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Ceramics International 31 (2005) 271–276

CERAMICS INTERNATIONAL

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Densification and mechanical properties of CaB_6 with nickel as a sintering aid

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Received 11 July 2003; received in revised form 25 February 2004; accepted 3 May 2004
Available online 3 August 2004

Abstract

The densification behavior and mechanical properties of CaB_6 with additions of nickel up to 35 wt.% were investigated. Sinterability was greatly improved by the addition of nickel. When 28 wt.% nickel was added, nearly full density was obtained. This improvement was attributed to the enhanced mobility of the melting of metals including the evaporated calcium or the formation of new phases in the Ca–B–Ni system at the grain boundaries. As a result of this improvement in the density, mechanical properties has been increased remarkably. Because of the elimination of pores, CaB_6 with 28 wt.% nickel has a maximum value of flexural strength and fracture toughness. The enhancement of the fracture toughness was due to a mixed mode of intergranular and transgranular fracture with a distinct step-cleavage pattern.

Keywords: C. Mechanical properties; Calcium boride; Densification

1. Introduction

Because of their strong bonds between the boron atoms, borides are particularly promising. They are characterized by high melting-point, high hardness, high chemical stability, high resistance to oxidation and wear and so on. All of these outstanding properties make it widely used in modern aircraft, parts of rocket engines and various other structures at high temperature [1].

Because their strong covalent B–B bonds inhibit diffusion, the production of refractory boride powders by hot-pressing and vacuum sintering is very difficult [2]. Up to now, calcium hexaboride polycrystalline has been made either under high pressure (3–5 GPa) [3] or at high temperature (2000–2200 °C) [4] in order to obtain high or full density bodies. These production methods impose a high demand on equipment and moulds, which increase production costs.

For certain purposes, it is desirable to produce a material with a density that is as high as possible, and at temperature that is as low as possible. Nonoxide ceramics such as TiB_2 have been found to be effective as sintering aid for CaB_6. However, either large amounts of second phase, or extremely high sintering temperatures are required for further densification and improvement of strength. Up to now, there have been a limited number of studies using metal, especially in large amounts, as sintering aids.

In the present study, the effect of nickel addition on the densification behavior of CaB_6 has been investigated. Mechanical properties, such as hardness, flexural strength and fracture toughness of CaB_6 have been measured and correlated with the variation in composition of the body.

2. Experimental procedure

The CaB_6 powder prepared by carbonboride method was ball-milled for 16 h. The average size and specific surface area of the CaB_6 powder were 14.73 μm and 0.68 m^2/g, respectively. The particle size distribution is illustrated in Fig. 1. Up to 35 wt.%, nickel was added as a sintering aid.

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0272-8842/$30.00
doi:10.1016/j.ceramint.2004.05.014

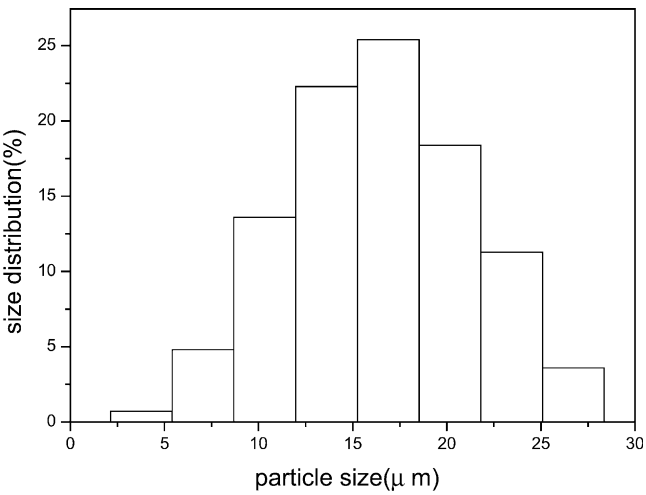

Fig. 1. Particle size distribution of the used CaB_6 powder.

