THEORETICAL STUDY OF HYDROGEN-SORPTION PROPERTIES OF LITHIUM AND MAGNESIUM BOROCARBIDES[*]

S.Yu. Zaginaichenko[1], D.A. Zaritskii[2], D.V. Schur[1,*], Z.A. Matysina[2], Nejat Veziroglu[3], M.V. Chymbai[1], L.I. Kopylova[1]

[1]Frantsevich Institute for Problems of Materials Science of NASU
3 Krzhyzhanovsky Str., Kiev, 03142, Ukraine
tel./fax: +38 (044) 424 0381; e-mail address: shurzag@ipms.kiev.ua
[2]Dnepropetrovsk National University
13 Nauchnaya Str., Dnepropetrovsk, 49050, Ukraine
[3]International Association for Hydrogen Energy
5794 SW 40 Street #303, Miami, FL, 33155, USA

The statistical theory of hydrogen-sorption properties of compounds of alkaline and alkaline-earth metals $M(BC)_nH_x$ ($M = Li, Mg; 0 \leq x \leq 12, n = 1,2$) has been developed in this paper in the expectation that such hydrogenated boron carbides will be the reliable materials for the reversible accumulation and storage of hydrogen in large quantities in perspective. The calculation of free energy of these crystals has been performed on the basis of molecular-kinetic notions, the equation of thermodynamic equilibrium of such system, determining the P-T-c phase diagram, has been derived in the present paper. The hydrogen solubility in these compounds has been ascertained in dependence on temperature and external pressure, the possibility of manifestation of hysteresis effect has been justified. The derived formulae allow to establish the P, T-conditions of high hydrogen content in boron carbide systems and can permit to select the optimum composition of material choosing for hydrogen storage, the regime of technological process, to develop the experimental technology for solving of the practical problems, if in this case the energetic parameters of these materials are known from independent experiments.

Keywords: statistical theory; hydrogenated boron carbides of metals; accumulation and storage of hydrogen; phase diagram; hysteresis effect; hydrogen concentration.

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ВОДОРОДНО-СОРБЦИОННЫХ СВОЙСТВ БОРОКАРБИДОВ ЛИТИЯ И МАГНИЯ

С.Ю. Загинайченко[1], Д.А. Зарицкий[2], Д.В. Щур[1,*], З.А. Матысина[1], Т.Н. Везироглу[3], М.В. Чимбай[1], Л.И. Копылова[1]

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[1]Институт проблем материаловедения им. И.Н. Францевича НАН Украины
д. 3, ул. Кржижановского, Киев, 03142, Украина
тел. / факс: +38 (044) 424-03-81; e-mail: shurzag@ipms.kiev.ua
[2]Днепропетровский национальный университет
д. 13, ул. Научная, Днепропетровск, 49050, Украина
[3]Международная ассоциация по водородной энергетике
5794 SW 40 ул. # 303, Майами, Флорида, 33155, США

В данной работе была разработана статистическая теория водородосорбционных свойств соединений щелочных и щелочноземельных металлов $M(BC)_nH_x$ (M = Li, Mg; $0 \leq x \leq 12$, n = 1,2), поскольку ожидается, что такие гидрированные карбиды бора будут перспективными материалами для обратимого накопления и хранения водорода в больших количествах. Расчет свободной энергии этих кристаллов был выполнен на основе молекулярно-кинетических представлений, и выведено уравнение термодинамического равновесия такой системы, определяющее фазовую диаграмму P-T-c. Установлено, что растворимость водорода в этих соединениях зависит от температуры и внешнего давления, подтверждена возможность проявления эффекта гистерезиса. Полученные формулы позволяют установить P-, T-условия высокого содержания водорода в карбидных системах бора и могут позволить выбрать оптимальный состав материала для хранения водорода, режим технологического процесса, разработать экспериментальную технологию решения практических проблем, в случае если энергетические параметры этих материалов известны из независимых экспериментов.

Ключевые слова: статистическая теория; гидрированные борокарбиды металлов; накопление и хранение водорода; фазовая диаграмма; эффект гистерезиса; концентрация водорода.

Сведения об авторе: д-р физ.-мат. наук, вед. научн. сотрудник отдела № 67 Института проблем материаловедения НАН Украины.

Образование: Днепропетровский национальный университет по специальности «Физик. Преподаватель физики» (1979 г.); Днепропетровский металлургический институт, аспирантура (1982 г.).

