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Some physical properties of compacted specimens of highly dispersed boron carbide and boron suboxide

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Abstract

Structure, shear modulus and internal friction (IF) of compacted specimens of boron carbide and boron suboxide have been investigated. Microtwins and stacking faults were observed along the {100} plane systems of polycrystalline specimens of boron carbide. Electrical conductivity of the specimens was that of *p*-type. Concentration of holes varied from 10^{17} to $10^{19}\,\mathrm{cm}^{-3}$. The IF was measured in the temperature range 80–300 K. It was shown that the IF of boron carbide and that of boron suboxide were characterized with a set of similar relaxation processes. Mechanisms of the relaxation processes in boron carbide and boron suboxide are discussed in terms of the Hasiguti model of interaction between dislocations and point defects.

Keywords: Boron suboxide; Boron carbide; Electrical conductivity; Activation energy; Internal friction; Shear modulus

1. Introduction

Boron carbide and boron suboxide have high potential opportunities to be successfully used in nuclear power engineering and chemical industries, in thermoelectric energy converters and composites. These materials can also be used for new elaborations in the area of creating technologies for wear-resistant coatings on the details of metallurgical equipment.

Specific conditions of fabrication of these materials determine dependence of a number of structure-sensitive physical properties on porosity of the specimens, size, shape and orientation of grains, concentration and distribution of point and linear defects in the bulk of the specimens. Most efficient ways for finding and identifying structure imperfections and their activation parameters are the methods of internal friction (IF) and transmission electron microscopy in conjunction with other traditional methods.

Present work is focused on the investigation of structural peculiarities of the specimens of boron carbide ($B_{12}C_3$, $B_{13}C_2$, B_8C) and boron suboxide (B_6O).

2. Experimental

The specimens were fabricated by hot pressing or sintering with subsequent compacting under high pressures. Measurements of the IF temperature dependence were performed in the temperature range 80–300 K at $\sim 1\,\mathrm{Hz}$ frequencies of torsion pendulum. Heating velocity varied between 1 and 3 K/min. Activation energy (H) of the process was measured by frequency shifts of the IF maxima. Frequency factor $\tau_0{}^{-1}$ was calculated from the condition $\omega\tau = 1$, where $\tau = \tau_0 \exp(H/kT)$. Electro-physical characteristics were estimated from the Hall coefficient and electrical conductivity measurements. Conductivity type was determined by signs of the Hall electromotive forces [1]. Structure of boron carbide specimens was studied by using the method of electron microscopy (JEM-200CX at accelerating voltage 200 kV).

Specimens for the investigation in transmitted light of electron microscope were prepared by chemical thinning

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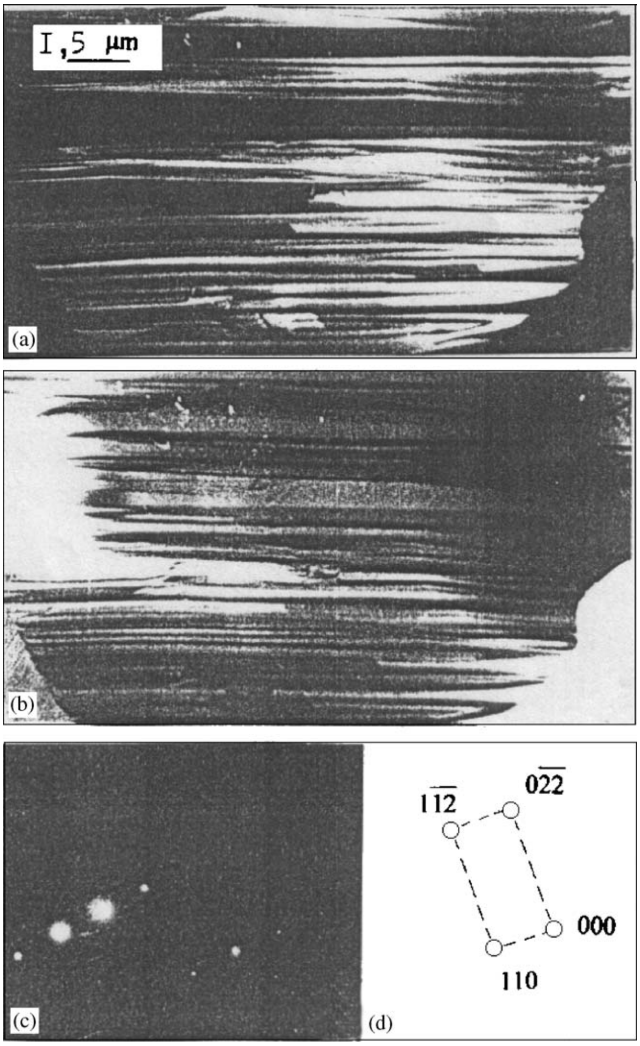

Fig. 1. Deformation twins in boron carbide: (a) light-field image; (b) dark-field image; (c) electron-diffraction pattern; (d) schematic representation of electron diffraction pattern along the axis [UVW] = [111].

of small slices of the specimens, with subsequent ion bombardment in argon flow. Investigation of the thinned specimens showed a presence of thin twinning packages different in width and concentration (Figs. 1 and 2). The observed difference in contrast of the images of planar defects can be attributed to the presence of stacking faults within twin packages.