Powder mixtures were hot-pressed in a 40 mm inner diameter circular graphite die for 1.5 h at 1750 °C under 32 MPa in a high vacuum. Nickel additions up to 20 wt.% was used. Considering the fast flow of the large amount of nickel, CaB_6 powder with 28 and 35 wt.% nickel was hot-pressed at 1650 °C under 32 MPa. The temperature was monitored by an optical pyrometer, which was calibrated using a thermocouple. The heating and cooling rates were 16 °C/min and furnace cooling, respectively.

All surfaces of sintered material were polished and the microstructure of the sintered sample and fractured surfaces were analyzed by scanning electron microscopy (JXA-840). Energy dispersive analysis of X-ray (EDAX) was used to detect nickel in the sintered matrix.

Hardness was measured on the polished surfaces using Rockwell apparatus. Four indentations were made for each preparation using 306 N loads. For bending strength testing, samples were cut and ground with dimensions of 4 mm × 3 mm × 30 mm. Bending strength was carried out by a three-point-bending with a crosshead speed of 0.5 mm/min and a span of 20 mm. The three-point single edge notched beam method (SENB) was used for evaluation of fracture toughness with 0.05 mm/min crosshead speed of and span of 20 mm. The dimensions of the fracture toughness samples were 4 mm × 2 mm × 30 mm, and a notch was cut with 0.2 mm in width and 1.5 mm in depth.

3. Results and discussion

The sintering behavior and microstructure of CaB_6 are changed markedly by the addition of nickel. The effect of nickel addition on the densification is illustrated by the SEM photographs in Fig. 2 Incomplete densification of the pure CaB_6 specimen hot-pressed at 1750 °C for 1.5 h is clearly seen in Fig. 2(a). With the addition of 20 wt.% nickel the specimen shows a significantly improved densification, as

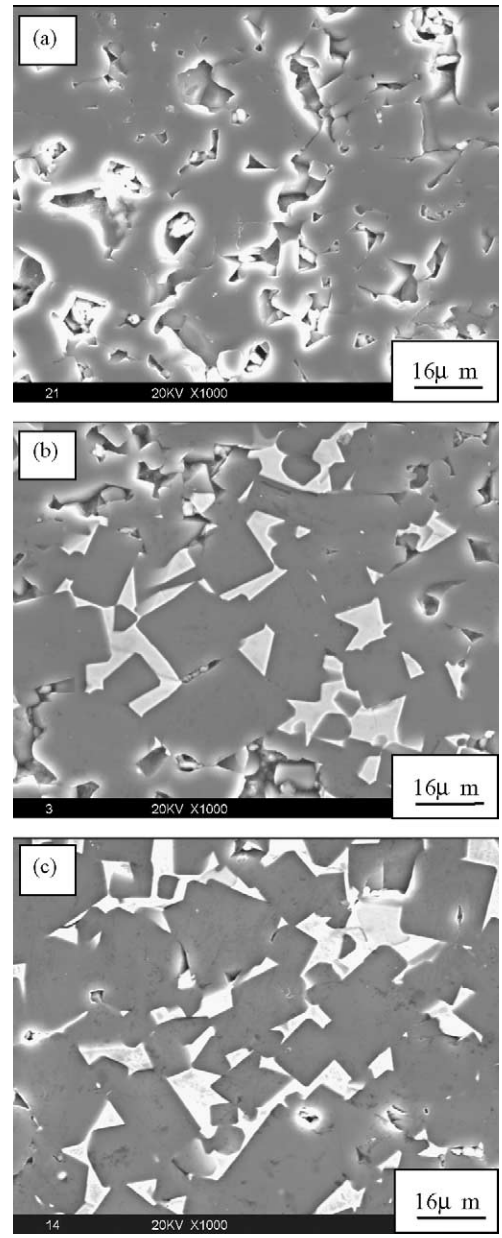

Fig. 2. SEM photographs of CaB_6 specimens hot-pressed at 1750 °C (a); CaB_6 with 20 wt.% nickel hot-pressed at 1750 °C (b) and CaB_6 with 28 wt.% nickel hot-pressed at 1650 °C (c).

shown in Fig. 2(b). When 28 wt.% nickel was added, nearly full density was obtained, although the temperature is 100 °C lower.

