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Rapid sintering of TiB_2 ceramics using Co as sintering aid under high pressure condition

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The improved TiB_2 ceramics were obtained in sintering process at the pressure of 5.5 GPa and temperature of 1550 °C in presence of metallic Co powder. The effect of Co content (ranging from 0 wt.% to 10.0 wt.%) on the phase composition, density, microstructure, Vickers hardness and thermal conductivity of TiB_2 ceramics was analyzed. A small amount of new phase Co_2B has been created in the reaction of TiB_2 and Co. The relative density of sintered TiB_2 ceramics reached 98.1 %. When the mass fraction of Co increased, the porosity increased, while the hardness first increased and then decreased. The maximal Vickers hardness values were equal to 33.3 GPa or 28.2 GPa when the used load was of 4.9 N or 9.8 N, respectively. The highest reached value of thermal conductivity was 88.9 $W \cdot m^{-1} \cdot K^{-1}$. The dense TiB_2 ceramics with improved hardness and thermal conductivity were ascribed to the high pressure sintering method and Co sintering aid. High pressure sintering method provides a new way for the preparation of ceramics materials.

Keywords: *titanium diboride; cobalt; high pressure; sintering*

1. Introduction

Titanium diboride (TiB_2) as one of the most important transition metal boride materials has attracted considerable interest, due to its excellent combination of exceptional hardness, high melting point, low density, good thermal conductivity, high electrical conductivity and chemical stability [1, 2]. The difficulty in densification of TiB_2 ceramics is one of the most important limiting factors for potential applications. The nature of covalent bonding, low self-diffusion coefficient are believed to be the causes of poor sinterability of TiB_2 ceramics. Thus, the fabrication of dense titanium diboride is a challenging task and requires high sintering temperature and long dwell time, however, such conditions lead to the significant grain growth which causes drop of mechanical properties [3]. To overcome these problems, a variety of metallic and nonmetallic sintering aids have been attempted to promote the densification process.

The addition of ceramic sintering aid can help the sintering to reach the density close to theoretical density, however, the mechanical properties can drop dramatically as has been reported [4–7]. The most frequently used metallic sintering aids are Ti, Cr, Co, Ni, Fe, Al, Ta, etc. [8–11]. Theoretical and experimental works show that the ceramic and metallic sintering aid system may be handled at lower temperature in a shorter time to form solid solution, eutectic and/or stable intermetallic phases with good elastic, electric and thermal properties [12–15]. So, the sintering aids can effectively suppress the grain growth and improve the properties of TiB_2. Cobalt (Co) is usually used to improve the relative density and mechanical properties of TiB_2 ceramics due to small wetting angle and good wettability of TiB_2 with Co at 1500 °C to 1600 °C [8].

There are many methods of preparation and sintering of ceramic materials, such as solid phase sintering, pressureless sintering, reaction sintering, and hot pressing sintering, etc. Because high pressure may change the equilibrium state, it could help to reduce the sintering temperature and shorten the

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dwell time. Moreover, high pressure method for material fabrication or sintering takes place in a closed environment, and the obtained sample is pure [16, 17]. Thus, high pressure method has an obvious advantage over conventional sintering process and is an effective way to fabricate or sinter materials of novel and improved properties.

In the present work, the improved TiB_2 ceramics were sintered in presence of metallic Co powder under high pressure condition. The effects of Co content on the phase composition, density, microstructure, hardness and thermal conductivity of TiB_2 ceramics were systematically investigated. The relationship between performance and Co content were analyzed.

