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Influence of carbon content on physicomechanical characteristics of boron carbide

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Abstract

Temperature and amplitude dependences of dynamic shear modulus (SM) and of internal friction (IF) have been measured on boron carbide samples with different carbon content. The samples were investigated at frequencies of torsion oscillations from 0.5 to 5 Hz and at amplitudes of oscillatory deformation from 5×10^{-6} to 1×10^{-2} at temperatures from 80 to 1000 K. It was shown that absolute values of SM, of critical amplitudes of oscillatory deformation and of shear elastic limit decreased with the decrease of carbon content in the samples. Simultaneously, activation energy of the intensive relaxation-type IF in the vicinity of 450–470 K was also decreased. Cyclic deformation at 1000 K provided additional decrease to physicomechanical characteristics while at annealing in vacuum at the temperatures of 1273 and 1773 K these structure-sensitive properties significantly increased. The observed changes of physicomechanical characteristics were attributed to possible changes of inter-atomic forces in the structure of boron carbide samples.

Keywords: Internal friction; Boron carbide

1. Introduction

Changes of B/C ratio in boron carbide provide changes to the lattice parameters thus affecting structure-sensitive physicomechanical characteristics of the material. However, fundamental studies on such problems have not yet been performed. Main objective of the present work was internal friction (IF) study of physicomechanical characteristics of boron carbide in the homogeneity range with carbon content of two edge compositions. Such investigations can give a valuable information on the nature of origination of defects and on their interaction as well as on the nature of their mobility, thus providing possibilities of specified variation of elastic, thermal and plastic properties of boron carbide. The compacted samples of boron carbide are characterized with a great number of defects such as dislocations, vacancies, twin boundaries. Treatment by annealing is capable to change a quantity and energetic condition of the defects. The rate of these changes can be controlled by measuring of the IF spectra and those of dynamic shear modulus (SM). In this connection, it was interesting to study structure-sensitive spectra of IF and SM of annealed compacted samples of boron carbide with different carbon content ($B_{4,3}C$ and $B_{6,5}C$) in a wide range of temperatures and amplitudes of oscillatory deformation.

2. Experimental

Influence of annealing on temperature and amplitude dependences of IF and SM were studied on the samples of $B_{4,3}C$ and $B_{6,5}C$. The samples were prepared by the following way: amorphous boron and carbon black were mixed and sintered for 2.5 h at 2170 K. The obtained powder of boron carbide was crushed in a ball mill (particle size was $< 5\,\mu m$) and then was compacted under pressure of 35 MPa at 2170 K. The samples were composed of 98.6% $B_{4.3}C$ and 98% $B_{6.5}C$, respectively. Major impurities were free carbon, boron oxide, iron, manganese and aluminum. Grain size of the compacted samples was $< 10\,\mu m$.

Annealing was performed for 5 h at 1273 and 1773 K in vacuum of 10^{-5} Pa. IF and MS were determined by the method of registration of damping logarithmic decrement

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and of frequency of free torsion oscillations on the laboratory experimental device [1]. Measurements were made at oscillation frequencies of ~1 Hz in vacuum of 10^{-5} Pa within the range of temperatures from 800 to 1000 K and at amplitudes of oscillatory deformation of 5×10^{-5}–5×10^{-3}. Velocity of heating was 2 °C/min. Dimensions of the samples were 0.5×0.5 (15–20) mm^3.

Real structure of the samples of boron carbide $B_{4,3}C$ annealed at 1273 K was investigated by the method of transmission electron microscopy (JEM-200 at the accelerated voltage of 200 kV). The samples for transmission studies were prepared by the argon plasma. Small openings were the most fitting areas for the transmission and electron diffraction studies. Electron microscopic investigations showed that along the transition areas between particles the image contrast was sharply changing due to overlapping of the fields of elastic deformation in the vicinity of dispersion phases or voids or impurities. Dislocation nodes, deformation twins and stacking faults observed in the structure of boron carbide were described in our earlier works [3,4].

