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THE STUDY OF THE STRENGTH CHARACTERISTICS OF REFRACTORY DODECABORIDES RARE EARTH METALS WITH A STRUCTURE OF UB_{12}

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This paper presents the results of experimental studies of thermal expansion, melting point, micro-hardness, elastic modulus and estimates of characteristic temperatures, the velocity of propagation of sound waves, the strength characteristics (Young's modulus, shear modulus, Poisson's ratio, fragility, etc.) for dodecaborides YB_{12}, TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}, YbB_{12}, LuB_{12}, ZrB_{12}.

Key words: refractory compounds, the mechanical characteristics, the characteristic temperature, Young's modulus, shear modulus, Poisson's ratio, brittleness.

Introduction. The refractory borides, carbides, silicides, oxides, etc. compounds have a number of remarkable properties: a wide range of electrical, magnetic properties, high melting point, high resistance to the action of acids and mixtures thereof, the absorption of radioactive radiation and other practically important properties. Problematic, however, is that the high brittleness, low ductility, and thermal stability, lack of knowledge of their mechanical properties such as modulus of elasticity (Young's modulus), the shear modulus, bulk modulus, Poisson's ratio and others [1], often limit the use of a wide term problems of strength of these compounds, especially with regard to the phase dodecaborides isomorphic with the structure of rare-earth metals such as UB_{12} - YB_{12}, TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}, YbB_{12}, LuB_{12}, ZrB_{12}. Mechanical properties of these compounds have hardly been studied. Therefore, consideration of problems in the broad sense of safety for these phases is highly relevant [2].

The mechanical properties of the rare earth metals dodekaborides phases is of interest not only from the point of view of their practical use as a durable, hard, abrasive materials, and from the relationship of these parameters with the thermal properties, the electronic structure, the type of the chemical bond therein. It is generally known that the hardness, friability, and other similar characteristics increases with the proportion of covalent bond. By the way, this is the type of chemical bond is prevalent in dodekaborides phases in consequence to preserve them icosahedrons B_{12}, inherent in the pure forest, as one of the hardest materials in nature.

The purpose of the paper is that on the basis of known relationships between mechanical parameters and thermal characteristics determined experimentally evaluate the strength parameters dodekaborides phases YB_{12}, TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}, YbB_{12}, LuB_{12}, ZrB_{12}.

Results and discussion. Dodecaborides rare earth metals borotermicheskogo synthesized by the reduction of oxides of metals using an excess of boron in the charge that allowed by the two-step process to obtain single-phase material [3]. Compact borides samples studied were fabricated by sintering preliminarily compacted powder briquettes dodecaborides crucibles zirconium diboride bed of a coarse powder of sinterable boride in argon at temperatures of 2100K to 2200K and holding for two hours. Cooling was carried out at temperatures 200degree/hour to 900K, and further - together with the furnace to room temperature. The resulting samples had a porosity of 15-20% and, according to X-ray and metallographic analyzes were single phase.

The samples for the study of the physical properties of the cut on the electric spark machine.

Thin sections for micro-hardness measurements of samples were prepared by sequential treatment for grinding wheels type ASO - 16 - 61 - 50 with a final polishing with diamond grit disks 100, 30, 3mkm. Identification of the structure after polishing produced by chemical etching. In this shot peening surface caused by polishing. The microhardness was determined on mikrotverdometre PMT-3 etalonirovannom carefully through the crystal NaCl at 300K. Loading time 10s, inductor loaded weights of 30, 50, 100, 150, 200g. At each loading was performed 30-50 microhardness measurements dodecaborides. It is established that, from a certain load (for dodecaborides 100g) microhardness dodecaborides almost independent of the load. Microhardness for dodekaboridnes phases were 3200, 3000, 2600, 2400, 2700,2800,3000,2900 kg/mm^2, respectively, for YB_{12}, ZrB_{12}, TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}, LuB_{12}. For dodecaboride ytterbium at loading 50g or more were observed chips (H_{30}=3300kg/mm^2).

For the calculation of the characteristic (Debye) temperature related to the speed of sound waves by (1)

$$\Theta^{Д} = \frac{h}{k}\left(\frac{3nN\gamma}{4\pi M}\right)^{\frac{1}{3}} \cdot v_m \qquad (1)$$

a quartz dilatometer investigated the thermal expansion dodecaborides and other values were determined in the formula (2)

$$\Theta^{Д} = 10{,}97\sqrt{\frac{Z \cdot C \cdot N^{\frac{2}{3}} \cdot \gamma^{\frac{2}{3}}}{M^{\frac{5}{3}} \cdot \alpha}} \quad [4]. \qquad (2)$$

The calculated values of the characteristic temperature practically coincided with the values of this parameter obtained from the X-ray spectra[5].