2. Experimental

The main raw materials were TiB_2 powders (purity $\geqslant$ 98.5 %, Dandong Chemical Engineering Institute Co., Ltd., China) with a mean particle size of 4 μm to 8 μm and Co metal powders (purity $\geqslant$ 99.5 %, Aladdin Chemistry Co., Ltd., China) with a mean particle size of 48 μm. The powder mixtures containing TiB_2 with different content of Co were mixed in an agate mortar for 3 h. Then, the mixed powders were cold-pressed into cylindrical samples with the diameter of 12 mm and the thickness of 5 mm. China-type large volume cubic high-pressure apparatus (CHPA, SPD-6×1200), tungsten carbide anvil, and experimental configuration used for TiB_2 ceramics sintering are shown in Fig. 1. The samples were processed at 5.5 GPa and 1550 °C. The temperature was measured in the experiment using a Pt-30%Rh/Pt-6%Rh thermocouple, which junction was placed near the sintered sample. The pressure was calibrated by the pressure-induced phase transitions of bismuth (Bi), thallium (Tl), and barium (Ba) [18]. Fig. 2 shows the preparation process curve for TiB_2 ceramics. Firstly, the pressure and temperature increased to 5.5 GPa and 1550 °C within 5 min and 3 min, respectively. Secondly, the temperature of 1550 °C remained constant for 20 min. Finally, the pressure and temperature decreased to atmospheric environment within 5 min.

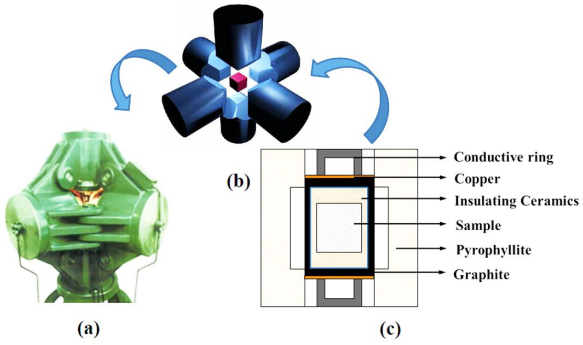

Fig. 1. (a) China-type large volume cubic high-pressure apparatus (CHPA), (b) tungsten carbide anvil, (c) experimental configuration used for TiB_2 ceramics sintering.

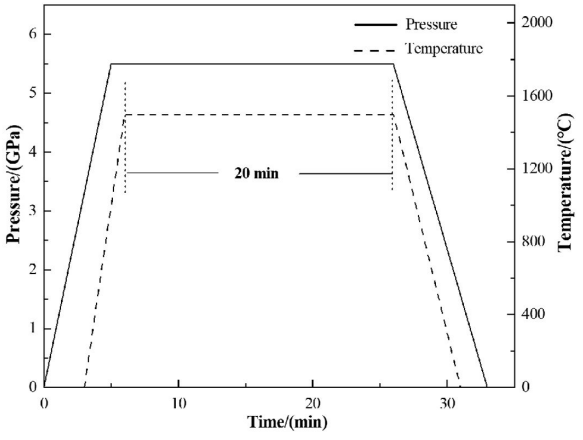

Fig. 2. Preparation process curve of TiB_2 ceramics sintering.

Phase identification was performed by X-ray diffraction (XRD). The density of the sintered samples was measured by the Archimedes method. Each sample was measured for 5 times and the bulk density was taken as the average value. The theoretical density of the materials was then calculated according to the formula: $\rho_{TD} = \frac{\rho_{TiB2}\rho_{Co}}{\omega_{TiB2}\rho_{Co}+\omega_{Co}\rho_{TiB2}}$. Here, ρ_{TD} is the theoretical density of TiB_2 ceramics with Co sintering aid, ρ_{TiB2} is the density of TiB_2, ρ_{Co} is the density of Co, ω_{TiB2} is the mass fraction of TiB_2, ω_{Co} is the mass fraction of Co. Microstructure was examined using scanning electron microscopy (SEM). Vickers hardness was measured using loads of 4.9 N and 9.8 N with 15 s dwell time. The thermal conductivity was

calculated from the relation $\kappa = \rho D C_P$. Here, ρ is the density of the sample, D is the thermal diffusivity of the sample which is measured on a LFA457 laser flash apparatus, and C_P is the heat capacity.

