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Structure features and fracture mechanisms of hexagonal boron nitride based composite materials

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The structure and fracture mechanisms of hexagonal boron nitride based composite materials with formation of new phases (mullite and sialon) during hot pressing has been studied. The composite microstructure was found to be textured oriented due to morphology of crystal boron nitride particles and to be essentially independent of the composite phase composition. It has been shown that fracture mechanisms vary within the temperature range of 20 to 1500°C. The fracture within 20–1200°C range is brittle with boron nitride exfoliation in (001) planes. The composite strength at above 1200°C is defined by the onset of weakening of grain boundary phase and tough character of its fracture.

Исследована структура и механизмы разрушения композиционных материалов на основе нитрида бора с образованием новых фаз (муллита и сиалона) в процессе горячего прессования. Установлено, что микроструктура композитов характеризуется ориентированной текстурой, обусловленной морфологией кристаллических частиц нитрида бора и практически не зависит от фазового состава композита. Показано, что механизмы разрушения изменяются в интервале температур 20–1500°C. Разрушение на участке 20–1200°C носит хрупкий характер с прохождением процессов расслоения нитрида бора по плоскостям (001). Прочность композитов при температурах выше 1200°C определяется началом разупрочнения зернограничной фазы и вязким характером ее разрушения.

Hexagonal boron nitride shows a unique combination of properties including low density, high heat resistance and thermal stability, chemical inertness and other advantages. However, its low hardness, strength and restricted corrosion resistance in oxidizing media at 1000°C and above hinder the industrial application of boron nitride in high-temperature materials. A great interest is paid to composite materials based on boron nitride that comprise additives contributing the governed phase and structure formation *in situ*, because a liquid phase resultant from the component interaction of some composites during hot pressing intensifies the process of material densification, thus enabling to increase the material strength and working temperature limit [1].

Earlier studies [2–5] have shown that aluminosilicates (mullite and sialon), when added to boron nitride based composites, could considerably increase the material properties such as strength, elasticity modulus, thermal stability, etc. It is also known that the microstructure of boron nitride based composites is a texture comprising platelets of boron nitride interlayered with aluminosilicates. This characteristic microstructure is due to the morphology of boron nitride particles. Having properties similar to those of graphite, boron nitride particles with high relative elongation are also able to efficiently resist crack propagation like fibrous composites with short fibers [2, 6].

From the practical point of view, for ceramics, thermal and mechanical properties

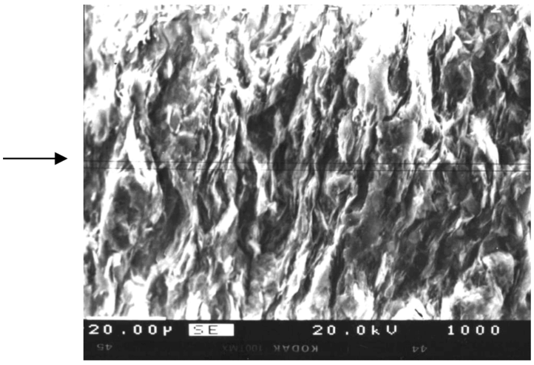

Fig. 1. Microstructure of fracture surface of a boron nitride based composite, ×1000 (Arrow shows the direction of hot pressing).

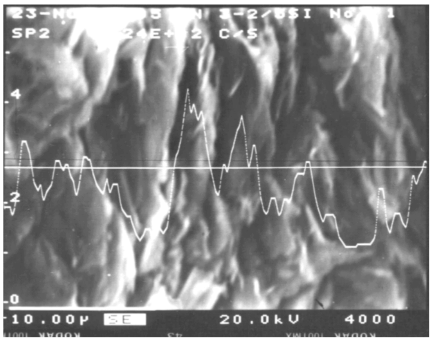

Fig. 2. Variation of the X-ray intensity profile for silicon along the cross-section of the fracture surface in composite, ×4000.

within a wide temperature range are of great importance [7]. It was found that the behavior of a ceramic composite under mechanical loading depends noticeably on its structure. The level of effect produced by elements and defects of the structure on decrease of ceramics strength properties was used [7, 8] to propose an empirical series (in the sequence of effect attenuation): macropores — interphase boundaries (and intercalations of low-melting phases especially) — micropores — boundaries of crystals — dislocations — vacancies. The presence of high order elements in a given structure is thus of most importance, and it is just these elements that govern the material behavior. Earlier, taking the sialon-BN system as an example, we have studied the effect of the composite structure upon ultimate bending strength [5]. It was shown that the porosity is the major factor influencing the strength values. Low porosity samples have the bending strength as high as 120 to 140 MPa, whereas it sharply decreases with increasing material porosity and at 18–23 %, ranges between 30 and 50 MPa. This work is aimed at the study of structure formation and fracture mechanisms of composite materials based on hexagonal boron nitride within 20 to 1500°C.

