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Review on the properties of hexagonal boron nitride matrix composite ceramics

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ABSTRACT

Novel hexagonal boron nitride (*h*-BN) matrix composite ceramics exhibit versatile and greatly improved properties compared with the traditional *h*-BN ceramics, such as excellent mechanical properties, high-temperature resistance, thermal shock resistance, ablation resistance, and molten metal erosion resistance. They have potential important applications in the field of aerospace, electronics, metallurgy, machinery, nuclear energy, etc. As such, much attention are paid by both academia and industry on materials science and technology. In this paper, the special crystal structure and unique characteristics of *h*-BN are firstly briefly introduced. Then, the state-of-the-art development on mechanical properties, thermal shock resistance, ablation resistance, ion erosion resistances, molten metal erosion resistance and the damage mechanisms of novel *h*-BN matrix composite ceramics under harsh serving environments are reviewed, including textured *h*-BN matrix composite ceramics with anisotropic properties targeted for heat management applications. Moreover, the possible future research focus on *h*-BN and *h*-BN matrix composite ceramics are also forecasted.

1. Introduction

Hexagonal Boron nitride (*h*-BN) is well known to be an important engineering ceramic. It has crystal structure analog of graphite. That is, within each layer, boron and nitrogen atoms are bound together by strong sp^2 covalent bonds, and the adjacent layers are integrated by weak van der Waals forces [1–5]. This special crystal structure provides *h*-BN a series unique combination of properties (see Table 1) [6–12], including low dielectric coefficient, low loss tangent, extremely high sublimation temperature of about 3000 °C (non-oxidizing atmosphere), excellent thermal shock resistance, and desirable machinability [12,14].

However, there exist some problems that limit the application of *h*-BN material, such as low strength and poor sintering properties. As the strong covalence of B-N bond has a rather low self-diffusion coefficient, it is difficult to obtain dense materials even if they are sintered under high temperature (>2000 °C) or assisted by pressure. In tradition, only several kinds of oxides, such as SiO_2 and B_2O_3, are used as sintered additives, and the mixed powders are often sintered without pressure-assistance. As a result, the *h*-BN ceramics show low relative density and poor properties, which constraint their application. While in most cases, *h*-BN are used as additives to adjust the properties of composite ceramics, for example, increasing thermal conductivity and improving processability [8,11–13].

In recent years, advanced sintering technologies (hot pressing sintering (HPS), hot isostatic pressing sintering (HIPS), Spark plasma sintering (SPS), etc.) and new types of sintering aid or reinforced phases (Al_2O_3, ZrO_2, CaO, Sialon, Si_3N_4, AlN, SiC, YAG, Y_2SiO_5, mullite, etc.) are applied to manufacture *h*-BN matrix composite ceramics, which render significantly improved performances for these materials in terms of mechanical, thermal and electric fields [5–13]. Thus, *h*-BN matrix composite ceramics with various properties have been commonly used in many high technology fields under extreme service environment, such as non-ferrous metal industry, chemical engineering, lubricating materials, high-temperature furnaces, and thermal protection systems [8,9,14–17].

In this paper, we focus on the homogeneous h-BN matrix composite ceramics that manufactured by sintering ceramic powders, recent progress of mechanical properties, thermal shock resistance, ablation resistance, ion erosion resistances, molten metal erosion resistance and anisotropic properties of novel *h*-BN matrix composite ceramics are reviewed. The damage mechanisms under extreme environment are discussed. In addition, the future devel-

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Table 1
Basic parameters for hexagonal crystal structure.

Crystal structure	Hexagonal	Group of symmetry	$P6_3mmc$
Density (g/cm^3)	2.28	Lattice constant at 297 K (nm)	0.25040 (a axis) 0.66612 (c axis)
Bulk modulus (GPa)	36.5	Moh's Hardness	1.5
Elastic constants at 300 K (GPa)	C_{11} 750 C_{12} 150 C_{33} 32 ± 3 C_{44} 3	Dielectric constant, static	5.06 (//to c axis) 6.85 (⊥ to c axis)
Debye temperature (K)	400	Specific heat (J/g K)	~0.8
Thermal conductivity (W/m K)	= < 0.3 (//to c axis) = < 6 (⊥ to c axis)	Thermal expansion, linear (×10^{-6}/K)	38 (//to c axis) −2.7 (⊥ to c axis)

