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Fabrication and oxidation behavior of LaB_6–ZrB_2 composites

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Abstract

LaB_6–ZrB_2 eutectic composites were sintered by hot pressing. The oxidation behavior of LaB_6–ZrB_2 eutectic composites was studied in the temperature range of 600–1300 °C. It was shown that the sample weight increased with increasing oxidation temperature and prolonging holding time. The rate of weight change was described by $k_p = 6.24 \times 10^{-4} \exp(-38,940/RT)\ g^2/m^2\ s$, but it changed according to the change of oxidation time at 1200 °C. Weight gain was evident in less than 1 h, but it slowed down subsequently due to the evaporation of B_2O_3. The rate of weight change increased abruptly at 1300 °C. The oxidation resistance of LaB_6–ZrB_2 composites was higher than that of monolithic LaB_6.

Keywords: A. Hot pressing; A. Sintering; LaB_6–ZrB_2 composites; Oxidation behaviors

1. Introduction

Lanthanum hexaboride (LaB_6) has excellent properties, such as high rigidity, low electron transmission work and high transmission stability [1–3]. It is widely used as cathode emission materials and structural materials [4,5]. However, LaB_6 will be oxidized when it is used at high temperature, which will not only shorten its life, but also degrade its properties at high temperature. Paderno et al. [6] fabricated the LaB_6–ZrB_2 composites by using a radio frequency heating zone melting method and found that the composites not only have good fracture toughness (up to 20–28 MPa m$^{1/2}$), high bending strength (up to 1200 MPa), but also have good electron emission properties. Chen [7] analyzed the oxidation behavior of LaB_6–ZrB_2 composites at high temperature and found the composites have excellent microstructure stability below 1650 °C. These researches all concern LaB_6–ZrB_2 single crystals. Few papers have systematically described the fabrication and oxidation behavior of LaB_6–ZrB_2 polycrystals. The aim of this work is to investigate the possibility of synthesizing LaB_6–ZrB_2 eutectic composite powders by "one step" method, i.e., the boron carbide method, and to analyze the hot pressing sintering technique for preparing LaB_6–ZrB_2 polycrystals. The oxidation behavior of the composites at high temperature was also studied.

2. Experimental

The LaB_6–ZrB_2 eutectic composite powders were synthesized using the boron carbide method. The raw materials were La_2O_3 with a purity of 99.9%, B_4C with a purity of 95%, ZrO_2 with a purity of 99% and carbon powder. The La_2O_3, ZrO_2, B_4C, and carbon powders were mixed in the desired molar ratio ($La_2O_3/ZrO_2/B_4C/C$ = 1:2:4:3).

The LaB_6–ZrB_2 polycrystals were sintered by hot pressing under vacuum. In this work the sintering was conducted at 1800 °C, with a holding time of 2 h and a pressure of 35 MPa.

The cuboids of 4 mm × 4 mm × 2 mm specimens were cut from the sintered bodies and machined with a 600-grit diamond wheel and subsequently polished with diamond slurries down to 1 μm. In order to easy to observe cross section after oxidation, a fine figure of V was made on the 4 mm × 4 mm section. Before oxidation, the samples were ultrasonically cleaned in acetone, alcohol and water and were dried in air at 200 °C.

Isothermal oxidation in air was carried out in an electric furnace heated at a rate of 10 °C/min. Polished specimens suspended at the end of a platinum wire, were inserted into

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the hot zone from above. After oxidation, the specimens were taken out from the furnace rapidly in order to measure the weight change.

The samples before and after oxidation were weighted using electronic balance with high sensitivity and the law of weight change was investigated. In this paper, the best technics of producing LaB_6–ZrB_2 powders and the oxidation products formed on the surface were analyzed by X-ray diffractometer (XRD). The microstructure of sintered polycrystals at different oxidation stages was observed through scanning electron microcopy (SEM).

Three-point-bend tests were used to determine the bending strength of the LaB_6–ZrB_2 polycrystalline with a loading rate of 0.5 mm/min and a span of 20 mm.