Область научных интересов: физические свойства металлов, упорядоченных сплавов, фуллеренов на уровне молекулярно-кинетической теории; теоретическое изучение фазовых превращений в системах «металл – водород» и углеродных материалах; определение растворимости водорода в этих твердых телах, сравнение теоретических результатов с экспериментальными данными.

Публикации: около 500, в том числе 7 монографий.

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Светлана Юрьевна Загинайченко Svetlana Zaginaichenko

Information about the author: D.Sc. in Physics and Mathematics, Professor, Senior Researcher at Laboratory no. 67 "Investigation of Processes and Systems of Hydrogen and Solar-Hydrogen Energy Transformation" in Institute for Problems of Materials Science of NAS of Ukraine.

Education: Dnepropetrovsk National University with degree of Physicist, Teacher of Physics, 1979; Dnepropetrovsk Metallurgical Institute, postgraduate studies, 1982.

Research interests: physical properties of metals, ordering alloys, fullerenes on the level of molecular-kinetic theory; theory of phase transformations in metal-hydrogen systems and carbon materials; determination of hydrogen solubility in these solids, comparison of theoretical results with experimental data.

Publications: about 500, including 7 monographs.

Сведения об авторе: канд. хим. наук, зав. отделом № 67 «Водородного материаловедения и углеродных наноструктур» Института проблем материаловедения НАН Украины.

Образование: Киевский политехнический институт по специальности «Химик-технолог» (1985 гг.); Институт проблем материаловедения НАН Украины, аспирантура (1990 г.).

Область научных интересов: водородное материаловедение и углеродные наноструктуры (синтез, свойства и применение); водородная и углеродная плазма; особенности процессов гидрирования материалов и углеродных наноструктур; применение материалов в качестве систем для хранения водорода.

Публикации: более 530, в том числе 9 монографий и 4 патента.

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Дмитрий Викторович Щур Dmitry Schur

Information about the author: Ph.D. in Chemistry, Professor, Chief of Laboratory no. 67 "Investigation of Processes and Systems of Hydrogen and Solar-Hydrogen Energy Transformation" in Institute for Problems of Materials Science of NAS of Ukraine, Kiev.

Education: Kiev Polytechnic Institute with degree in Chemical Engineering, 1985; Institute for Problems of Materials Science of NAS of Ukraine, postgraduate studies, 1990.

Research interests: hydrogen materials science and carbon nanostructures (synthesis, properties and application); the hydrogen and carbon plasma; the peculiarities of the hydrogenation processes of materials and carbon nanostructures; the use of materials as systems for hydrogen storage.

Publications: more than 530, 9 monographs, 4 patents.

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Турхан Н. Везироглу
T.N. Veziroglu

Сведения об авторе: д-р наук (теплообмен), профессор, президент Международной ассоциации водородной энергетики, член 18 научных организаций.
Образование: Городской профессиональный колледж, Имперский колледж науки и техники (Великобритания), Лондонский университет по специальности «машиностроение» (1946 г.); доктор наук по теплообмену (1951 г.).
Награды: Лауреат нескольких международных наград.
Опыт работы: профессор, заведующий кафедрой технического факультета в университете Майами (1962–1979 гг.); директор Института чистой энергии (США), Coral Gables, Флорида (1974–2009 гг.); основатель и директор Международного центра технологий по водородной энергетике, Стамбул, Турция (2004–2007 гг.); почетный профессор университета Майами (2009 – по настоящее время); основатель и президент Международной ассоциации водородной энергетики (1976 – по настоящее время); почетный главный редактор Международного научного журнала «Альтернативная энергетика и экология» (ISJAEE).
Область научных интересов: неустойчивость двухфазного потока; внутренняя теплопередача; солнечная энергия; глобальное потепление; экологические проблемы; возобновляемые источники энергии и система использования водородной энергии.
Публикации: более 350, редактор 160 книг и трудов конференций, соавтор книги «Солнечная водородная энергетика: сила, которая сохранит Землю».

