testing bar was polished using polishing machinery with diamond slurries down to 1 μm. The edges of all testing bars were chamfered to minimize the stress concentration induced by the machining flaw. Bending strength was measured by the three point bending test method (test specimen dimension, 3×4×35 mm, span, 25 mm, crosshead speed, 0.5 mm/min). Fracture toughness (K_{IC}) was evaluated by a single edge-notched bending test (SENB), the dimension of testing bar was 2×4×35 mm with a notch of 0.3 mm width and 2 mm depth. At least seven specimens were tested for each experimental condition. Hardness of the TiB_2 ceramics was tested by means of Rocke hardness tester (HRA), the applied load was 60 kg.

3. Results and discussion

3.1. Sintering processing features

Fig. 1 shows the relationship between sintering time and relative density. Initially the density of sample increases quickly with increasing of the sintering time (initial few minutes), later on, the density increases slowly. This indicates that the sintering mechanisms are different at different sintering stages: plastic flow and diffusion creep respectively are the main sintering mechanisms at initial sintering stage and last sintering stage, respectively.[9]

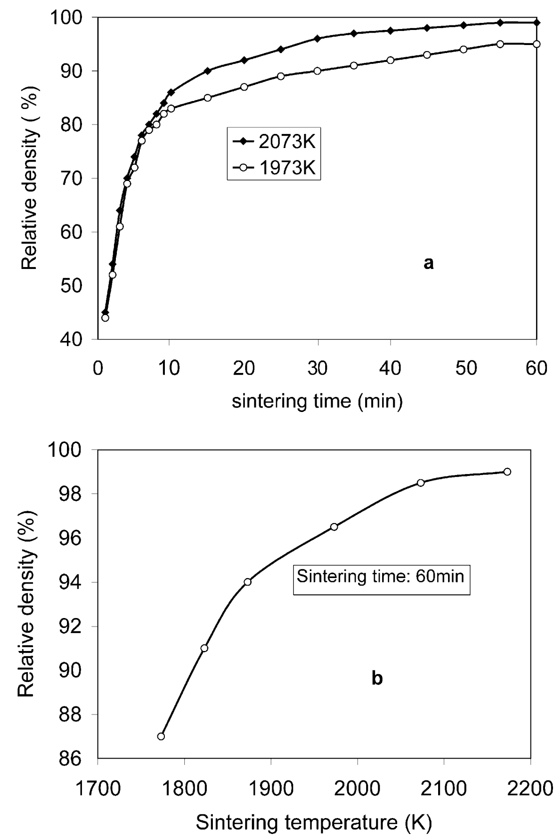

Fig. 1. Influence of sintering time and temperature on relative density.

Hot pressing temperature has a remarkable influence on the density of sintered sample (Fig. 1b): at low temperature, density of sample is lower, with increasing of sintering temperature, sample density increases quickly. At 2173 K, the TiB_2 ceramics is nearly fully dense. This result indicates that in order to prepare TiB_2 ceramics with high density, the higher sintering temperature is necessary.

3.2. Growth of TiB_2 grain and microstructure characteristics

At high sintering temperatures, TiB_2 grains will grow quickly and irregularly, and it is known that grains size and shape of TiB_2 ceramics can have an important influence on the mechanical properties.[10] In order to prevent the grain growing irregularly, the optimum hot pressing parameters have to be chosen by experiments.

Fig. 2 shows the influence of sintering temperature and time on the average grain size. When temperature is lower than 1973 K, the grains grow slowly, when sintering temperature is more than 2100 K, the grains grow quickly. At 2173 K, the average TiB_2 grain size is bigger than 12 μm, and the biggest grain is more than 20 μm. Fig. 3 shows the SEM photograph of the sample sintered at 2173 K, many irregular TiB_2 grains can be found.

