PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 1 (2017) P. 58-63
DOI: 10.15330/pcss.18.1.58-63

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 1 (2017) С. 58-63

PACS: 61.72.FF, 64.70.KD, 64.70.D, 65.40.BA ISSN 1729-4428

N.Yu. Filonenko

The Physical and Thermodynamic Functions of Borides

State Establishment "Dnipropetrovsk Medical Academy of Health Ministry of Ukraine", 9 Dzerzhinsky Str., Dnipro 49044, Ukraine, e-mail: natph2016@gmail.com

In the paper the physical properties and thermodynamic functions of borides X_2B (X=W, Mo, Mn, Fe, Co, Ni та Cr) are studied with accounting for fluctuation processes. We use the microstructure analysis, the X-ray structural and the durometric analyses to determine the physical properties of alloys. In the paper it is determined the phase composition and physical properties of borides. In this paper for the first time it is determined the thermodynamic functions of borides using the Hillert and Staffansson model with accounting for the first degree approximation of high-temperature expansion for the free energy potential of binary alloys. We obtain the temperature dependences for such thermodynamic functions as Gibbs free energy, entropy, enthalpy and heat capacity C_p along with their values at the formation temperature for X_2B (X=W, Mo, Mn, Fe, Co, Ni та Cr). The approach under consideration enables to give more thorough from the thermodynamic point of view description of borides formed from the liquid. The outcomes of the thermodynamic function calculation for borides are in good agreement with experimental data and results of other authors.

Key words: borides, Gibbs energy, entropy, enthalpy, heat capacity, fluctuation process

Article acted received 24.11.2016; accepted for publication 05.03.2017.

Introduction

The W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides have a body-centered tetragonal cell with 12 atoms per cell and belong to the structural type of $CuAl_2$ $D_{4h}^{18} - I4/mcm$ [1-5].

The W-B, Mn-B, Fe-B, Co-B, Ni-B, Mo-B and Cr-B systems were studied both experimentally and theoretically [6-12]. In the Refs. [6-12] the authors give results of calculation for Gibbs energy of borides using the models that can be applied only for equilibrium conditions. The objective of this paper is to study physical properties and thermodynamic functions of borides, their temperature dependences with consideration of the first degree approximation of high-temperature expansion for the free energy potential of binary alloys.

I. Materials and research technique

The investigation was carried out on specimens with boron content of 5 - 9.5 % (wt.), the rest is metal X (X=W, Mo, Mn, Fe, Co, Ni та Cr), for which is used burden consisting of metal with content 99.99 %, amorphous Boron (with Boron content of 97.5,0 % (wt.)). The smelting of specimens was carried out in Taman furnace with graphite hearth, melting of specimens was carried out in alundum sagger under argon atmosphere. The cooling rate for alloys amounted to 10 K/s. To ascertain alloy chemistry the chemical and spectrographic analysis were used [13]. The microhardness of various phase components was determined by using a PMT-3.

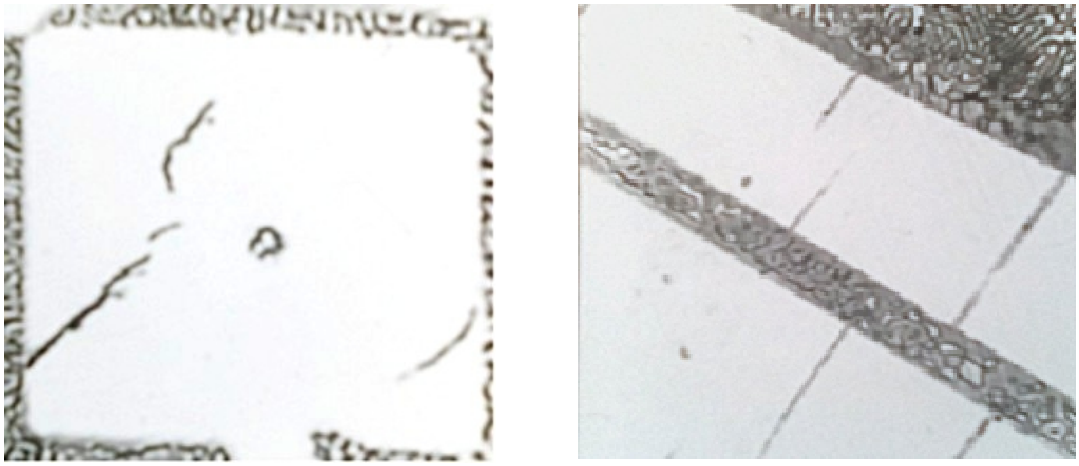
The phase compositions of the alloys were determined by the method of X-ray spectral microanalysis in a JSM–6490 microscope and with the help of a Neofot-21 optical microscope.