3. Results and discussion

3.1. Synthesis techniques

The XRD analysis results of LaB_6–ZrB_2 eutectic composite powders with a holding time of 2 h at different temperatures were shown in Fig. 1. It can be seen that only B_4C phase existed at 800 °C, which showed that La_2O_3 had reacted with B_4C and ZrO_2 had reacted with B_4C and C. The diffraction peaks of B_4C powder were not detected when the temperature attained 1000 °C, but the LaB_6 and ZrB_2 phases did not appear. They began to appear at 1200 °C, at the same time a transition phase $LaBO_3$ produced. Of the three phases, the intensity of the diffraction peaks of the ZrB_2 phase was the strongest. At 1400 °C, the transition phase disappeared and only the LaB_6 and ZrB_2 phases remained. So the optimal conditions for synthesizing the LaB_6–21%ZrB_2 composite powders were a holding time of 2 h at 1400 °C, under vacuum.

Fig. 2 shows scanning electron micrographs of LaB_6–ZrB_2 composite powder, LaB_6 powder and ZrB_2 powder. From the figure, the microstructure of LaB_6–ZrB_2 composite powder was similar to that of ZrB_2 powder, but different to that of LaB_6 powder.

By experiment, compared with LaB_6 powders, the LaB_6–ZrB_2 composite powders had good uniform extension. They were easy to mix and allow to obtain polycrystalline materials with high density by hot pressing. In this experiment, the relative density of LaB_6–ZrB_2 polycrystalline attained $0.97D_{\mathrm{theor}}$ and the bending strength (290 MPa) was higher than that of LaB_6 single crystal (200–250 MPa).

3.2. Oxidation behavior

3.2.1. XRD analysis

Fig. 3 shows X-ray spectra of LaB_6–ZrB_2 composite polycrystalline before and after oxidation at different temperatures for a holding time of 6 h. There were only LaB_6 and ZrB_2 peaks before oxidation and a similar result was obtained for the sample exposed in air at 600 °C for 6 h. When the temperature attained 800 °C, LaB_6 was oxidized and produced white $LaBO_3$, yet ZrB_2 was not oxidized, which indicated the beginning oxidation temperature of LaB_6 was lower than that of ZrB_2. With increasing oxidation temperature, the intensity of LaB_6 diffraction peaks decreased and $LaBO_3$ increased. So, it can infer that the following oxidation reaction of LaB_6 from 800 to 1000 °C was occur:

$$4LaB_6(s) + 21O_2(g) = 4LaBO_3(s) + 10B_2O_3(s) \qquad (1)$$

However, the B_2O_3 phase was not detected. It was believed that the samples were quenched in air during the course of drawing the samples rapidly out of the furnace and that the liquid B_2O_3 was not able to crystallize before solidification.

When the samples were exposed to air at 1100 °C, the $LaBO_3$ phase disappeared and $La(BO_2)_3$ and ZrO_2 diffraction peaks were detected, suggesting these oxidation