3. Results and discussion

Concentration of boron and carbon in the structures of different specimens after compaction is not reproducible. However X-ray diffraction patterns of the specimens defined by formulas $B_{12}C_3$, $B_{13}C_2$ and B_8C show a single phase with stoichiometry of boron carbide.

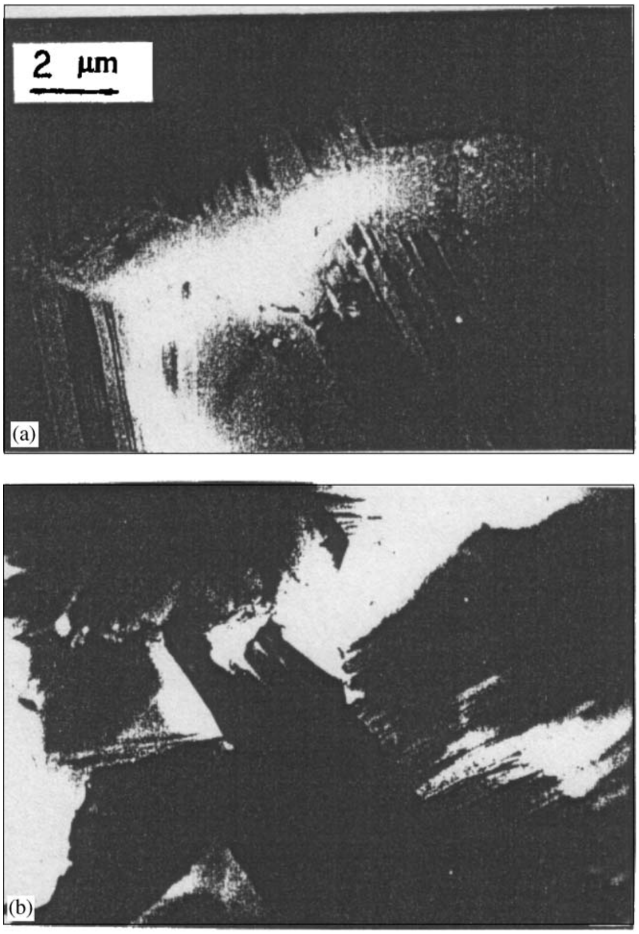

Fig. 2. Electron micrographs of boron carbide.

In the IF temperature spectrum of specimens with formula $B_{12}C_3$ at frequencies of about 0.9 Hz and at temperatures 115, 140, 180–190, 200 and 250 K were found superimposed maxima (Fig. 3, curve 1). Increase of frequency promotes shifting of the maxima (except for the maximum at 180–190K) toward high temperatures, this indicating to their relaxation origin. Values of activation energy of the relaxation maxima are 0.15, 0.20, 0.30 and 0.50 eV; corresponding frequency factors are 4×10^5, 2×10^7, 2×10^8 and $7\times10^{10}\,s^{-1}$. Position of the IF maximum at 180–190 K is not dependent on torsion oscillation thus demonstrating hysteretic origin of the IF. The maximum is completely suppressed by hydrogen annealing for 3 h at 950 K. Hysteretic maximum at 180–190 K is not observed in the IF temperature spectrum of boron carbide having formula $B_{13}C_2$ (Fig. 3, curve 2), however all the other relaxation maxima are shifted to lower temperatures. Activation energy and frequency factor of the relaxation maxima at 110, 135, 195 and 245 K are, respectively, 0.10, 0.18, 0.25, 0.45 eV and 3×10^5, 1×10^7, 1×10^8, $5\times10^{10}\,s^{-1}$. In the vicinity of the maxima are observed negligible defects of dynamic shear modulus (Fig. 3, curve 2′).