It has been previously reported that above 1300 °C, atomic calcium enters the vapor–gas phase at high vacuum [5]. In this case, the elements in the second phases area were detected using EDAX, and nickel, cobalt, calcium and iron were found as is shown in Fig. 3 and the contents of these elements were illustrated in Table 1. Cobalt and iron were the impurity in the nickel powder. And accordingly, calcium was formed due to the evaporation of CaB_6 at high temperature. However, there was a great difference of calcium

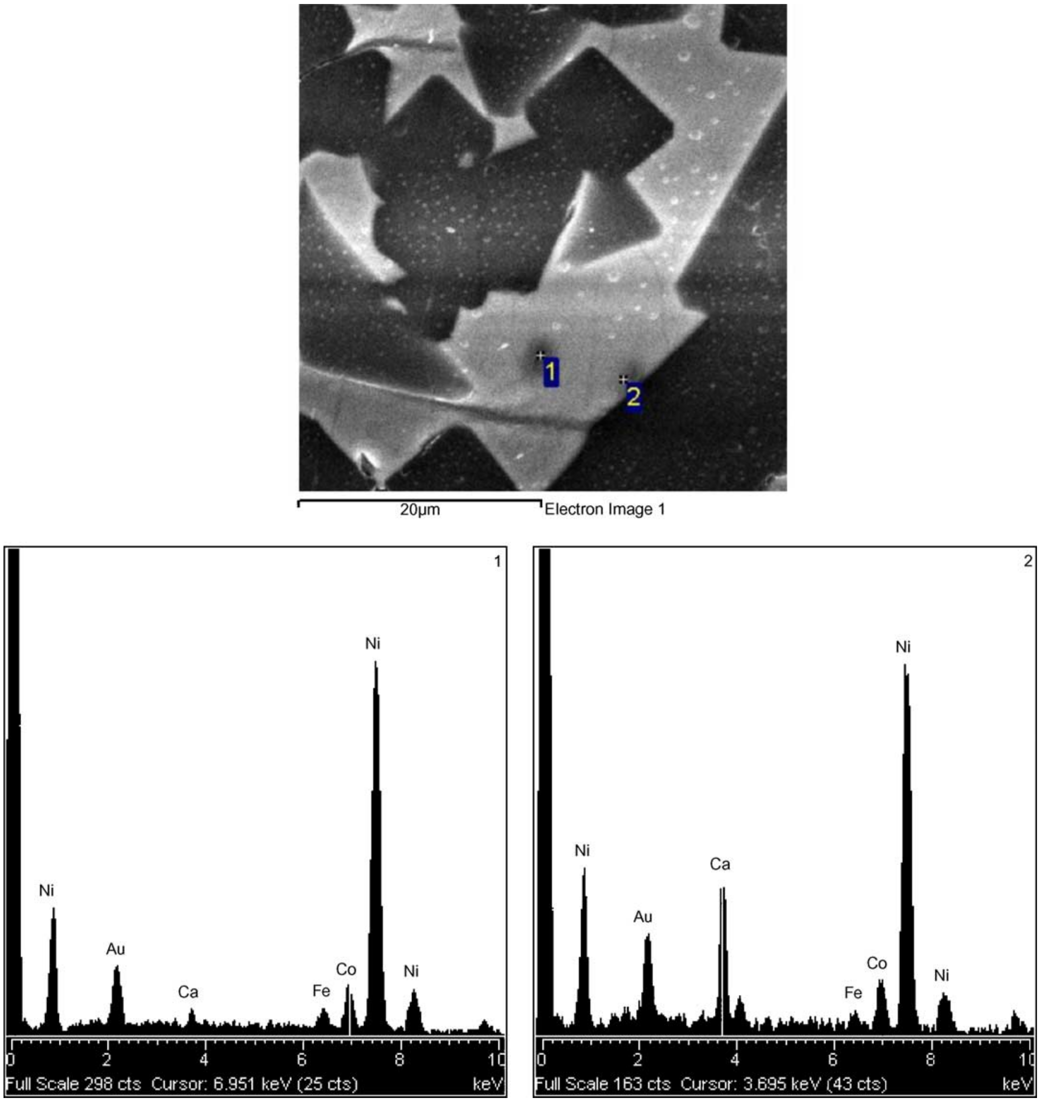

Fig. 3. EDAX profiles of second phase in CaB_6 with 35 wt.% nickel hot-pressed at 1650 °C.

content in the point 1 and 2, which further confirmed the evaporation of calcium from the boundary to the center of the rich-nickel areas. Previous studies showed that chemical reactions could occur in the Ca–B–Ni system [6]. Even though boron was not detected due to detection limitations, the evaporation of calcium resulted in the production of free boron. A possible reaction among calcium, boron and nickel at such high temperature was deemed to have occurred. The improved sinterability, therefore, was attributable to the melting