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**FORMATION ENTHALPY OF BLi INTERMEDIATE PHASE****ENTALPIA TWORZENIA FAZY MIĘDZYMETALICZNEJ BLi**

The formation enthalpy of the BLi ( $B_{48}Li_{52}$ ) intermetallic phase was measured with the use of the water reaction and the direct reaction calorimetric method. The phase was prepared of weighed amounts of B and Li in a glove-box filled with high purity argon. The BLi phase was confirmed with using the X-ray diffraction investigations. The experiments were carried out with the use of a water reaction calorimeter (water reaction calorimetric technique) at 25°C (298 K) in air, as well as a direct reaction calorimeter at 752°C in high purity argon. The formation enthalpy value obtained for the BLi phase in the case of the water reaction calorimetric method equaled  $-30.3 \pm 2.2$  kJ/mole of atoms and in the case of the direct synthesis technique -  $29.4 \pm 2.0$  kJ/mole of atoms.

*Keywords:* Boron-lithium system, calorimetry, thermochemistry, hydrogen storage

Entalpia tworzenia fazy międzymetalicznej BLi ( $B_{48}Li_{52}$ ) została zmierzona przy użyciu metody rozpuszczania w wodzie oraz metody bezpośredniej reakcji. Faza była wytworzona w komorze manipulacyjnej w atmosferze oczyszczonego argonu z odpowiednich naważek B oraz Li. Eksperymenty zostały przeprowadzone przy użyciu kalorymetru wodnego (technika kalorymetryczna pozwalająca na pomiar reakcji z wodą) w 25°C (298 K) w powietrzu, a także przy użyciu metody bezpośredniej reakcji w 752°C w atmosferze argonu o wysokiej czystości. Uzyskana wartość entalpii tworzenia fazy BLi w przypadku kalorymetrycznej metody reakcji z wodą wynosiła  $-30,3 \pm 2,2$  kJ/mol atomów a w przypadku metody bezpośredniej reakcji: -  $29,4 \pm 2,0$  kJ/mol atomów.

**1. Introduction**

Hydrogen is thought to be the future fuel for vehicles and the power industry. In comparison with the traditional sources of energy, which, during combustion, emit great amounts of carbon dioxide, hydrogen is a fully ecological and high energy fuel, which, in the course of combustion, gives water as the product. However, the main problems with the usage of hydrogen on a large scale concern its storage in a safe form. Therefore investigations at many laboratories all over the world are concentrated on the search for a technology of safe hydrogen storage. One of such ways is the chemical bonding of hydrogen in the form of metals or semimetals hydrides of a relatively low decomposition temperature. Lithium-boron tetra-hydride ( $LiBH_4$ ) is one of such compounds which contain up to 18.5 wt. % of hydrogen. Although binary Li-B alloys or multi-component borides can be used for hydrogen storage or as anode material in high temperature lithium batteries or accumulators, because of their low density and electrochemical properties comparable to lithium, the thermodynamic properties of the boron-lithium system are practically unknown. One should also mention that the phase diagram, in the entire range of compositions, is also unknown. Such situation has been most probably caused by the huge experimental difficul-

ties, especially at high temperatures, connected with the great difference between the melting temperatures of the elements and the considerable vaporization of Li at temperatures higher than 1000°C (1273 K). In spite of this, the first experiments with B-Li alloys were initiated by Andrieux and Barbetti [1] already in 1932. They identified the  $B_6Li$  intermediate phase by the electrochemical technique and, in 1974, Rupp [2] confirmed its existence using the X-ray diffraction method. In the course of the following years, new phases from the B-Li system were identified at some laboratories by means of the structural and electrochemical methods and by way of density and electrical resistivity measurements ([3]  $B_4Li$ , [4]  $B_3Li$ , [5, 6, 7],  $B_2Li$ , [8] BLi, [3, 9, 10]  $B_4Li_5$  ( $B_5Li_7$ ), [10]  $BLi_3$  and [11]  $B_{14}Li_3$ ,  $B_{19}Li_6$ ). The last to prepare and investigate, by Mair at al. [11], was the  $B_3Li$  ( $B_6Li_2$ ) phase. The structural study revealed that it consists of 6 atoms of boron and 2 atoms of lithium, and that its structure is tetragonal (tP16) and belongs to the space group P4/mbm.

