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Sintering Densification of Boron Carbide Materials and Their Research Progress

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Abstract

Boron carbide (B_4C) has excellent high-temperature oxidation resistance, high hardness, low relative density, high melting point and excellent abrasive resistance, which is widely used in fields such as refractories, wear-resistant materials and lightweight protective materials. The research progress and application of B_4C materials in China and overseas in recent years were summarized. The influences of sintering processes (pressureless sintering, hot-pressing sintering, hot isostatic pressing sintering, spark plasma sintering and microwave sintering) and sintering additives (simple substances, oxides and carbides) on the B_4C densification were analyzed. The development of B_4C materials was prospected.

Key words： boron carbide; refractories; densification; preparation method; sintering additive; research progress

1 Introduction

Boron carbide has excellent properties such as oxidation resistance, high hardness, low density, high melting point and excellent wear resistance, which is widely used in the fields of refractory materials, wear-resistant materials and lightweight protective materials[1-3]. However, due to the high covalent bonding ratio of 93.9% in the crystal structure of boron carbide, and the existence of an oxide layer on the surface of boron carbide with poor surface activity, the relative density is still lower than 90% when the sintering temperature reaches 2 300 °C without applying pressure and sintering aids[4]. The poor sintering seriously limits the application of boron carbide materials. With the development of science and technology, there are more and more preparation methods for boron carbide materials, which provide new opportunities for the wide application of boron carbide. To this end, the influence and mechanism of the sintering process and sintering additives on the sintering densification of boron carbide were reviewed, the main application areas of boron carbide materials were discussed, and the development direction was pointed out.

2 Sintering Densification of Boron Carbide

2.1 Pressureless Sintering

The main advantages of pressureless sintering are the simple process, the low cost and the direct availability of the desired product shape, avoiding secondary processing and thus reducing the production cycle[4]. Subramanian, *et al.*[5] obtained boron carbide ceramics with a relative density of 86.6% by pressureless sintering at 2 275 °C for 60 min using boron carbide fine powder with $d_{50}=1.02\ \mu m$. Yin, *et al.*[6] prepared boron carbide ceramics using boron carbide ultrafine powder with $d_{50}=0.56\ \mu m$ at 2 220 and 2 250 °C for 60 min, respectively, the relative densities of the obtained products were 78.6% and 82.5%, and the average grain sizes were 28 and 50 μm, respectively. Compared with the raw materials, the size of boron carbide particles in the sintered products increased significantly, which reduced the mechanical properties of boron carbide ceramics.

The relative density of boron carbide materials prepared by pressureless sintering is low, the sintering temperature is too high, and the boron carbide grains in the obtained products are obviously coarsened, which affect the mechanical properties of the products. Therefore, many researchers tried to add different kinds of sintering aids during the sintering process to improve the densification of pressureless sintered boron carbide ceramics. The effective sintering aids mainly include monomers, oxides, and carbides.

The introduced monolithic sintering aids mainly include Al

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powder, Ti powder, and carbon. Mashhadi, *et al.*[7] investigated the effect of adding Al powder as a sintering aid on the densification behavior of pressureless sintered boron carbide. The results showed that when 4 *mass*% of Al powder was added to boron carbide, B_4C/Al composite ceramics could be produced by pressureless sintering at 2 050 °C for 60 min under argon atmosphere with the density as high as 96%, which was increased by about 45% compared with boron carbide ceramics prepared under the same conditions without adding Al powder. During the sintering process, Al atoms replaced C atoms on the C–B–C triatomic chain in the B_4C crystal structure, forming various solid solution ceramic phases such as AlB_2 and Al_3BC, which caused lattice distortion and increased the defect density, thus promoting the bulk diffusion of grain boundaries and lattices. Metal monomers such as Ti reacted with boron carbide to form metal borides, which promoted sintering densification while also using the products as reinforcing phases to produce diffusion strengthening of ceramics. Liu, *et al.*[8] prepared B_4C–TiB_2 composite ceramics by pressureless sintering with 2.5–5 μm B_4C powder and high purity Ti powder as raw materials. The results showed that B_4C–TiB_2 composite ceramics with the relative density, flexural strength and fracture toughness of 96.1%, 293.6 MPa and 4.05 $MPa \cdot m^{1/2}$ could be produced by adding 5 *mass*% Ti powder and holding at 2 250 °C for 60 min in argon atmosphere. Compared with the B_4C ceramics prepared without adding Ti under the same conditions, the relative density, flexural strength and fracture toughness were increased by about 21%, 140% and 100%, respectively. In addition to metal monomers, carbon is also an important sintering aid. Lee, *et al.*[9] prepared B_4C/C composite ceramics by pressureless sintering using B_4C and carbon as raw materials. The results showed that when 3 *mass*% carbon was added as a sintering aid, B_4C/C composite ceramics could be obtained with the relative density of 97% by heating to 2 250 °C at a heating rate of 30 $°C \cdot min^{-1}$, and the average grain size of the obtained products was 2.03 μm, smaller than the products without carbon addition under the same conditions (2.32 μm). During the sintering process, the oxide layer on the surface of boron carbide particles was removed by reaction with carbon, increasing the surface energy of boron carbide and the rearrangement stress of boron carbide particles, and reducing the viscosity coefficient of boron carbide powder, thus enhancing the ability of plastic flow, which could effectively improve the relative density of the products. The added carbon distributed at the boron carbide grain boundaries, which could inhibit the surface diffusion and evaporation of boron carbide, and control the grain boundary movement during the sintering process, preventing the excessive grain growth[10].