Information about the author: Ph.D. in Heat Transfer, Professor, President of International Association for Hydrogen Energy, a member of 18 scientific organizations.
Education: the City and Guilds College, the Imperial College of Science and Technology, University of London with degrees in Mechanical Engineering, 1946, advanced studies in engineering, 1947; Ph.D. in Heat Transfer, 1951.
Awards: recipient of several international awards.
Experience: University of Miami, Engineering faculty, Department Chairman, Professor, 1962–1979; Clean Energy Research Institute, Coral Gables, Fl, Director, 1974–2009; International Centre for Hydrogen Energy Technologies, Istanbul, Turkey, Founding Director, 2004–2007. University of Miami, Professor Emeritus, 2009–present. International Association for Hydrogen Energy, Founding President, 1976–present. Honorary Editor-in-Chief of the International Scientific Journal for Alternative Energy and Ecology (ISJAEE).
Research interests: two-phase flow instabilities; interstitial heat transfer; solar energy; global warming; environmental problems; renewable energy sources and hydrogen energy system.
Publications: more than 350, editor of 160 books and proceedings, co-author of the book "Solar Hydrogen Energy: the Power to Save the Earth".

1. Introduction

Since the exciting discovery in 2001 of superconductivity in compound MgB_2 with an unusually high transition temperature ($T_c = 39$ K) [1], interest in simple compounds of boron and light elements has undergone a renaissance. Doping on both the Mg and B sites has led both theorists and experimentalists to the investigation of structurally related compounds [2]. The $M(BC)_n$ phases (M = alkaline-earth or rare-earth metal, n = 1,2) triggered an enormous interest as compounds with structurally similar features, namely graphite-like layers [3, 4]. Although the physical properties of $M(BC)n$ compounds family have been widely investigated, some of their structures are still debated, especially with respect to the position of B atoms versus C atoms.

In the case of MgB_2C_2 and LiBC compounds, for instance, the recent discovery of various potentially interesting properties [5–10] has revived the interest of the scientific community. The structure of the LiBC and MgB_2C_2, both containing BeC layers isoelectronic to graphite, have been investigated in detail in many experimental and theoretical works [11–14].

Interest in the intercalated heterographites, as LiBC and MgB_2C_2 [15–17], has going to be renewed thanks to the considerable progress made in graphite research, whose lattice points might be entirely occupied by carbon (graphene layers) and stacked along the direction perpendicular to the layer plane (graphite) or alternatively substituting carbon by boron and adding a layer formed by electron-donor elements, as lithium and magnesium, between the heterographene layers.

For the first time LiBC compound was prepared in 1995 by Nesper's group [4, 18] who also determined some of their physical and chemical properties. LiBC is a layered boron carbide consisting of alternating graphene-like (BC)-sheets [4, 19, 20] separated by intercalated Li^+ ions. It normally crystallizes in primitive hexagonal lattice with space group symmetry P6$_3$/mmc (Fig. 1). LiBC borocarbide is structurally and electronically similar to the superconductor MgB_2, except for the replacement of Mg by Li and by replacement of B by C at every second position along in-plane covalent bonds as well as along the hexagonal axis, what leads to doubled unit cell along the hexagonal axis [8, 13, 16, 21–29]. LiBC was experimentally subjected to very high pressures [13, 24] and experiments revealed that crystal structure of LiBC remains stable up to 60 GPa. The BeC distance of 1589 Å in LiBC is comparable with that in MgB_2C_2 [29].

A related layered borocarbide MgB_2C_2 has been suggested [29–31]. Magnesium diboride dicarbide, MgB_2C_2, compound made of alternate boronecarbon and metallic sheets constitute an important class of the alkaline-earth metal boron carbides. The structure of MgB_2C_2 contains analogously graphite-like but slightly

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puckered boronecarbon layers (formed nets of condensed six-membered rings) [29, 32–42] and for MgB_2C_2 a high-pressure Pnnm phase was also synthesized and structurally characterized [14]. Yan and collaborators