The number of articles on the measurements of the thermodynamic properties of B-Li alloys is low, probably, because of the problems connected with conduction of the experiment (the great difference between the melting temperatures, the vaporization of Li at elevated temperatures, the reactivity of Li with the elements of the apparatus and the very pure at-

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mosphere of the noble protective gas, both for the preparation and the performing of the experiments). Two articles [3, 7] are related to the discharge behavior of B-Li alloys between 400-600°C (673-873 K). The next ones [3, 12-18] show the reaction heat effects of boron and lithium during the thermal analysis studies, whereas the description of the preparation method and the studies of various properties of boron-lithium alloys or phases can be found in works [19, 20].

On the basis of the literature information on the investigations of the B-Li system, Okamoto, in [21], presented all the phases which were suggested in the literature ( $B_{13}Li$ ,  $B_6Li$ ,  $B_{14}Li_3$ ,  $B_4Li$ ,  $B_3Li$ ,  $B_2Li$ ,  $BLi$ ,  $BLi_3$ ), and in 2003, for the first time, Borgstedt and Gumiński [22] proposed the B-Li phase diagram. The last mentioned authors, for the critical assessment, also considered the liquidus and solidus data [23] for the B-Li alloys, within the concentration range between 0.5 and 1 mole fraction of lithium.

The investigations of the enthalpy of formation of the BLi phase were initiated in 2010 at A. Krupkowski Institute of Metallurgy and Materials Science of Polish Academy of Sciences. They have been a part of the ZAMAT research program, which concerned new materials and technologies. The program has been financed by both the European Union and the Polish Government.

This paper is a continuation of the study on the heat of formation of the intermediate phases from the B-Li system, in which the authors present the results of the X-ray structural analysis of the prepared phase and the experimental data on the formation enthalpy of the BLi phase performed by two different calorimetric techniques.

## 2. Experimental

### 2.1. Calorimetric study

The measurement of the formation enthalpy of the  $B_nLi_m$  compound by the calorimetric reaction technique is based on the determination of the heat effects accompanying the reaction of the components of the phase and the phase or compound with the suitable substance and was described in our previous work [24].

The direct synthesis method is based on the measurement of the reaction energy effect of the components (B, Li) of the intermediate compound (phase), at the temperature of such a reaction. The heat effect is measured by the thermopile of the calorimeter, whose calibration constant was earlier established, assuming that the synthesis of the compound is described with the following chemical reaction:



where:  $T_c$  is the temperature of the components before the introduction into the crucible and  $T_r$  is the crucible temperature at which the reaction goes on,  $Q$  is the heat effect measured by the calorimeter at the temperature  $T_r$  and  $X_B$  and  $X_{Li}$  are the mole fractions of the components (B, Li).

In such a case, the formation enthalpy  $\Delta_f H$  at the temperature  $T_c$  is calculated according to the following reaction:

$$\Delta_f H = Q - (X_B \Delta H_B + X_{Li} \Delta H_{Li}) \quad (2)$$

In Eq. 2,  $X_B$  and  $X_{Li}$  are the mole fractions of the reacted components (B, Li) and  $\Delta H_B$  and  $\Delta H_{Li}$  are the enthalpy changes of solid boron and lithium between the temperatures  $T_c$  and  $T_r$ . Therefore, the solid crystalline and amorphous boron and the solid lithium at temperature  $T_r$  were assumed as the reference state.