of the metals in the grain boundaries and the formation of new phases [6]. In general, as we can see from the microstructure, under the current circumstances (high temperature and pressure), the metals melted and penetrated into the corner of CaB_6 particles, which to some extent resembled the morphology of CaB_6 powder.

Table 1
Second phase element analysis results in CaB_6 with 35 wt.% nickel hot-pressed at 1650 °C

Element	Weight (%)	Atomic (%)
Point 1		
Ca	1.27	1.85
Fe	2.16	2.26
Co	8.90	8.81
Ni	87.66	87.08
Point 2		
Ca	10.99	15.32
Fe	1.53	1.53
Co	8.78	8.32
Ni	78.69	74.83

As a result of the improved density, the hardness of CaB_6 was clearly enhanced. The effect of nickel addition on hardness of CaB_6 is shown in Fig. 4. With the increasing amount of nickel, the hardness values were gradually enhanced up to 20 wt.% nickel. These increases were presumably due to the decrease in porosity. The hardness decrease of the specimen with 28 and 35 wt.% nickel was

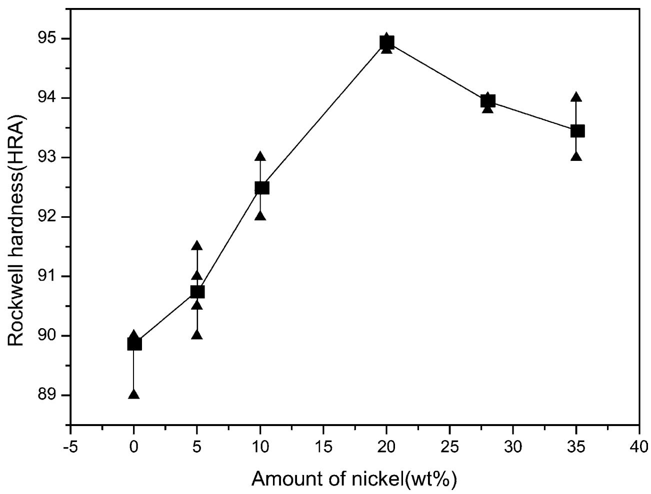

Fig. 4. Effect of nickel additions on the hardness of CaB_6.

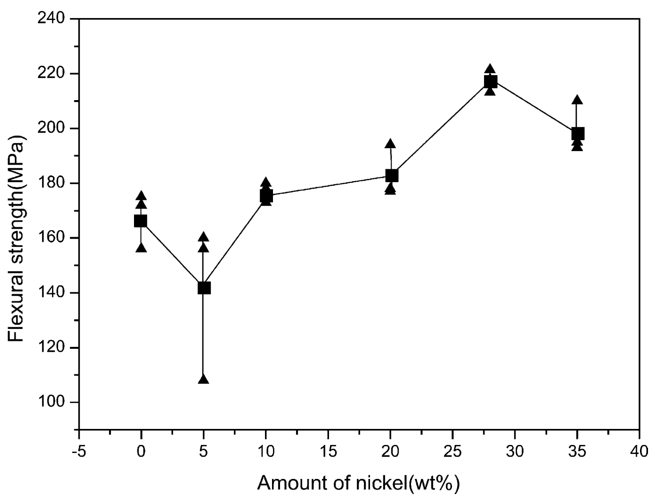

Fig. 5. Flexural strength of CaB_6 with different amounts of nickel.

