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Preparation, structure and some properties of boron crystals with different content of ^{10}B and ^{11}B isotopes

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Abstract

The present work deals with the analysis of data on preparation and investigation of boron with different content of ^{10}B and ^{11}B isotopes. It was established that influence of isotopes on the structure and physical–mechanical properties of boron varies with regard to the type and percentage of an applied isotope. Microhardness of the specimens was measured at room temperatures. Peculiarities of changes observed in the values of microhardness, thermal expansion coefficients and characteristics of the relaxation processes are discussed from the point of view of probable changes in inter-atomic forces created due to substitution of natural boron atoms with their isotopes.

Keywords: Boron isotope; Lattice parameters; Thermal expansion coefficient; Microhardness; Dislocations; Stacking faults; Internal friction; Diffraction pattern

1. Introduction

In recent years, study of the influence of ^{10}B and ^{11}B isotope content on the properties of boron and boron-containing materials became a matter of special interest. However, fabrication of such materials is connected with some difficulties, this being a reason for rather a restricted number of works on their investigation and application perspectives in modern technique.

2. Experimental

Present work is focused on the fabrication and investigation of materials with different content of ^{10}B and ^{11}B isotopes. Crystalline powders of ^{10}B and ^{11}B isotopes obtained by electrolysis of KBF_4 salts of appropriate isotopes (known as Cooper method) were used as initial materials. Atomic share of ^{10}B in crystalline powder of ^{10}B isotope was 87.8 at%; mass fraction of the basic material—95.1%, a sum of natural boron mass fraction and impurities of carbon, silicon, iron, nickel, lead, was not less than 99.0%; powder density—2.19 g/cm^3, bulk density—1.60 g/cm^3. Atomic share of ^{11}B in crystalline powder of ^{11}B isotope was 98.4%; basic material mass fraction—97.2%, accompanying impurities were: carbon—1.4%; iron—0.30%; aluminum 0.15%; nickel—0.3%; powder density—2.35 g/cm^3; bulk density—1.65 g/cm^3.

The sintered billets of boron with different content of ^{10}B and ^{11}B isotopes were melted in electro-resistance furnace of the СШВ-1.2,5/25-*И*1-type following the elaborated special mode. The sintered rods with different content of ^{10}B and ^{11}B isotopes were refined on a laboratory installation for floating zone melting.

3. Results and discussion

Structure of the specimens was investigated on a diffractometer HZG-4A-type, at Cu$K\alpha$ irradiation with Ni filter. The bulk specimens with different content of ^{11}B isotope as well as the rods made by floating zone method had polycrystalline structure of β-rhombohedral

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Table 1
Lattice parameters calculated by diffraction patterns of zone-melted boron specimens with different content of ^{11}B isotope

^{11}B isotope content (at%)	Lattice parameters (Å)	
	a	*c*
13	10,940	23,814
60	10,940	23,811
81.8	10,942	23,810
90	10,935	23,762
95	10,932	23,757
98.2	10,930	23,765
99.8	10,928	23,750

modification. Program package CSD was used for the analysis of the diffraction maxima. The results of estimation of the lattice parameters are given in Table 1. As seen from the data, an increase of ^{11}B isotope content in the specimen results in slight decrease of the parameters.

With the goal of evaluating an isotope content effect on boron, a comparative study of the unit cell parameters of the specimens with sharp distinctions of isotope content was performed. Two zone-refined boron specimens have been studied: (a) with a ratio $^{10}B/^{11}B$—19/81 (where the unit cell parameters were well established), (b) with a ratio $^{10}B/^{11}B$—87/13, i.e., the samples with 81% ^{11}B and 87% ^{10}B isotope content.

Parameters *a* and *c* were defined with high accuracy on the diffractometer HZG-4A by scanning method. Scanning step was 0.05°, for nearby maxima it was 0.02°. Impulse counting for each step was 10–20 s. A program packet for each scanning and analysis of the maxima profiles was of CSD type. From the obtained 25 reflexes, the best 15 were selected. Their profiles were treated with the goal of establishing their accurate location. The obtained parameters were: $a = 10.9409$ (3) Å; $c = 23.8107$ (6) Å; $\Delta a = 0.0008$ (6) for the specimen with 87% ^{10}B isotope content; $a = 10.9401$ (3) Å; $c = 23.8112$ (6) Å for the specimen with 81% ^{11}B isotope content.