The calibration constant was established before the measurements with the use of solid boron as the tested material, similarly to the water reaction calorimetric method described above. The experimental procedure is described below. A suitable amount of boron was inserted into a molybdenum crucible at room temperature. The construction of the crucible is demonstrated in Fig. 1. Next, the calorimeter was heated up to the measurement temperature and after equilibrating (constant base line), an appropriate quantity of lithium was added to the crucible, and the change of the crucible temperature (heat effect) was measured up to the moment when the base line was achieved. After the measurement had been finished, the formation enthalpy was calculated from the heat effect of the reaction of boron and lithium.

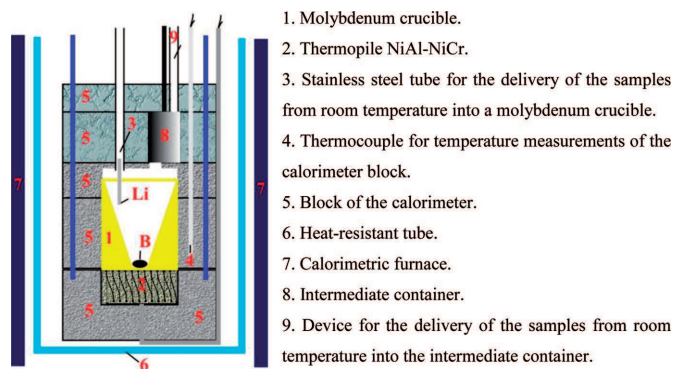


Fig. 1. Construction of the crucible used in the direct reaction calorimetric method

### 2.2. Preparation and identification of BLi phase

The BLi phase necessary for the water reaction calorimetric experiments, was prepared in a glove-box with a high purity argon protective atmosphere by the synthesis of crystalline boron [24] (pieces of purity 99.9 wt.%) and lithium (rod of purity 99.9 wt.%) delivered by Alfa-Aesar. The proper amounts of B and Li were slowly heated up to 1000°C (1273 K), and annealed for 4 hours. The furnace temperature was then lowered to 850°C (1123 K) and the sample was annealed for 4 days. The phase prepared was identified by the X-ray analysis. This method is the primary method of research, which is based on modern crystallography and used to test single crystals, ceramics and polycrystalline materials. In this technique a diffraction pattern obtained by the deflection of X-rays through the lattice of atoms in a crystal is recorded and analyzed to determine the lattice structure. For the analysis the diffractometer Bruker D8 Discover was used with the applied radiation Cu K alpha, with the voltage 30 kV, and the current 40 mA. The measured diffraction pattern of prepared BLi phase is shown in Fig. 2.

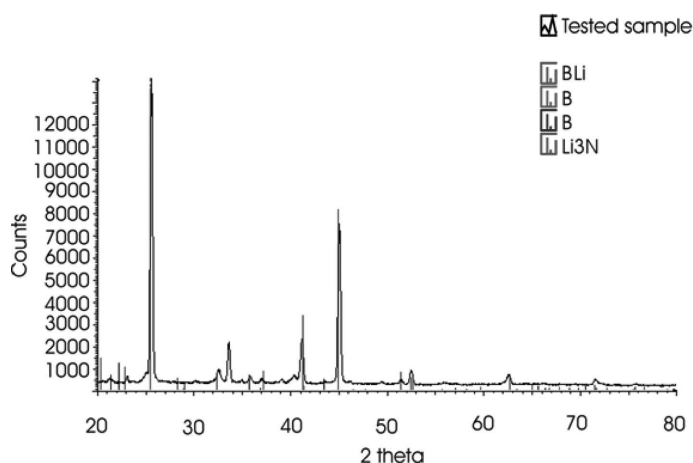


Fig. 2. Diffraction pattern of BLi phase (black) in the background of BLi (red line), boron (purple and blue lines) and  $\text{Li}_3\text{N}$  (green line)

According to PDF data base the card number of the defined  $\text{LiB}$  phase is 00-052-1033 [25].

It is visible that the BLi phase is dominating in the sample, with a slight amount of  $\text{Li}_3\text{N}$  and boron. The presence of  $\text{Li}_3\text{N}$  could be the effect of the reaction of  $\text{N}_2$  of the air in the course of the X-ray diffraction study. Therefore, the produced sample of the BLi phase could be used for the calorimetric studies, as such a low quantity of boron could not significantly influence the experimental value of formation enthalpy.

