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The effects of rare-earth oxide additives on the densification of pressureless sintering B_4C ceramics

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Abstract

Boron carbide ceramics used as neutron absorbing materials in fast breeder reactor were fabricated with boron carbide powders and different rare-earth oxide additives by pressureless sintering. The effects of rare-earth oxide as well as phenolic resin on densities and mechanical properties of the composites were studied. The addition of Dy_2O_3, Eu_2O_3, and Sm_2O_3 was found to be beneficial in the densification of B_4C ceramics. B_4C with 4 wt% rare-earth oxide and 18 wt% phenolic resin, exhibiting bulk density of 90–96% T.D., flexural strength of 276–358 MPa, could be prepared by pressureless sintering at 1960–2080 °C, which are capable of meeting the requirement of fast breeder reactor.

Keywords: A. Sintering; C. Mechanical properties; E. Nuclear applications; B_4C

1. Introduction

Boron carbide is a promising material used as the neutron absorbing material of control rods in nuclear reactors, because of its superior properties such as large neutron absorption cross-sections through the $^{10}B\ (n,\alpha)^7Li$ reaction for a wide energy range of neutrons, high melting temperature, light weight, low neutron induced radioactivity, chemical stability and refractory character [1–3].

However, the application of B_4C ceramics is restricted by its low strength and fracture toughness as well as poor sinterability [4]. Due to the presence of very strong covalent bonds, the high resistance to grain boundary sliding and absence of plasticity, densification of stoichiometric boron carbide is extremely difficult. Many efforts have been made to improve the densification of B_4C by introducing sintering aids including metals (Al [5], Si [6] and Ti [7]), oxides (Al_2O_3 [8], TiO_2 [7] and ZrO_2 [9]), carbides (SiC [10], TiC [11]), borides (TiB_2 [12]) and C [13].

Rare-earth oxides have been reported to be excellent sintering aids in ceramics. Goldstein et al. [14] prepared B_4C/metal boride composites using Y_2O_3, La_2O_3 as sintering aids; such composites exhibit a sintering aptitude higher than that of monolithic B_4C ceramic. Taking into account that some rare-earth elements are characterized by huge neutron absorption cross-sections (e.g. Promethium, Samarium, Europium, Gadolinium, and Dysprosium) [15], the superiority of rare-earth oxides as sintering aids in boron carbide may not only accelerate the densification, but also enhance the neutron absorption properties in nuclear applications.

In the present work, the effects of rare-earth oxides as well as phenolic resin on the sintering behavior and mechanical properties of B_4C ceramics were investigated using commercially available B_4C powders. The microstructure and mechanical properties of specimens were examined.

2. Experimental

Commercially available B_4C powder (W1.5, Mudanjiang Boron Carbide Co. PR China) was used as received. The powder has a B:C ratio of ~3.9, an average particles size

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of 1.6 μm and an oxygen content of 1.7 wt%. The additives used in this work were Dy_2O_3, Eu_2O_3, Sm_2O_3 and phenolic resin. The sources of rare-earth oxide were micron high purity (99.9%) powders supplied by Beijing Founde Star Co. The phenolic resin (PF-2123) was supplied by Jinan Shengquan Co.

The powders of Dy_2O_3, Eu_2O_3, and Sm_2O_3 were added to B_4C powder respectively, to give 0–8 wt% additive mixtures. The addition of phenolic resin was 18 wt%. The mixed powders were processed with media made up of high-purity B_4C balls and methanol for 24 h by ball milling. Green specimens were formed via cold isostatic pressing (120 MPa). Sintering was performed at 1960–2160 °C, under argon, in a graphite resistance furnace, with a 120 min dwell time for all the specimens studied.