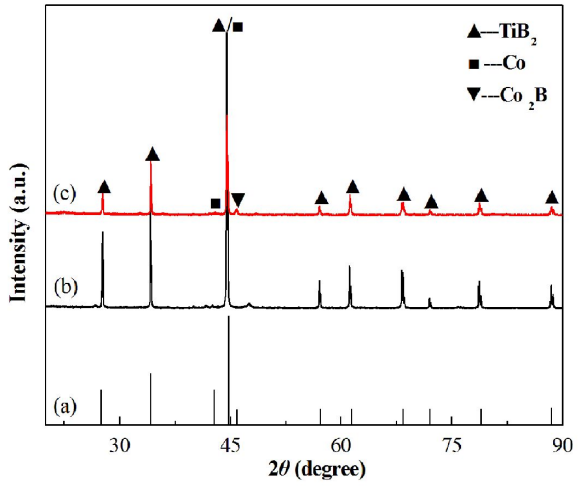

Fig. 3. XRD patterns of the TiB_2 ceramics with Co (10.0 wt.%) sintering aid: (a) standard pattern, (b) before sintering, and (c) after sintering.

3. Results and discussion

3.1. Phase composition

XRD patterns of the TiB_2 ceramics with Co before and after sintering are shown in Fig. 3. It can be seen that TB_2, Co and cobalt boride Co_2B were detected in the sintered samples. According to the previous literature [6, 9], boride ceramics sintered with metal sintering aid reacted with each other and produced a new compound of intermediate phase. The new produced intermediate phase is usually brittle which has a negative impact on the mechanical and other properties. Here, the cobalt boride compound peaks could be indexed as the brittle Co_2B, which may be formed due to reaction of TiB_2 with Co. However, the peak of Co_2B is very weak, which indicates that its content is very low. Further, high pressure and rapid sintering within 20 min could suppress effectively the generation of brittle phase (Co_2B) in the TiB_2 ceramics.

3.2. Relative density and microstructure

Fig. 4 shows the relative density of TiB_2 ceramics sintered with 0 wt.% to 10.0 wt.% Co. It can be seen that, at 5.5 GPa and 1550 °C, pure TiB_2 without Co was sintered till it achieved a low relative density of 92.2 %. In contrast, under the same pressure and at the same temperature, the relative density of TiB_2 ceramics sintered with the Co sintering aid reached the maximum value of 98.1 %, quite near the density of the solid (nonporous) ceramics. Hence, the relative density after sintering with Co aid was higher than the one without Co. It is evident that the presence of Co can significantly improve the densification of the TiB_2 ceramics. Better densities were achieved with the relative density of 98.1 % and 98.0 % when the content of Co was 5.0 wt.% and 7.5 wt.%, respectively.

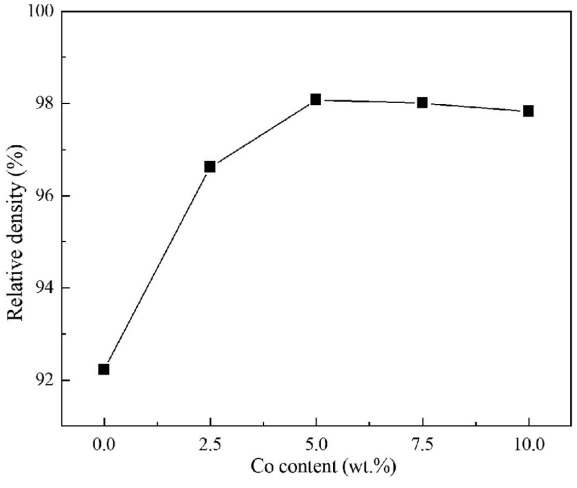

Fig. 4. Relative density of the TiB_2 ceramics with different Co contents.

