RESEARCH METHODS AND PROPERTIES OF POWDER MATERIALS

INTERACTION IN THE SYSTEM Li−B AND SOME PROPERTIES OF LITHIUM BORIDE PHASES

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Theoretical prerequisites are given for the formation of boride phases in castings. Lithium borides LiB_2 and LiB_{10} are synthesized and identified by x-ray photoelectron spectroscopy and x-ray phase and chemical analyses. Lithium diboride is a rather unstable compound which easily decomposes in weak mineral acid solutions. In contrast the decaboride is highly resistant to corrosive media. It decomposes completely in $HNO_3-H_2O_2$ and $H_2SO_4-HNO_3$ mixtures. A small amount of boron hydride is released as a result of lithium decaboride reaction with acids. Some physical properties (magnetic susceptibility, resistivity) are studied. The physicochemical properties of the Li−B system resemble those of the Be−B system. The highest lithium boride LiB_{10} pertains to covalent crystals and like boron it possesses semiconducting properties.

The Li−B phase-equilibrium diagram has not been studied and there are no reliable data for lithium boride phases [1]. Compounds of boron with lithium are mentioned for the first time in [2]. In the 1950s a series of articles was published by a group of authors (Markovskii, Shamrai, Mikhheeva, and others [1]) in which different methods were studied for preparing lithium boride phases. A suggestion arose that lithium boride is close in composition to LiB_6. In [3, 4] the opinion was expressed that in the Li−B system there exists a boride solidifying in the structural type CaB_6. The author in [5] studied the reaction of lithium with boron over a wide range of concentration and first indicated that in this system there exist borides of the compositions LiB_{2-x} ($x \leq 0.15$) and LiB_{10}. The first boride is a very unstable compound which hydrolyses in air forming lithium hydroxide. In the 1960s Secrist [6] with reaction of lithium and boron carbide in an inert atmosphere obtained lithium decaboride LiB_{10} which accompanied boron carbide and lithium. According to x-ray data for LiB_{10} tetragonal syngony is indicated. In [7] in sinters which are a mixture of lithium metal with Li_3B and Li_5B_4 an attempt was made to estimate the electrical resistivity and Hall effect. From a review of numerous publications it can be seen that the existence and phase composition of boride phases in the Li−B system is not currently clear.

If we consider theoretical prerequisites for forming lithium boride phases then they are reduced to the following. Lithium relates to s-elements. The energy stability of the s-configurations decreases with an increase in the first quantum number. That is with a changeover from Li to Na and K there is an increase in the energy potential for participation of s-electrons of the metal in organizing bonds on reaction with boron. Among the alkali metals lithium exhibits the least affinity for boron. This follows from the fact that for lithium in the s-shell there is only electron. In view of this in the lattices of the lithium borides formed the concentration of nonlocalized electrons is extremely small. With formation of Me−B bonds in lithium borides the s-configuration deforms which leads to an increase in electron cloud asymmetry, and this appears in the symmetry of the crystal lattice. Compounds take a lower structural order than for borides of sodium and potassium, and more so for magnesium and aluminum with which in accordance with the rule of diagonals affinity for alkali metals is observed [8-11]. According to Brewer and others [10] for a series of nontransition metals, and this relates to the metals of group I, the type of crystal structure displays a clear correlation with the number of valence electrons in an isolated atom of the element. Lithium, magnesium, and aluminum which exhibit 1, 2, and 3 valence electrons, have correspondingly BCC-, HCP-, and
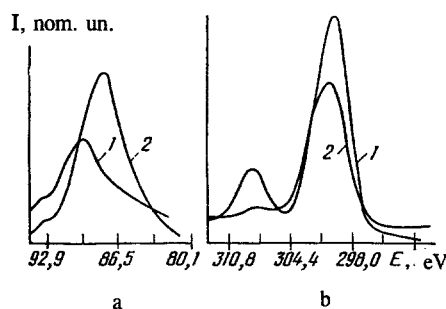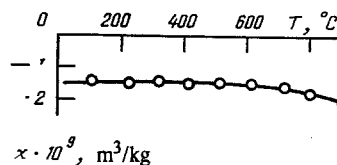
Fig. 1. X-ray photoelectron spectra of 1s-electrons of lithium (a) and boron (b) in borides LiB$_2$ (1) and LiB$_{10}$ (2).

Fig. 2. Temperature dependence of the magnetic susceptibility of LiB$_{10}$.

FCC-structures. In the first two the energy characteristics of the spectrum markedly affect formation of the structure. The concentration of nonlocalized electrons may be determined in terms of the intensity of s → d, s → p and d → p transitions or in terms of the acceptor capacity of the d-subshell. For the lithium the d-subshell is absent, but for potassium it plays a decisive role. Stable interatomic bonds in transition metals give rise to spd-hybrid functions and naturally all of the electrons of this hybrid affect formation of the crystal structure and its symmetry [8]. In forming borides a marked role is played by the dimensional factor [12]. The atomic radii of lithium, magnesium, and aluminum are close: 0.157; 0.160 and 0.143 nm respectively. The electronegativity of the lithium atom is 1.0 (1.2 for magnesium and 1.5 for aluminum). Following from these theoretical ideas it is possible to suggest that in the Li−B system there exist compounds with lower crystal lattice symmetry than in the system Na−B and K−B, and also with the structure of the type AlB$_2$.

