Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 2253–2257

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Sintering process and high temperature stability investigation for nano-scale CaB_6 materials

Lin Zhang *, Guanghui Min, Huashun Yu, Hui Yu

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, PR China

Received 27 January 2010; received in revised form 2 February 2010; accepted 7 May 2010

Abstract

Calcium hexaboride (CaB_6) polycrystalline was prepared from its nano-scale powders using vacuum hot-pressing method under 1750 °C, 32 MPa for 5 min. SEM, FESEM and AFM were employed to observe morphology and compared with its bulk material sintered under 1550 °C. Observations showed the structure of the nano-scale CaB_6 bulk has the regions with high and low compactness degree due to CaB_6 nanometer powder aggregations. The hardness, bending strength and fractural toughness were 79.7 HRA, 198.7 MPa and 3.73 MPa $m^{1/2}$, respectively, better than those of CaB_6 micron-polycrystalline sintered under the same sintering parameters. DSC and TG were tested to investigate high temperature stability. Only one exothermic peak (1117.2 °C) appeared in nano-polycrystalline which began at 1080 °C and area was -167.7 J/g, showing its stability is much better than CaB_6 nano-micron composite polycrystalline and micron-polycrystalline.

Keywords: Calcium hexaboride; Nano-scale powder; Vacuum hot-pressing; Mechanical property; High temperature stability

1. Introduction

Calcium hexaboride (CaB_6) has very important values both in research and application due to its good combination of mechanical properties, chemical stability and unique physical properties [1–4], which show a potential application in advanced instruments industry. In order to further probe the natures of this material, the recent research focused on the physical properties of its ultrafined or nano-scale material. Superfine [5] and submicron CaB_6 cubic particles [6], CaB_6 nanowires [7,8] have already been synthesized. It was discovered that the physical properties such as magnetic performance and optical property [9] are different from its micron-powders, which highlighted the research significance of nano-scale CaB_6.

In this paper, the vacuum hot-pressing method was employed to prepare CaB_6 polycrystalline bulk from its nano-powders. The sinterability of nano-powders was analyzed and compared with CaB_6 micron-powders and its nano-micron composite powders. High temperature stability of polycrystalline bulk material was also tested and analyzed in this work.

2. Experimental procedure

Nanometer CaB_6 powders (average particle size 80 nm), micron-scale CaB_6 powders (average grain size 5 μm) were used as raw material in this study, which were prepared by ourselves (Boride Research Group of Shandong University, P. R. China). Their mixture powders were mingled by planetary high energy mill (model: QM-1SP(2L)) using carnelian balls as media for 10 h at a rotate speed of 380 rpm.

A high purity graphite mould whose inner diameter is Ø 40 mm was used to fill nano-scale CaB_6 powders and then was put into vacuum hot-pressing sintering furnace which working vacuum degree is 6.67×10^{-2} Pa. The powders were heated by high pure graphite heater at a rate of 16 °C/min to the schedule temperatures 1550 and 1750 °C. After 32 MPa pressure was brought to bear on powders for 5 min, the material was cooled with furnace. In order to compare the high temperature stability, the polycrystalline bulks of CaB_6 micron-powders and CaB_6 nano-micron composite (nanometer powders content was 10 wt.%) were pressed under the same parameters.

Crystal slicing machine was used to cut one polycrystalline bulk to five samples which size were 30 mm × 4 mm × 3 mm. The samples were polished by different sizes boroncarbide (B_4C) powders as abrasive. Atomic force microscope (AFM, model: AFM-IIa) and scanning electron microscope (SEM,

---

* Corresponding author. Tel.: +86 531 88395639; fax: +86 531 88395639.
E-mail address: zhanglin2007@sdu.edu.cn (L. Zhang).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.06.005

model: Hitachi S-2500) were used to examine microstructure. Field emission scanning electron microscope (FESEM, model: JSM-6700F) was employed to observe fractural morphology. Differential Scanning Calorimetry (DSC, model: Netzsch DSC404C) was used to analyze the oxidation behavior with elevated temperature.

