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Boron carbide nanoparticles for high-hardness ceramics: Crystal lattice defects after treatment in a planetary ball mill

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ABSTRACT

Deformation features of the boron carbide lattice treated in a planetary ball mill are studied in our work. It is shown that such treatment causes a decrease in the B_4C grain size and cracking along the $\{20\bar{2}1\}_h$ planes, whereas the same treatment in the presence of silicon results in the appearance of twins along the $\{10\bar{1}1\}_h$ planes. Distorted stacking faults along $(10\bar{1}4)_h$ are observed. *Ab initio* simulations shown, that among low-index crystallographic planes $\{20\bar{2}1\}_h$ and $\{10\bar{1}1\}_h$ have the smallest values of specific surface energy which favors the formation of defects and cracks.

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1. Introduction

Studies of the high-intensity treatment effect on the structural states of the composite components and the connection between their structures and the properties of the composite are of great interest in the course production of high-temperature nanostructured ceramics with grain size below 20 nm. One of the main ceramic powder nanostructuring methods is treatment in a planetary ball mill with acceleration (shock load). Such a treatment can be analogous to the shock-wave treatment methods that are particularly relevant for the processing of high-hardness carbides, borides, nitrides, with the purpose of changing their structural state. Thus, the goal of the present work is to study the boron carbide (B_4C) structure, since it is widely used for production of high-hardness ceramics.

Boron carbide has a set of prominent chemical, physical and mechanical properties [1]. Boron carbide (B_4C) is a hard, strong, and light-weight material with a wide variety of applications. It is used, for example, in military equipment, as a neutron-absorbent material, for abrasive and wear-resistant parts, etc. B_4C and other ceramics possessing high hardness are used under conditions of

intense shock loading, therefore it is necessary to describe their durability under such conditions. The process of deformation of boron carbide was studied in a number of works. Stress-induced structural transformation of boron carbide has been reported in static indentation [2–4], dynamic indentation [5,6], and scratching experiments [4]. In [4], the TEM observations have shown large amorphized zones formed within the indentation contact area. Amorphous and nanocrystalline B_4C were observed in [7]. The dynamic indentations resulted in a greater level of structural change compared with the static indentation. A lower hardness, fracture toughness, and a greater level of damage under dynamic loading compared with static loading, could be attributed to the formation of a greater amount of localized amorphous phase that is weaker than the original crystalline phase in boron carbide [5,6]. Localized contact loading resulted in the disorder in the region under the indenter [2].

In the present work we study the boron carbide deformation under dynamic loading in a planetary ball mill. Some of the experiments were conducted with the presence of silicon in the planetary mill: its concentration varied from 0 to 99.5% (by mass). The deformation mechanism in the presence of silicon is different from the one without Si when a direct contact of B_4C grains takes place. Since the hardness of silicon ($H = 10$ GPa) is much lower than that of B_4C (about 40 GPa [8]), the yield strength $\tau^* \approx H/3$ of silicon is 4 times lower than that of boron carbide, and Si acts as a soft damping

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material separating the B_4C grains. Another reason to use silicon is that the composition of these two materials is promising for the development of thermoelectrics [9].

1.1. Experimental and theoretical methods

We analysed powders consisting of B_4C and Si with different mass content of Si: 99.5% Si and 0.5% B_4C , 99% Si and 1% B_4C , 95% Si and 5% B_4C , and pure B_4C . Precursor components were treated in a Fritsch Planetary Micro Mill PULVERISETTE 7 premium line with a ceramic drum and Si_3N_4 milling balls. Milling time was 2 h, and the size of the particles approached 10–15 nm. The obtained samples were studied in a JEM-2010 transmission electron microscope (TEM) with EDS and EELS attachments. In samples, where the concentration of boron carbide was very low, we chemically dissolved the samples in a mixture of nitric and etching acids.

Ab initio calculations were performed using density functional theory (DFT) [10,11] in the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [12], as implemented in the VASP package [13]. The plane-wave energy cutoff was equal to 400 eV, while the Brillouin zone was sampled using a $4 \times 2 \times 1$ Monkhorst–Pack [14] grid for simulated slabs and a $4 \times 4 \times 2$ grid for the bulk phase. Atomic structure optimization was carried out until the maximum interatomic force became less than 0.05 eV/Å. To avoid artificial interactions between periodic replicas of the studied slabs, a vacuum interval at least 10 Å was introduced in all 2D supercells. The thickness of the slab was set not less than 10 Å.