Low-temperature (80–300 K) measurements of the IF temperature spectrum of the $B_{4,3}C$ sample annealed at 1273 K revealed four maxima at 115, 140, 200 and 240 K. Temperatures of the maxima changed together with the change of the oscillation frequency that certifying for the relaxation origin of the maxima. The estimation results of activation characteristics are given in Table 1. Comparison of the data with those of the initial samples [3,4] showed that annealing provided sharp decrease to the intensities of the maxima at 115 and 200 K as well as to the IF background. The values of activation energies of all the maxima were decreased by 10–15%.

Room temperature cyclic deformation at the amplitudes of 1×10^{-3} did not provide any significant changes to the character of the IF spectrum in the temperature range of 80–300 K. The changes became noticeable when the background and intensity of the maxima at 140 and 250 K increased after the cyclic deformation (number of cycles was 200) at temperatures <600 K. Annealing of the samples for 3 h at 450–470 K after the deformation decreased the intensities of the background and of the IF maxima. In such conditions, the IF at the indicated relaxation maxima practically did not change in rather a wide range of amplitudes of oscillatory deformations (5×10^{-5}–1×10^{-3}). After annealing at 1773 K the maxima at 115 and 200 K were fully suppressed and the IF background and activation characteristics of the rest two maxima in the area of 140 and 240–250 K were decreased (see Table 1).

Annealing at 1273 K decreased the maxima observed in the IF spectra of the samples $B_{6,5}C$ even to more extent (Fig. 1, curve 1). After annealing of the initial samples at 1773 K in the spectrum of the IF there were observed only two maxima at 140 and 240 K with relatively low values of activation energy and of frequency factor. At temperatures from 80 to 600 K the intensities and activation characteristics of the indicated maxima were slightly changing at increasing of the amplitude of oscillatory deformation.

Table 1
Activation characteristics of the relaxation processes in boron carbide

Samples of boron carbide	Temperature of the IF maximum (K)	Activation energy (eV)	Frequency factor ($!^{-1}$)
$B_{4,3}C_3$ after annealing at 1273 K, 5 h	110–115	0.10	4×10^{5}
	135	0.18	3×10^{7}
	200	0.28	5×10^{7}
	240	0.45	4×10^{10}
	450	0.90	4.5×10^{12}
	830	2.3	6×10^{13}
$B_{12}C_3$ after annealing at 1773 K, 5 h	132	0.17	3×10^{7}
	240	0.42	3×10^{10}
	480	1.12	7×10^{12}
	830	2.35	8×10^{13}
$B_{13}C_2$—initial	110	0.10	4×10^{5}
	135	0.18	3×10^{7}
	200	0.27	4×10^{7}
	240	0.45	3×10^{10}
	470	0.90	5×10^{12}
	825	2.25	4×10^{13}
$B_{13}C_2$ after annealing at 1273 K, 5 h	110	0.10	4×10^{5}
	130	0.17	3×10^{7}
	190	0.25	2×10^{7}
	235	0.41	3×10^{10}
	450	0.85	4.5×10^{12}
	820	2.20	4×10^{13}
$B_{13}C_2$ after annealing at 1773 K, 5 h	130	0.16	1×10^{7}
	230	0.40	3×10^{10}
	480	1.20	7×10^{12}
	820	2.10	3×10^{13}

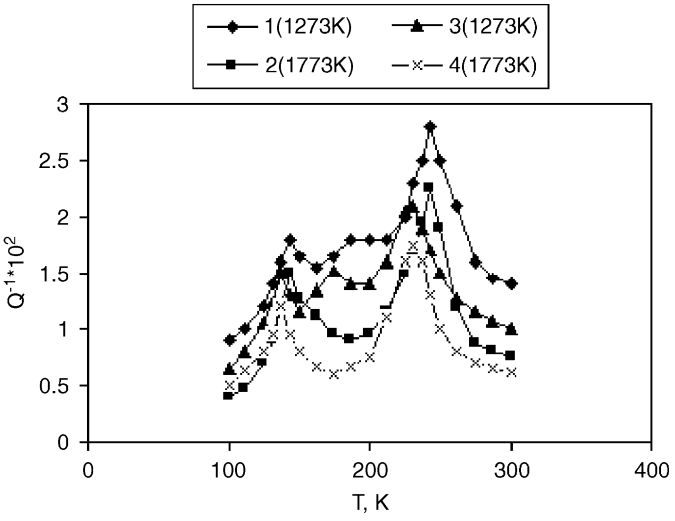

Fig. 1. IF spectrum of annealed samples $B_{4,3}C$ (1.2) and $B_{6,5}C$ (3,4). 1,3—after annealing at 1273 K, 5 h. 2,4—after annealing at 1773 K, 5 h.