Formation of lithium hexaboride with a structure of the CaB$_6$ type is hardly probable. This emerges from the main rules for forming hexaborides of the CaB$_6$ type by alkaline earth and rare earth metals formulated by Samsonov [13]: For alkali metals there are no (n − 1)-d-levels close to the ns-levels which take part in organizing the Me−B bonds; values of second ionization potential for alkali metals exceed the critical levels (11.5-12.0 eV); in the outer ns-level there is only one electron and not two as for alkaline earth and rare earth metals.

A study of the Li−B system is of considerable scientific interest since data about the phase composition of lithium borides and their physicochemical properties will make it possible to trace how the structure and properties of borides change with a changeover from alkali metals to beryllium magnesium, and then to alkaline earth metals in which a s → d transition may be realized causing occurrence of another type of bond.

In the present work the problem was set of obtaining the lower (LiB$_2$) and higher (LiB$_{10}$) borides of lithium and also of studying some physicochemical properties of these compounds.

In order the synthesize lithium boride phases there was use of lithium carbonate Li$_2$CO$_3$ (MRTU 6-09-4843−67) and amorphous boron with a purity of 99.6% (MRTU 6-02-292−64). Borothermal reduction of Li$_2$CO$_3$ was performed in argon and in a vacuum. The reduction products were subjected to chemical analysis. Lithium was determined iodimetrically [14] and boron was determined volumetrically in solution [15] (previously the product was fused with alkali at 700°C, and the melt was dissolved in dilute (1:1) hydrochloric acid). Lithium borides were identified by x-ray photoelectron spectroscopy (XPS) and x-ray phase analysis. X-ray phase analysis was carried out by the powder method and recording was performed with CuK$_\alpha$-radiation in a URS 50-I unit. X-ray spectra were interpreted by comparing interplanar distances with hose provided in [5].

The behavior of lithium decarbide and some modifications of boron in mineral acids and hydrogen peroxide under stationary conditions (a three-necked flask held at the solution boiling temperature for 1 h) was studied. At the end of a test the content of lithium and boron in the insoluble residue and the filtrate was determined.

The stability of lithium boride in a vacuum was studied by the Knudsen effusion method. Magnetic susceptibility was measured by the Faraday method in vacuum of ~6.6·10^{-1} Pa, and specific electrical resistivity was determined potentiometrically by direct passage of current through sintered cylindrical specimens 0.8 cm in diameter and 10-12 cm high. Specimen porosity was 3-10%. Specific electrical resistivity was extrapolated by the equation

TABLE 1. Comparative Characteristics of the Chemical Stability of Lithium Boride and Some Modifications of Boron*

Reagent	T, °C	LiB_{10}	B_{am}	β-B	α-B
H_2O	100	93,4	99,3	99,5	98,8
HCl $(d=1,19)$	115	91,5	92,0	100,0	87,0
HCl $(1:1)$	110	89,9	94,3	93,3	97,8
HCl $(1:10)$	102	79,2	97,7	98,5	96,1
H_2SO_2 $(d=1,84)$	280	98,2	97,3	98,4	68,1
H_2SO_4 $(1:1)$	120	—	97,8	97,8	63,8
HNO_3 $(d=1,4)$	110	2,8	0	0	0
H_2O_2 (30%)	100	12,8	0	—	—
$H_2C_2O_4$ (6%)	120	81,5	—	—	—

*The content of insoluble residue, % (wt.), is shown.

$$\rho_0 = \rho_n \frac{2-3n}{2},$$

where n is porosity.

X-ray photoelectron spectra were obtained in a U IEE-15 spectrometer. In making measurements a constant vacuum of $3.03\cdot10^{-2}$ Pa was maintained. The source of photons was K_α-radiation of magnesium (1253.6 eV). The bond energy for the core electrons of boron and lithium was determined with an accuracy of $\pm(0.1-0.2)$ eV. Calibration was carried out for 1s-lines of carbon for which a bond energy of 285.0 eV was adopted.

According to chemical and x-ray analysis data the powders were single phase and the weight content of lithium and boron in them approximated the calculated content: 23.8% Li and 74.9% B in LiB_2, 5.8% Li and 93.4% B in LiB_{10}. Lithium diboride solidified in structural type AlB_2 (spatial group $D_{6h}^1 - P6/mmm$); LiB_{10} has a tetragonal structure close to that of tetragonal boron (spatial group $D_{2d}^8 - P\bar{4}n2$) which is in good agreement with data in [5-7].

It was established by the XPS method that the spectrum of the core electrons of lithium and boron in borides mainly consists of two lines: One of them corresponds to the bond energy of the core electrons of lithium and boron in the Li−B bond and the other characterizes the charge condition of both components combined with oxygen (Fig. 1).