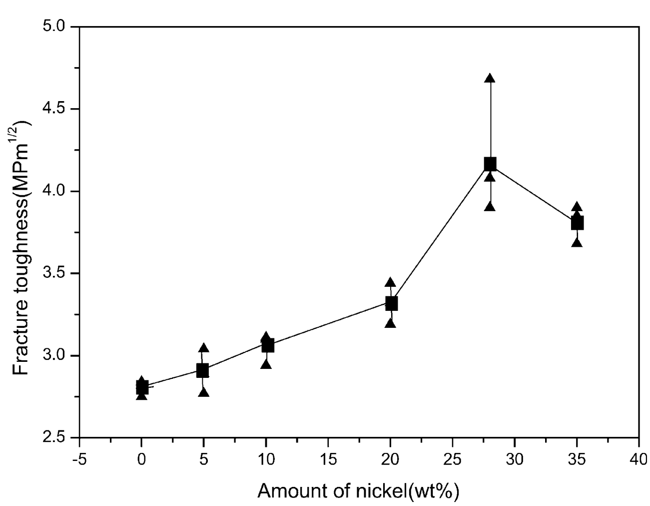

Fig. 6. Fracture toughness of CaB_6 with different amounts of nickel.

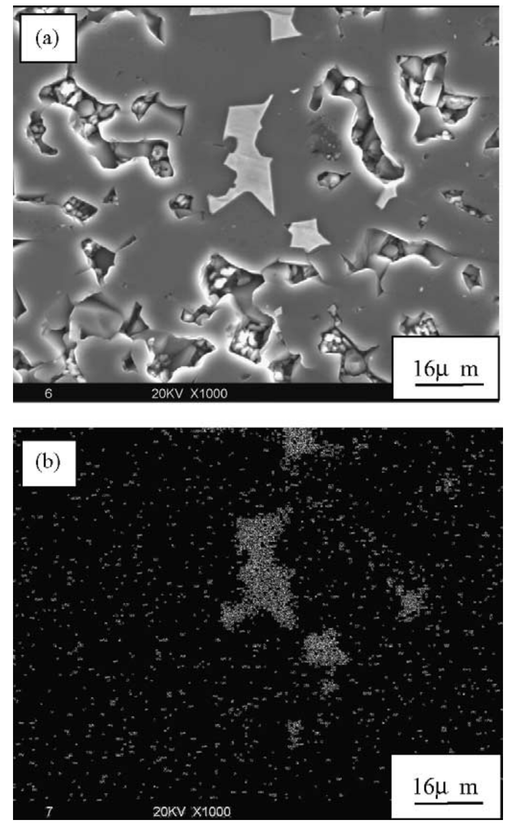

Fig. 7. SEM photograph of CaB_6 with 5 wt.% nickel specimens hot-pressed at 1750 °C (a) and nickel distribution (b).