[43] have recently provided an extensive study of structural and thermodynamic properties of insulating MgB_2C_2. The BeC distances within the layers range are from 1562 to 1595 Å [29].
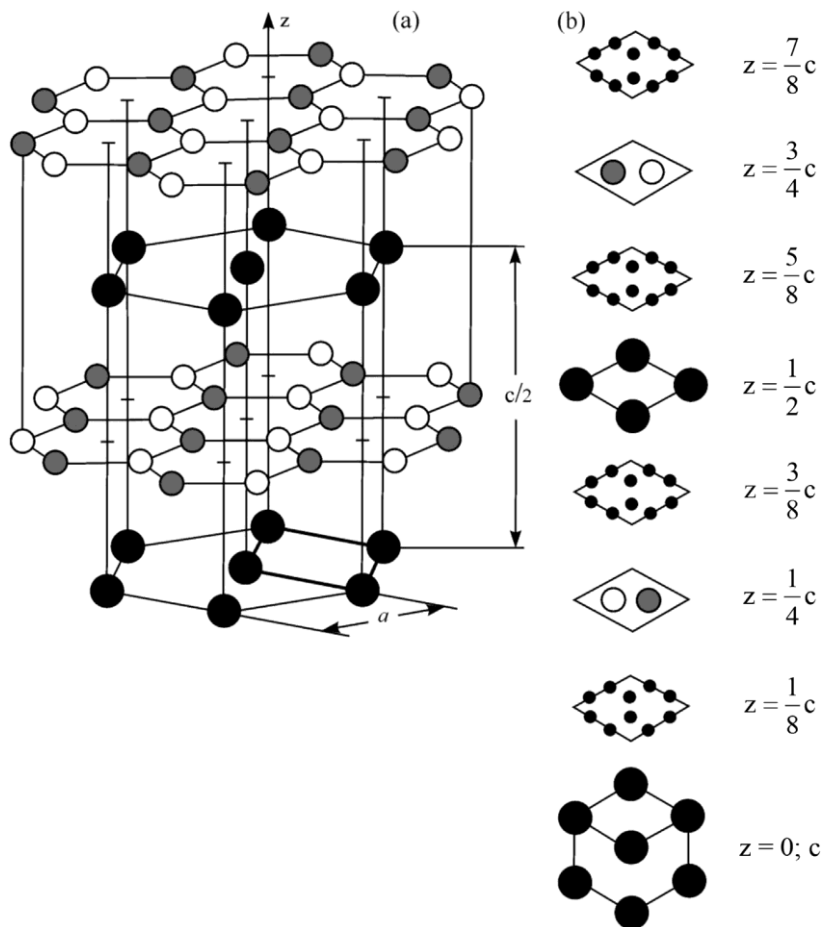

Fig. 1 – The hexagonal crystal structure of stoichiometric LiBC, illustrating the similarity to MgB_2: (a) spatial projection and (b) its projection onto the planes perpendicular to the z axis at different z. Sites of first type corresponding to lithium atoms (●), sites of second type corresponding to boron atoms (●) and carbon atoms (○) and triangular interstitial sites for hydrogen atoms (●). B and C alternate along the c axis, doubling the unit cell

Рис. 1 – Гексагональная кристаллическая структура стехиометрического LiBC, иллюстрирующая сходство с MgB_2: *a* – пространственная проекция и *b* – его проекция на плоскости, перпендикулярные оси z при разных z; Участки первого типа, соответствующие атомам лития (●), участки второго типа, соответствующие атомам бора (●) и атомам углерода (○), и треугольные промежуточные участки для атомов водорода (●). В и С чередуются вдоль оси *c*, удваивая элементарную ячейку

Recently the investigation of new hydride systems as boron carbides of alkaline and alkaline-earth metals has been began due to their prospects for the reversible hydrogen storage [44], their experimental study has been started to assess the P-T-conditions for the solution of practical problems.

In recent years the hydrogen-sorption properties of magnesium- and lithium-containing systems have been studied intensively to develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the scientific goals for reversible on-board hydrogen storage. The Li- and Mg-based systems have great advantages in the question of alloys searching for accumulation and storage of hydrogen and as environmentally safe sources of energy. The magnesium and lithium intermetallics, borohydrides and borocarbides have important benefits in their use as materials slightly polluting the surrounding medium and are pure environmentally.

In the last years, hydrogen storage systems (including LiBC, $Mg(BC)_2$) have been developed and tested [45]. Some interest in Li- and Mg-borocarbides shifted from

their superconductivity to the energy storage applications and hydrogen storage is one promising topic in this area. In general hydrides are interesting candidates for hydrogen storage applications [46], especially those formed from light elements like boron and alkaline and alkaline-earth metals. Nakamori et al. [47]. reported hydrogen containing derivatives of LiBC synthesized from lithium hydride precursors. Their compound was claimed to be thermally stable up to 700 K and thereafter should release the hydrogen to form pure LiBC. It was also claimed that LiBC and $Mg(BC)_2$ systems could be an interesting candidates for hydrogen storage applications in another works [26, 44, 48, 49].

In the present consideration the theoretical study of hydrogenated borocarbides of metals $M(BC)_nH_x$, where M = Li, Mg, $0 \leq x \leq 12$, n = 1,2 is performed respectively for alkaline Li and alkaline-earth Mg metals, the dependence of hydrogen concentration on temperature and external pressure is calculated.