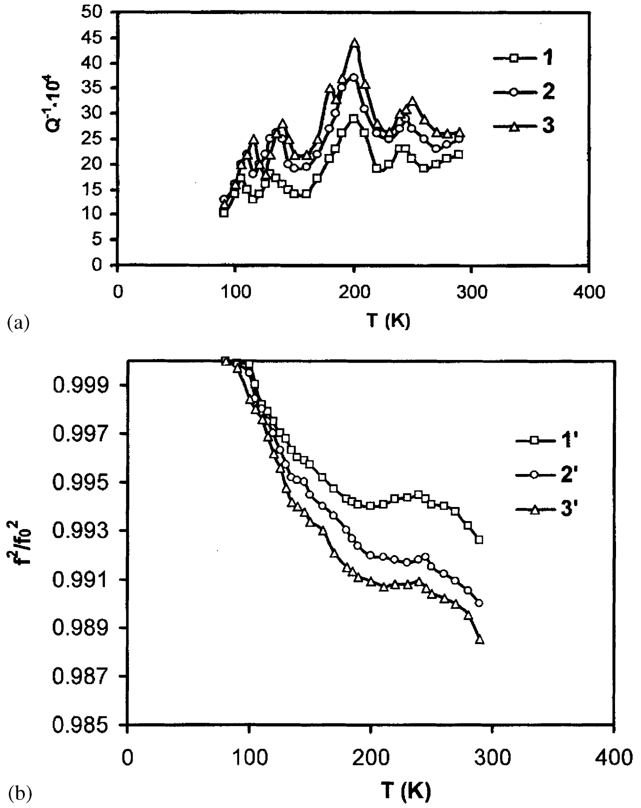

Fig. 3. IF (Q^{-1}) (a) and relative shear modulus (f^2/f_0^2) (b) of boron carbide with different boron content. 1–1′—$B_{12}C_3$, $f_0 = 0.9$ Hz; 2–2′—$B_{13}C_2$, $f_0 = 1$ Hz; 3–3′—B_8C, $f_0 = 0.9$ Hz.

Hydrogen annealing of the specimen for 3 h at 950K provides decrease of the IF background. Amplitude dependence of the IF at room temperature and above the critical amplitude of torsion oscillations ($\sim 5 \times 10^{-4}$) is rather weak.

Boron carbide specimens enriched with boron (B_8C) are characterized with the maxima at 110, 132, 200 and 240 K (Fig. 3, curve 3). Temperatures of the maxima depend on frequency of oscillations, i.e. they have relaxation origin. The calculated values of activation energy are 0.12, 0.15, 0.28, 0.38 eV and frequency factors are 3×10^5, 8×10^6, 1×10^8, $2 \times 10^{10}\,s^{-1}$, respectively. Temperature dependence of shear modulus is shown in Fig. 3 (curve 3′). Vacuum (10^{-3} Pa) annealing for 5 h at 1000 K does not affect activation energy and intensity of the relaxation processes, while hydrogen annealing for 3 h at 950 K provides decrease of intensities of the maxima at 110 and 200 K.

IF spectrum of the hot pressed specimen of polycrystalline boron suboxide (B_6O) was studied in the temperature range from 80 to 300 K. In our previous work [2] two small IF maxima were revealed in the specimen of boron suboxide at 110 and 260 K at the frequency of about 1 Hz. The maxima were imposed on the temperature-dependent IF background, their activation energy being 0.25 and 0.70 eV, respectively. In the present work IF maxima occur at 115, 200 and 240 K at ~1 Hz (Fig. 4, curve 1). IF background of the specimen increases together with the increase of temperature. The maxima at 200 and 240 K are distorted due to their being overlapped. Shear modulus defects observed in the vicinity of the maxima are shown in Fig. 4 (curve 1′). Temperature of the maximum at 200 K does not depend on oscillation frequency, this noting to its hysteretic character. The two other maxima have relaxation origin; their activation energies are 0.15 and 0.5 eV and frequency factors are 1×10^7 and $5 \times 10^{10}\,s^{-1}$, respectively. Spectrum of the IF is amplitude dependent. Intensities of the maxima at 200 and 240 K sharply arise as a result of cyclic deformation at 300 K (where number of cycles is 500; amplitude of torsion oscillations—5×10^{-4}). Such changes may be due to the increase of concentration of defects responsible for the formation of the maxima.

After vacuum annealing for 5 h at 1270 K, hysteretic IF is suppressed to ~200K; intensity of the maximum at 240 K decreases by 20% and the height of the maximum at 110 K slightly reduces. Annealing weakens temperature dependence of the IF background at temperatures from 80 to 300 K. Relaxation processes at 110 and 240 K