The sintering time is another important factor that affects grain growth (Fig. 2). The TiB_2 grains increase with increasing of sintering time during hot pressing sintering processing, and at lower temperature, the grain growth speed is slower than that at high temperature. Low sintering temperature and short sintering time can limit TiB_2 grain growth, but at this processing condition, the density of sample is very low. For example, at 1973 K, the average grain size is about 5 μm; the relative density is only 95%. In hot pressing sintering processing, the grain growth mechanisms is diffusion moving of grain boundaries, increasing of sintering temperature cause increasing of diffusion coefficient, and also increase the grain growth speed.

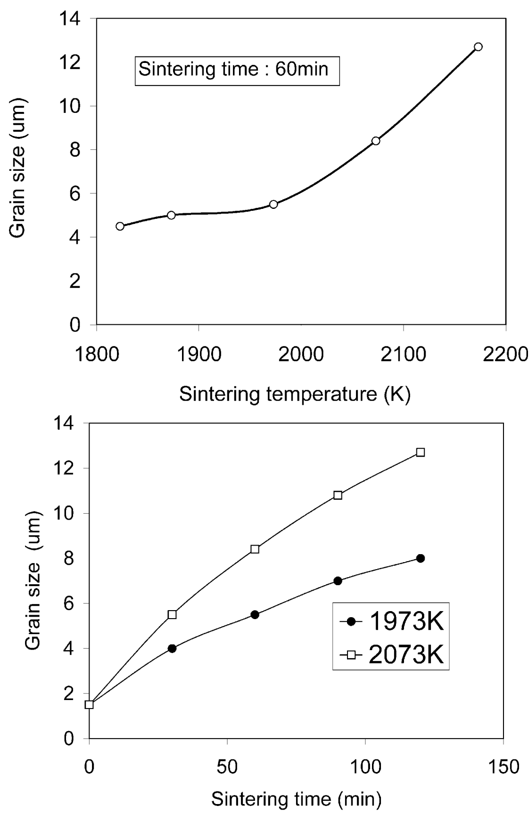

Fig. 2. Influence of sintering temperature and time on average grain size of TiB_2 ceramics.

For single-phase ceramic materials, the following equation can be used to describe the relation between sintering time and average grain size[11]

$$G = G_0 + K\ t^n \tag{1}$$

where, G is the average grain size, G_0 is the initial grain size, t is sintering time and n is the growth coefficient. Theoretically the n is about 0.5, but due to the fact that impurity and pores on the grain boundary will impede grain growth, the grain growth coefficient decreases. At low sintering temperature, the more pores at the grain boundary impede grain boundary moving and decreases grain growth coefficient, grains grow slowly. At high sintering temperature, density increases, pore decreases, the impeded force of grain boundary moving decreases, hence the grains grow quickly.

From the above experimental results and analysis, it can be found that an increase of sintering temperature and time can increase the sample density, but also increase grain size. Producing TiB_2 materials with high density and small grain size (fine-grain microstructure) is very difficult. The key processing parameters are sintering temperature and time. We believe that the quick hot pressing sintering at high temperature is the best sintering process for TiB_2 ceramics.

The typical microstructure of the TiB_2 ceramics hot pressed at 2073 K for 60 min is shown in Fig. 4. It is clear that the grain size is fine and uniform.

Fig. 5 shows the typical grain boundary structure and dislocation inside the crystalline of TiB_2. From Fig. 5a, it can be seen that the grain boundary is clear, and no second phase is found. In the sample prepared at a higher temperature, many dislocations can be found (see Fig. 5b), which can decrease mechanical properties of