It was shown that at temperatures from 300 to 1000 K the IF of the compacted samples of $B_{4,3}C$ had an exponentially increasing background with superimposed

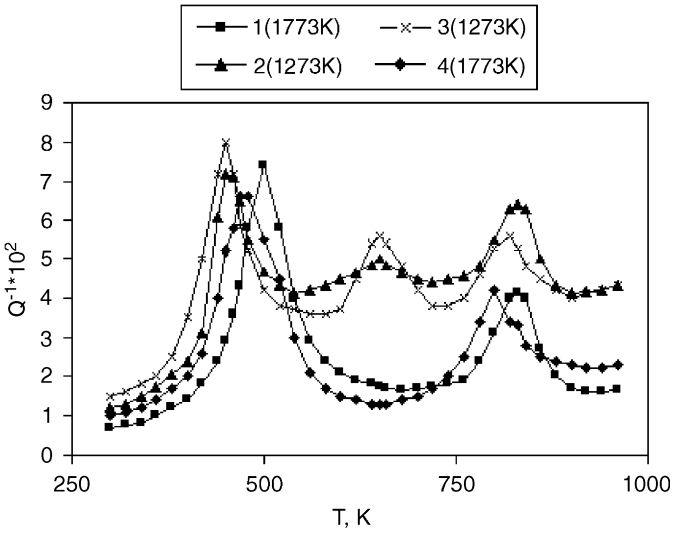

Fig. 2. IF spectrum of compacted samples $B_{4,3}C$ (1.2) and $B_{6,5}C$ (3,4). 2,3—after annealing at 1273 K, 5 h. 1,4—after annealing at 1773 K, 5 h.

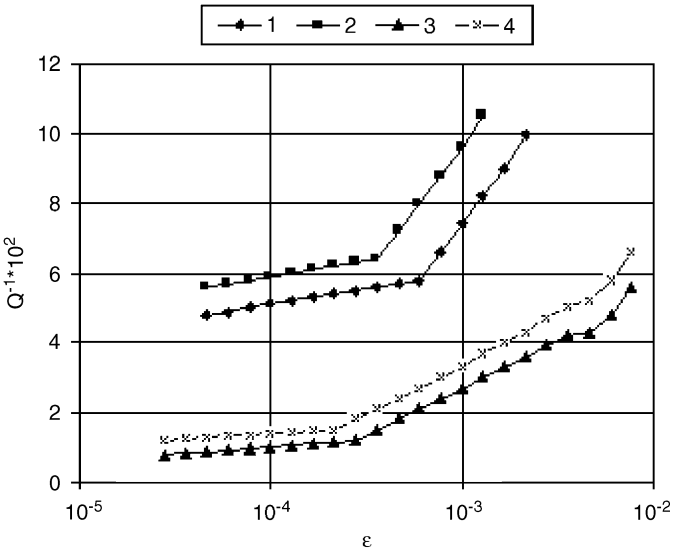

Fig. 3. Amplitude dependence of the IF of the compacted samples of boron carbide: $B_{4,3}C$ initial—(1) and after annealing at the 1773 K, 5 h—(2); $B_{6,5}C$ initial—(3) and after annealing at the 1773 K, 5 h—(4).

relaxation maxima in the vicinity of 470 and 830–850 K. The background of the nonrelaxation maximum at 650 K also increased [5]. After annealing at 1273 K the exponentially increasing background decreased however the relaxation maxima were broadened (Fig. 2). Temperatures and activation characteristics of these maxima were decreased by 10–15% if compared with the initial IF spectrum (see Table 1). The IF spectra of the sample of $B_{6,5}C$ were similar to those of the sample $B_{4,3}C$. Distinctive feature was a slight decrease of the activation characteristics of high-temperature IF in the samples of $B_{6,5}C$ after annealing at 1273 and 1773 K. Annealing of the samples for 5 h at 1773 K sharply depressed the nonrelaxation IF at 650 K, and increased the temperature of the first relaxation maximum up to 490 K. Activation characteristics of the samples of $B_{6,5}C$ were also increased (see Table 1), however those of the relaxation processes at 830 K slightly decreased.