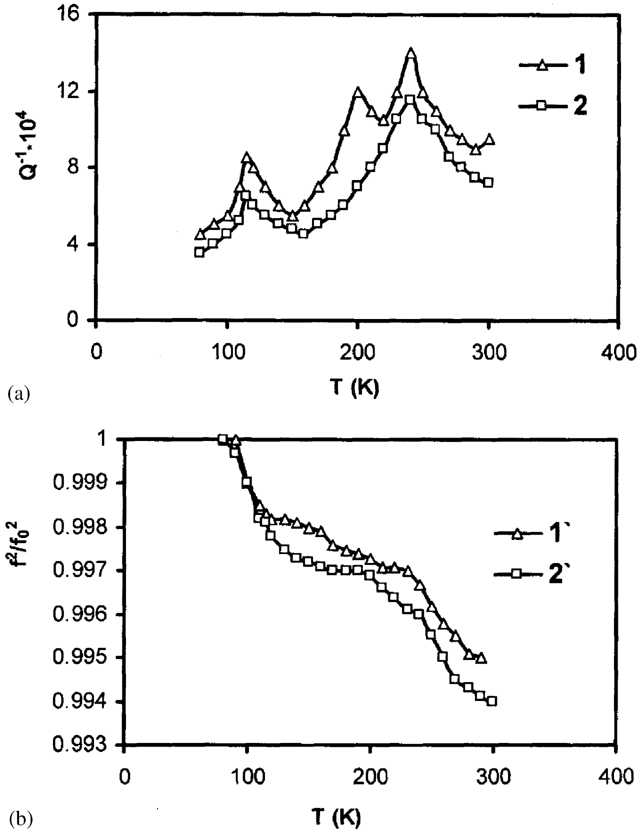

Fig. 4. IF (Q^{-1}) (a) and relative shear modulus (f^2/f_0^2) (b) of boron suboxide. 1–1′ (initial), $f_0 = 1$ Hz; 2–2′ (annealed in vacuum for 5 h at 1270K), $f_0 = 5$ Hz.

in the vacuum annealed specimens (Fig. 4, curve 2) have high values of activation energy (0.18 and 0.60 eV, respectively). The same is appropriate to say about the specimens annealed in hydrogen for 3 h at 970 K.

It is well known that boron carbide and boron suboxide have similar structures where isolated atoms of carbon and oxygen basically occupy equivalent crystallographic positions on the trial axis of appropriate unit cells. Therefore, activation characteristics of the IF relaxation maxima are similar. Behavior after thermal treatment or after cyclic deformation of the IF spectra in these materials is also similar.

By activation characteristics and behavior, studied under the influence of deformation and annealing, the IF maxima found at temperatures from 80 to 300 K, may be considered in terms of the model earlier developed by Hasiguti for the dislocation-type maxima in deformed metals [3] and covalent crystals [4]. Essence of the mechanism of Hasiguti-type relaxation consists in detachment of geometric kinks on the dislocations from point defects (impurities or vacancies). According to Ref. [5] there are three perfect burgers vectors in each rhombohedral plane of the dislocation structure of boron carbide, namely $\bar{a}_1$, $\bar{a}_2$ and $\bar{a}_1 - \bar{a}_2$ in the (001) plane; each of these vectors can dissociate into a pair of Shockley partial Burgers vectors. Since the relation $|\bar{a}_1 - \bar{a}_2| > |\bar{a}_1| = |\bar{a}_2|$ is quite realizable for the structure of boron carbide, we may suppose that greater activation energy is necessary for the detachment of geometrical kink on the $\bar{a}_1 - \bar{a}_2$ dislocations, than for the detachment of geometrical kinks on the $\bar{a}_1$ or $\bar{a}_2$ dislocations. Issued from the above mentioned, possible mechanisms for the IF maxima in boron carbide are the following:

Maximum at 115 K is due to the detachment of the assembly of geometrical kinks; maximum at 200 K—to the detachment of a single geometrical kink on dislocations with Burgers vector $\bar{a}_1$ or $\bar{a}_2$.

Maximum at 140 K is appropriately due to the detachment of the assembly of geometrical kinks from point defects; maximum at 250 K—to a single geometrical kink on dislocations with Burgers vector $\bar{a}_1 - \bar{a}_2$.

Hysteretic maximum at 180–190 K is supposed to be due to destruction of metastable complexes of point defects (impurities of H_2, N_2, O_2 and vacancies) in a stress field at torsion oscillations.

Dislocation structure of boron suboxide has not yet been studied. Therefore, it is impossible to discuss the mechanisms of low-temperature IF maxima in the observed crystals. Presence of dislocations in the specimens of boron suboxide may be supposed only due to the changes of intensities in the observed maxima.

One of the possible mechanisms of formation of the IF maximum at 115 K in boron suboxide may be the detachment from point defects of the assembly of geometrical kinks on the dislocations with Burgers vector $\bar{a}_1$ or $\bar{a}_2$. The IF maximum at 240 K may be due to the detachment from point defects of single geometrical kinks on the same dislocations.

4. Conclusions

IF study of boron carbide and boron suboxide showed very similar IF spectra and identical values of activation characteristics before as well as after thermal treatment or after cyclic deformation. Probably, all the above mentioned is due to the well-known identity of the crystalline structures of these materials.

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