Oxides were introduced as sintering aids, mainly including Al_2O_3, TiO_2, Y_2O_3, and CeO_2. Lee, *et al.*[11] prepared boron carbide ceramics with relative density of 96% by pressureless sintering at 2 150 °C with 3 *mass*% Al_2O_3 powder added. The obvious promotion of sintering densification is due to the formation of low melting point liquid phases such as $AlB_{12}C_2$ by B_4C and Al_2O_3 at high temperatures. Liu, *et al.*[8] prepared B_4C–TiB_2 composite ceramics by pressureless sintering at 2 250 °C for 60 min with 5 *mass*% TiO_2 added, and the density was increased from 79.6% to 89.3% compared with the boron carbide ceramics prepared under the same conditions without TiO_2. During the sintering process, the addition of TiO_2 resulted in the *in situ* generation of TiB_2 on the boron carbide surface, where Ti atoms replaced C atoms, causing distortion of the boron carbide crystal structure, increasing the defect concentration, promoting material transport, and improving the relative density. Zhu, *et al.*[12] produced B_4C–SiC composite ceramics with the relative density of 96.4% by adding 5 *mass*% CeO_2 as the sintering aid and holding at 2 150 °C for 1 h. It was due to the *in situ* generation of CeB_6 on the surface of boron carbide and the formation of B-rich transition zones between B_4C and CeB_6 grains such as $B_{38.22}C_6$ and $B_{51.02}C_{1.82}$, which increased the sintering driving force by introducing local lattice distortion, while the thermal conductivity of CeB_6 was higher than that of B_4C, which was conducive to heat transfer and uniform sintering.

Since oxide additives react with B_4C during the sintering process, the emission of gas is not conducive to the densification of boron carbide. Therefore, carbides are often introduced in boron carbide as sintering aids[13], mainly including TiC, ZrC, NbC, Cr_3C_2, *etc.* Similar to metal oxides, transition metal carbides *in situ* react with B_4C substrates, producing borides and carbon, and no gas will escape during the whole process. As a result, the formed second phase more tightly bounds to the B_4C matrix, which results in higher relative density and generally better mechanical properties. Li, *et al.*[14] prepared B_4C–Cr_3C_2 composite ceramics by pressureless sintering using B_4C with an average particle size of 374 nm and Cr_3C_2 powders with an average particle size of 1.0–1.5 μm. The results showed that B_4C–Cr_3C_2 composite ceramics with relative density and flexural strength of 93.1% and 440 MPa, respectively, could be produced by adding 30 *mass*% Cr_3C_2 and holding at 2 070 °C for 60 min. The CrB_2 was formed by the *in situ* reaction of Cr_3C_2 and B_4C, which diffusely distributed around the B_4C particles and played an role of enhancement.

Therefore, the introduction of sintering aids can significantly increase the relative density of the boron carbide materials or reduce the sintering temperature required to achieve the same relative density during pressureless sintering. However, the sintering temperature cannot be effectively reduced by just adding sintering aids, and the sintering temperature still needs to reach over 2 000 °C to achieve the relative density more than 90%. Therefore, researchers have started to focus on new sintering methods such as hot-pressing sintering and spark plasma sintering.