At room temperatures the values of absolute SM of the samples of $B_{4,3}C$ and $B_{6,5}C$ were 198 and 185 GPa, respectively. After annealing for 5 h at 1273 K these values increased up to 200 and 190 GPa. Annealing of the samples for 5 h at 1773 K increased the values of absolute SM up to 205 and 195 GPa. Comparison of the results showed that increase of the annealing temperature from 1273 to 1773 K did not cause any noticeable changes to the values of SM of the samples $B_{4,3}C$ and $B_{6,5}C$.

Background of the IF in the samples of boron carbide clearly revealed a dependence on the oscillation amplitude in the area of high temperatures (~850 K). On the curves of the IF amplitude dependence of the initial samples of $B_{4,3}C$ (Fig. 3, curve 1) and of $B_{6,5}C$ (Fig. 3, curve 3) there were observed two intervals of a slight and then of a sharp increase of the IF intensities separated from each other by a critical amplitude of oscillatory deformation. A value of the critical amplitude of $B_{4,3}C$ was higher than that of $B_{6,5}C$. The IF of the initial samples sharply increased in the area of high amplitudes of oscillatory deformation.

Annealing at temperatures of 1273 and 1773 K decreased the critical amplitude of oscillatory deformation and the IF background intensity at high amplitudes. Two critical amplitudes of oscillatory deformation appeared on the curves of amplitude dependence of damping after the annealing (Fig. 3). Critical values of the oscillatory amplitudes are given in Table 2. The values of the first and the second critical amplitudes of the samples of $B_{6,5}C$ were relatively low if compared with those of the samples of $B_{4,3}C$. The values of the both critical amplitudes of oscillatory deformation decreased together with the increase of the measurement temperatures (see Table 2).

According to some theoretical considerations [2], at critical amplitudes of oscillations the dislocation segments break off from weak (first critical amplitude) and from strong (second critical amplitude) centers of pinning. Generally, it is supposed that impurity atoms and vacancies are weak centers while complexes of point defects, dispersion phases and nodes of intersecting dislocations are strong centers. Estimations of the energy of breaking off from dislocations and of the bonding energy of dislocations with different centers of pinning at different temperatures (600–800 K) were performed by the method described in Ref. [6]. The results of the estimations are given in Table 2. They show that the values of the energy of bonding of the dislocations with the centers of their pinning for the samples of $B_{4,3}C$ and of $B_{6,5}C$ are different and that they are dependent on the annealing temperature.

Table 2
Physicomechanical characteristics of the samples of boron carbide

Samples of boron carbide	Shear modulus (Gpa)	I critical amplitude		II critical amplitude		I limit of elasticity (Gpa)		II limit of elasticity (Gpa)		Link energy at I critical amplitude (eV)	Link energy at II critical amplitude (eV)
		600 K	800 K	600 K	800 K	600 K	800 K	600 K	800 K		
$B_{12}C_3$ initial	198	8×10^{-4}	4×10^{-4}			0.158	0.079			0.2	
$B_{12}C_3$ after annealing at 1273 K, 5h	200	6×10^{-4}	3.35×10^{-4}	7.5×10^{-3}	1.13×10^{-3}	0.120	0.087	1.50	0.23	0.18	0.45
$B_{12}C_3$ after annealing 1773 K, 5h	205	5×10^{-4}	2.9×10^{-4}	7×10^{-3}	1.22×10^{-3}	0.102	0.060	1.43	0.25	0.17	0.42
$B_{13}C_2$ initial	185	6×10^{-4}	3.3×10^{-4}			0.111	0.061			0.18	
$B_{13}C_2$ after annealing at 1273 K, 5h	190	5×10^{-4}	3×10^{-4}	6.5×10^{-3}	1.2×10^{-3}	0.095	0.057	1.235	0.228	0.17	0.42
$B_{13}C_2$ after annealing at 1773 K, 5h	195	4.5×10^{-4}	$\mathbf{2.7\times10^{-4}}$	6.2×10^{-3}	1.19×10^{-3}	0.087	0.053	1.209	0.232	0.16	0.40