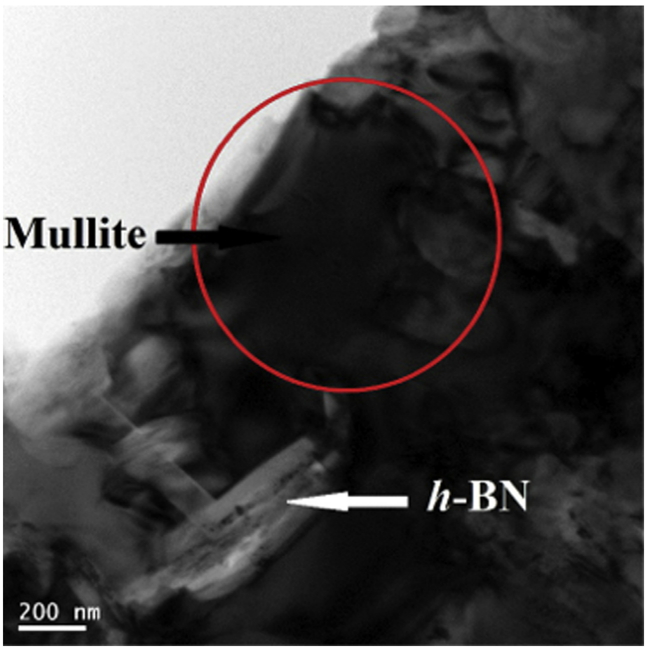

Fig. 1. TEM micrographs of *h*-BN-MAS composite ceramics with 50 wt.% MAS hot-pressed at 10 MPa.

oping directions of *h*-BN and *h*-BN matrix composite ceramics are pointed out.

2. Fabrication methods

As one of the strongest covalently bonded ceramic materials, BN-based materials are difficult to be sintered due to the low coefficients of atomic diffusion and anisotropic plate-liked structure. Therefore, sintering aids are usually incorporated and the sintering had to be conducted at high temperature under pressure. The typical fabrication methods for h-BN matrix composite ceramics include pressureless sintering, hot pressing sintering, spark plasma sintering, and hot isostatic pressing sintering.

Pressureless sintering is usually conducted under vacuum or certain atmosphere environment, and it is widely used to densify the covalently bonded ceramics with incorporation of the sintering aids. Now, pressureless sintering method have been widely used in many kinds of composite ceramics, such as Si_3N_4, SiC and AlN matrix ceramics [18,19]. However, for BN matrix composite ceramics, it is rather difficult to eliminate pores and other defects with pressureless sintering due to the plate-liked structure of h-BN grains. Thus, even though high sintering temperature is employed in the process of pressureless sintering and high content of sintering aids are used, the relative density of the sintered ceramics are still not high enough. Hexagonal boron nitride ceramic had been fabricated by pressureless sintering at 2100 °C using submicrometer h-BN powders without any sintering additive [20]. The as-prepared h-BN ceramic just showed flexural strength of 30.7 MPa and a low bulk density of 1.31 g/cm^3.

Hence, BN-based materials are generally produced by pressure assisted sintering. Hot pressing is a processing technique allowing the compact forming and sintering simultaneously achieved under axial pressure, which is a more effective way to fabricate h-BN matrix ceramics with relatively high densities. The anisotropic plate-liked structure of h-BN tend to form the triangle structure and prevent the densification of h-BN ceramics. The axial pressure during hot pressing process is very beneficial to destroy the triangle structure and obtain the sintered ceramics with relative high density. Meanwhile, the hot pressed h-BN matrix composites with the sintering additive is also beneficial to the particle plastic flow and compact densification. It is widely used to densify a variety of h-BN-based ceramics with high density and excellent comprehensive properties. In general, hot pressing could make it possible to achieve a relative high density of more than 90% and provide the final products with good comprehensive properties such as a combination of mechanical and physical properties [9,11,14,21–23].

Spark plasma sintering (SPS) is a very effective way to sinter ceramic powders quickly to its full density at a relatively lower temperature compared to conventional hot pressing methods [24], it was regarded that the electrical arc discharge occurs on the particle surfaces under the pulse current promotes material sintering. In addition, due to the shorter sintering time of SPS when compared with the hot pressing, the grain growth is significantly confined, thus leading to fine and homogeneous grains, which benefits the mechanical properties of the materials [25–27]. However, the relative high cost of SPS equipment restricts its wide applications.

Hot isostatic pressing (HIP) can be used for densifying the pre-sintered components, consolidating powders, and interfacial bonding that involves simultaneous application of high temperature and pressure [28]. It is also distinguished from the conventional unidirectional pressing such as hot pressing and spark plasma sintering. In the process of HIP, a rather high isostatic pressure (150 ~ 200 MPa) is usually employed [28,29] to eliminate pores and other defects of h-BN-based ceramics and at the same time, higher relative density of more than 95% could be achieved eventually. According to our recent research, when a post-treatment of HIP was conducted on the sintered h-BN-based ceramics, the bulk density of the samples increased from 1.81 g/cm^3 to 2.32 g/cm^3, which is pretty close to the full density.

Now, it is urgently necessary to develop the highly dense and large-scale h-BN-based ceramics structural parts to meet the industry requirements or to expand product applications in more fields. Generally, by the pressure assisted sintering process, only sintered bodies with simple shapes can be obtained. Fortunately, the BN matrix composite ceramics have better machinability, the component parts with complex shapes can be manufactured by the following machining services. But the cost of their corresponding components are significantly increased. So, the basic scientific