As issued from these data the boron lattice parameters slightly decrease with the increase of ^{11}B isotope content.

Relative elongation of the specimens (both bulk and zone-melted rods) with the dimensions $4 \times 4 \times (10–12)$ mm^3 was measured on a vacuum quartz dilatometer with inductive sensor. Heating temperature varied from 20° to 900°C. Accuracy of measurements of the specimens with different content of ^{11}B isotope was $\pm 3\%$. Temperature dependence of relative elongation is shown in Figs. 1–3.

On the curve of temperature-dependent elongation of boron containing 19.0 at% of ^{10}B isotope, deviations from linear changes within the area of temperatures 250–400°C and 500–550°C were observed. Character of the changes is reproducible. The indicated anomalies were observed also in the specimens where ^{10}B isotope content was 40.0, 60.0 and 97.2 at%. At elevated temperatures (600–850°C), the curve of temperature-dependent elongation of the specimen with 97.2 at% ^{10}B isotope content had linear character. As temperature starts to rise, the deviations from the expected linear increase of the elongation occur on the α (T) in the form of bends; they are better expressed at temperatures from room to 500°C. Such changes are in good correlation with the results of Ref. [1], where α (T) of β-boron was calculated based on X-ray analysis data.

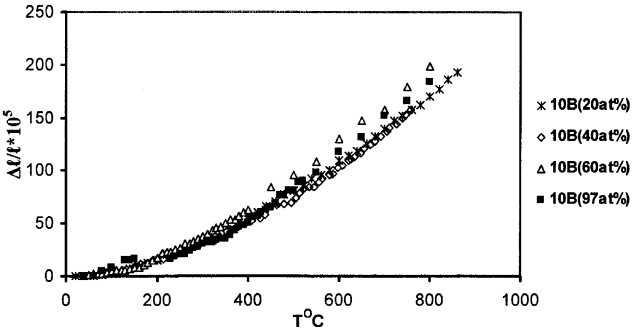

Fig. 1. Temperature dependence of relative elongation of β-boron samples with different ^{10}B isotope content.

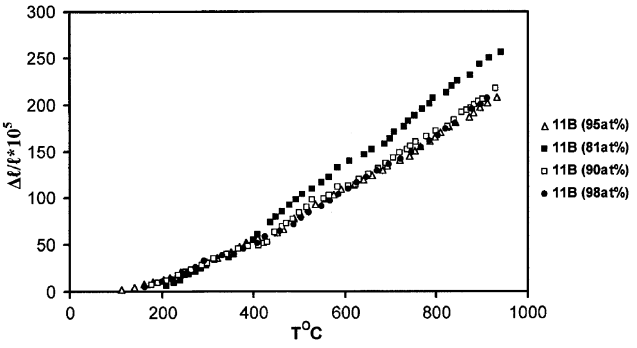

Fig. 2. Temperature dependence of relative elongation of zone-melted β-boron samples with different content of ^{11}B isotope.

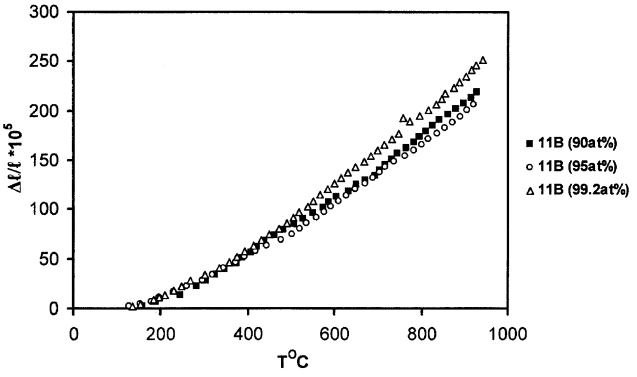

Fig. 3. Temperature dependence of relative elongation of β-boron samples with different content of isotope ^{11}B melted in BN crucible.

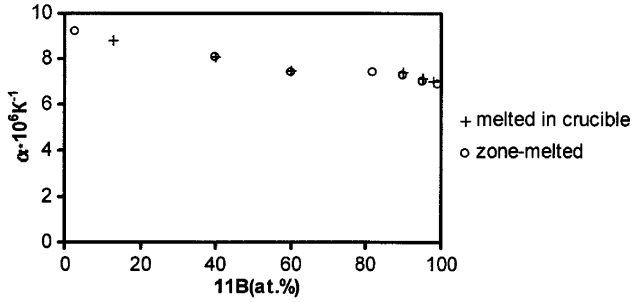

Fig. 4. Thermal expansion coefficient (α) for the samples with different content of isotopes ^{10}B and ^{11}B. $T = 900$°C.