The compactness degree was tested by pycnometer method according to Archimedes law. Hardness values were achieved by Rockwell hardness tester (model: HRS-150) with load 150 kgf and eight points of each sample were tested to get the mean value. Bending strength and fractural toughness were measured by portal type microcomputer control electron universal tester (model: CMT5105). All above mechanical properties data for one bulk measured from its five samples in order to reduce the experimental error.

3. Result and discussion

Fig. 1 showed the SEM images of CaB_6 polycrystalline bulk which were made of nanometer powders sintered at different temperature. A number of pores were observed in CaB_6 nano-scale polycrystalline at 1550 °C as shown in Fig. 1(a). The average size of the large pores was about 100 μm in length and 20 μm in width. Almost no nano-particles could be found in the large pores, and the pores became smaller in dense area. The high magnification observation showed the polycrystalline still has the powder-like morphology, which indicated that sintering has not fully completed at 1550 °C.

The microstructure of CaB_6 nano-scale polycrystalline changed significantly when the temperature increased to 1750 °C. SEM observation (Fig. 1(b)) showed the microstructure consisted of the regions with high and low compactness degree. With the elevation of sintering temperature, the edges circularization of pores occurred due to the diffusion of atoms. From Fig. 1(c), the large pores left in samples sintered at 1550 °C were divided by neck growth and tangled into network-like structure. And it was obvious that the tiny pores in dense area closed and shrank, so the densification microstructure achieved eventually as shown in Fig. 1(d).