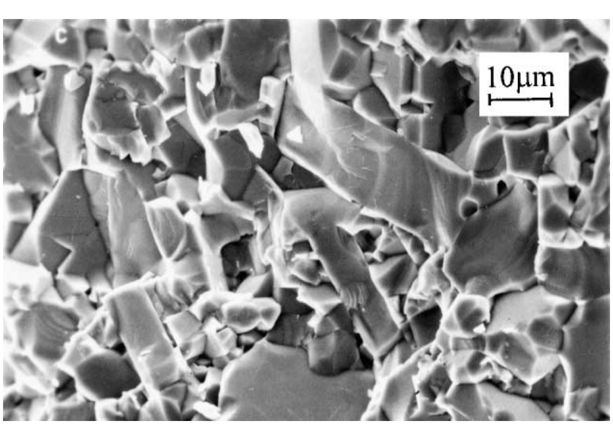

Fig. 3. SEM photography of the TiB_2 ceramics sintered under 2173 K for 60 min.

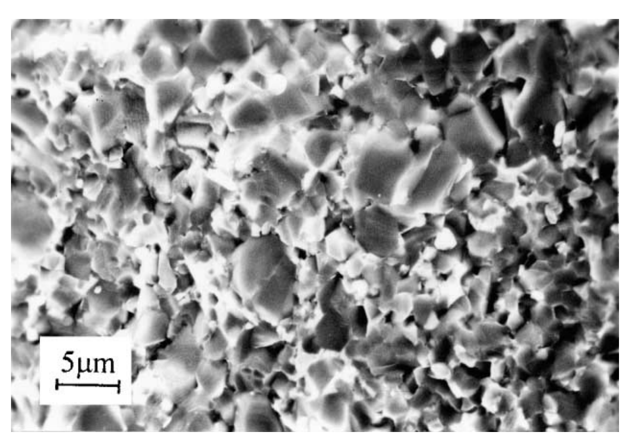

Fig. 4. Typical microstructure for TiB_2 ceramics sintered at temperature of 2073 K.

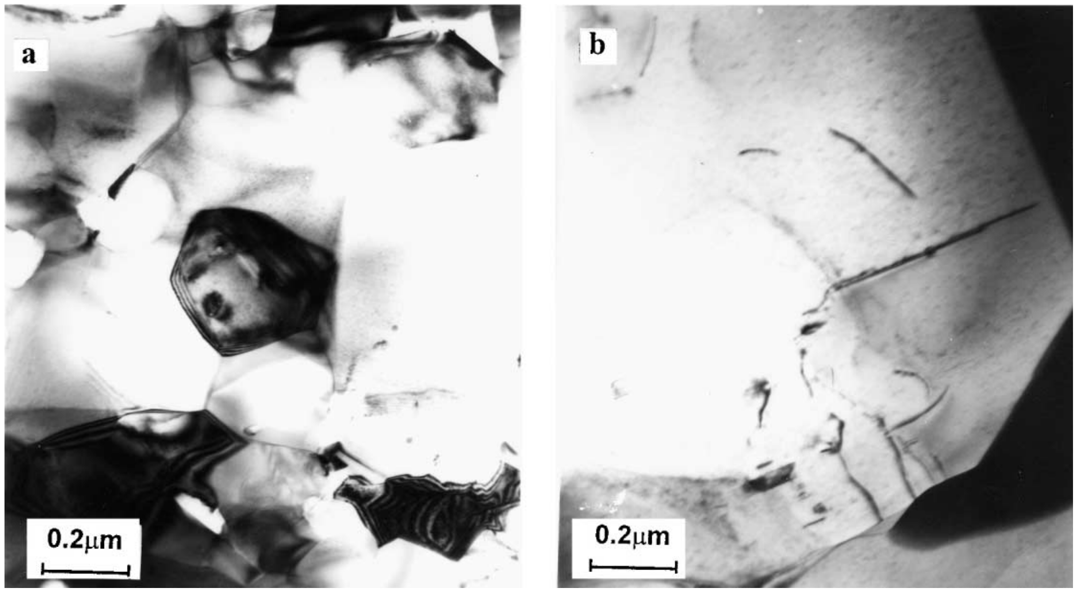

Fig. 5. Typical grain boundary structure and dislocation inside crystalline of TiB_2.

ceramic materials. The likely reasons induced the dislocation are TiB_2 crystal grain deformation and quick grain growth during hot pressing sintering. Controlling sintering processing parameters can decrease the dislocations. In the sample prepared at a temperature of 2073 K (see Fig. 5a), there is almost no dislocation.