Microstructure of ceramic materials significantly affects their mechanical properties. The microstructure of the sintered TiB_2 ceramics without Co sintering aid is shown in Fig. 5a. Plenty of pores tended to evenly distribute in the ceramics and resulted in the low relative density (92.2 %). The low relative density of TiB_2 ceramics with pores may have an effect on mechanical and other properties. Influence of Co content (from 2.5 wt.% to 10.0 wt.%) on TiB_2 microstructure was also experimentally monitored. As can be seen from Fig. 5b to Fig. 5e, the addition of Co changed the sinterability

and microstructure of the TiB_2 material. The pore dimension decreased and well distributed Co particles at the grain boundaries filled the interspaces between the grains. Meanwhile, the Co filled the pores resulting in the relative density increase up to 98.1 %. In addition, from Fig. 5f, it can be seen that the grain size of the final TiB_2 ceramics is about 2 μm to 3 μm, which is consistent with the raw material. Thus, if the TiB_2 ceramics with Co were sintered at 1550 °C, this sintering temperature was too low to result in the grain growth. In other words, the improvement in the ceramics density can be attributed to the application of rapid sintering for 20 min and low sintering temperature suppressing the grain growth.

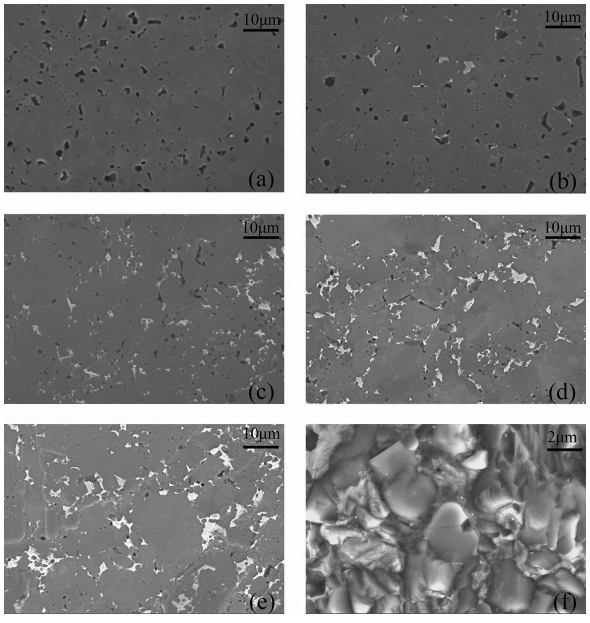

Fig. 5. SEM images of polished surfaces of the TiB_2 ceramics with different Co contents: (a) 0 wt.% of Co, (b) 2.5 wt.% of Co, (c) 5.0 wt.% of Co, (d) 7.5 wt.% of Co, (e) 10.0 wt.% of Co.

3.3. Vickers hardness

Vickers hardness is one of the tests conducted on materials. The Vickers hardness of TiB_2 ceramics samples vs. Co content (in wt.%) is shown in Fig. 6. According to the calculation formula, $Hv = 1.8544\frac{P}{d^2}$ [1], the Vickers hardness values of TiB_2 ceramics sintered with different Co content

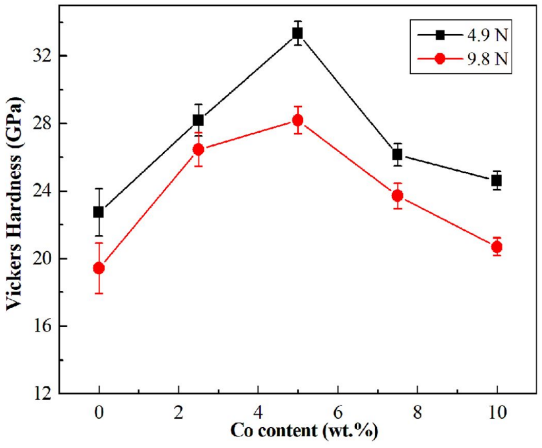

Fig. 6. Vickers hardness of the TiB_2 ceramics sintered with different Co contents at 5.5 GPa and 1550 °C.