Melting points dodecaborides metals were determined by Pirani-Altertuma (drop method), which consists in measuring the optical micropyrometer intensity of blackbody radiation in the center of the sample is heated by electricity. By heating the sample hole in it will seem brighter than the surrounding surface, which loses heat by radiation. Upon reaching the melting point of the hole formed in the middle drop and darkens it. Measured at this point, the temperature is the melting temperature of the material - dodecaborides.

The experimental and calculated values dodecaborides characteristics are summarized in Table 1.

Table 1

Boride	Mol. weight $M \cdot 10^{-3}$, kg/mol	Density $\gamma \cdot 10^{3}$, kg/m^3	Heat capacity C, Dg/(mol·K)	Microhardness H_{100}, kg/mm^2	Coef. of thermal expansion $\alpha \cdot 10^{-6}$, K^{-1}	The characteristic temperature Θ, K		Mean square vibration of the atom $\sqrt{\overline{u}^2} \cdot 10^{-10}$, m	T_m, K
						calculated	[9]		
YB_{12}	218,732	3,444	158304,71	3200	3,2	1052	1094	0,029	2950
TbB_{12}	288,656	4,540	160523,71	2600	3,6	900	834	0,042	2400
DyB_{12}	292,232	4,611	160398,11	2400	4,6	850	871	0,026	2550
HoB_{12}	294,732	4,655	160398,11	2700	3,6	872	886	0,026	2750
ErB_{12}	296,982	4,706	161277,34	2800	3,7	872	888	0,026	2600
TmB_{12}	298,732	4,756	160146,90	3000	3,8	868	886	0,027	2750
YbB_{12}	302,732	4,820	158262,84	-	3,7	845	858	0,028	-
LuB_{12}	304,732	4,868	160146,90	2900	3,4	878	878	0,029	2650
ZrB_{12}	220,952	3,611	158304,71	3000	3,5	976	976	0,029	2750
UB_{12}	367,732	5,855	133180,24	-	4,7	-	758	0,024	2500

Using the formula

$$v_m = \frac{\Theta^{Д}}{\frac{h}{k}\left(\frac{3nN\gamma}{4\pi M}\right)^{\frac{1}{3}}} \text{ [6]} \tag{3}$$

forward speed of propagation of sound waves in polycrystalline samples dodecaborides rare earth metals and the relation

$$v_t = \sqrt{\frac{G}{\gamma}} \tag{4}$$

find the shear modulus

$$G = \gamma \cdot v^2 \tag{5}$$

for boron and dodekaboridnes phases (Table 2).

Representations of Koester and Frantsevich by the formulas:

$$f(\mu) = \frac{3{,}34 \cdot 10^7 \cdot T_{пл}^{\frac{3}{2}}}{A \cdot \gamma^{\frac{1}{2}} \cdot C \cdot V^{\frac{3}{2}} \cdot \Theta^3} \tag{6}$$

$$f(\mu) = \left[\left(\frac{1+\mu}{3(1-\mu)}\right)^{\frac{3}{2}} + 2\left(\frac{2(1+\mu)^{\frac{2}{3}}}{3(1+2\mu)}\right)^{\frac{3}{2}}\right]^{\frac{2}{3}} \tag{7}$$

we estimate the Poisson's ratio and compare it with those of the borides TiB_2 and ZrB_2.

From the relation $G = \frac{E}{2(1+\mu)}$ find a Young's modulus of dodecaborides and then the coefficient of elasticity

$$E = 2G(1+\mu). \quad (8)$$

Compare this value with the values obtained from the formula of Frenkel

$$\alpha = \frac{nk}{nR_0^3 E}; \quad (9)$$

$$E = \frac{nk}{\alpha \cdot n \cdot R_0^3} [7] \quad (10)$$

and claims Frantsevich

$$\Theta^{Д} = \frac{1{,}6818 \cdot 10^3 \cdot \sqrt{E}}{M^{\frac{1}{3}} \cdot \gamma^{\frac{1}{6}}}, \; E = \frac{\Theta^2 M^{\frac{2}{3}} \gamma^{\frac{1}{3}}}{1{,}6818^2 \cdot 10^6} [8] \quad (11)$$

experimental (Table 2) of our studies modulus dodekaboridnes phases as described for the determination of the values for the rectangular beam, clamped at one end.

The elastic modulus of phases MeB_{12} calculated by the formula

$$E = \frac{6P\left(\frac{l}{h}\right)^2}{\alpha \cdot b \cdot h} \quad (12)$$

where P - load the sample (N); l - length of the sample (m);

h - thickness of the sample (m); b - width of the sample (m);

$\alpha = \frac{\lambda}{L}$ (λ - arc deflection, L - length) - the angle associated with the arc trough.

It is possible to take into account the values of the mechanical properties of boron $G=0{,}32 \cdot 10^{12} N/m^2$, $E=0{,}39 \cdot 10^{12} N/m^2$ and $\mu=-0{,}39$ [9].

It is noteworthy that the obtained values of Young's modulus for dodecaborides virtually the same as those based on equations (8), (10), (11).