Fig. 1 illustrates the crystalline structure of LiBCHx [44] with possible positions of hydrogen atoms. Some positions of hydrogen atoms can be vacant. Distribution

of boron and carbon atoms can be ordered (Fig. 2) [41, 50], but in this case the ordering arrangement of B, C atoms in the crystal lattice is ignored. Two atoms M, B and C at once fall into the unit cell of crystal and 24 positions of H atoms are shown.

The hydrogen atoms positions are triangular interstitial sites, which are surrounded by one atom M, B and C at the same distances r and by three interstices of H atoms at a distance r_0 (Fig. 1). For lithium metal the lattice parameters a, c and distances r, r' are equal to (in Å).

$$a = 2,7154; \quad c = 6,9907;$$

$$r = \frac{\sqrt{a^2 + c^2/4}}{4} = 1,1065; \quad (1)$$

$$r' \approx \frac{a}{3} = 0,9051$$

To solve the setted problems the calculation of free energy for examined systems and its minimization are performed on the basis of the molecular-kinetic concept using the simplifying assumptions. The crystal lattice is taken geometrically perfect without considering small lattice distortions in the case of alkaline-earth metals. Based on the lattice geometry the hydrogen atoms arrangement is taken to be in the trigonal interstices, in doing so the introduction of hydrogen atoms does not distort the crystal lattice. Lattice distortion is not taken into account because, as is well known, the interstitial hydrogen atoms in metallic alloys only increase the lattice parameter without changing the lattice [51–53]. Therefore we allowed for the interaction energies of

atomic pairs on the interatomic distance and for activity of hydrogen atoms on the external pressure. The method of average energies is used in a model of pair interaction of the nearest neighbouring atoms, ignoring the correlation in substitution of lattice sites and interstitial sites by atoms.

2. Theory

2.1. Free energy of crystal

The calculation of free energy is carried out by the known formula [54, 55].

$$F = E - kT\ln W - kTN_H \ln \lambda, \quad (2)$$

where E is the internal configuration energy determined by the sum of interaction energies between the nearest atomic pairs MH, BH, CH, HH (the interaction energies of atomic pairs MB, MC, BC are included into the energy E_o), W is the thermodynamic probability of distribution of hydrogen atoms at interstitial sites, which is defined by the combinatorial rules, N_H is the number of hydrogen atoms in the crystal, λ is their activity, k is Boltzmann's constant, T is the absolute temperature.

The internal configuration energy E is determined by the following expression

$$E = E_0 + N_{MH}u_{MH} + N_{BH}u_{BH} + N_{CH}u_{CH} + N_{HH}u_{HH}, \quad (3)$$

where N_{MH}, N_{BH}, N_{CH}, N_{HH} are the numbers of indicated nearest atomic pairs, u_{MH}, u_{BH}, u_{CH}, u_{HH} are their energies of interaction.
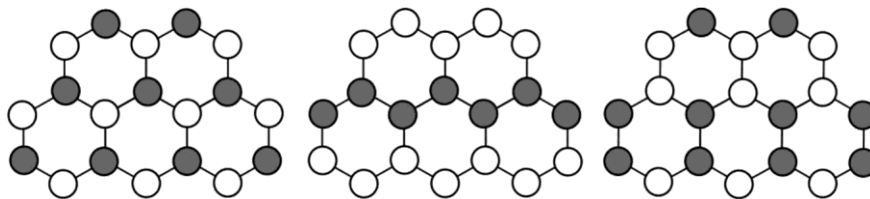

Fig. 2 – The possible types of orders in distribution of boron and carbon atoms over their positions [41, 50]
Рис. 2 – Возможные типы порядков в распределении атомов бора и углерода по их положениям [41, 50]

The calculation of the numbers of atomic pairs according to the crystalline structure (Fig. 1) gives the following results

$$N_{MH} = 12Nc, \quad N_{BH} = 12Nc, \\ N_{CH} = 12Nc, \quad N_{HH} = 36Nc^2, \quad (4)$$

where N is the number of M, B, C atoms respectively, 12N are the numbers of positions of hydrogen atoms and

$$c = N_H / 12N, \quad x = 12c \quad (5)$$

are concentrations of hydrogen atoms in the relationship to the number of their positions and in the relationship to

the number of metal atoms M.