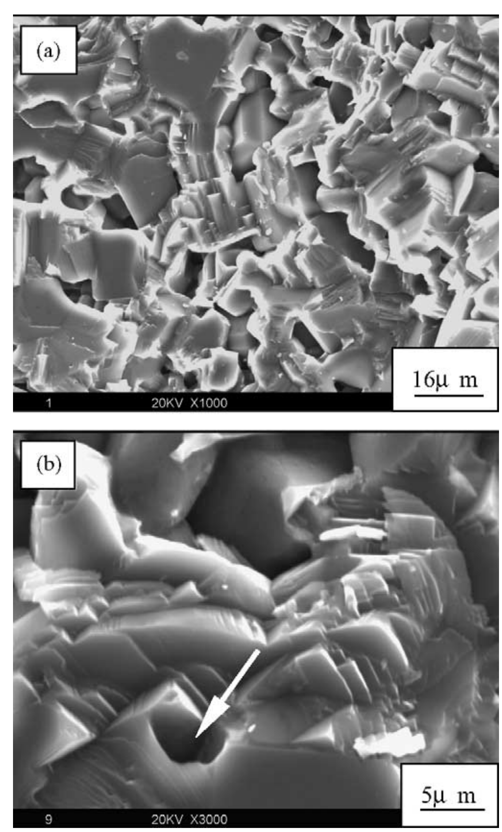

Fig. 8. Fracture surfaces of pure CaB_6 specimens hot-pressed at 1750 °C.

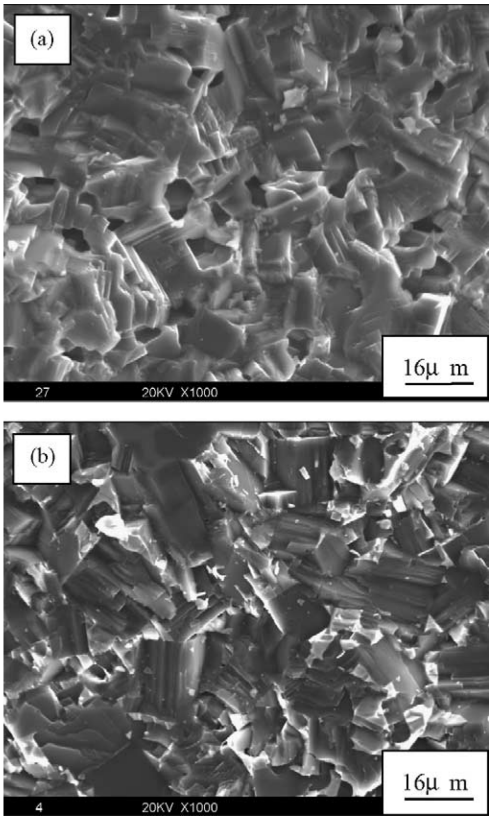

Fig. 9. Fracture surfaces of hot-pressed specimens CaB_6 with 10 wt.% nickel (a) and CaB_6 with 28 wt.% nickel (b).