Young's modulus dodecaborides earth elements ($\approx 0{,}2 \; 10^{12} N/m^2$) much less than the Young's modulus of pure boron ($0{,}32 \; 10^{12} N/m^2$) and zirconium and titanium diboride ($0{,}42 \; 10^{12} N/m^2$).

Table 2

Boride	Densit $\gamma \cdot 10^3$, kg/m^3	The characteristic temperature Θ, K	Melting point [5]	Velocity of sound v, m/s	Shear modulus $G \cdot 10^{12} N/m^2$		Poisson's ratio	Young's modulus $E \cdot 10^{12}$, N/m^2			
					From v	From E [8]		Calculated by us	[7]	(11)	Experimental
YB_{12}	3,444	1094	2950	7520	0,165[x] 0,195	0,180	0,31	0.27	0.18	0.23	0.25
TbB_{12}	4,540	900	2400	6000	0,160	0,141	0,36	0.20	0.22	0.18	-
DyB_{12}	4,611	850	2550	5740	0,150	0,151	0,37	0.20	0.21	0.19	0.19
HoB_{12}	4,655	872	2750	5880	0,160	0,166	0,34	0,21	0,20	0,22	0,190
ErB_{12}	4,706	872	2600	5888	0,160	0,143	0,30	0,22	0,20	0,20	0,195
TmB_{12}	4,756	868	2750	5820	0,160	0,157	0,33	0.21	0,20	0.21	0.197
YbB_{12}	4,820	845	-	5688	0,156	0,154	0,35	0.20	0.20	0,20	0,198
LuB_{12}	4,868	878	2650	5900	0,170	0,141	0,36	0,22	0.19	0,18	-
ZrB_{12}	3,611	976	2750	6520	0,154	0,156	0,39	0,19	-	0.19	0,20
TiB_2	-	615	2900	-	0,130 [9]	-	0,42	0.37 [9]	-	-	-
ZrB_2	-	481	3040	-	0,120 [9]	-	0,42	0,35 [9]	-	-	-
B	2,340	1200	-	16200[5] 15600 – рассч.	0,320 [5]	-	0,39	0.39 [5]	-	0,33	-

[x] Published data [10].

This result indicates that the metal component in the rare earth element dodekaboridnes phase plays the role of a plasticizer that reduces the strength characteristics of said phases compared with a pure boron.

An important mechanical feature of refractory compounds, and borides, in particular, there brittleness. To assess the fragility of the work [11] proposed to use the value of the mean-square fluctuations of atomic complexes $\sqrt{\overline{u}^2}$ and work $m\Theta^2$. The authors [11] assume that the growth occurs as the brittleness of these parameters decrease.

As can be seen from Table 3, a clear conclusion about the fragility dodekaboridnes phases in comparison with other higher borides of MeB_2, MeB_4, MeB_6, MeB_{12} today do not seem possible since failure studies of these characteristics (Table 3), but lower values $\sqrt{\overline{u}^2}$ indicate a high brittleness of the phases MeB_{12}.

Table 3

Boride	Mean square vibration of the atom $\sqrt{\bar{u}^2}\cdot 10^{-10}$, m	$m\cdot\Theta^2$	Θ, K	$E\cdot 10^{12} N/m^2$	$G\cdot 10^{12} N/m^2$	Microhardness H, kG/mm^2
YB_4	0,028	99	670	-	0,29 [11]	2850
YB_6	0,047	131	570	-	0,27 [11]	2575
YB_{12}	0,029	436	1094	-	0,165 [11] 0,195	2500
TbB_4	0,023	147	661	-	-	1897
TbB_6	0,047	177	690	-	-	2300
TbB_{12}	0,025	389	900	0,20	0,160	2600
DyB_4	0,022	184	698	-	-	1896
DyB_6	-	-	-	-	-	-
DyB_{12}	0,026	352	850	0,20	0,160	2400
HoB_4	0,029	91	514	-	-	1684
HoB_6	-	-	-	-	-	-
HoB_{12}	0,026	371	872	0,21	0,160	2700
ZrB_2	0,081	196	765	0,15	0,120	2252
ZrB_{12}	0,029	350	976	0,19	0,160	2750

Conclusions. The experimental data of increased values of micro-hardness, high melting point and the characteristic temperatures at significantly low values of the coefficient of thermal expansion and the values of the phases MeB_{12} strength properties comparable to those of pure boron indicate that dodecaborides rare earth metals with the structure of UB_{12} - refractory compounds with high strength properties, require further study, particularly with regard to the mechanism and the nature of their mechanical properties, the characteristics of the electronic structure and chemical bonding.

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INDIRECT OBSERVING OF THE LOW-FREQUENCY GRAVITATIONAL WAVES ASSOCIATED WITH A GAMMA-BURST GRB 051103 BY ANALYSIS OF LIGO'S DATA

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