Make use of X-radiation diffraction analysis, which was realized in a DRON-3 diffractometer in the monochromatized Fe-Kα-radiation.

II. Results and discussion

The microstructure of the W-B, Mn-B, Fe-B, Co-B, Ni-B, Mo-B and Cr-B as-cast alloys at boron content over 33.3 % (atomic) contains plane-faced borides (Fig. 1, a, b).

The structure of borides consists of alternating planes of iron atoms (forming the identical square grids) and planes of boron atoms [14]. The occurrence of the planes of different packing density has to enable the sharp growth anisotropy of boride. Anisotropy and interatomic forces result in that boride crystals are right regular square prisms in shape and grow in (011)



a **b**

Fig. 1. Microstructure of alloys with boron content of 7 % (w.) Fe-B (a), Co-B (b)

Table 1

Crystal lattice parameters for borides with boron content of 7 % (w.)

Borides	Lattice constant, (exp)		Lattice constant (tab)		Reference
	a,Å	c, Å	a, Å	c, Å	
W_2B	5.565	4.741	5.564	4.740	[2]
Mn_2B	5.147	4.21	5.148	4.208	[2]
Fe_2B	5.1074	4.2464	5.109	4.249	[3]
Co_2B	5.016	4.21	5.016	4.22	[3]
Ni_2B	5.01	4.246	4.993	4.249	[4]
Mo_2B	5.542	4.736	5.543	4.735	[2]
Cr_2B	5.1287	4.282	5.1283	4.2818	[5]

Table 2

Dependence of size of crystallites L, level of microstresses, density of dislocations ρ in borides with boron content of 7.0 % (wt.)

Borides	Size of Crystallites L, Å	Level of Microstresses M	Density of Dislocations $\rho\times10^{10}$, sm^{-2}
W_2B	856	$5.01\cdot10^{-3}$	8.64
Mn_2B	584	$2.12\cdot10^{-3}$	6.79
Fe_2B	452	$2.13\cdot10^{-3}$	6.52
Co_2B	872	$3.85\cdot10^{-3}$	6.92
Ni_2B	692	$1.63\cdot10^{-3}$	7.6
Mo_2B	892	$3.23\cdot10^{-3}$	6.87
Cr_2B	815	$4.04\cdot10^{-3}$	7.79

direction. In this direction the bond is strongest and growth rate of prisms, based on (011) face, leads to their impurity and defect enrichment, which gives rise to inhomogeneities such as pores, cracks and others (Fig. 1, a, b).

Determinations of lattice parameter of the phases by using X-radiation analysis show their correlation to tabular data (Table 1).

For the W_2B boride we observed a slight increase of microstrain degree and dislocation density compared to other borides (Table 2).

The obtaining of thermodynamic functions values for the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides is quite difficult. Thereby, accounting for the first degree approximation of high-temperature expansion for the free energy potential in the Hillert and Staffansson model enables to determine the thermodynamic functions of borides and their temperature dependences theoretically.

2.1. Gibbs energy for the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides.

Gibbs energy of the phase is known to be a function of variables $G = G(p,T,y)$, where p is pressure, T denotes temperature, y represents weight content of the elements. For mole fraction of components in compound or alloy the condition $\sum_{i=1}^{2} y_i = 1$ holds.