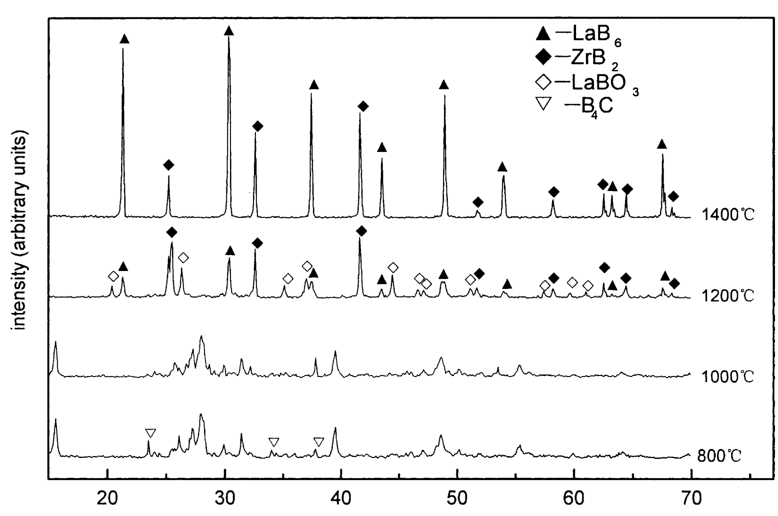
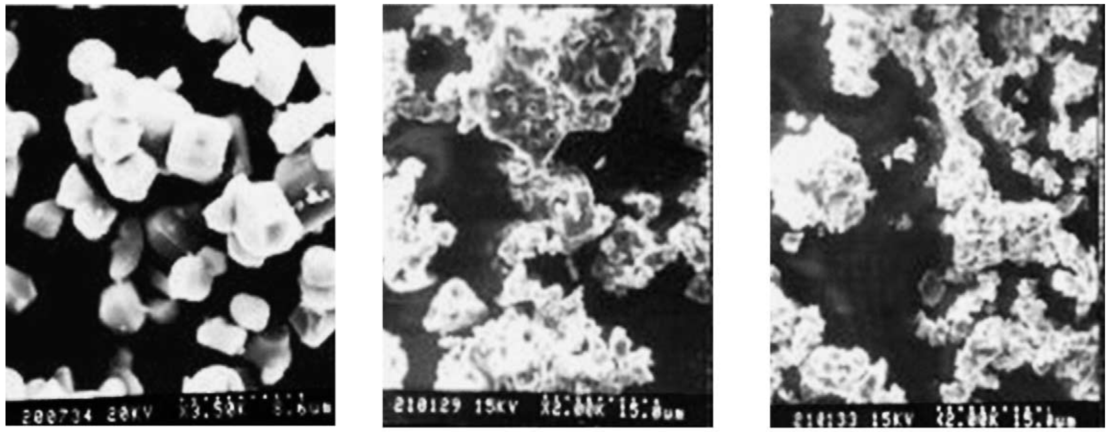


Fig. 1. XRD patterns of the products obtained at different temperatures for 2 h holding time.



(a) (b) (c)

Fig. 2. SEM micrographs of different powder: (a) LaB_6 powder; (b) LaB_6–ZrB_2 composite powder; (c) ZrB_2 powder.

reaction were occurred at 1000–1100 °C. ZrB_2 was oxidized completely to ZrO_2 at 1100 °C.

$$LaBO_3(s) + B_2O_3(s) = La(BO_2)_3(s) \tag{2}$$

$$ZrB_2(s) + 2.5O_2(g) = ZrO_2(s) + B_2O_3(s) \tag{3}$$

The appearance of $La(BO_2)_3$ can be explained by the La_2O_3–B_2O_3 phase diagram, which shows that when there is more B_2O_3 than La_2O_3, $La(BO_2)_3$ will appear.

When the oxidation temperature attained 1200 °C, La_2O_3 phase appeared on the surface structure due to the evaporation of B_2O_3. LaB_6 was oxidized completely until 1300 °C and only La_2O_3 phase and ZrO_2 phase were detected at 1300 °C.

3.2.2. Effect of temperature on oxidation of the LaB_6–ZrB_2 eutectic composites

The oxidation behavior of LaB_6–ZrB_2 composites was studied in the temperature range 600–1300 °C, and the specific weight changes versus time were shown in Fig. 4.

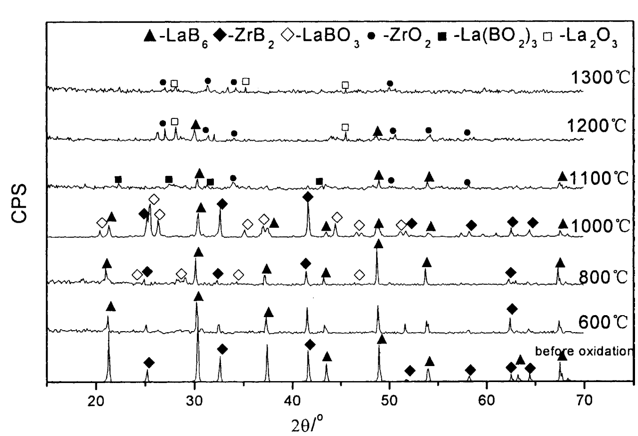


Fig. 3. XRD spectra of oxidation results of LaB_6–ZrB_2 polycrystalline at different temperatures with 6 h holding time.

