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Aluminium oxynitride–hexagonal boron nitride composites with anisotropic properties

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ABSTRACT

Structure of hexagonal boron nitride (h-BN) consist of hexagonal layers with strong covalent bonds and weak van der Waals bonds between them. Such specific structure and usually plate-like grains cause anisotropic properties of h-BN based materials. The aim of the present work was preparation of composites in the aluminium oxynitride–hexagonal boron nitride system with anisotropic properties. SHS technique was used to obtain complex powders with both phases synthesized *in situ*. Mixtures of aluminium, aluminium oxide and different amount of boron were combusted in nitrogen and the powders were hot-pressed. The h-BN grains in the composites show plate-like shapes and crystallographic orientation. The specific microstructure and texture result in anisotropy of thermal properties; thermal conductivity was few times higher in the direction perpendicular to hot-pressing force and parallel to the longer diameter of h-BN grains. The texture effect is stronger than the effect of the h-BN content.

1. Introduction

Boron nitride exists in three polymorphs that are isostructural and isoelectronic with carbon. Structure of hexagonal boron nitride (h-BN), analogue of graphite, consists of a system of the hexagonal layers within which strong covalent bonds exist between B and N atoms and weak van der Waals bonds link these layers. Thanks to such specific structure, h-BN shows unique properties set: high thermal conductivity, high electrical, temperature and oxidation resistance, high melting point, outstanding thermal shock resistance, good chemical inertness and poor wettability with molten metals, glasses or salts [1]. That is why h-BN products are widely applied as high temperature and refractory materials, heat-sinks in power industry and microelectronics, windows transparent to microwaves, lubricants and seals. It is worth noticing that materials based on h-BN demonstrate anisotropic properties due to its structure and usually plate-like shapes of grains e.g. thermal conductivity for highly oriented materials reach even hundreds W/m·K along the basal plane and only a few in the direction perpendicular to this plane [2,3].

Hexagonal boron nitride is often used as inclusions in composites with metal [4], polymer [5] or ceramic matrix [6]. The reported results show that addition of h-BN into ceramic matrix can significantly enhance thermal shock resistance such as in the β-SiAlON/h-BN [7] or in SiC/h-BN composites [8]. Presence of h-BN influences also a reaction between material and the atmosphere. Xu et al. studied ZrO_2/h-BN composites, which have good oxidation resistance up to 1200 °C thanks to the presence of Zr-B compounds and formation of protection layer [9]. Similar effect was observed in hot pressed SiC/h-BN material; borosilicate glass film acts as a protective layer and decreases an oxidation rate [10]. Eichler and Lesniak reported on h-BN/ZrO_2 and h-BN/ZrO_2/SiC composites, which are refractory materials for steel industry (thin-strip casting and continuous casting processes) due to their excellent corrosion resistance, wear behaviour and high-temperature compressive strength [1].

Considering layered structure of h-BN, most of material properties strongly depend on the h-BN crystals orientation. Buchheit et al. examined mechanical and thermal properties of SiC-AlN-h-BN composites with enhanced thermal shock resistance [11]. Hardness, fracture toughness and strengths did not vary significantly with HP pressure direction nevertheless meaningful anisotropy was noticed in elastic modulus and thermal properties. Resulting values were lower than those of SiC specimens but based on assumptive criteria they work to increase thermal shock resistance in the SiC/AlN/BN material. Duan et al. succeed in fabrication of textured h-BN composites with mullite as a sintering additive [12]. The results revealed that *c*-axis of h-BN grains were preferentially oriented parallel to pressure direction. It was also found that increase of pressure used in hot-pressing process enhanced

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the texture development [13]. Further investigations showed strong anisotropy in mechanical properties with diversified fracture mechanisms as a consequence of textured microstructure of this material. Pressure- or field-assisted sintering techniques (HP, HIP, SPS) are usually used to consolidate such materials due to their strong covalent bonds and hence limited diffusivity of the system [3,12].

The second component of the investigated composites, aluminium oxynitride with spinel-type structure (γ-alon), is characterized by a specific combination of properties such as good thermal conductivity, resistance to high temperature corrosion in liquid metals, good mechanical properties, high transparency from ultraviolet to near-infrared and high dielectric constant [14]. Powders of γ-alon and h-BN can be successively obtained using self-propagating high-temperature synthesis (SHS) [15,16].

The present work is focused on preparation of materials composed of γ-alon and hexagonal boron nitride and investigation their properties. Such composites can be used as components of some metallurgical systems (e.g. for continuous casting) that have direct contact with molten or hot metals and a high thermal conductivity is necessary. Anisotropy of thermal conductivity makes additional opportunity to receive a heat sink in a direction perpendicular to a plane of contact with a hot metal which can reduce an insulating layer. SHS technique was used to obtain complex powders with both phases synthesized *in situ* in one-step process what restricts grain growth and increases homogeneity of the powder mixture.