As it is known, the sublattice model by Hillert and Staffansson [15] enables to calculate Gibbs energies of the phases for equilibrium state. The potentials within the Hillert and Staffansson model don't take an account for the first degree approximation of high-temperature series for binary alloy thermodynamic potential that must be borne in mind when deriving the Gibbs energy for the phases formed from liquid and involving fluctuation

Table 3

Temperature dependence of Gibbs energy and enthalpy value corresponding to the formation of borides

Borides	Equation of Gibbs energy	G_m^{MeB}, (Дж/моль)	Reference	ΔH_m^{MeB}, (Дж/моль)	Reference
W_2B	$-72687+5.3T-2.3\cdot10^5T^{-1}$	-58872.79	First-principles calculation	-83543.1	First-principles calculation
	$-97250+1.787T$	-413310.24	[9]	-87000	[9]
Mn_2B	$-35264-0,35T-8,8\cdot10^5T$	-36389.38	First-principles calculation	-32856.35	First-principles calculation
	$-31254+0.293T$	-30705.2	[27]	-38600	[34]
	$-31651,9-6,17T$	-43208.31	[7]	-31700	[32]
Fe_2B	$-29726+2,5T-10^5T^{-1}$	-26217.7	First-principles calculation	-31630	In this paper
	$-29365+6,54T$	-22244.5	[28]	-24294.83	[35]
	$-31000+3,37T$	-25362	[29]	-32600.72	[36]
Co_2B	$-32128+2.1T-2.6\cdot10^5T^{-1}$	-28989.99	First-principles calculation	-25345.82	First-principles calculation
	$-26900.0-1.41T$	-29117.9	[8]	-26400	[37]
	$-28564+5,077T$	-20588.89	[30]		
Ni_2B	$-35157+1,36T-1,5\cdot10^5T^{-1}$	-32971.4	First-principles calculation	-27363.90	First-principles calculation
	$-22500+2.5T$	-21500	[10]	-21129.22	[10]
	$-24100,75+4,017T$	-17380.32	[25]	-24670	[25]
Mo_2B	$-50269+5.2T+2.4\cdot10^5T^{-1}$	-37054.36	First-principles calculation	-37895.10	First-principles calculation
	$-42800+2.43T$	-35775.71	[21]	-42860	[21]
	$-42176+2T$	-37030	[22]		
Cr_2B	$-32947+0.78T-1.3\cdot10^6T^{-1}$	-31514.66	First-principles calculation	-42930.90	First-principles calculation
	$-30848+1.48T$	-28001.96	[32]	-41417.6	[40]
	$-28285-0.33T$	-28903.09	[31]		

processes into consideration. As we know from theory of binary alloys, the partition function of such a system cannot be computed exactly, but according to Kirkwood technique it may be written in the form of infinite series in powers of 1/T [16-17].

So, we define Gibbs energy for boride with accounting for the first degree approximation as:

$$G_m^{MeB} = y_{Me}\,{}^0G_{Me} + y_B\,{}^0G_B + RT\left(2y_{Me}\ln y_{Me} + y_B\ln y_B\right) + y_{Me}y_BL_{Me:B} - \frac{L_{Me;B}^2y_{Me}^2y_B^2}{2ZRT}, \qquad (1)$$

where Z is coordination number, which equals Z=12 for boride [2-3].

Using data for pure components ${}^0G_{Me}$, ${}^0G_B$ [19-20] and information on interaction energy of components in the phase $L_{Me:B}$ from the papers [7, 9, 20-26], we obtain temperature dependences of Gibbs energy for borides.

Table 3 contains computational data on Gibbs energy and enthalpy of borides at temperature of their formation.

As we can see from Table 3, obtained values of Gibbs energy are in good agreement with those of other authors.

Thus, obtained temperature dependences of Gibbs energies of borides enable to determine their values in high-temperature region, as well as Gibbs energies of formation of these phases from the liquid.

2.2. Entropy, enthalpy and heat capacity C_p for borides.

One of the most important thermodynamic characteristics of the phase is entropy. The entropy of