Below 1100 °C, the oxidation behavior is parabolic with

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t \tag{4}$$

where Δm is the increasing weight of LaB_6–ZrB_2 sample; A, surface area; k_p, kinetic constant. Oxidation rates follow Arrhenius's law:

$$k_p = B \exp\left(\frac{-Q}{RT}\right) \tag{5}$$

where Q is the activation energy of oxidation; B, a coefficient; R, gas constant; T, oxidation temperature (K).

By calculation, Q in the range 600–1000 °C was 38.94 kJ/mol, $k_p = 6.24 \times 10^{-4} \exp(-38,940/RT)\ g^2/m^2\ s$.

By weight and calculation, the rates of weight change per minute were shown on Table 1. It showed that the rate of weight change of LaB_6–ZrB_2 composites was lower than that of LaB_6 at the same temperature. So the oxidation resistance of LaB_6–ZrB_2 composites was higher than that of monolithic LaB_6.

When LaB_6–ZrB_2 was exposed to air at temperatures higher than 1200 °C, the weight change curves deviated from parabolic behavior. Thus, the oxidation proceeded in accordance with the parabolic law during the initial stage, implying that the formed oxide layer acts as a protective layer, causing the oxidation rates to be determined by the diffusion of oxygen through the oxidation layer. The scaling rate increased obviously at 1100 °C due to the beginning of ZrB_2 oxidation. At 1200 °C, during the first 2 h, a rapid weight

Table 1
The rate change of LaB_6–ZrB_2 composites and LaB_6

Temperature (°C)	Rate of weight change per minute (mg/cm^2 min)	
	LaB_6–ZrB_2 composites	LaB_6
600	0.0077	0.00775
800	0.01153	0.01273
1000	0.0185	0.0216

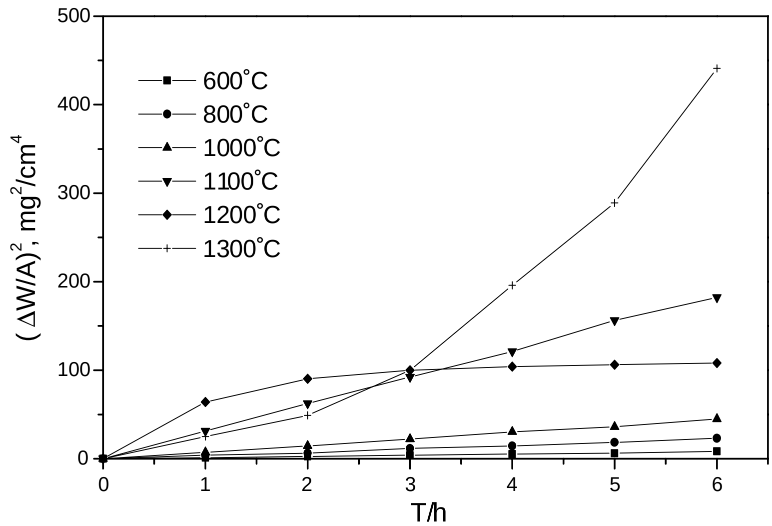


Fig. 4. The weigh change of LaB_6–ZrB_2 eutectic composites.

gain occurred. However, this weight gain was followed by a slight loss, as shown in Fig. 4 due to the evaporation of B_2O_3. At 1300 °C, the oxidation productions became La_2O_3 and ZrO_2, so the rate of weight change increased abruptly.