2. Discussion of results

It is known that the crystal lattice of boron carbide can be represented in two ways: as a rhombohedral one with $a = 0.516$ nm and $\alpha = 65.7^\circ$, and as a hexagonal one with $a = 0.56$ nm, $c = 1.207$ nm [1]. TEM studies have shown that all the samples after the treatment contained cracks. When pure boron carbide was subjected to ball milling, no twins, polytypes or other crystal lattice defects (apart from cracks) were observed. At the same time, in the samples where Si concentration prevailed (about 95% and more), we observed both twins and stacking faults. Fig. 1a shows a fragment of a B_4C particle from the sample with silicon constituting 99.5% of its mass. The particle is twinned. As it follows from the corresponding Fourier transform (Fig. 1b), the twinning plane is $\{10\bar{1}1\}_h$. Since the amount of the boron carbide particles in the material subjected to milling was very small, they were completely surrounded by silicon parti-

cles and were deformed through the surrounding silicon layer. In this case, Si served as a pressure-transferring medium. Apparently, such conditions result in the appearance of twins and stacking faults in B_4C . Twinning in boron carbide is described in a number of works [15–21]. The twin structure in B_4C [15] is verified as (0001)-type planar defects. Boron carbide nanolumps on the surface of multiwall carbon nanotubes had a twinning plane $(10\bar{1}1)_h$ [16]. The $\{10\bar{1}1\}_h$ twins of the growth type were found in [17]. High density of the $\{10\bar{1}1\}_h$ twins and stacking faults was observed in hot-pressed $B_{13}C_2$ samples [18]. It was shown that the $\{10\bar{1}1\}_h$ twins were found in the B_4C specimens hot-pressed below 2000 °C [19]. Boron carbide nanowires were characterized by twins and stacking faults with $\{10\bar{1}1\}_h$ plane [20]. The twins formed in bulk boron carbide are usually deformation twins. Asymmetric B_4C twins with a $(100)_r$ twinning plane were found in [21]. Cyclic $\{100\}_r$ -type twinning was observed in [22]. Using the orientational relationship (OR) between the hexagonal and rhombohedral lattices of boron carbide, it is easy to demonstrate that $\{100\}_r$ in rhombohedral and $\{10\bar{1}1\}_h$ in hexagonal coordinates are equivalent. Therefore, the twins at $\{10\bar{1}1\}_h$ observed in our studies, appearing as a result of B_4C treatment in a planetary ball mill, are similar to the deformation and growth twins observed in other works. It is worthwhile noting that the twinning plane contains icosahedra connected by the intericosahedral bonds (Fig. 3a) which connect atoms in the polar sites of the neighboring icosahedra and originate from the sp-hybridized orbitals.

Fig. 2a shows some almost parallel lines (bands) in boron carbide that resemble cracks. The crystal structures on both sides of these lines are the same, but they are slightly disoriented, as could be seen in the Fourier transform in Fig. 2b. The reflection spots are doubled and slightly broadened. The widths of the lines (most probably, cracks) do not exceed 1 nm and they are equal to the width of several interplanar distances for these lattices. They are located in the $\{20\bar{2}1\}_h$ -plane. In total, we examined 16 particles containing such deformation bands. In 12 particles these bands located in the $\{20\bar{2}1\}_h$ -planes.

B_4C compound contains boron icosahedra interspersed with chains consisted of three carbon atoms aligned along c axis. In the $B_{13}C_2$ compound one of these atoms could be replaced by boron one as it is represented in [23]. Fig. 3b represents a B_4C structure where a $\{20\bar{2}1\}_h$ -plane is shown schematically (in a hexagonal cell). The figure does not include all the atoms in cell to avoid overloading the scheme.

The bands similar to those in Fig. 2 were observed in some other works. Usually they are treated as amorphous bands. It was found that boron carbide deforms by atomic-scale amorphous band for-

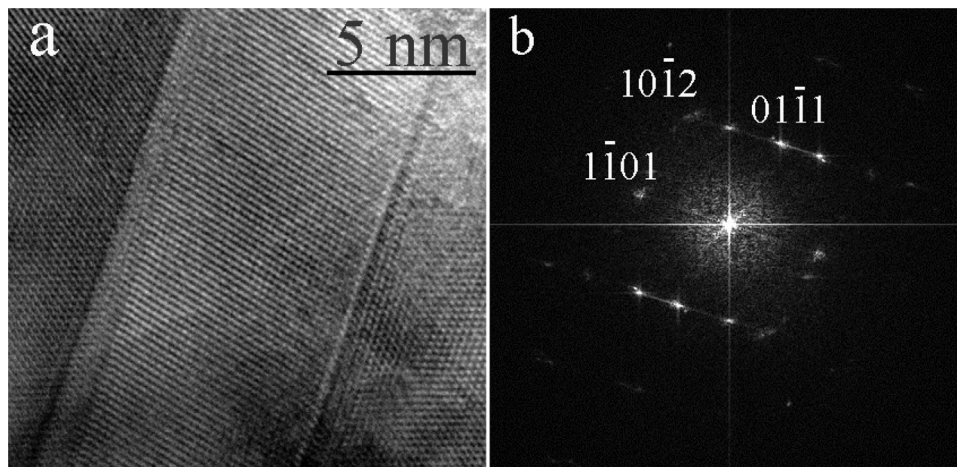


Fig. 1. B_4C after the treatment in planetary mill with silicon constituting 99.5% of powder mass. a) Twinning in boron carbide at $\{10\bar{1}1\}_h$ plane. b) A Fourier transform of the image in (a).

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