Substituting these numbers in Eq. (3), we find the configuration energy as follows

$$E = E_0 + 12N(u_{MH} + u_{BH} + u_{CH})c + 3u_{HH}c^2 \quad (6)$$

Thermodynamic probability W is defined by the relation

$$W = \frac{(12N)!}{N_H!(12N - N_H)!} \quad (7)$$

and using Stirling formula $\ln X! = X(\ln X - 1)$ for large X

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numbers we find the natural logarithm of thermodynamic probability

$$\ln W = -12N[c\ln c + (1 - c)\ln(1 - c)] \qquad (8)$$

Considering the derived formulae (5, 6, 8) in accordance with the expression (2) we find free energy of alloy $MBCH_X$ in the following form

$$F = E_0 + 12N(U_i c + 1/U'c^2) + \\ +12kTN[c\ln c + (1 - c)\ln(1 - c)] \qquad (9)$$

where the following designations are used

$$U_i = u_{MH} + u_{BH} + u_{CH}; i = 1; 2 \text{ for } M \\ = Li, Mg, U' = 6u_{HH} \qquad (10)$$

We note that in the general case energies U_i depend on the chemical nature and concentration of metal atoms, on the system composition including boron and carbon, on the order of distribution of boron and carbon atoms in their positions. However, the dependence of energies U_i on the composition is not taken into account in the present consideration.

In view of dependence of activity of hydrogen atoms on pressure [29] as follows

$$\lambda_i = D_i P^{1/2} \qquad (11)$$

(D_i is the constant of proportionality), the obtained formula (9) determines the dependence of the free energy of alloy on temperature, pressure, hydrogen concentration and energetic constants.

2.1. Hydrogen solubility

In the state of thermodynamic equilibrium the solubility of hydrogen is determined by its limiting concentration. The last is found from the condition of free energy minimum

$$\partial F / \partial c = 0, \qquad (12)$$

whence it follows that

$$c = (1 + \frac{1}{\lambda_i}\exp \frac{U_i + U'c}{kT})^{-1} \qquad (13)$$

which defines the P-T-c phase diagram in terms of Eq. (11).

The plots of temperature and pressure dependences of hydrogen solubility can be constructed by formula (13). For the construction of temperature dependence of hydrogen concentration c = c(T) formula (13) can be written as

$$kT = - (U_i + U'c) / \ln \frac{c}{(1 - c)\lambda_i} \qquad (14)$$

We can set in formula (14) the value of concentration c in the range [0, 1] at the certain values of energetic constants and determine the temperature. As an example, we take such energies U_i, U_0 [56–58].

$$U_i = 0,152; 0,157; 0,162; U' = -0,134. \qquad (15)$$

Fig. 3 illustrates the plots of hydrogen concentration c = c(T) constructed by formula (14) for the activities of hydrogen atoms $\lambda = 1$ and 0,8 with the use of energies (15). As evident from this figure, the plots of temperature dependence c = c(T) are determined by two branches: the rising and falling. Variations in energy U_i cause the change of character of hydrogen solubility dependence with increasing temperature. In the case of Fig. 3 (a) the hydrogen concentration increases with a rise in temperature and can reach the value c = 0,5 (x = 6). The reduction in energy U_i (Fig. 3b) leads to the decrease of the maximum possible concentration of hydrogen in crystal to the value c z 3 (x = 4). In this case the up-tending branch of curve of the dependence c = c(T) corresponds to the unstable state or to the process of hydrogen desorption with temperature increase (if at the beginning the crystal was saturated with hydrogen). The increasing energy U_i (Fig. 3c and d) produces either the increase of hydrogen solubility up to the value c = 0,5 (x = 6) or even greater increase in the hydrogen concentration as the result of transition from the falling branch to the rising branch in the considered dependence c = c(T).

The activity of hydrogen atoms λ depends on the crystal structure and the chemical nature of metal atoms and it has an effect on the hydrogen solubility. The bonds of hydrogen with the crystal lattice weaken with decreasing activity of these atoms, hydrogen atoms more slightly interact with atoms of crystal, would easier absorb or desorb and these processes will occur at a lower temperature. This is illustrated in Fig. 3 (e). In this case an increase of hydrogen solubility can runs either along a curve 1–1 (if the crystal already contain hydrogen initially) or by a curve 2–2 with the transition to the upper branch of the curve. In both cases a decrease in activity l will cause the value of maximum solubility of hydrogen to increase.