Fig. 5 showed scanning electron micrographs of the surfaces of oxidized LaB_6–ZrB_2 at different oxidation conditions. When the specimen was exposed to air at 1000 °C for 6 h, some parts of the surface became rough, as shown in Fig. 5a. According to the XRD analysis, this was because parts of LaB_6 grains were oxidized to $LaBO_3$. Increasing the oxidation temperature to 1100 °C a continuous oxide layer composed of an amorphous phase La $(BO_2)_3$, ZrO_2, and LaB_6 was formed making the surface of sample rougher (Fig. 5b). As the oxidation temperature increased to 1200 °C, many cracks appeared on the oxidation surface which perhaps resulted from the difference in the coefficient of thermal expansion between the oxide layer and LaB_6 and many cavities were generated on the surface which was probably caused by the evaporation of B_2O_3 (Fig. 5c). From Fig. 5d, some large holes exist on the surface of oxidation film, so the film could not protect the inside structure at this time.

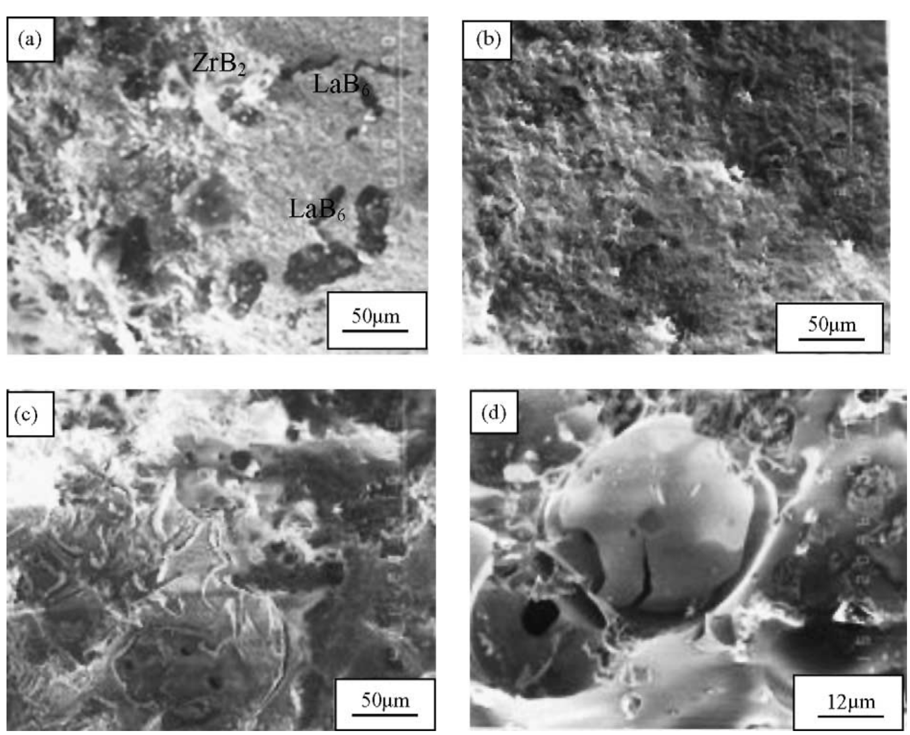


Fig. 5. Microstructures of the surfaces of the oxidized LaB_6–ZrB_2 eutectic composites at different conditions: (a) 1000 °C, 6 h; (b) 1100 °C, 6 h; (c) 1200 °C, 6 h; (d) 1300 °C, 6 h.

4. Conclusions

The LaB_6–ZrB_2 composite powders were synthesized by "one step" method, i.e., the boron carbide method. Polycrystalline materials with high density were obtained by hot pressing sintering.

LaB_6 is oxidized earlier than ZrB_2; The oxidation resistance of LaB_6–ZrB_2 composites is higher than that of monolithic LaB_6.The rate of weight change of LaB_6–ZrB_2 composites obeys the parabolic law below 1100 °C; The rate of weight change decreases at 1200 °C due to the evaporation of B_2O_3; The rate of weight change increased abruptly at 1300 °C. When the oxidation temperature is high, many cracks appear on the oxidation surface which perhaps resulted from the difference in the coefficient of thermal expansion between the oxide layer and LaB_6 and some holes appear due to the evaporation of B_2O_3. The films have could not protect the inside structure at 1300 °C.

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