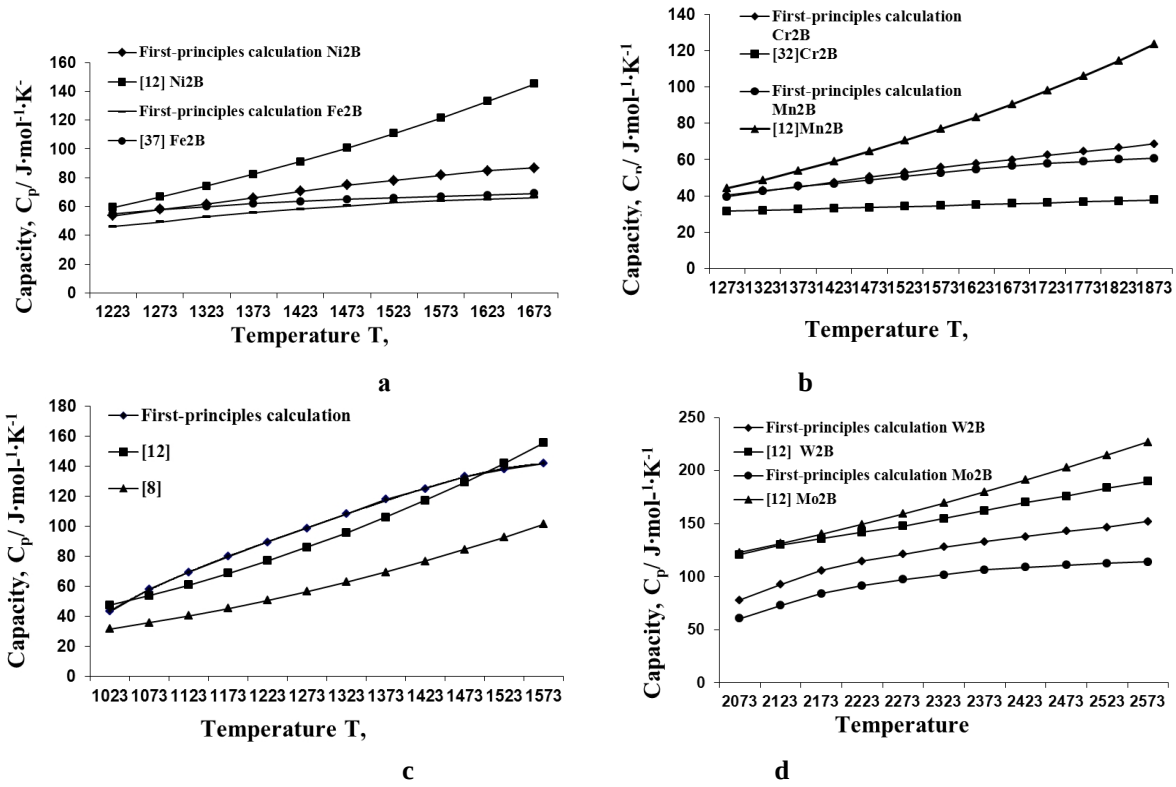


Fig. 2. Temperature dependence of heat capacity C_p for borides: Fe_2B та Ni_2B (a), Cr_2B та Mn_2B (b), Co_2B (c), W_2B та Mo_2B (d).

borides one can determine from the formula:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -R\left(y_{Me}\ln y_{Me} + y_B \ln y_B\right) - \frac{L_{Me:B}}{2ZRT^2} y_{Me}^2 y_B^2$$

The accounting in Gibbs energy for the first degree approximation of high-temperature expansion of thermodynamic potential enables to determine the enthalpy of borides. To calculate the enthalpy of borides we use relation [33]: $\Delta H = \Delta G + T\Delta S$.

Temperature dependence of enthalpy of the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B phases has the form:

$$H^{W_2B} = -127698 + 21.3T - 3.1\cdot 10^5 T^{-1},$$
$$H^{Mn_2B} = -35126 + 1.36T - 5.2\cdot 10^5 T^{-1},$$
$$H^{Fe_2B} = -32527 + 0{,}5T + 10^5 T^{-1},$$
$$H^{Co_2B} = -26458 + 0.8T - 2{,}3\cdot 10^5 T^{-1}$$
$$H^{Ni_2B} = -30208 + 1.7T - 2{,}45\cdot 10^5 T^{-1},$$
$$H^{Mo_2B} = -43698 + 2.3T - 3.1\cdot 10^5 T^{-1}$$
$$H^{Cr_2B} = -48123 + 2.7T - 1.5\cdot 10^5 T^{-1}$$

Table 3 gives the comparison results of borides' enthalpy values obtained in this paper with those obtained experimentally and by calculation by other authors.

So, the outcomes of this research (Table 3) are in good agreement with those of other authors [10, 21, 25, 32-37].

We calculate heat capacity for the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides using the formula

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \frac{L_{Fe:B}^2}{RZT^2}\cdot y_{Fe}^2 y_B^2.$$

As result, the obtained temperature dependence of heat capacity C_p for borides (Fig. 2) matches with data of Refs. [12, 33, 37, 40].