In order to evaluate the dependence of hydrogen solubility on the external pressure formula (13) can be written in terms of formula (11) as

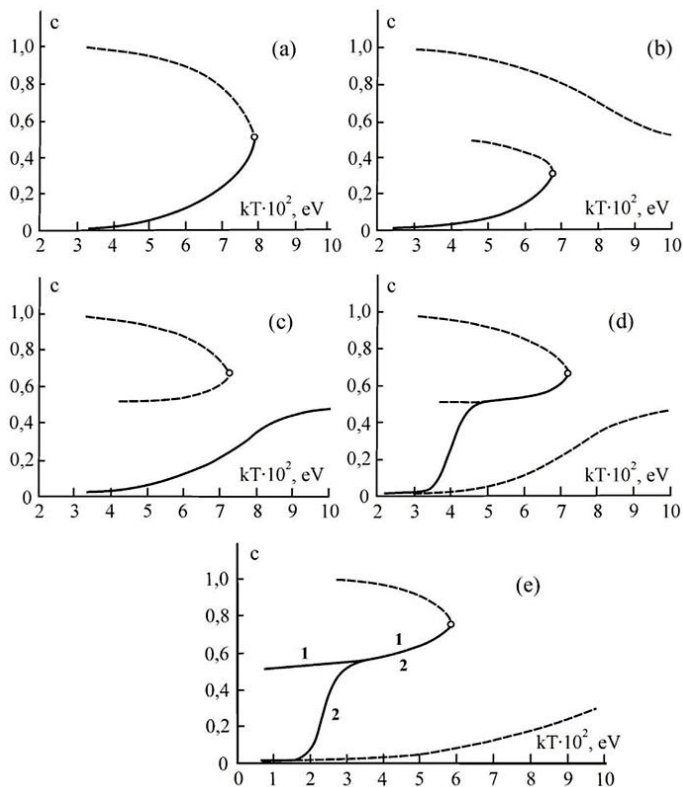$$\ln P = 2[ln \frac{c}{(1 - c)D} + \frac{U_i + U'c}{kT} \qquad (16)$$

Fig. 3 – Calculated temperature dependences of the atomic concentration of hydrogen accumulated in the boron carbides of metals constructed via formula (14) for the values of the energy parameters (15) (in eV) U_i = 0.157 (a), 0.152 (b), 0.162 (c–e) and U' = 0.314 and activity of hydrogen atoms I = 1(a–d) and I = 0.8(e). The solid portions of the curves correspond to the possible accumulation of hydrogen with increasing temperature. Circles indicate the extreme points on the curves

Рис. 3 – Расчетные температурные зависимости атомной концентрации водорода, накопленного в карбидах бора металлов, построенные по формуле (14) для энергетических параметров (15) (в эВ) U_i = 0,157 (a), 0,152 (b)), 0,162 (c–e) и U ' = 0,314 и активность атомов водорода I = 1 (a–d) и I = 0,8 (e): сплошные участки кривых соответствуют возможному накоплению водорода при повышении температуры; круги обозначают крайние точки на кривых

We estimate the values lnP for different temperatures prescribing the values of hydrogen concentration for certain values of U_i, U' and D. Fig. 4 illustrates the plots of pressure dependence of accumulated hydrogen concentration constructed for energies U_i = 0.157 eV, U' = –0.314 eV and activity coefficient D = 1 at different temperatures equal in eV to kT = 0.052, …, 0.070. As is evident from Fig. 4, the character of hydrogen concentration dependence on the value lnP is the same for all temperatures: at first with

increased value lnP the rise of concentration is smooth, then hydrogen concentration increases sharply to a large value c ≥ 0.8 and thereafter the smooth rise of concentration c continues again up to the maximum value c → 1 (x = 12). The shaded regions characterize the hysteresis effect. As is seen from Fig. 4, with increased temperature the hysteresis loop converges, shortens and disappears as a result of absorption–desorption process.
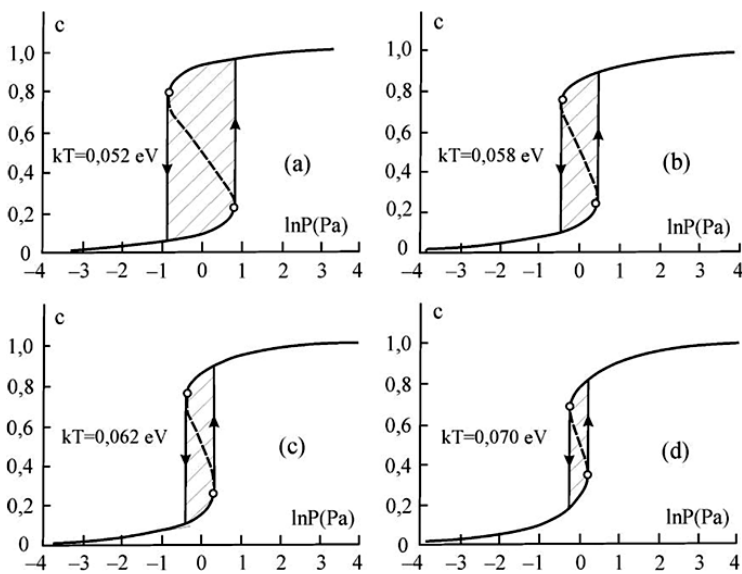