For the study, composite materials of the $BN\text{-}Al_2O_3\text{–}SiO_2\text{–}Si_3N_4$ system were chosen prepared by powder metallurgy techniques, containing up to 70 % boron nitride and having different ratios of oxide and nitride phases. The powder mixtures were prepared using the mixing in an attrition device that provided high intense comminuting followed by agglomeration. The samples of composite materials were obtained by hot pressing in graphite molds at 1500–1700°C and 20 MPa pressure. The phase composition of the samples was examined by X-ray diffraction using a DRON-3M diffractometer. The microstructure was examined by a CAMEBAX-SX-50 scanning electron microscope. The composite strength was determined by three-point bending of the samples shaped as square beams of $3.0\times4.0\times30$ mm^3 size with span of 20 mm on a 1246 P-2 testing machine [9]. The samples were tested within the temperature range of 20 to 1500°C under vacuum at minimum residual pressure near 10^{-5} Torr. The fracture toughness was estimated by the SEVNB method which provided bending of a V-notched beam [10, 11].

While preparing a composite, the structure formation in a material was found to start at the step of mixing. High-intense treatment in the attrition device results in deformation of BN particles with their intrinsic plate-like morphology remaining intact, while their surfaces having particles of oxides and nitrides thereon. Electron microscopy data revealed that the composite microstructure, regardless of the phase composition, features an expressive texture orientation (Fig. 1) due to crystal morphology of initial boron nitride particles. Thus, during hot pressing, the particles are arranged with their developed surfaces in parallel to each other, causing formation of morphologic texture in the composite. According to the X-ray phase analysis, the aluminosilicate component of composite may be single-phased or multi-phased (depending on initial ratio of components) and comprise mullite, sialon, cristobalite, or their mixture. X-ray spectral analysis shows the aluminosilicate matrix to be distributed rather uniformly among the BN particle packets (Fig. 2). Referring to [6], a similar distribution of matrix phase in the composite has advantage over that for disperse inclusions,

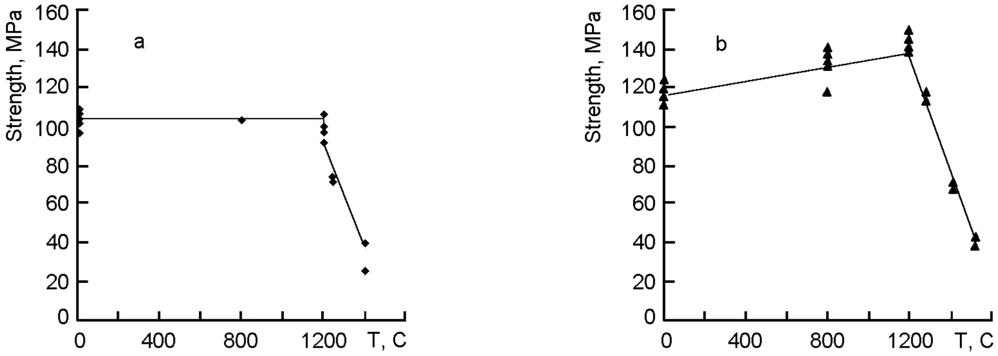

Fig. 3. Temperature dependences of bending strength of boron nitride based composite materials:: a) BN-mullite; b) BN-sialon.

since the aluminosilicate phase forms a continuous skeleton and contributes directly to the stress redistribution.

As the testing results have shown, introduction of the aluminosilicate phase provides an opportunity for activation of hot pressing processes of boron nitride based composites and to obtain denser and stronger ceramics [5]. This phase also influences the fracture mechanisms of composites at various temperatures, which is due to the amount and refractoriness of grain boundary phase that also comprises glass phase. The temperature strength dependence of BN-mullite and BN-sialon composites was found to have similar patterns. The diagrams (Figs. 3a,b) include two characteristic ranges. In the 20–1200°C range, the fracture is mainly brittle with exfoliation of boron nitride in (001). This is also accompanied with some shape change of BN packages, starting from the temperature of 800°C (Figs. 4a, b). The composite strength above 1200°C features the onset of grain boundary phase weakening and tough fracture. This is evidenced by some microstructure peculiarities of the samples fractured at 1300–1500°C, such as strong shape change of boron nitride packages, absence of a substructure therein and relief-free surface, and also more uniformly distributed elements of additive along the fracture surface (Figs. 5 a,b). The latter is explained by the matrix layer presence at the fractured surface that might be formed during its melting under loading at the testing temperatures. It should be noted that for the BN-sialon composite at up to 1200°C, an increase of strength is observed. A similar effect was described also for sintered β-sialons between 800 and 1100°C [12]. Such a behavior is characteristic for brittle materials exhibiting the brittle-tough transition at certain temperatures. This effect is enhanced by softening of interparticle phase comprising also glass phase. Tough decrease of interparticle phase with the temperature rise causes an increase of apparent plasticity of the material as a whole and simultaneously some increase of its strength.