2.2 Hot-pressing Sintering

Properties such as densities, mechanical properties and microstructures of boron carbide materials prepared by hot-pressing sintering are affected by hot-pressing parameters such as sintering temperature, heating rate, pressure and sintering time[15]. Compared with pressureless sintering, the additional sintering driving force is applied by pressure during hot-pressing sintering, which can significantly reduce the sintering temperature and shorten the densification time. Gao, *et al.*[16] found that the temperature required to prepare near fully densified boron carbide-based composite ceramics was reduced by about 200 °C under pressure of 100 MPa compared with the pressure of 30 MPa. Zhang, *et al.*[17] prepared boron carbide materials by hot-pressing sintering at 1 900 °C with different pressures (30–110 MPa). The results showed that the relative density of products increased from 87.9% to 99.8% when the applied pressure increased from 30 to 110 MPa, while other conditions remained consistent. The applied pressure can reduce the starting temperature of densification and shorten the densification process.

In order to further reduce the sintering temperature and improve the properties of boron carbide materials, sintering aids are also often introduced in hot-pressing sintering. Zhang, *et al.*[18] prepared B_4C–Si composite ceramics in a vacuum hot-pressing sintering furnace using boron carbide powder with purity of 96.0 *mass*% and particle sizes of 3–5 μm and silicon powder with purity of 99.8 *mass*% and particle sizes of 1–2 μm as raw materials. The results showed that when 15 *mass*% Si powder was added, B_4C–Si composite ceramics with the relative density, flexural strength and fracture toughness of 98.7%, 447.2 MPa and 4.62 MPa · $m^{1/2}$, respectively, were produced at 1 830 °C for 30 min under 40 MPa. The presence of SiB_6 during the sintering process significantly improved the flexural strength and fracture toughness of the composites, and the addition of SiC whiskers also enhanced the mechanical properties of the composites. Yue, *et al.*[19] prepared B_4C–TiB_2 composite ceramics by hot-pressing sintering from boron carbide and TiO_2 with an average particle size of 1 μm. The results showed that when 43 *mass*% TiO_2 was added, B_4C–TiB_2 composite ceramics with the density, flexural strength and fracture toughness of 98.2%, 458 MPa and 8.7 MPa · $m^{1/2}$, respectively, could be produced at 1 950 °C for 60 min under 30 MPa. The *in situ* reaction between B_4C and TiO_2 was utilized to promote material diffusion during the sintering process and facilitate sintering densification, while the crack deflection and formation of fine grains caused by the difference in thermal expansion coefficients between the B_4C matrix and the *in situ* generated TiB_2 particles improved the toughness of the material.

In conclusion, the preparation of boron carbide ceramics by hot-pressing sintering has many advantages, such as high relative density and small grain sizes, and the temperature required for hot-pressing sintering generally 100–200 °C lower than that for pressureless sintering to obtain the same relative density of boron carbide products. However, the amount of products for once hot-pressing sintering is small, and the shape of the products is fixed, which make it difficult to process later and be costly.

2.3 Hot Isostatic Pressing Sintering

In the industrial process, the matrix with certain residual porosity is generally obtained by pressureless sintering, and then the residual porosity is eliminated by hot isostatic pressing sintering, which obtains ceramic materials with the highest relative density[20]. Cho, *et al.*[21] prepared fully dense boron carbide ceramic by hot isostatic pressing sintering with the 93.0% relative density boron carbide ceramic obtained by pressureless sintering as the raw material. Larsson, *et al.*[22] prepared boron carbide ceramics by hot isostatic pressing sintering and investigated the effect of adding boron monomer on the sintering of boron carbide. The results showed that under the conditions of holding at 1 850 °C for 1 h and 160 MPa, the relative density of the products was increased from 97% to 99.1% when 20 *mass*% boron was added, while the B_4C particle size in the products was reduced from 4.3 to 2.8 μm. The addition of boron could effectively improve the relative density and control the grain sizes of the products.

The boron carbide products prepared by hot isostatic pressing sintering have a relative density closed to the theoretical relative density and almost no porosity. The higher the relative density, the higher the strength of the boron carbide materials. However, hot isostatic pressing sintering equipment is extremely expensive and the production cost is high, which makes it difficult to be applied on a large scale at present.