Analysis of the curve shows that velocity of growing of $\Delta\ell/\ell$ within the area of temperatures from 250°C to 400°C is being reduced while at temperatures from 700°C to 900°C it increases. It was established that the higher the ^{11}B isotope content in the specimens the more is the elongation. At high temperatures ($\sim$900°C) such changes are more distinctly revealed. Average meanings of the thermal expansion coefficient $\alpha = (\Delta\ell/\ell\,\Delta T)$ were calculated on the linear parts of the dependence $\Delta\ell/\ell(T)$ at different temperatures from 400°C to 900°C. Fig. 4 shows that the value of α decreases with the increase of ^{11}B isotope content.

Room-temperature measurements of microhardness were performed for both, zone-refined and crucible-melted specimens, on the device of "ПМТ-3"-type. Processing of surfaces of the specimens was carried out using diamond saw with subsequent mechanical polishing. Loading weight was 100 g/mm^2. Hardness measurement error was 3%. The results of measurements are shown in Table 2. Table 2 and Fig. 5 show that the increase of the content of ^{10}B or ^{11}B isotopes in boron specimens promotes increasing of microhardness.

Temperature dependence of internal friction (IF) and shear modulus of polycrystalline boron specimens were studied by using the method of registration logarithmic decrement and frequency of free attenuation torsion oscillations. Specimens with the dimensions $0.4 \times 0.4 \times (12\text{–}15)$ mm^3 were cut from the zone-refined specimens as well as from the crucible-melted ones. The IF and proportional to shear modulus square frequency oscillations were evaluated at temperatures from 20°C to 800°C within the frequency range from 0.5 to 5 Hz and relative deformation 5×10^{-5}–2×10^{-3}. The IF and activation energy of the observed maxima were calculated by the method described in Ref. [2].

Content of ^{10}B isotope in two specimens of zone-refined boron was 19.0% and 97.2%, respectively, and that in two crucible-melted boron was 40.0% and 70.0%. The results of IF and shear modulus measurements are shown in Fig. 6.

IF spectrum of natural boron measured at low frequencies of $\sim$1 Hz is characterized with two maxima

Table 2
Microhardness of boron specimens with different content of ^{10}B and ^{11}B isotopes

^{11}B isotope content (at%)	Microhardness (kg/mm^2)	
	Melted in BN crucibles	Zone melted
3	3300	3800
13	3250	3700
30	3200	3400
40	3050	3350
60	3600	3050
81.8	—	3280
90	3800	4330
95	4000	4090
99.2	4050	4450

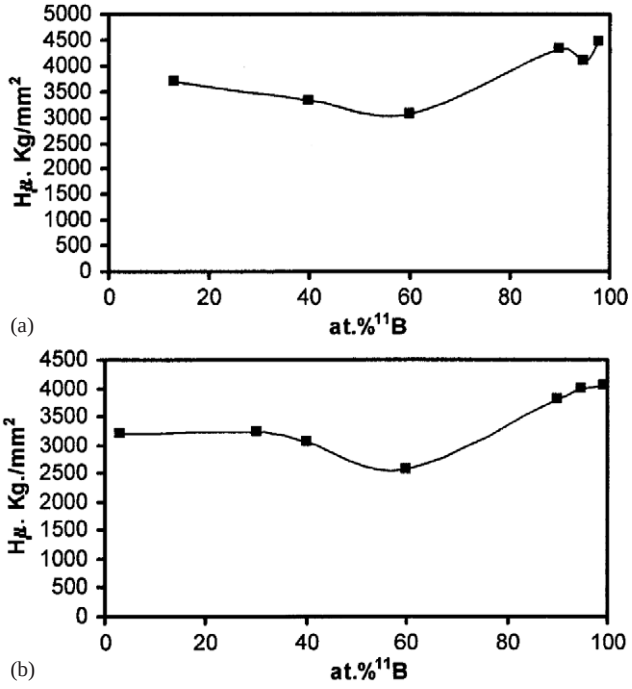

Fig. 5. Dependence of a microhardness on the isotope ^{11}B content in the samples, obtained by: (a) zone-melting; and (b) melting in BN crucible.

of relaxation-type at 250°C and 450°C and a non-relaxation maximum at 300°C. Intensity of the maximum at 450°C is moderate ($\sim$0.01). It increases with the decrease of grain size. Values of activation energy do not depend on grain size. Non-relaxation IF maximum at 300°C has average intensity ($\sim$0.05). At the occurrence of the IF maximum, one can observe decrease of shear modulus. Value of the modulus defect is proportional to the IF intensity. IF spectra of the specimens with different ^{10}B isotope content have similar maxima; however, their intensities are somehow different. Activation characteristics of the relaxation maxima are shown in Table 3.