Fig. 4 – Calculated plots of dependences of the concentration of accumulated hydrogen in the boron carbides of metals on the external pressure constructed via formula (16) for the values of the energy parameters (in eV) U_i = 0.157, U' = 0.314, coefficient of activity of hydrogen atoms D = 1 and temperatures corresponding to kT = 0.052; 0.058; 0.062 and 0.070 eV (a–d). The hatched regions (a) characterize the hysteresis effect. The dashed portions of the curves correspond to the nonequilibrium state of the system. Circles in the curves note the extremum points

Рис. 4 – Расчетные графики зависимости концентрации накопленного водорода в карбидах бора металлов от внешнего давления, построенные по формуле (16) для энергетических параметров (в эВ): U_i = 0,157, U ' = 0,314, коэффициента активности атомов водорода D = 1 и температур, соответствующих kT = 0,052; 0,058; 0,062 и 0,070 эВ (a-d). Заштрихованные области (a) характеризуют эффект гистерезиса; пунктирные участки кривых – неравновесное состояние системы; кружки – точки экстремума

The study of pressure dependence $c = c(P)$ on extremum allows to determine the hydrogen concentrations corresponding to the extreme points which define the shape of the hysteresis loop.

From the condition

$$\partial P / \partial c = 0 \qquad (17)$$

we find the formula

$$P \left(\frac{kT}{c(1-c)} + U' \right) = 0 \qquad (18)$$

and the solution of this equation yields the values of concentrations c_1, c_2 for the extreme points

$$c_{1;2} = 0.5 \pm \sqrt{0.25 + kT/U'} \qquad (19)$$

The estimation by the formula (19) of concentrations c_1, c_2 for different temperatures gives the following values

$c_1 = 0.79$; $c_2 = 0.21$ at $kT = 0.052$ eV,
$c_1 = 0.76$; $c_2 = 0.24$ at $kT = 0.058$ eV,
$c_1 = 0.73$; $c_2 = 0.27$ at $kT = 0.062$ eV, (20)
$c_1 = 0.66$; $c_2 = 0.34$ at $kT = 0.070$ eV,
$c_1 = c_2 = 0.5$ at $kT = 0.0785$ eV,

i.e. the concentration values c_1, c_2 converge as the temperature increases and at the temperature of $kT = eU'/4$ they have the same value $c_1 = c_2$, in this case the hysteresis loop disappears.

Hence the derived formulae (14), (16) for hydrogen concentration can allow one to choose the composition of material, to bring in a new regime of manufacturing process and to select the P-T-conditions for implementation of the optimal accumulation of hydrogen for the purpose of its reversible storage.

A technologically important problem is the storage of hydrogen, that is required e.g. for the use of fuel cells as mobile energy sources. Porous or layered materials as borocarbides are candidates for these applications and larger layer distances in $M(BC)_nH_x$ could improve the storage properties [46].

3. Conclusions

The statistical theory of hydrogen solubility in boron carbides of alkaline Li and alkaline-earth Mg metals has been developed. The free energy of the systems have been calculated as a function of temperature, pressure, energetic parameters and activity of hydrogen atoms. The condition of thermodynamic equilibrium of the investigated systems have been derived and examined. The equation defining the P-T-c diagram of the systems

being studied have been found. The temperature and pressure dependences of hydrogen solubility in these compounds have been ascertained, the special features of these dependences have been established from the conditions of thermodynamic equilibrium. The plots of these dependences have been constructed, they define the temperature, pressure and concentration area of the system realization.

The process of hydrogen absorption–desorption in the studied systems has been investigated. The possibility of hysteresis effect manifestation has been justified, its decrease and disappearance with a rise in temperature have been shown in the present paper.

The knowledge of energetic parameters of interatomic interactions from independent experiments can permit to solve the practical problems: to examine the hydrogen absorption–desorption processes in boron carbides of different alkali and alkali-earth metals, to select the optimum variant in the materials choosing for hydrogen storage and accumulation, to establish the optimum P-T-conditions for the purpose of hydrogen reversible storage.

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