2.4 Spark Plasma Sintering

The preparation of boron carbide materials by spark plasma sintering is characterized by rapid temperature rise, short sintering time, low sintering temperature and high sintering efficiency. Spark plasma sintering can fully control the growth of boron carbide grains, which results in fine grain sizes, high relative density and excellent mechanical properties[23]. Ghosh, *et al.*[24] prepared boron carbide materials with the relative density of 96% by spark plasma sintering under 80 MPa at 1 750 °C for only 2 min, and when the holding time was 5 min, the relative density of the product was increased to 99.2%. Chen, *et al.*[25] prepared boron carbide ceramics by spark plasma sintering with boron powder and graphite powder as raw materials, which made the synthesis and compaction of boron carbide complete once. The results showed that the starting temperature of boron carbide densification was around 1 650 °C, and boron carbide ceramics with relative density of 98.2% were obtained by sintering at 1 800 °C, and the Vickers hardness and Young's modulus reached 48.8 and 264.5 GPa, respectively. Therefore, high relative density boron carbide ceramics can be obtained at lower temperatures by spark plasma sintering. Zhang, *et al.*[26] studied the difference of hot-pressing sintering and spark plasma sintering for the densification of boron carbide ceramics. The results showed that boron carbide ceramics with relative density of 91.2% could be obtained by hot-pressing sintering at 10 °C · min^{-1} to 1 900 °C for 1 h and 40 MPa. Under the same conditions, the boron carbide ceramics with relative density of 93.9% could be obtained by spark plasma sintering for just 6 min. Therefore, the sintering time can be shortened by 90% by spark plasma sintering, which can greatly improve the production efficiency in comparison with the two sintering methods.

Using spark plasma sintering to prepare boron carbide materials has many advantages, but the size of the products is significantly limited, and the shape is simple. Due to the fast cooling, residual large internal stresses will be in the products, which will adversely affect the mechanical properties of the material.

2.5 Microwave Sintering

Microwave sintering is a new type of sintering process, which has many advantages such as fast temperature rise, uniform temperature field and energy saving and environmental protection. The main working principle is to use the dielectric loss through the interaction between microwave and the material itself to heat, which is a viable way to rapidly prepare high relative density boron carbide ceramics[27]. Dyatkin, *et al.*[28] produced boron carbide ceramics with relative density of 95.9% with micron-sized pure boron carbide powder as the raw material by microwave sintering at 1 400 °C, and the boron carbide particles did not grow significantly. Katz, *et al.*[29] used microwave sintering to prepare boron carbide ceramics from ultrafine boron carbide powder. The results showed that the boron carbide ceramics with an average particle size of 20 μm and relative density of 95% were produced by microwave sintering at 2.45 GHz for 12 min at 2 000 °C. The presence of twins and microcracks in the microstructure had a toughening effect, and the energy consumption of microwave sintering was 18% lower than that of induction hot pressing.

Microwave sintering has a low sintering temperature, usually below 1 500 °C, fast heating rate, uniform temperature field, and high energy efficiency, which is a green and environmentally friendly sintering method. However, microwave sintering equipment is expensive and has high requirements for the type of materials and the homogeneity of the sample. The microwave parameters should be specially designed according to the sample properties, which makes it difficult to apply on a large scale at present.

3 Application of Boron Carbide Materials

3.1 Refractory Materials

Boron carbide is mainly used as an antioxidant and a sintering agent for refractory materials. The addition of boron carbide can significantly improve the oxidation resistance of carbonaceous refractories. The antioxidant mechanism of boron carbide mainly includes[2]: (1) it is preferentially oxidized, reducing the partial pressure of oxygen inside the material, thus protecting the carbon from massive oxidation; (2) B_2O_3, the product of boron carbide oxidation, covers the surface of the material, blocking the pores and reducing the diffusion rate of O_2 on the surface of the specimen, thus reducing the oxidation of carbon; (3) the liquid phase B_2O_3 reacts with the oxides in the material such as MgO, which produces the high viscosity and low melting point borate, forming a liquid phase on the surface of the material protective layer, thus preventing O_2 from contacting with carbon to achieve the effect of protecting carbon. Wang, *et al.*[30] investigated the effect of B_4C and Si on the antioxidant properties of low carbon MgO–C bricks. The results showed that the addition of B_4C could significantly improve the antioxidant capacity of low carbon MgO–C bricks, and the antioxidant properties could be best improved with 0.5 *mass*% B_4C and 3 *mass*% Si. Campos, *et al.*[31] studied the effect of the addition of B_4C on the structure and properties of MgO–C refractories. The results showed that the appropriate addition of B_4C could enhance the antioxidant and slag corrosion resistance of MgO–C refractories. In practical production applications, it is important to determine the optimal addition of B_4C.

