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Pressureless sintering of boron carbide with Cr_3C_2 as sintering additive

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Abstract

In this study, chromium carbide (Cr_3C_2) was selected as the sintering additive for the densification of boron carbide (B_4C). Cr_3C_2 can react with B_4C and form graphite and CrB_2 in situ, which is considered to be effective for the sintering of B_4C composites. The sintering behavior, microstructure development and mechanical properties of B_4C composites were studied. The density of B_4C composite increased with the increase of Cr_3C_2 content and sintering temperature. The formation of liquid phase could effectively improve the densification of B_4C composites. The abnormal grains began to appear at 2080 °C. The bending strength could reach 440 MPa for the 25 wt% and 30 wt% Cr_3C_2 samples after sintering at 2070 °C.

Keywords: Boron carbide; Liquid phase sintering; Cr_3C_2

1. Introduction

B_4C is a covalently bonded compound with extremely high hardness (the third hardest material known after diamond and c-BN), relatively low density (2.52 g/cm^3) and high neutron absorption cross section. Owing to its outstanding properties, it has been used as wear resistant linings such as sandblasting nozzles, lightweight armor for individual protection, and control rods in nuclear reactors, etc.[1,2] However, the application of B_4C is restricted due to the difficulty in attaining high density B_4C ceramics. Nearly full dense B_4C ceramics have been routinely produced by hot pressing (HP) or hot isostatic pressing (HIP). But the application of the HP or HIP is limited due to the simple shaped, small sized and costly product. Compared with HP and HIP, pressureless sintering method is promising to fabricate B_4C ceramics with complex shape and large size at low cost.[1,2]

At present, the sintering of pure B_4C to high density is difficult through pressureless sintering. Various kinds of sintering aids have been added to obtain high density product, such as C, SiC, AlF_3, etc.[1–9] These sintering aids can obviously improve the properties of B_4C ceramics, though the additives usually increase the specific density. The best known additive, carbon,[2,3,10,11] is considered to enhance the densification by removing the negative species, boron oxide, on the B_4C surface at low temperature and forming the eutectic liquid phase at grain boundary at high temperature.[2,11] Carbon has usually been introduced in the form of carbonaceous precursor (phenolic resin,[2,10] polysaccharide,[12] etc.) or carbon black.[11,13] Carbon can also be provided through in situ reaction between B_4C and metal carbide additive. The densification and mechanical property can also be improved by simultaneously formed borides. Sigl et al.[14] used titanium carbide (TiC) as sintering additive. The performance of B_4C was improved by in situ-formed TiB_2, but postsintering HIP was required to further enhance the densification. Other metal carbides additives also have been reported.[15] However, Cr_3C_2 has rarely been employed as sintering aid for pressureless sintering of B_4C.[16]

Due to the relatively low sintering temperature, liquid phase sintering is usually selected as an alternative route for the densification of boron carbide. High density B_4C ceramics had been prepared using Al or Al_2O_3 as additives[17,18] which was proposed to be able to form liquid phase and thus improve the densification through liquid phase sintering. Yamada et al. chose CrB_2 as

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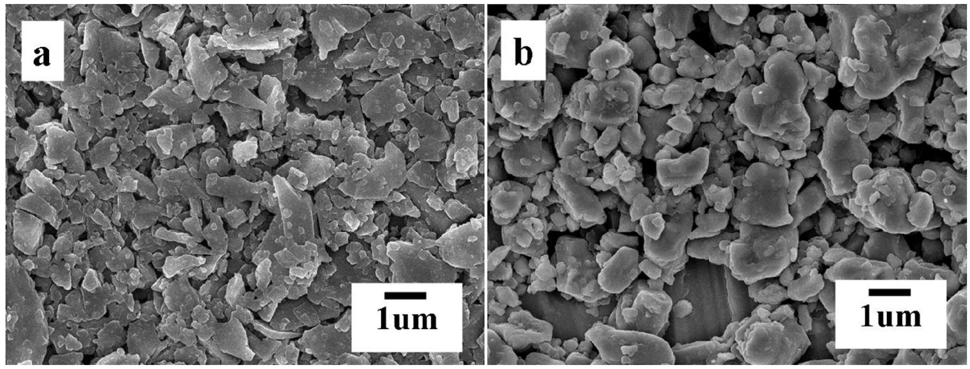

Fig. 1. Photographs of the B4C (a) and Cr3C2 (b) powder.

sintering aid and obtained high density B_4C,[19,20,21,22] which was also attributed to liquid phase sintering in the B_4C–CrB_2 system. Moreover, The Cr was found to be able to diffuse into the grains of B_4C, which may also contribute to the densification.[23]

In this work, the sintering of B_4C ceramics using Cr_3C_2 as the sintering additive is studied. Slip casting was used to prepare green samples with homogeneous microstructure and high reliability. The sintering behavior and microstructure evolution of B_4C–Cr_3C_2 composites were investigated. The liquid phase formation in the B_4C–Cr_3C_2 system was also studied.