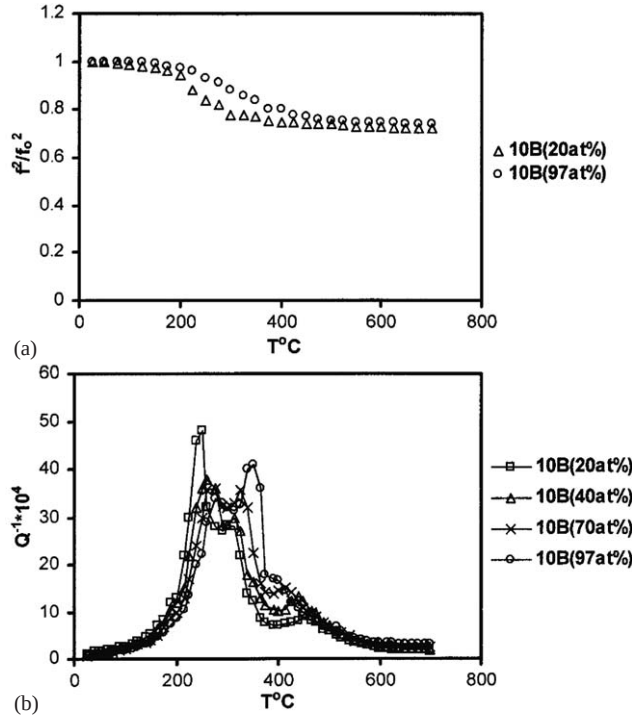

Fig. 6. Temperature dependence of IF (Q^{-1}) and relative shear modulus (f^2/f_0^2) in boron samples with different ^{10}B isotope content.

Table 3
Activation characteristics of the relaxation maxima

^{10}B isotope content (at%)	Temperature of IF maxima (°C)	Activation energy (eV)	Frequency factor (s^{-1})	Relative intensity of the IF maxima
19.0	240	1.2	8×10^{12}	0.15
	450	2.2	6×10^{14}	0.005
60.0	270	1.3	1×10^{13}	0.01
	430	2.0–2.1	3×10^{14}	0.03
70.0	275	1.35–1.4	2×10^{13}	0.01
	410	1.9	1×10^{14}	0.015
97.2	280	1.5	5×10^{13}	0.012
	380–390	1.8	1×10^{14}	0.015

Intensity of the non-relaxation processes significantly increases in the vicinity of 300°C with the increase of ^{10}B isotope content. This process is analogous to that described for boron in Ref. [3]. The process can be explained by transformations occurring in the complexes or small phases located in twinning packs and stacking faults of the β-boron structure. As seen from Table 3, activation characteristics of the relaxation processes in the vicinity of 400°C decrease with the increase of ^{10}B isotope concentration. This process can be attributed to the motion of stacking faults along the

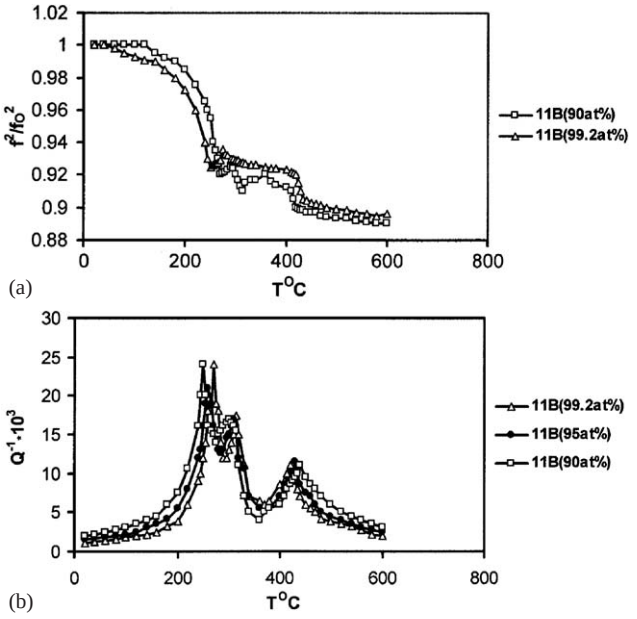

Fig. 7. Temperature dependence of IF (Q^{-1}) and relative shear modulus (f^2/f_0^2) of crucible-melted β-boron samples with different ^{11}B isotope content.