3.3. Mechanical properties

A three point bending test and a single edge-notched bending test (SENB) were used to evaluate the mechanical properties of TiB_2 ceramics; the results are shown in Fig. 6 and Table 2. Rise in sintering temperature can increase bending strength and fracture toughness remarkably due to the densification increase. An increase of sintering time leads to a decrease of bending strength, however, the fracture toughness increases continuously with an increase of sintering time.

In ceramic materials, microstructure, specially the flaw structure, has obvious influence on the mechanical property. Pore and micro-crack are the typical flaw structures. Eq. (2) can be used to describe the relationship between materials' strength and porosity.

$$\sigma = \sigma_0 \exp(-k\alpha) \quad (2)$$

where, σ is the materials strength, σ_0 is the strength of materials without any defect, α is residual porosity. This equation indicates that strength will increase with decreasing of porosity, this agrees with our results.

Influence of grain size on the strength can be expressed by Eq. (3),

$$\sigma = \sigma_0 + kd^{-m} \quad (3)$$

where, σ is mechanical strength, d: grain size, k and m: experimental coefficients. This equation indicates that the materials' mechanical properties increase with decreasing of grain size. In this paper, when sintering temperature is over 2073 K, the density of samples is almost constant. In this case, the materials' strength will be controlled by grain size. In hot pressing sintering, longer time leads grains to grow quickly and irregularly (see Section 3.2), which is one of the reasons causing strength reduction, because this non-uniform grain

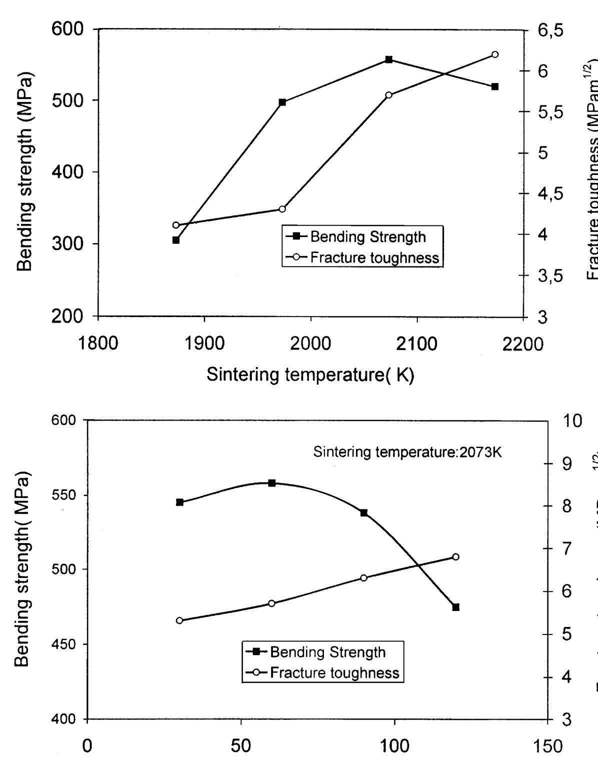

Fig. 6. Influence of sintering parameters on mechanical properties.

Table 2
Bending strength and fracture toughness

Producing parameters	Bending strength		Fracture toughness	
	σ_f (MPa)	Standard deviation (MPa)	K_{IC} (MPam$^{1/2}$)	Standard deviation (MPam$^{1/2}$)
Temperature (K)				
1873	305	40.7	4.1	0.67
1973	498	34.5	4.3	0.59
2073	558	30.1	5.7	0.43
2173	521	45.8	6.2	1.12
Sintering time (min)				
30	545	32.7	5.3	0.54
60	558	30.1	5.7	0.43
90	538	37.2	6.3	0.51
120	475	41.5	6.8	0.63

growth can induce micro-crack between crystal grains.