3. Discussion of the results

It was shown [3–5] that in the samples of boron carbide prepared by the method of melting or compacting there was observed an intensive IF relaxation maximum in the vicinity of 450–470 K. Activation energy and frequency factor of the IF maximum were ~1 eV, and $\sim5\times10^{12}c^{-1}$, respectively. IF maximum was created due to the movement of twin boundaries in the system of {100}. Activation energy of the relaxation maxima in the samples of $B_{4,3}C$ was rather weak (0.1–0.5 eV) within the range of low temperatures; by activation characteristics they were similar to the maxima described in Ref. [7].

Changes of the activation characteristics of the relaxation maxima at 450–470 K can be attributed to the following: at annealing temperatures (~1273 K) the impurities around twinning dislocations transfer into the solid solution and form strong local bonds with boron atoms and vacancies. If twinning dislocations are free of the pinning effect of impurity atmospheres in the field of the internal and external stresses they will need less activation energy for moving. Increase of the annealing temperature together with the impurity transfer in the lattice provides thickening of twinning lamella and of slowly moving twinning packs. Activation energy necessary for the moving of these packs is much higher. It is well known that in the model presented by the authors in Ref. [8] carbon-saturaded composition, near B_4C, comprises $B_{11}C$ icosahedra and (primarily) C–B–C chains. Between B_4C and $B_{13}C_2$, C–B–C chains are progressively replaced by C–B–B chains. It seems that a comparatively low value of activation energy of the initial and the annealed samples of $B_{4,3}C$ is caused by the presence of less rigid bonds in the C–B–B chain if compared those to the C–B–C chain located along the trigonal axis of boron carbide. This must be a reason explaining why the values of dynamic mechanical characteristics as are SM, critical amplitudes of oscillatory deformation and shear elastic limit are rather high. These characteristics depend on the forces of inter-atomic interactions and on the efficiency of bonding of twinning and perfect dislocations as well as of stacking faults with the centers of point pinning. Existence of four weak relaxation maxima in the area of 80–300 K must be provided by the existence of different relaxation centers. The maxima at 115 and 200 K are thermally non-stable: they are decreased upon annealing and the values of their activation energies are changed; frequency factor of the maxima decreases by 5–6 orders of magnitude if compared to the frequency factor of impurities and vacancies.

The relaxation maxima at 140 and 250 K were thermally stable. Activation characteristics of these maxima are comparable with those of the analogous IF maxima provided by interaction of dislocations with point defects [7].

4. Conclusion

The experiments showed that in the samples of $B_{4,3}C$ and of $B_{6,5}C$ the values of activation energies of the above

described maxima coincide with the values of the energy of breaking off of dislocation segments from weak and from strong points of pinning at the first and at the second critical amplitudes of oscillatory deformation. Possible mechanism of the origination of the IF maximum at 140 K may be break off of the dislocation segments from impurity atoms or from the vacancies. The IF maximum at 240 K may be due to the break off of the dislocation segment from the complexes "impurity atom-vacancy". Presence of full dislocations and a character of their distribution along the system of (100) planes was investigated in Ref. [9].

At annealing the bonds between dislocation and point defects are breaking. These defects provide elongation of the segments on dislocations. Correspondingly, tension force of the segments decrease. Therefore, breaking off of the pinned dislocation segments will be realized at comparatively low activation energy after annealing of the samples of $B_{4,3}C$ and $B_{6,5}C$ at 1273 and 1773 K. It is supposed that the differences observed in the samples of $B_{4,3}C$ and $B_{6,5}C$ in the values of the discussed activation energies of the low-temperature IF maxima are provided by the presence of more rigid bonds like C–B–C chains—icosahedra in the lattice of $B_{4,3}C$.

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