{100} system planes [4]. Such changes of activation parameters may be induced by decrease of the formation energy of stacking faults.

IF spectrum of the specimen with $\sim$90.0 at% ^{11}B isotope content measured at a frequency of $\sim$5 Hz and relative deformation of $\sim10^{-5}$, is characterized with two maxima of relaxation-type at 270°C and 420°C and a non-relaxation maximum at 315°C (Fig. 7). Intensities of the maxima at 315°C and 420°C are comparable with intensities of the analogous maxima observed in relatively pure polycrystalline natural boron obtained in similar conditions (BN crucible); however, intensity of the main relaxation maximum ($\sim$250–270°C) is by 5–8 times lower. Activation energies of relaxation processes at 270°C and 420°C are 1.25 ± 0.2 and 1.90 ± 0.2 eV, respectively. Corresponding frequency factors are 5×10^{13} and $2\times10^{14}\,s^{-1}$. Room-temperature absolute value of dynamic shear modulus is 180 GPa. Defects of dynamic shear modulus are characteristic for all three IF maxima. Values of shear modulus defects are proportional to the intensity of IF maxima. Physical–mechanical characteristics of boron specimens with different content of ^{11}B isotope are shown in Table 4.

It was established that with increase of the ^{11}B isotope content, intensity of the relaxation maxima in the area of 270°C and 420°C increase. Simultaneously, the maximum at 420°C shifts to higher temperatures and its activation energy increases up to 10%. The maximum at 270°C slightly shifts to lower temperatures and its activation characteristics slightly decrease. As for the non-relaxation process at 300–315°C, it is thermally

Table 4
Activation characteristics of the relaxation maxima

^{11}B isotope content (at%)	Temperature of IF maxima (°C)	Activation energy (eV)	Frequency factor (s^{-1})	Room-temperature shear modulus (GPa)
90	270	1.30 ± 0.2	5×10^{13}	180
	420	1.90 ± 0.2	2×10^{14}	
	315	—	—	
95	260	1.25 ± 0.2	1×10^{13}	195
	430	2.00 ± 0.2	5×10^{14}	
	310	—	—	
99.2	255	1.15 ± 0.2	5×10^{12}	210
	435	2.20 ± 0.2	8×10^{14}	
	305			

stable with the increase of ^{11}B isotope content in contrast to the analogous maximum found in single crystals of pure boron [2].

The specimens with relatively high ^{11}B isotope content are characterized with rather increased values of shear modulus. With this, the amplitude of oscillation deformation significantly increases where the IF amplitude dependence at temperatures of about 400–450°C occurs. Increase of shear modulus is in good correlation with the decrease of thermal expansion coefficient and boron lattice parameters with the increase of ^{11}B isotope content. Increase of the amplitude may be attributed to increase of blocking forces of partial dislocations.

It is supposed that the observed changes in activation characteristics of the IF relaxation maximum at 250–270°C are provided by enhancement of mobility of twin boundaries. Increase of activation characteristics of the maximum at 420–430°C may be due to the strengthening of inter-atomic (inter-icosahedra) forces with increase of ^{11}B isotope content.

4. Conclusion

Structure and physical–mechanical characteristics of zone-refined and crucible-melted boron have been studied. It was established that the values of lattice parameters, microhardness, thermal expansion coefficient, and absolute shear modulus non-monotonously increase with increase of the concentration of ^{10}B isotope. Basing on the analysis of IF spectra it was shown that in the specimens with high content of ^{10}B isotope, activation energy of the motion of twin boundaries in the vicinity of 250°C decrease; however, activation energy of stacking faults in the vicinity of 400°C increase. The changes of physical–mechanical characteristics were explained from the point of view of the increase of inter-atomic (inter-icosahedral) forces upon increase of the content of light ^{10}B isotope in boron structure.

Acknowledgments

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