at 5.5 GPa and 1550 °C range from 22.7 GPa to 33.3 GPa with the load of 4.9 N, while, 19.4 GPa to 28.2 GPa with the load of 9.8 N. Compared to the previous literature [6, 9], the Vickers hardness of TiB_2 ceramics sintered using Co as a sintering aid under high pressure condition is higher than for these ceramics sintered under pressureless or hot pressing conditions. The hardness measured in TiB_2 ceramics sintered without Co was low, and the values were 22.7 GPa and 19.4 GPa, with the loads of 4.9 N and 9.8 N, respectively. The relatively lower hardness could be caused by the massive residual porosity. However, the positive influence of Co sintering aid on the hardness can be seen and the maximum hardness values were up to 33.3 GPa and 28.2 GPa, with the loads of 4.9 N and 9.8 N, respectively. It can be deduced that, residual pore were filled with Co. The dense microstructure was the primary factor to improve the mechanical properties. In addition, high pressure method is beneficial to densification, and can lead to the increase of hardness. Furthermore, the hardness of the TiB_2 ceramics was reduced as the additive Co increased up to 10.0 wt.%. The reason could be the excess of Co which has lower hardness.

3.4. Thermal conductivity

The transport of heat energy through the bulk material depends on such parameters as density ρ,

thermal diffusivity D and heat capacity C_p. The reports on thermal conductivity of TiB_2 ceramics are rare. In our work, the thermal conductivity of the TiB_2 ceramics sintered with different Co contents at 5.5 GPa and 1550 °C ranged from about 77.3 $W \cdot m^{-1} \cdot K^{-1}$ to 88.9 $W \cdot m^{-1} \cdot K^{-1}$, which is shown in Fig. 7. The thermal conductivity of pure TiB_2 without Co was 77.3 $W \cdot m^{-1} \cdot K^{-1}$. As the Co weight fraction increased up to 5.0 wt.% the TiB_2 ceramics exhibits thermal conductivity of 88.9 $W \cdot m^{-1} \cdot K^{-1}$. The thermal conductivity of TiB_2 ceramics shows a slight decrease with an increase in Co doping from 5.0 wt.% to 10.0 wt.%. Many factors may affect the change in thermal conductivity. It can be explained as follows: the decrease in porosity, subsequently, the increase in relative density resulted in the thermal resistance increase with the Co content from 0 wt.%. to 5.0 wt.%. However, as the Co content increased and reached 10.0 wt.%, the quantity of brittle Co_2B phase increased and it distributed uniformly in the grain boundaries, which could raise thermal resistance. Then, the thermal conductivity of TiB_2 ceramics decreased.

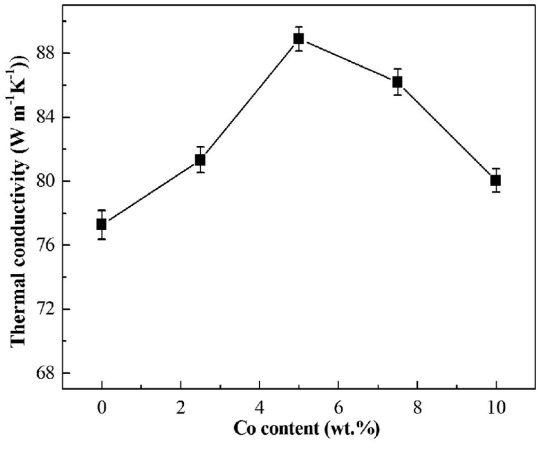

Fig. 7. Thermal conductivity of the TiB_2 ceramics sintered with different contents Co at 5.5 GPa and 1550 °C.

4. Conclusions

TiB_2 ceramics with different amounts of Co sintering aid were rapidly fabricated via high pressure method. High pressure method significantly improved the densification of the TiB_2 ceramics. It can be concluded that the hardness and thermal conductivity of the TiB_2 ceramics can be improved under high pressure conditions and by adding Co sintering aid. As the Co content increased, the hardness and thermal conductivity of TiB_2 ceramics first increased then decreased slightly, which could be caused by the change in the pore volume fraction, the generation of new phase (Co_2B) and the excess of Co.

Acknowledgements

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