The bond energy of 1s-electrons of boron in pure rhomboheral boron is 187.8 eV. The bond energy for 1s-electrons of boron in borides differs from this value by an amount up to 1.6 eV [16]. The bond energy for 1s-electrons of lithium in lithium metal is 54.8 eV. In the reaction products of the original materials corresponding to the compositions LiB_2 and LiB_{10} an increase is detected in the bond energy of 1s-electrons for lithium up to 56.2 eV compared with pure lithium and there is a reduction in bond energy for 1s-electrons of boron to 187.2 eV compared with pure boron. The first indicates that in lithium borides the electron density in metal atoms is reduced, and the second is a result of transfer of part of the charge from lithium atoms to boron atoms. These results place lithium borides in a single series with borides of calcium, scandium, titanium, and some chromium borides [16]. With a change-over from LiB_2 to LiB_{10} the bond energy for 1s-electrons of lithium decreases from 56.7 to 55.2 eV, and the bond energy for 1s-electrons of boron increases from 187.2 to 187.7 eV. On the basis of the data obtained it is possible to say that in LiB_2 the proportion of the iron component of the Me−B bond is high whereas in LiB_{10} rigid covalent B−B bonds prevail. This feature of the electron structure and type of chemical bond in lithium borides LiB_2 and LiB_{10} governs their physicochemical properties.

Lithium diboride is not of considerable interest since it is very unstable and it easily dissolves in methanol and weak solutions of mineral acids. On reaction of LiB_2 with methanol it is more probable that alcoholates of the type CH_3OMe form.

The results of studying the stability of LiB_{10} powder in dry and moist air and in vapor above water and concentrated sulfuric acid are provided in Table 1. The main mass of the powder comprised particles with a size of 500-3000 nm. Lithium decaboride is relatively stable in air at room temperature. In vapor above water the weight gain after two weeks was 73.4% which may probably be connected with adsorption of moisture (about 70%) and formation of lithium hydroxide (3.4%). On holding LiB_{10} in vapor above sulfuric acid (96.5%) the weight hardly changed.

With action of sulfuric and hydrochloric (concentrated and dilute) acids on lithium decarboride there is marked dissolution of it. Complete dissolution of LiB_{10} is observed in mixtures of H_2O_2 + HNO_3, H_2SO_4 + HNO_3, and H_2O_2 + $K_2S_2O_8$. It should be noted that with reaction of LiB_{10} with acids considerable amounts of boron hydrides separate which are

absorbed: diborane by water and tetraborane by a solution of potassium hydroxide (20% by weight). During reaction of diborane with water, tetraborane with alkali, and subsequent neutralization of the alkaline solutions by hydrochloric acid there is formation of boric acid which is determined by normal titration. The behavior of lithium boride in different chemical reagents is suggested as a basis for the chemical analysis of lithium boride phases.

The rate of evaporation was determined for LiB_{10} in the temperature range 1240-1330 K in a vacuum of $\sim 6.6 \cdot 10^{-2}$ Pa using an evaporator made of molybdenum and a diaphragm $0.43 \cdot 10^{-3}$ m in diameter made of tantalum. The overall evaporation rate of LiB_{10} at 1240 K was $2.2 \cdot 10^{-3}$, and at 1330 K it was $7.4 \cdot 10^{-3}$ kg/m^2·sec. These values are lower by 2.5-3 orders of magnitude than the evaporation rate for pure metal. It is possible to expect that lithium boride LiB_{10} is similar to other metal borides on heating in a vacuum which dissociate into the component elements and the overall evaporation rate is governed by evaporation of lithium from the solid phase.

The temperature dependence was measured for magnetic susceptibility of LiB_{10} in the temperature range from room temperature to 1000°C (Fig. 2). It is well known that lithium is paramagnetic with $\chi = +2.4 \cdot 10^{-9}$ m^3/kg, and boron is diamagnetic with $\chi = -0.62 \cdot 10^{-9}$ m^3/kg. For lithium boride diamagnetism is established. It can be seen in Fig. 2 that up to 450°C the value of χ does not depend on temperature and above it there is a small increase. This path of the dependence is determined by the nature of the compounds. Specific magnetic susceptibility ($-1.5 \cdot 10^{-9}$ m^3/kg), which markedly exceeds in absolute value that calculated by the addition rule ($-0.3 \cdot 10^{-9}$ m^3/kg), indicates that lithium decaboride should relate to covalent crystals. The specific electrical resistivity of LiB_{10} is $\sim 3 \cdot 10^3$ Ω·cm and with an increase in temperature it decreases which is typical for semiconductors.

On the basis of these studies it is possible to draw the following conclusions. In physicochemical properties the Li−B system is close to the Be−B system. Lithium boride phases, as for beryllium, may be separated into two groups: lower borides which relate to LiB_2, and higher borides whose representative is LiB_{10}. The lower boride is distinguished by a high capacity for hydrolytic decomposition with formation of boron hydrides whose amount decreases with an increase in the boron content in boride. The higher boride LiB_{10} relates to covalent crystals and it exhibits semiconductor properties similar to boron.

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