The density of the sintered specimens was measured by the Archimedes' method and the relative density was then calculated by comparison with the theoretical density. The approximate theoretical density of each specimen is estimated by calculating the composition of each phase by the rule of mixtures based on the theoretical densities of boron carbide, graphite and other rare-earth. Phase composition of the ceramic bodies was determined by X-ray diffraction. A scanning electron microscope (SEM, ZEISS EVO-18) was used for the microstructural studies. The flexural strength was measured by the three-point bending test in a mechanical testing machine (INSTRON-5569).

3. Results and discussion

3.1. Densification behavior

Fig. 1 shows the relative densities of the B_4C ceramic specimens containing different sintering aids (Dy_2O_3, Sm_2O_3, and Eu_2O_3) sintered at 2160 °C. The contents of sintering aids are ranging from 0–8 wt%. It is shown that when the rare-earth oxides were added separately, the effect of Dy_2O_3 on the densification of B_4C ceramic is notable to a certain extent, relative density increases for Dy_2O_3 content up to 4 wt%, 78.5% of theoretical density is obtained, whereas, the addition of Sm_2O_3 and Eu_2O_3 are not so effective in enhancing the sinterability of B_4C.

Relative densities of specimens sintering at different temperatures with 18 wt% phenolic resin and 4 wt% rare-earth oxides are shown in Fig. 2. Compared with the low densities of the specimens in Fig. 1, it can be seen that carbon addition facilitated the densification process evidently. Relative density of 91.6% with specimen of 18 wt% phenolic resin sintered at 1960 °C could be achieved; moreover, the relative density increased to as high as 96% when sintered at 2160 °C.

Rare-earth additions are found to be excellent in lowering the sintering temperature. The relative density of specimen with Dy_2O_3 and phenolic resin sintering at 2040 °C is 96.6%, which achieves the similarly high relative density of specimen sintering at 2160 °C with only phenolic resin additive, indicating that the addition of Dy_2O_3 lowering the sintering temperature for about 120 °C. When the sintering temperature is increased, the relative density remained unchanged. The relative densities of the specimens with Eu_2O_3 and Sm_2O_3 increase with the increase of sintering temperature at the beginning. The optimal sintering temperature is observed to be 2080 °C and 2040 °C, with the relative densities of 96.3% and 96.0% respectively, which is also higher than that of specimens without rare-earth additives, showing that the addition of Eu_2O_3 and Sm_2O_3 is also beneficial for a higher densification rates. When the sintering temperature increased continually, the densities of the specimens with Eu_2O_3 and Sm_2O_3 decreased apparently.

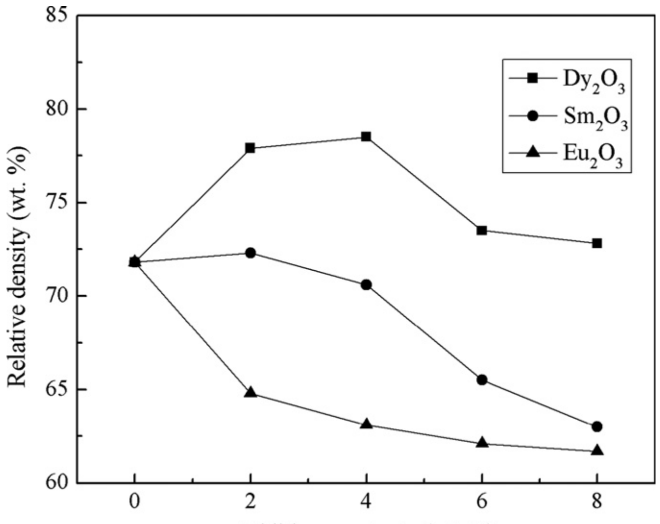

Fig. 1. Relative density of B_4C ceramics sintered at 2160 °C with different rare-earth oxides.