Judge by the results obtained we can conclude that accounting for contribution of the first degree approximation of high-temperature expansion of the free energy potential for binary alloys in the Hillert and Staffansson models enables to calculate such thermodynamic quantities of the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides as entropy, enthalpy, heat capacity and their temperature dependences.

This approach makes it possible to give more thorough from the thermodynamic point of view description of borides as well as monoborides formed from the liquid.

Conclusions

In paper are considered structural and physical properties of the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides in binary alloys with boron weight content of 5.0-10.0 % (wt.), the rest is metal.

It should be noted that thermodynamic functions of the phases enable to predict physical and chemical properties of alloys under variable environmental conditions such as temperature, pressure and so on. The well-known computational techniques for thermodynamic functions of the phases can be applied only at equilibrium conditions and do not account for fluctuation processes. Thereby, in the paper the temperature dependences of such thermodynamic functions as Gibbs energy, entropy, enthalpy and heat capacity C_p for the W_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B and Cr_2B borides are obtained with accounting for the first degree approximation of high-temperature series of the free energy potential.

The obtained calculation results for thermodynamic functions of borides are in good agreement with experimental data.

Filonenko N.Y. – Lecturer of the Physics Chair.
.

[1]. A. Friedrich, B. Winkler, E.A. Juarez-Arellano, L. Bayarjargal, Materials 4, 1648 (2011).
[2] G.V. Samsonov, T.I. Serebryakova, V.A. Neronov, Borides (Atomizdat, Moscow, 1999).
[3] Yu.B. Kuzma, Crystal chemistry of borides (Vishcha school, Kiev, 1983).
[4] C.T. Zhou, J.D. Xing, B. Xiao, J. Feng, X.J. Xie, Y.H. Chen, Computational Materials Science 44, 1056 (2009).
[5] M. Sekar, N.V. Chandra, S. Shekar, G. Shwetha, G. Vaitheeswaran, V. Kanchana, Journal of Alloys and Compounds 654, 554 (2016).
[6] B. Halemans, P. Wollemans, J.R. Roos, Metallkd 85 (10), 676 (1994).
[7] Weihua Sun, Yong Du, Shuhong Liu, Baiyun Huang, and Chao Jiang, Journal of Phase Equilibria and Diffusion 31 (4), 357 (2010).
[8] P.K. Liao and K.E. Spear, Bulletin of Alloy Phase Diagrams 9 (4), 452 (1988).
[9] H. Duschanek and P. Rogl, Critical Journal of Phase Equilibria 16 (2), 150 (1995).
[10] O.Teppa and P. Taskinen, Materials Science and Technology 9, 205 (1993).
[11] Edmund Storms and Barbara, Journal of Physical Chemistry 8 (4) 318 (1977).
[12] B. Xiao, J. Feng, C.T. Zhou, J.D. Xing, X.J. Xie, Y.H. Cheng, R. Zhou, DFT theory Physica B. 405, 1274 (2010).
[13] S.V. Твердохлебова, Вісник Дніпропетров. Nat. Un-tu. Ser. Fizika. Radiotelektronika (12/1), 100 (2007).
[14] A.S. Pomelnikova, M.N. Shipko, MA Stepovich, Surface. X-ray, synchronous and neutron studies 3, 99 (2011).
[15] M. Hillert, L. Staffonsson, Acta Chemica Scandinavica 24 (10), 3618 (1970).
[16] M.I. Shakhparonov, Introduction to the molecular theory of solutions (State Publishing House of Technical and Theoretical Literature, Moscow, 1956).
[17] L. Zhirifalko, Statistical physics of the solid body (Mir, Moscow, 1975).
[18] Richard A. Roble and David R. Waldbaum Thermodynamic Properties of Minerals and Related Substances at 298.15 ° K (25.0 ° C) and One Atmosphere (1.013 Bars) Orton memorial library the OHIO State University 155 S. Oval Drive. 1970, p. 262.
[19] SGT data for pure elements A T Dinsdale NPL Materials Center, Division of Industry and Innovation, National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK. P. 174.
[20] Y.Q. Liua, X.S. Zhao, J. Yanga, J.Y. Shenb, Journal of Alloys and Compounds 509, 4805 (2011).
[21] K.E. Spear and P.K. Liao, System Alloy Phase Diagrams 9 (4) 457 (1988).
[22] Y. Yang, Y.A. Chang, Intermetallics 13, 121 (2005).
[23] Yongcheng Liang, Zheng Zhong, Wenqing Zhang, Computational Materials Science 68, 222 (2013).
[24] Tatsuya Tokunaga, Hiroshi Ohtani; And Mitsuhiro Hasebe, SystemMaterials Transactions 46 (6) 1193 (2005).
[25] Wei-Hua Sun, Yong Du, Yi Kong, Hong-HuiXu, Wei Xiong, Shu-Hong Liu Int. J. Mat. Res. (Formerly Z. Metallkd.) 100, 59 (2009).
[26] J. Miettinen, G. Vassilev, Metallurgy and Materials 59 (2) 601 (2014).
[27] P.K. Liao and K.E. Spear, Bulletin of Alloy Phase Diagrams 7 (6), 543 (1986).
[28] N.Yu. Філоненко, Фізика і хімія твердо тіла 12 (2), 370 (2011).
[29] Hiroshi Ohtani, Mitsuhiro Hasebe, and Taiji Nishizawa, Ternary Phase Diagram. Transactions ISIJ. 28, 1043 (1988).
[30] Y.Q. Liua, X.S. Zhao, J. Yanga, J.Y. Shenb, Journal of Alloys and Compounds 509, 4805 (2011).
[31] P.K. Liao and. K.E Spear, Bulletin of Alloy Phase Diagrams 7 (3) 232 (1986).
[32] J. Miettinen, G. Vassilev, Archives of metallurgy and materials 59 (2) 601 (2014).
[33] I.P. Bazarov, Thermodynamics (Higher School, Moscow, 1991).
[34] Bing Wang, Li Xiang, Xu Yuan Wang, and Yu Feitu, J. Phys. Chem. C. 115, 2142935 (2011).
[35] S. Sato and O. J Kleppa, Metallurgical Transactions B-Process Metallurgy 13 (2), 251 (1982).