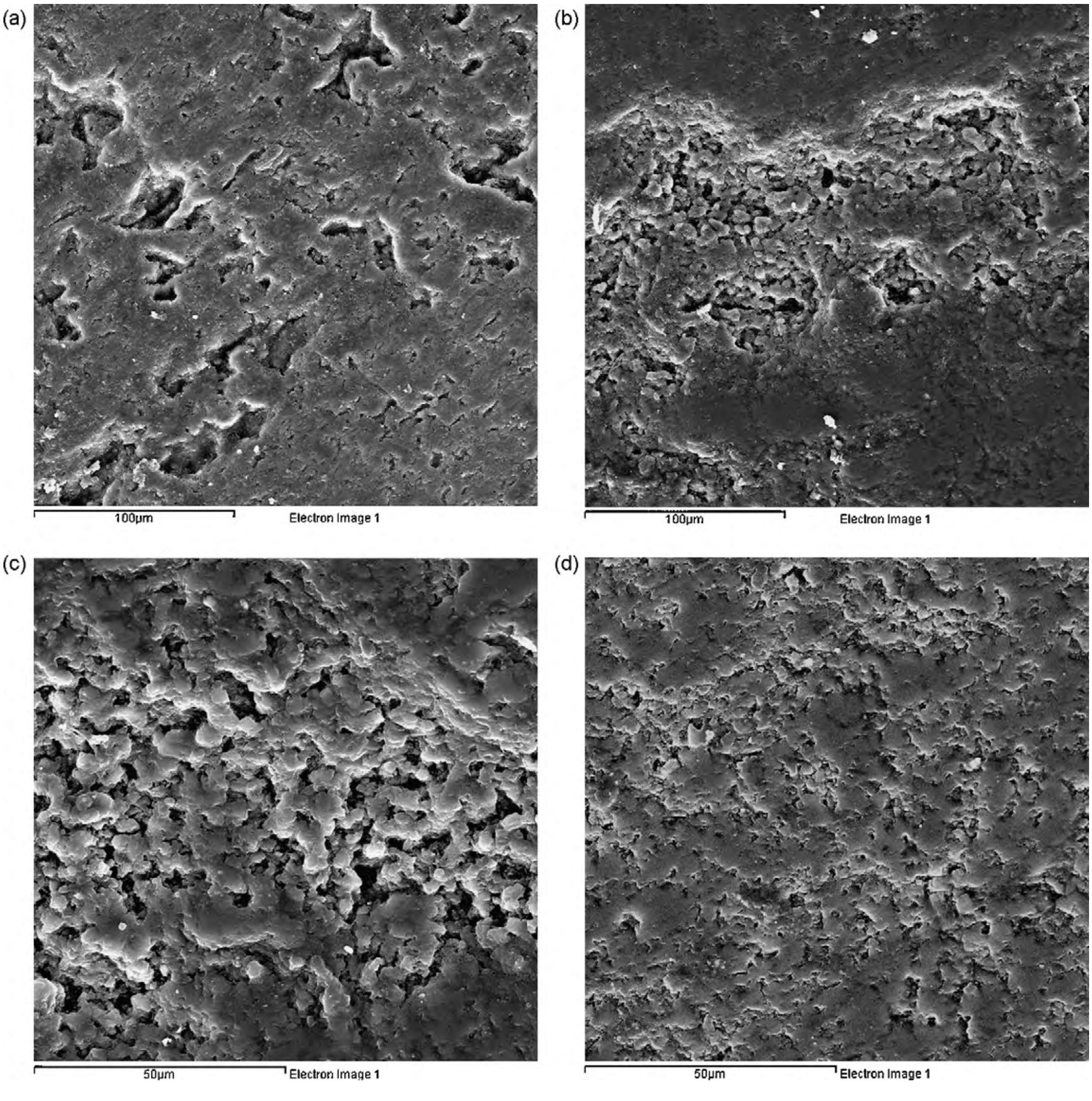

Fig. 1. SEM of morphologies of CaB_6 polycrystalline made of nanometer powders sintered under different temperatures: (a) 1550 °C, (b)–(d) 1750 °C.

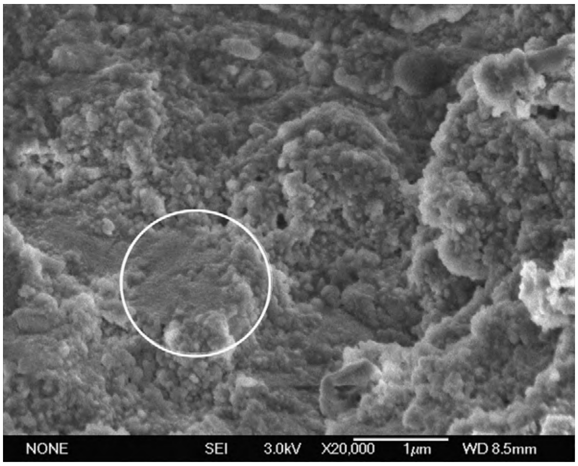

Fig. 2. FESEM observation to fracture surfaces of CaB_6 nano-scale polycrystalline sintered under 1750 °C.

Due to having large specific area, agglomerates were inevitable in nano-powders. At initial and middle stages of sintering [10], firstly, the interior agglomerate particles densified as well as pores eliminated, which resulted in the big pores grew up in the boundaries of agglomerates. Surface diffusion played a predominant role during this processing. There was no remarkable shrink densification of billet. With the sintering developing, the grains turned coarse in dense area, and the shrinkage of large pores would be introduced by compressive stress from dense area, which led to densification finally.

Fig. 2 showed FESEM observation to fracture surface of CaB_6 polycrystalline sintered from nano-scale powders at 1750 °C, which indicated that the fracture mode is intergranular type. The morphology of nano-scale grains was obvious in addition to the circle part marked in the image, where partial particles melted together. AFM two-dimensional and corresponding three-dimensional images of CaB_6 nano-scale polycrystalline at 1750 °C (Fig. 3) confirmed the above result. There was no abnormal grain growth resulting from nano-CaB_6 powders sintered at 1750 °C, but the corresponding three-dimensional image has large bump areas of local peaks which meant grains fusion took place.