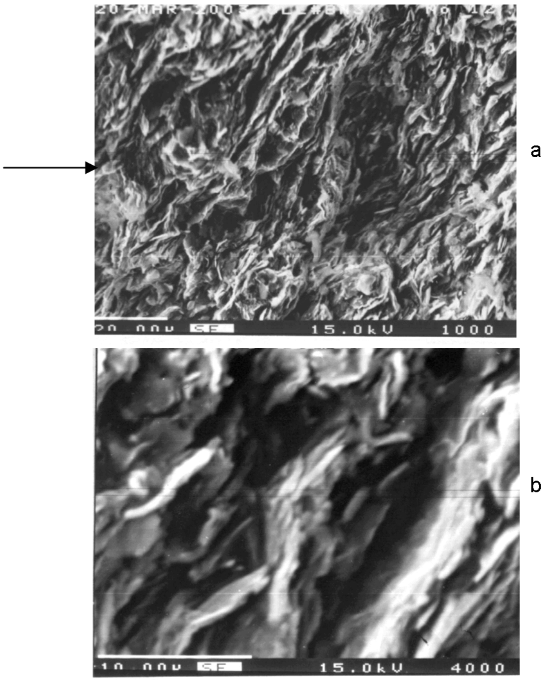

Fig. 4. Typical microstructure of sample fracture surfaces of BN-sialon at $T = 800$–1200°C: a) General view, ×1000 (Arrow shows the hot pressing direction); b) blown-up image showing exfoliation in particle packages, ×4000.

Changing fracture mechanism of the boron nitride based composite is also confirmed by the temperature dependence of fracture toughness. A maximum has been revealed in the temperature dependence of stress intensity factor K_{1c} in the BN-sialon composite at 1200–1300°C. So, at 20–1000°C, the K_{1c} value is at a level of 2.2 to 2.3 MPa·m$^{1/2}$

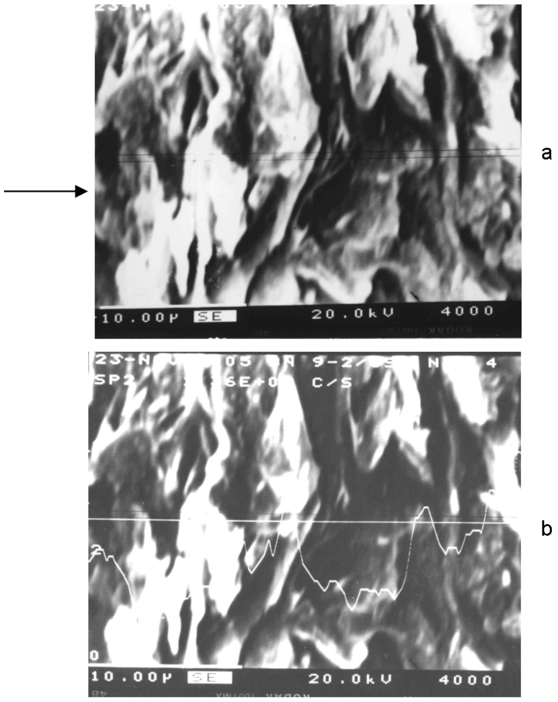

Fig. 5. Typical microstructure of fracture surface of BN-sialon at $T = 1500°C$: a) general view, ×4000 (Arrow shows the hot pressing direction); b) variation of the X-ray intensity profile for silicon along the cross-section of the fracture surface at 1500°C, ×4000.

and increases to 2.7–3.2 MPa·m$^{1/2}$ at 1200–1300°C. Such an increase of fracture toughness can be explained by softening of grain boundary phase and blunting of the crack which occur at high temperatures. A further temperature rise up to 1400–1500°C causes no crack propagation hindering by grain boundary phase because exhausting margin of safety, and both fracture toughness and strength of specimens lower.

To conclude, during preparation of hot pressed samples based on hexagonal boron nitride and aluminosilicate phase, it has been found that structure formation defines the behavior of fracture mechanisms and favors conditions for improving strength characteristics. The temperature strength dependence of composites BN-mullite and BN-sialon has two characteristic ranges. The fracture within 20–1200°C is mainly of brittle nature with exfoliation of boron nitride in (001). The composite strength above 1200°C is defined by the onset of grain boundary phase weakening and tough behavior of its fracturing. Changing fracture mechanism of the boron nitride based composite is also confirmed by the temperature dependence of fracture toughness, which has a maximum at 1200–1300°C.

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Особливості структури та механізми руйнування композитних матеріалів на основі графітоподібного нітриду бору

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Досліджено структуру та механізми руйнування композитних матеріалів на основі нітриду бору з утворенням нових фаз (муліту та сіалону) у процесі гарячого пресування. Встановлено, що мікроструктура композитів характеризується орієнтованою текстурою, обумовленою морфологією кристалічних часток нітриду бору, та практично не залежить від фазового складу композиту. Показано, що механізми руйнування змінюються в інтервалі температур 20–1500°C. Руйнування на ділянці 20–1200°C має крихкий характер з проходженням процесів розшарування нітриду бору у площинах (001). Міцність композитів при температурах понад 1200°C визначається початком знеміцнення зернограничної фази та в'язким характером її руйнування.