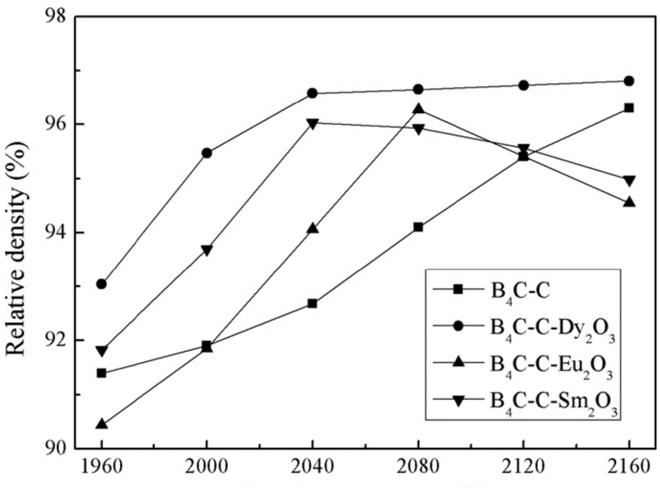

Fig. 2. Influence of different rare-earth oxides and phenolic resin on densification of B_4C ceramics.

3.2. Mechanical properties

The mechanical properties of the fabricated B_4C matrix ceramics are listed in Table 1. It is shown that the flexural strength of B_4C matrix ceramics increase obviously with the addition of rare-earth oxides. Specimens sintered at 1960 °C possess a lower strength due to its lower relative density (90–93%). The relative density of specimen without rare-earth additions sintered at 2160 °C is 96.2%, with a relatively low flexural strength of 234 MPa. While specimens with rare-earth additives sintered at 2040 °C or 2080 °C are able to achieve the similarly high relative densities, with flexural strength of more than 300 MPa (specimen BD: 358 MPa; specimen BE: 325 MPa; specimen BS: 303 MPa).

3.3. X-ray diffraction

X-ray diffraction patterns of selected sintered samples of B_4C with different additives are shown in Fig. 3. For pure B_4C (Fig. 3a), free carbon phase is detected besides B_4C phase. When Dy_2O_3 is added (Fig. 3b), no traces of Dy_2O_3 phase was found, while a new phase, DyB_4, is detected, which indicates that some B_4C might react with Dy_2O_3 to generate a boride. When phenolic resin is added (Fig. 3c), the phase composition is B_4C and carbon, similar to the situation in pure B_4C. In the specimen which Dy_2O_3 and phenolic resin are added together (Fig. 3d), four fundamental crystallographic phases are detected in the sintered samples: B_4C, DyB_2C_2, Dy_2C_3 and C, which mean that the rare-earth might react with B_4C and pyrolytic carbon. Compared with the results shown in Fig. 3b, it is considered that when rare-earth oxides and phenolic resin are added together, rare-earth oxides react with B_4C, resulting in the formation of rare-earth borides (DyB_4), and then the excessive amount of pyrolytic carbon involved in the reaction with rare-earth borides, generated DyB_2C_2 and Dy_2C_3 phase, thus the diffusion between B and C atoms was accelerated, which promote the densification of B_4C ceramics.

Table 1
Compositions, relative density and mechanical properties of B_4C matrix ceramics.

Specimen	Composition	Sintering temperature (°C)	Relative density (%)	Flexural strength (MPa)
BP	B_4C—18 wt% PF	1960	91.6	192 ± 9
		2160	96.2	234 ± 22
BD	B_4C—18 wt% PF—4 wt% Dy_2O_3	1960	93.1	287 ± 12
		2040	96.6	358 ± 6
BE	B_4C—18 wt% PF—4 wt% Eu_2O_3	1960	90.4	276 ± 17
		2080	96.3	325 ± 12
BS	B_4C—18 wt% PF—4 wt% Sm_2O_3	1960	91.8	284 ± 18
		2040	96.0	303 ± 20

3.4. Microstructure

The microstructures of the specimens with different sintering aids can be seen in Fig. 4. In the Fig. 4b, rare-earth particles appear as white spots due to the larger atomic weight compared to B and C. The fracture surface of monolithic B_4C was quite smooth (Fig. 4a), with a few pores dispersed in the matrix. However, the fracture surface of specimen with 4 wt% of Dy_2O_3 (Fig. 4b) was relative rough and rare-earth particles were dispersed in intergranular areas. It is also apparent that the grain size in these samples is smaller than that of the rare-earth additive-free samples, which indicates that the addition of rare-earth prohibit the grain growth of B_4C particles, resulting in enhanced mechanical properties of B_4C matrix ceramics.