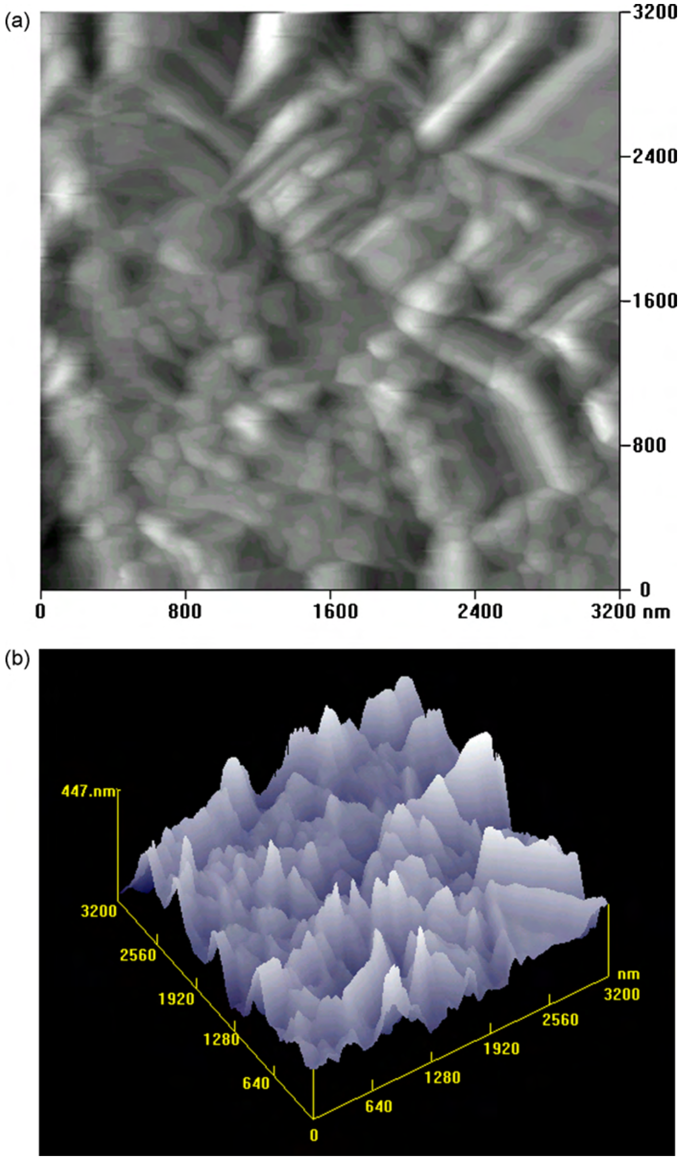

Fig. 3. AFM two-dimensional (a) and corresponding three-dimensional (b) pictures of CaB_6 nano-scale polycrystalline sintered under 1750 °C.

Table 1 provided the hot-pressing parameters and mechanical properties of sintered CaB_6 polycrystallines made from nano-powders, micron-powders and composite powders. For samples sintered by CaB_6 nano-powders, as sintering temperature increasing from 1550 to 1750 °C, the densification of polycrystalline improved from 86.2 to 92.1%. The volume fraction of pores decreased sharply. At the same time, the resulting Rockwell hardness, bending strength and fractural toughness of the specimen increased as well. Hardness and fractural toughness increased from 73.4 HRA, 3.23 MPa $m^{1/2}$ to 79.7 HRA, 3.73 MPa $m^{1/2}$, respectively. Especially, sintering

Table 1
Hot-pressing parameters and the mechanical properties of sintered CaB_6 polycrystallines.

No.	Temperature (°C)	Pressure (MPa)	Densification (%)	Rockwell hardness (HRA)	Bending strength (MPa)	Fractural toughness (MPa $m^{1/2}$)
1	1550	32	86.2	73.4	80.81	3.23
2	1750	32	92.1	79.7	198.7	3.73
3[a]	1750	32	90.2	83.6	167.3	2.80
4[a]	1750	32	93.2	92.6	331.7	3.06

Note: Bulk No. 1 and 2 were CaB_6 polycrystalline sintered from nano-scale powders, while No. 3 was from micron-scale powders and No. 4 was sintered from CaB_6 nano/micron composite powders containing 10 wt.% nano-powders.

