Chemical reactions in the preparation of B_4C - CeO_2 composites

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Abstract. The B_4C - CeO_2 composites were prepared by pressure-free infiltration method. The chemical reactions and products of CeO_2 and B_4C in the temperature range of 20~1500 were studied by TG-DTA and X-ray diffraction analysis. The results show that the B_4C and CeO_2 reaction products are CeB_4 , B , $CeBO_3$ in 550~1240 and the product of CeO_2 reaction with B_4C is CeB_6 in the temperature range of 1240~1300°C.

1 Introduction

Boron carbide is characterized by many excellent properties, such as supernormal hardness (35~45 GPa), low density (2.5 g/cm³), high chemical stability and wear resistance, and excellent neutron absorption. But the high hot pressing sintering cost and low toughness restrict the widespread application of boron carbide [1-3]. For this reason, scholars at home and abroad have done a lot of research on boron carbide reinforced metal matrix composites [4,5]. Therefore, the aim of this paper is to determine the type, quantity and temperature range of B_4C and CeO_2 reaction phases, which can provide theoretical basis for preparing good mechanical properties of Boron carbide composites.

Fig.1. Micrograph of B_4C powder

2 Empirical method

The purity of boron carbide (B_4C) of the alloy raw material is 98.5 wt%, the residual carbon is about 0.5 wt%, the other residues are iron and other impurities composition volume average distribution particle size is 4.820 μm, as shown in Fig.1. The morphology is irregular rhombohedral structure, and some particles have adhesion phenomenon. The purity of cerium dioxide (CeO_2) is 99.9 wt%, the volume average distributed particle size is 22.942 μm, as shown in Fig.2.

Fig.2. Micrograph of CeO_2 powder

The pressure of 769 yp-60E powder press is 40 MPa, and the holding time is 10 min. The sintering process was carried out in a tubular high temperature electric furnace by heating to 500°C, 1240°C, 1300°C and 1900°C, respectively. The sintering time was 120 min, and the whole sintering process was carried out under the condition of argon as a protective gas. The experiment of X diffraction method was carried out on a Japanese D/max 2400 diffraction instrument using Cu α radiation.

3. Results and discussion

3.1. DTA curve and XRD phase analysis

Fig. 3 shows the B_4C - CeO_2 DTA curve. There are two endothermic peaks on the DTA curve with temperature ranges of 550~1120°C and 1240~1300°C. This indicates that chemical action occurs between CeO_2 and the B_4C during sintering. the result will lead to the change of

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phase composition in the sintered material. The span of the two endothermic peaks varies greatly. The first peak from 550°C to 1120°C, the span of the temperature zone is 570°C, and the peak changes slowly, which indicates that the chemical reaction in the temperature zone is more complex, and the multiple reactions are carried out continuously. The span of the second peak is only 60°C, and the peak is sharp, which indicates that the chemical reaction rate is faster in this temperature region. To further determine the change of chemical reaction and phase composition within each peak, the starting and ending temperature of each peak on the DTA curve was selected for sintering experiments, and the samples obtained by sintering were XRD analyzed.

Fig.3. DTA curve diagram of the reaction of B_4C and CeO_2

Fig. 4(a) is the xrd result of the sintered sample 500°C before the starting point of the first heat absorption peak on the dta curve. there are only B_4C and CeO_2 diffraction peaks in the figure, which proves that at 500°C temperature, no chemical reaction and no new phase generation occur in this B_4C and CeO_2 .

Fig. 4(b) is the XRD result of the sintered sample at the starting temperature of the second heat absorption peak on the dta curve. the results show that in addition to B_4C , CeO_2 , CeB_4 , B, $CeBO_3$ diffraction peaks appear in the sintered products, indicating that at 550~1240 temperature, the B_4C and CeO_2 reaction generated products are CeB_4 , B, $CeBO_3$, which also verifies that the chemical reaction in this temperature region is more complex, and the multiple reactions are inferred continuously.

Fig. 4(c) is the XRD result of the sintered sample at the temperature of the second endothermic peak on the dta curve. The results show that in the sintered samples at this temperature, in addition to B_4C and CeB_4 , B, $CeBO_3$ generated at 550~1240 temperature, new diffraction peaks of product CeB_6 appear, but no CeO_2 diffraction peaks are found. this result, compared with Figures 4(a) and 4(b), can prove that at 1300°C temperature, the reaction of CeO_2 with the same temperature is strengthened at high temperature, so that the CeO_2 is completely consumed. The CeB_6 was generated in 1240 °C and 1300 °C.

Fig.4. XRD pattern of the reaction of B₄C and CeO₂ (a) 500°C (b) 1240°C (c) 1300°C (d) 1900°C

The sintering temperature of the preforms prepared for B₄C and CeO₂ is usually 1800~2000°C, so the sintering experiments under 1900 °C were carried out again. The XRD results of the sintered samples are shown in figure 4(d). The results showed that only B₄C and CeB₆ were found in the sintered products. This indicates that at 1900°C temperature, CeB₄, B, CeBO₃ intermediate products have disappeared and they and b₄c have completely reacted to form CeB₆.

3.2 Chemical reaction analysis during heating

The results of DTA and XRD experiments can be inferred that with the increase of sintering temperature, the chemical reaction of CeO₂ with B₄C and its carbon is divided into three stages. The main chemical reaction equations of each stage are inferred as follows:

Phase I CeB₄, B, CeBO₃ generated at 550~1240°C temperatures

Phase II CeB₆ generated at the temperature range of 1240 °C and 1300°C

Phase III total reaction generation CeB₆ 1900°C CeB₄, B, CeBO₃ and B₄C

4 Conclusions

The chemical reactions and products of CeO₂ and b₄c in the temperature range of 20~1500°C were studied by TG-DTA and X-ray diffraction analysis. The starting temperature range of each reactant is: at 550~1240°C temperature, B₄C and CeO₂ reaction products are CeB₄, B, CeBO₃. Within the temperature range 1240~1300°C, CeO₂ react in situ with the B₄C and its carbon in situ the product is CeB₆. When the temperature reaches 1900°C, CeB₄, B, CeBO₃ intermediate products have disappeared, and they and B₄C have completely reacted to form CeB₆.

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