In addition to an antioxidant, boron carbide can also be used as a sintering aid for refractory castables. B_2O_3, the oxidation product of boron carbide, which is liquid phase at lower temperatures, promotes the densification of the material by liquid phase sintering. Tu, *et al.*[32] investigated the effect of B_4C on the properties of Al_2O_3–SiC–Si_3N_4 iron trough channel castables. The results showed that with the addition of B_4C, the B_2O_3 liquid phase from B_4C oxidation can promote the material flow, increase the relative density of the product and improve the properties of the material, and the overall performance of the iron trough castables reaches the best when the mass fraction of B_4C is 0.4%. In addition, the effect of boron carbide on the mechanical properties of MgO–Si_3N_4 castables was also studied. The analysis showed that the oxidation of boron carbide produces liquid phase during the heating process, which promotes the sintering of the material, resulting in dense material and increased cold strength[33].

3.2 Wear-resistant Ceramics and Protective Materials

Boron carbide is only second to diamond and cubic boron nitride in hardness at room temperature (50 GPa), and its constant high temperature hardness (>30 GPa) is higher than theirs, which makes it ideal for use in high temperature conditions. It also has a high modulus of elasticity (448 GPa). Therefore, one of the most important uses of boron carbide is an abrasive medium to crush, grind and polish high hardness materials such as various cemented carbides and industrial ceramics.

The production process of boron carbide is mature and the yield is high, therefore, the cost of boron carbide material is significantly lower than diamond for the same application in the field of abrasive materials. Due to its high hardness, the use of boron carbide ceramics as grinding devices is not easy to contaminate the material, and at the same time, boron carbide ceramics also have good wear-resistance, low wear rate and high cost performance. Therefore, the wear resistant parts made from boron carbide ceramics also have a wide range of applications such as rust remover nozzle for the maintenance of the ship's hull and high-pressure jet nozzle for water cutting. In addition, boron carbide ceramic parts are also widely used in corrosion and wear resistant parts of gas turbines, journal bearings of nuclear power plant cooling systems, pneumatic slide valves and hot extrusion dies[34].

The high hardness, high modulus of elasticity and low relative density of boron carbide make it the best choice for lightweight protective materials such as bullet-proof helmets and undershirts for human safety, and bullet-proof armor for tanks, armored vehicles and helicopter gunships for military equipment protection. However, due to the high cost of preparing high relative density boron carbide ceramics, it is mainly used in special industries with high requirements for protection performance. The expansion of conventional applications is depending on further improvement of the sintering process of boron carbide to reduce the cost[35].

3.3 Temperature Difference Thermocouple

Boron carbide is a promising thermoelectric material because of its low thermal conductivity, good thermal stability, high temperature electric conductivity and large Seebeck coefficient. The Seebeck coefficient and the electric conductivity of boron carbide increase with the temperature, so the boron carbide has high thermoelectric conversion efficiency and obvious advantages in thermoelectric conversion, especially its high temperature resistance, which makes its application in high temperature environment attract much attention. The excellent thermoelectric properties of boron carbide are also reflected in the good linear relationship between its potential difference and temperature, so boron carbide materials can be used to make thermocouples. At present, the temperature difference thermocouple prepared by using the combination of boron carbide thermoelectric properties and stability can be applied to the detection and control of high temperature parts with high reliability, which can achieve long-term and accurate measurement at high temperatures[36].

4 Conclusions

Boron carbide materials have many excellent properties and are widely used in the fields of refractory materials, abrasive ceramics and protective armor, but the application of boron carbide ceramics is greatly restricted due to the high sintering temperature and many problems such as densification difficulties and low toughness. Conventional pressureless sintering is difficult to prepare boron carbide ceramics with high relative density, and high temperature sintering for a long time will cause grain coarsening and reduce the mechanical properties of the material. Rapid sintering can avoid grain growth, which is conducive to the densification and the mechanical properties of boron carbide itself; the applied pressure can provide sintering driving force, reduce the sintering temperature and shorten the densification process. Sintering aids promote the densification of boron carbide in sintering process mainly by increasing the defect concentration, promoting material transfer, controlling grain growth and other action mechanisms.

In summary, the future development direction of sintering densification of boron carbide materials mainly includes that: the mixed application of various sintering processes to make full use of their advantages reducing the sintering densification temperature, reducing sintering costs, and improving the relative density of sintered products; the comprehensive utilization of different kinds of sintering additives to improve the relative density to the greatest extent without damaging the excellent mechanical properties of boron carbide itself and improving the bending strength, fracture toughness and other properties of boron carbide ceramics.

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