[a] Data from Ref. [11].

temperature had significant influence on bending strength. For instance, the bending strength of CaB_6 polycrystalline sintered at 1750 °C was elevated to 198.7 MPa, almost 145% increase obtained compared with that of the nano-polycrystalline sintered at 1550 °C, whose value was only 80.81 MPa.

According to Fig. 1, the pores of sintered polycrystalline were large at 1550 °C and had not particles inside, which reduced the mechanical properties dramatically. However, the particles could contact each other resulting in circularization and close of pores, thus the large pores were separated to small agglomerate pores at 1750 °C, which was beneficial to bending strength. Due to fine-grained materials with large percentage of grain boundaries, the path of crack proportion was not straight (Fig. 2). The finer the grains were, the longer the distance used. Furthermore, due to the small size of initial crack, the critical stress enhanced, for the crack size was equivalent to the finer grain size of polycrystalline materials. Thus, fractural toughness of the bulk from nano-scale CaB_6 powders at 1750 °C, 32 MPa were better than those of the bulk from micron-scale CaB_6 and nano-micron composite containing 10% nano-powders under the same hot-pressing parameters circumstance [11]. The values were increased by 33.2 and 21.9%, respectively (as seen in Table 1).

DSC technique was used to study the thermal effects from room temperature to 1300 °C of CaB_6 polycrystalline sintered at 1750 °C, 32 MPa from nano-scale powders, the heating rate was 10 °C/min. No protection gas was used in order to simulate the actual oxidizing environment. Fig. 4 was the DSC results of nano-scale, micron-scale as well as nano-micron composite CaB_6 polycrystallines.

As shown in Fig. 4, a couple of exothermic peaks (1055.0 and 1122.2 °C) appeared in micron-scale CaB_6 polycrystalline, whose areas were −112.25 and −311.4 J/g, respectively. This result agreed with two oxides (Ca–B–O and Ca–O) in sintered CaB_6 with additional Nickel as reported in Ref. [12]. However, only one peak (1117.2 °C) was found in nano-scale CaB_6 polycrystalline and the area of peak was −167.7 J/g. The DSC curve of nano-scale CaB_6 polycrystalline was similar with nano-micron composite CaB_6 polycrystalline (in which nano-powders weight ratio was 10%), which also had one exothermic peak in large area (−1061 J/g).

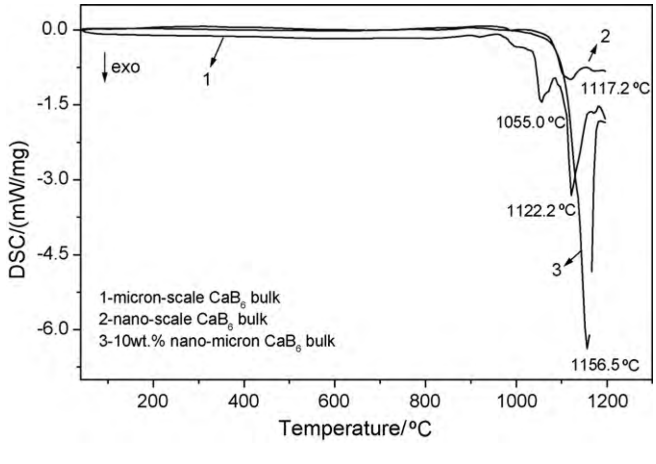

Fig. 4. DSC curves of the CaB_6 polycrystalline samples prepared under 1750 °C and 32 MPa for 5 min.