Experimental results show that fracture toughness increases continuously with an increase of sintering temperature and sintering time. Fracture toughness is a property that materials resist to the propagating of cracks. Increase of sintering temperature makes TiB_2 ceramics more dense, porosity decreases, hence fracture toughness increases. Longer sintering time leads to bigger crystal grain with a pillar shape; this kind of microstructure can impede the crack propagating by the mechanism of crack deflection, which absorbs much energy of micro-crack expansion, fracture toughness increases enormously.

From Table 2, it can be found that the standard deviation of strength and fracture toughness increases at high hot pressing temperature and long sintering time, the possible reason is the uneven microstructure caused by quick and abnormal grain growth.

4. Conclusion

From above experiment study and analysis, following conclusions can be summarised:

1. Hot pressing sintering can improve density of TiB_2 ceramic. At initial sintering stage, sintered density increases quickly, at the last stage materials density increases slowly.
2. Sintering temperature and sintering time have obvious influence on the grain growth of TiB_2 ceramic. When sintering temperature is lower than 2073 K, grains grow slowly and uniformly. At higher temperature, grains grow quickly and irregularly. Long sintering times also lead to grain bigger. Hence quick hot pressing sintering at high temperature is the best sintering processing for TiB_2 ceramic (short sintering time and high temperature).
3. Sintering temperature and time have remarkable influence on mechanical properties, at proper sintering parameters, the bending strength, fracture toughness and hardness reach respectively 558 MPa, 5.7 MPam$^{1/2}$ and 93 HRA.

Acknowledgements

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References

1. Cutler, R. A., *Engineering Materials Handbook, Ceramic and Glass, Vol. 4*. ASM International, Materials Park, OH, 1991 (pp. 787–811).
2. McLeod, A. D., Haggerty, J. S. and Sadoway, D. R., Electrical resistivities of monocrystalline and polycrystalline TiB_2. *J. Am. Ceram. Soc.*, 1984, **67**(11), 705–708.
3. Matkovich, V. I., *Boron and Refractory Borides*. Springer, Berlin, 1977 (p. 172).
4. Baik, S. and Becher, P. F., Effect of oxygen contamination on densification of TiB_2. *J. Am. Ceram. Soc.*, 1987, **78**(8), 527–530.
5. Einarsrud, M. A., Hagen, E., Pettersen, G. and Grande, T., Pressureless sintering of titanium diboride with nickel, nickel boride, and iron additives. *J. Am. Ceram. Soc.*, 1997, **80**(12), 3013–3020.
6. Park, J. H., Lee, Y. H., Koh, Y. H., Kim, H. E. and Baek, S. S., Effect of hot-pressing temperature on densification and mechanical properties of titanium diboride with silicon nitride as a sintering aid. *J. Am. Ceram. Soc.*, 2000, **83**(6), 1542–1544.
7. Yuan, R. Z., Composite materials and compositing technology by SHS. *International Journal of Self-Propagating High-Temperature Synthesis*, 1997, **6**(3), 265–275.
8. Wang, W. M. and Fu, Z. Y. *et al.*, Self-propagating high-temperature synthesis of TiB_2 powder. *Journal of Wuhan University of Technology*, 1995, **10**(2), 34–39.
9. Wang, W., Fu, Z. and Yuan, R., Microstructure study of TiB_2/NiAl composites fabricated by SHS. *J. Chin. Cera. Soc.*, 1996, **24**(1), 470–476.
10. Case, E. D. and Smyth, J. R., Grain size dependence of microcrack initiation in brittle materials. *J. Mater. Sci.*, 1980, **15**(1), 149–153.
11. Kingery, W. D., *Introduction to Ceramics*. Wiley, New York, 1976 (p. 411).