2. Experiment

Commercially available metallic aluminium (Benda Lutz, pure grade, 99.5%), γ-aluminium oxide (TM-300D TAIMICRON, Taimei Chemicals Company, purity >99.99%) and amorphous boron (Fluka, 15580 Aldrich, purity >96%) powders were used as the reagents. Average particle sizes of the powders were 17 μm for Al, 1 μm for B and 10 nm for Al_2O_3. The weight proportions between the powders were established as follow: $(1-x)(0.2Al+0.8Al_2O_3)-xB$, where $x = 0.025$, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.50 and 0.70. The appropriate amount of the powders were mixed for 12 h in isopropyl alcohol using a ball mill and zirconia grinding media. The dried powder mixtures, about 50 g each, were placed in a graphite container in the form of loose, porous bed. The container was then placed in a high-pressure reactor filled with pure (99.8%) nitrogen under pressure of 2.5 MPa. SHS reaction between the substrates and nitrogen was initiated by high electric current flow through the graphite container for several seconds. The combustion started rapidly and combustion wave was propagating through the substrate powders for several seconds and the synthesis was accomplished. The SHS products were crushed and ground for 6 h in rotary–vibratory mill with corundum balls using dry propanol as a milling medium. Then, after evaporation of the alcohol, the powders were granulated and subjected to hot pressing (Thermal Technology Inc.) at 1900 °C for 1 h under 25 MPa in nitrogen flow.

Phase composition of the obtained powders and hot-pressed samples was analysed by X-ray diffractometer (Empyrean system, Panalytical). Rietveld refinement allowed evaluating the quantitatively phase composition. Apparent density of the composites was determined according to the Archimedes method and relative densities were calculated using the rule of mixture. Morphology of the synthesized powders and sintered specimens were examined using scanning electron microscopy (Nova NanoSEM 200, FEI). Thermal diffusivity and specific heat capacity of the sintered materials was measured by the laser flash method (LFA 427, Netzsch). The thermal conductivity, k, was calculated from the well know equation: $k = \alpha \times d \times C_p$, where: α is thermal diffusivity, d is density and C_p is specific heat capacity.

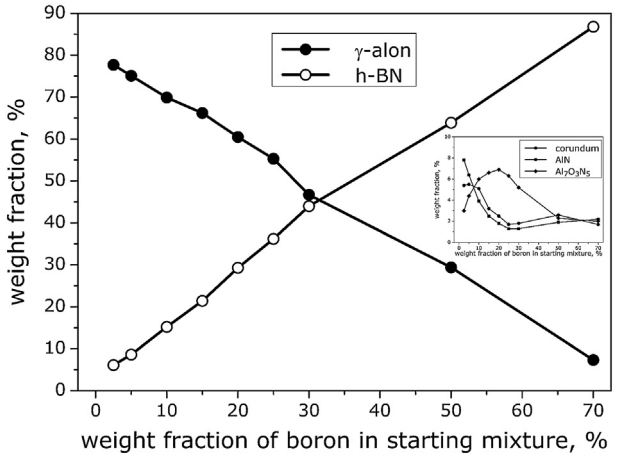

Fig. 1. Phase composition of the SHS-derived powders in the Al—B—O—N system. Size of the markers corresponds to measurement uncertainty.

XRD analysis and thermal diffusivity measurements were used to describe orientation of the h-BN grains and anisotropy of thermal properties of the sintered samples, respectively. Rectangular samples were cut out from the cylinder-shaped ones with the one plane parallel and the second plane perpendicular to a direction of the force applied during hot-pressing. The diffraction patterns, taken in the Bragg–Brentano geometry, as well as thermal diffusivity were measured applying these surfaces. The crystallographic orientation (texture) of h-BN grains was defined by the ratio of the volume fraction of crystallites in a textured sample with a specific orientation to the texture axis to the same volume fraction for a random (or untextured) sample. The function of the crystallite orientation chosen for this work is the March–Dollase function that has been incorporated in software packages (HighScore Plus) used to analyse powder diffraction data [17].

3. Results and discussion

The XRD analysis reveals that the SHS-derived powders are composed mainly of γ-alon and hexagonal boron nitride, Fig. 1, Small amounts of aluminium nitride, rhombohedral aluminium oxynitride $Al_7O_3N_5$ and non-fully reacted corundum are also present in the powders (inset in Fig. 1). The phase content of the powders depends on the quantitative composition of the starting mixtures. It means that nitridation of aluminium and boron run independently of each other and γ-alon is formed in the reaction between aluminium nitride and corundum.

The high-temperature SHS reaction lead to strongly agglomerated product. It can be observed that crushed and ground powders are composed of angular, isometric and plate-like shaped grains with sizes from 200 nm to few micrometers, Fig. 2.

The hot-pressed samples are composed mainly of γ-alon and hexagonal boron nitride; in the samples prepared from the powders with higher amount of γ-alon small amounts of aluminium nitride are also present, Fig. 3. Essential changes in the phase composition between powders and sintered samples suggest assumption that chemical reaction occurs during densification process. The phase composition of the sintered samples is strongly connected with the phase composition of the SHS obtained powders.

X-ray diffraction patterns taken from the two perpendicular surfaces of the samples (Fig. 4) clearly indicate strong orientation of the platelet h-BN grains with flat surface corresponding to the (0 0 0 2) plane of the h-BN structure. The h-BN grains were orientated in-plane, perpendicular to hot-pressing direction. On the surface, perpendicular to hot-pressing direction more intensive are reflexes derived from (0002) plane and on the surfaces parallel