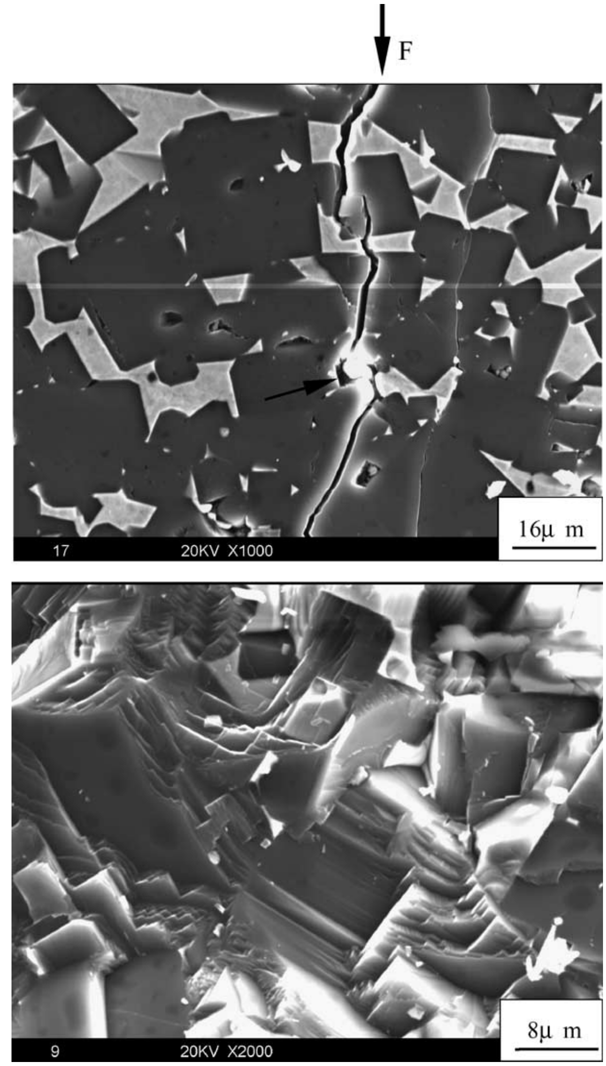

Fig. 10. Crack propagation in CaB_6 with 35 wt.% nickel (a) and fracture surfaces of hot-pressed specimens CaB_6 with 35 wt.% nickel (b).

deemed to be controlled by the rule of mixtures. When the porosity has been controlled to a limited degree, the comparatively soft nickel can lower the hardness of CaB_6.

The addition of nickel also had great effect on the flexural strength and the fracture toughness of CaB_6, as illustrated in Fig. 5 and Fig. 6. The specimen with 5 wt.% nickel has the lowest strength value in these materials, although its relative density is slightly higher than that of the pure CaB_6. The SEM photograph of this specimen is shown in Fig. 7(a). On the nickel distribution photograph, it's clear that the small amount of nickel was randomly filled in grain boundaries. So the inhomogeneity of nickel is partially responsible for the poor property.

When 28 wt.% nickel was added, the highest strength was obtained, which was apparently due to the reduction in the number and size of many pores acting as fracture origin. However, the strength decreased slightly with further nickel addition.

Different from the flexural strength, the fracture toughness increased steadily with the addition of nickel up to 28%, which has reached a top value in Fig. 6. The predominant reason is that the addition of nickel greatly decreased the number and size of the pores.

Fig. 8 shows the fracture surfaces of CaB_6 polycrystalline. It is worth emphasizing that the fracture mode of CaB_6 polycrystalline was a mix of intergranular and transgranular type. As shown in Fig. 8(b), the regular pore is considered to be due to the pull-out of a small particle. The fracture surfaces of CaB_6 with 10 and 28 wt.% nickel specimen are shown in Fig. 9. As a consequence of nickel addition, the specimens were clearly densified. As for CaB_6 with 28 wt.% nickel sintered specimens, the fracture routes are more complex and the ratio of transgranular to intergranular type is enhanced. The existence of terraces and steps makes the fracture area increase, which results in a high fracture energy and hence a high fracture toughness.

In order to make clear investigation of fracture mode, the Vickers indenter was used to make an indentation on the surface of CaB_6 with 35 wt.% nickel under the pressure of 306 N. The load direction was indicated in Fig. 10. It was noted that the crack passed through the nickel area and the path was not so straight. As the arrow indicated, the pore has been the fracture origin, the crack was propagated along the pore and formed the intergranular fracture failure. Combined with Fig. 10(b), the main fracture mode was transgranular, and the particle was severely laniated. In some areas, there were serrated edges, which was the result of the intense integrity between two particles. The transgranular fracture surface is distinct with step-cleavage pattern, which is a significant contribution to the improvement of fracture toughness.

4. Conclusions

The sinterability and mechanical properties of CaB_6 with additions of nickel up to 35 wt.% were investigated. When 28 wt.% nickel was added, nearly full density was obtained at 1650 °C under 32 MPa.The improvement in sinterability was attributed to the enhanced mobility of the metals including the evaporated calcium or the formation of new phases in the Ca–B–Ni system at the grain boundaries.

Flexural strength and fracture toughness had their top values with 28 wt.% nickel. When the amount of nickel was 5 wt.%, the flexural strength was the lowest partially because of the inhomogeneity of small amount of nickel.

The enhancement of the fracture toughness was due to the mixture mode of intergranular and transgranular type with a distinct step-cleavage pattern. With the addition of nickel, the fracture routes become more complex and the proportion of transgranular fracture increased.

Acknowledgement

This research was jointly supported by Shandong Outstanding Young Scientist Foundation (2000) and Shandong High Technology Foundation (GXB991).

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