Although the exothermic peak position of nano-scale CaB_6 polycrystalline (1117.2 °C) was ahead of that of nano-micron composite polycrystalline (1156.5 °C), both of their exothermic peaks started at about 1080 °C. The area of exothermic peak in nano-scale CaB_6 was much smaller than the others, which indicated that the high temperature stability of nano-scale CaB_6 bulk materials was the best. The microstructure of nano-scale CaB_6 polycrystalline had high and low compactness degree regions, and grains in high dense area contacted closely which made the diffusion of oxygen atoms along the grain boundary become difficult. Thus, the antioxidation ability was improved finally. In the nano-micron composite polycrystalline, the nanometer particles filled in the boundaries of micron-scale particles, so the surface of composite polycrystalline became more compact to prevent the diffusion of oxygen atoms.

4. Conclusions

(1) CaB_6 polycrystalline bulk was successfully prepared using hot-pressing method at 1750 °C, 32 MPa for 5 min in vacuum. The microstructure of nano-scale CaB_6 has the regions with high and low compactness degree. No abnormal grain growth was observed, but some partial particles melted together.

(2) The densification, hardness, bending strength and fracture toughness were 92.1, 79.7 HRA, 198.7 MPa and 3.73 MPa $m^{1/2}$, respectively. These properties were better than those of CaB_6 micron-scale polycrystalline. The fracture mode was intergranular type.

(3) The high temperature stability of nano-scale CaB_6 polycrystalline was much better than that of nano-micron CaB_6 composite polycrystalline and micron-scale polycrystalline. The nano-scale CaB_6 polycrystalline oxidized began at 1080 °C. Only one exothermic peak appeared (1117.2 °C) and its area was −167.7 J/g.

Acknowledgements

This research was supported by China Postdoctoral Science Foundation Funded project (no. 20090461202) and Key Project of the Natural Science Foundation of Shandong Province, China (no. Z2007F09).

References

[1] C. Hotta, M. Ogata, H. Fukuyama, Ferromagnetism in CaB_6, Journal of Physics and Chemistry of Solids 63 (2002) 1505–1509.

[2] R. Monnier, B. Delley, Point defects, ferromagnetism, and transport in calcium hexaboride, Physical Review Letters 87 (15) (2001) 1572041–1572044.

[3] Z.H. Dou, T.A. Zhang, C. Hou, S.X. Xu, H. Yang, H. Li, Elementary research on CaB_6 prepared by SHS, The Chinese Journal of Nonferrous Metals 14 (2) (2004) 322–326.

[4] M. Song, I.S. Yang, J.Y. Kim, B.K. Cho, Raman scattering study of calcium hexaboride, Vibrational Spectroscopy 42 (2006) 288–291.

[5] L. Zhang, G.H. Min, H.S. Yu, Reaction mechanism and size control of CaB_6 micron powder synthesized by the boroncarbide method, Ceramics International 35 (2009) 3533–3536.

[6] L. Shi, Y.L. Gu, L.Y. Chen, Low temperature synthesis and characterization of cubic CaB_6 ultrafine powders, Chemistry Letters 32 (10) (2003) 958–959.

[7] J.Q. Xu, Y.M. Zhao, C.Y. Zou, Q.W. Ding, Self-catalyst growth of single-crystalline CaB_6 nanostructures, Journal of Solid State Chemistry 180 (9) (2007) 2577–2580.

[8] T.T. Xu, J.G. Zheng, A.W. Nicholls, Single-crystal calcium hexaboride nanowires: synthesis and characterization, Nano Letters 4 (10) (2004) 2051–2055.

[9] L. Zhang, Synthesis, microstructure and properties of submicron and nanosized CaB_6 materials, PhD Dissertation, 2007.

[10] R.L. Coble, Sintering crystalline solids. I. Intermediate and final state diffusion models, Journal of Applied Physics 32 (5) (1961) 787–792.

[11] L. Zhang, G.H. Min, H.S. Yu, Morphology characteristics and mechanical properties of nano/micron calcium hexaboride sintered body, Journal of Inorganic Materials 25 (1) (2010) 87–90.

[12] L. Zhang, G.H. Min, L.X. Yang, High temperature oxidation of CaB_6–28 wt% Ni sintered body, International Journal of Modern Physics B 23 (6) (2009) 1166–1171.