[36] M. Mihalkovic, M. Widom, Physical Review 70 (14), 144107 (2004).
[37] B.V. Mikhajlovskij, V.I. Goryacheva, I.B. Kutsenok, Zhurnal Fizicheskoj Khimii 73 (4). 763 (1999).
[38] Bing Wang, De Yu Wang, Zhenxiang Cheng, Xiaolin Wang and Yuan Xu Wang Chem. Phys. Chem. 14, 1245 (2013).
[39] Raju S. et al., Asian Nuclear Prospects 1 (2012).
[40] Konga Yi, Xiongb Wei, Haibo Guoc, Weihua Suna, Yong Dua, Yichun Zhoud CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 34, 245 (2010).

Н.Ю. Філоненко

Фізичні та термодинамічні властивості боридів

Державний заклад «Дніпропетровська медична академія МОЗ України», вул. Володимира Вернадського, 9, 49044 Дніпропетровськ, Україна, e-mail: natph2016@gmail.com

У роботі досліджено фізичні властивості та термодинамічні функції боридів X_2B (X = W, Mo, Mn, Fe, Co, Ni та Cr) з урахуванням флуктуаційних процесів. Для визначення фізичних властивостей сплавів використовували мікроструктурний, рентгеноструктурний та дюрометричний аналізи. В роботі було визначено фазовий склад сплавів та фізичні властивості боридів.

Вперше визначено термодинамічні функції боридів з використанням моделі Хіллерта і Стеффансона та з урахуванням першого ступеня наближення високотемпературного розвинення термодинамічного потенціалу бінарних сплавів. Для боридів X2B (X = W, Mo, Mn, Fe, Co, Ni та Cr)отримано залежності від температури таких термодинамічних функцій, як енергія Гіббса, ентропія, ентальпія й теплоємність Ср, а також визначено їх значення при температурі утворення. Використаний у даній роботі підхід дає можливість надати найбільш повний з термодинамічної точки зору опис боридів, що утворюються з рідини.

Отриманірезультати розрахунків термодинамічних функцій боридів добре узгоджуються з експериментальними даними та даними інших авторів.

Ключові слова: бориди, енергія Гіббса, ентропія, ентальпія, теплоємность, флуктуаційний процес.