2. Experimental procedure

B_4C powder (Dalian Jinma Group, China) with average particle size of 374 nm and specific surface area of 12.10 m^2/g and Cr_3C_2 (Zhuzhou SanLi Carbide Material Co., LTD., China) powder with the particle size in the range of 1.0–1.5 μm were used as starting materials. Fig. 1 shows the morphology of the B_4C and Cr_3C_2 powders. The B_4C particles are plate-like while the Cr_3C_2 particles are more spherical. The addition content of Cr_3C_2 was in the range of 5–30 wt% (based on the weight of B_4C).

In order to prepare well dispersed slurries, the B_4C powder was firstly treated using acid solutions. The purity of the B_4C powder could reach above 99% after treatment. The as-treated B_4C and Cr_3C_2 powder were dispersed and mixed in aqueous media using TMAH (Tetramethyl ammonium hydroxide, Analytical, Sinopharm Chemical Reagent Co., Ltd., China) as the dispersant and ball milled to achieve 50 vol.% slurries using SiC as milling media. After milling, the slurries were cast into plaster mold. The solidified green samples were removed from the mold and dried at 100 °C for 12 h. The as-dried green samples were then calcinated at 900 °C for 1 h in vacuum. Then, the sintering was conducted at the temperatures of 1200 °C, 2030 °C, 2050 °C, 2070 °C, 2080 °C, 2100 °C and 2150 °C respectively for 1 h with the heating rate of 10 °C/min in flow argon atmosphere. In order to study the shrinkage rates of samples with and without Cr_3C_2 as additives, the shrinkages of B_4C and B_4C + 10 wt% Cr_3C_2 were recorded using a Thermo-Optical-Measurement Automatic system (Tomac, Fraunhofer Institute for Silicate Research, Germany). The Tomac system was also used to collect the video pictures of the sample to verify the liquid phase formation during sintering.

After sintering, the density of B_4C sample was measured using Archimedes's method. Phase components were identified using X-ray diffraction (XRD, D/max 2550 V, Rigaku, Japan). The microstructure of the sample was observed using a field emission scanning electron microscopy (FESEM, JSM-6700F, Hitachi, Japan) with an energy dispersive X-ray spectrometer (EDS, INCA, Oxford instruments, Britain) for chemical analysis. The chemical analysis was also carried out using an electron probe micro-analyzer (EPMA, JXA-8100, JEOL, Japan). The three-point flexural strength of the sintered sample was measured using a material testing system (Mold 5566, Instron Corp., UK) with the span width of 30 mm and the crosshead speed of 0.5 mm/min.

3. Result and discussion

3.1. Reactions and components of composites

$$2B_2O_3 + 6C = B_4C + 6CO \quad (1)$$

$$1.5B_4C + Cr_3C_2 = 3CrB_2 + 3.5C \quad (2)$$

XRD patterns show that the as-treated B_4C powder is mainly composed of B_4C, with a small amount of B_2O_3 and graphite

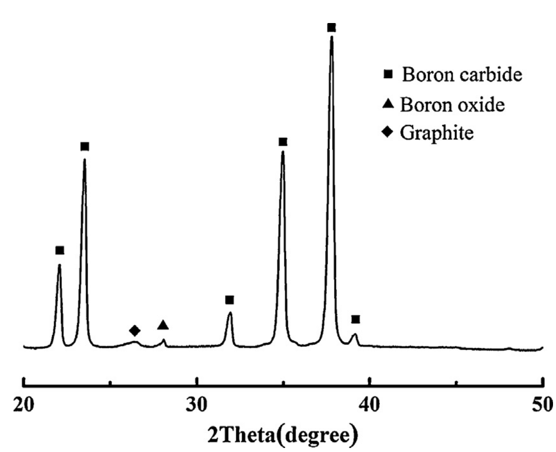

Fig. 2. XRD pattern of the as-treated B_4C powder.