4. Conclusions

B_4C matrix ceramics were fabricated by pressureless sintering B_4C powders, Dy_2O_3, Eu_2O_3, and Sm_2O_3, as well as phenolic resin. Introduction of rare-earth oxides and phenolic resin contributed to enhancement of densification rate and mechanical properties for B_4C matrix ceramics. For specimen with addition of 4 wt% rare-earth oxides and 18 wt% phenolic resin, the relative density of 90–96% and flexural strength of more than 300 MPa were obtained after sintering at 1960–2080 °C.

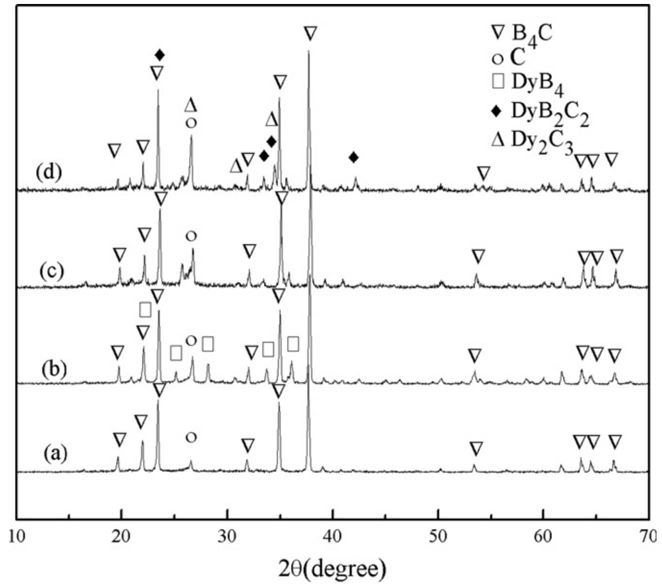

Fig. 3. XRD patterns of B_4C specimens: (a) pure B_4C; (b) B_4C—4 wt% Dy_2O_3; (c) B4C—18 wt% phenolic resin; and (d) B_4C—4 wt% Dy_2O_3—18 wt% phenolic resin.

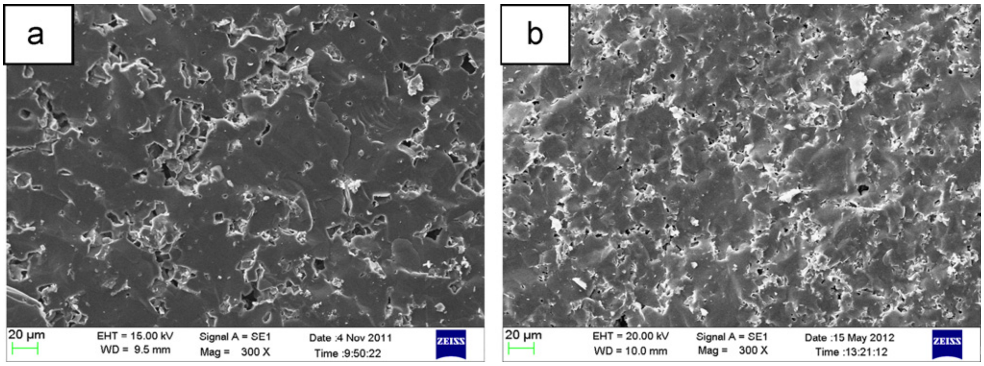

Fig. 4. Microstructures of specimen sintered at 2040 °C for 2 h: (a) B_4C with 18% phenolic resin; and (b) B_4C with 4 wt% of Dy_2O_3 and 18% phenolic resin.

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