### 3. Results and discussion

The room-temperature water solution calorimeter shown in our earlier work [24] was used as first for the determination of the formation enthalpy of the BLi phase. During the dissolution of the BLi phase, the medium (water) was mixed with a stirrer and the values of the thermoelectric power were registered. The experiments were conducted in a glass crucible. The determination of the calibration constant was performed with the use of four inorganic compounds: lithium and sodium hydroxides, as well as ice and potassium permanganate. Values

of heat of solution in water were taken from the Handbook of Chemistry and Physics [26]. The obtained results of the calibration constants together with the values of the heat of solution were taken from [24].

The chemical compounds for the calibration were held in the glove-box to avoid their reaction with the water. The samples were weighted before the experiment and then transferred into the water reaction calorimeter in a small tightly closed bottle, from which lumps of samples were fast thrown into the water. The energy effects of the reaction were recorded. The measurement of the formation enthalpy of the  $\text{CaLi}_2$  compound was performed additionally, as a test. The comparison of the results of the  $\text{CaLi}_2$  formation enthalpy obtained with the use of the solution calorimetric method (Al and Sn as solvents) [27] as well as the water reaction calorimetric method (this work) determined the use of the latter for the measurement of the BLi formation enthalpy (the formation enthalpy of  $\text{CaLi}_2$  determined on the basis of the reaction heat effects of Ca, Li and the phase in water was  $-3.5 \pm 0.9$ , and by the solution in Al and Sn, it equaled  $-2.7 \pm 1.3$  and  $-2.9 \pm 1.9$  kJ/mol at. [27], respectively).

The heat of the lithium reaction with the water was experimentally determined for 6 samples and the results were taken from [24].

In the following stage, the heat effects of the reaction of the BLi phase were measured. The time of the reaction and stabilization of the calorimeter baseline was about  $3/4$  hour. The phase samples were weighted in the glove-box and quickly brought into the calorimeter in a small tightly closed bottle to protect them against the reaction with the air components ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ). Directly before the measurement, the bottle was opened and the sample was introduced into the water. The values of heat effects and the formation enthalpy are shown in Table 1, together with the average values and the standard deviation. The calculations were conducted with the assumption of two standard states of boron: amorphous and crystalline, and the results are shown in Table 1. The transition heat value of the crystalline boron into the amorphous one at room temperature was taken from [28].

TABLE 1  
Heat effects and formation enthalpy of BLi phase at 25°C (298 K) obtained by water reaction calorimetric method

Phase	T [K]	No of sample	Heat effect $\Delta H^{\text{ef}}$ [kJ/mol at.]	Enthalpy of formation $\Delta_f H$ [kJ/mol at.]	Heat effect $\Delta H^{\text{ef}}$ [kJ/mol at.]	Enthalpy of formation $\Delta_f H$ [kJ/mol at.]
			Amorphous boron		Crystalline boron	
BLi	298	1	-74,0	-32,8	-75,8	-31,0
		2	-73,8	-32,9	-75,6	-31,1
		3	-70,6	-36,2	-72,4	-34,4
		4	-75,4	-31,3	-77,2	-29,5
		5	-77,3	-29,5	-79,1	-27,7
		6	-75,3	-31,4	-77,1	-29,6
		7	-76,2	-30,5	-78,0	-28,7
		Average value	-74,7	-32,1	-76,5	-30,3
		Standard error	2,2	2,2	2,2	2,2

As it was mentioned earlier, the boron did not react with water and after the reaction, it was accumulated at the bottom of the crucible in the form of powder. The X-ray diffraction pattern of the powder obtained after the reaction of BLi with the water showed mainly the amorphous boron and a small amount of boron of different crystallographic structures [24].

For the measurement of the formation enthalpy of the BLi phase by the direct reaction, the same calorimeter which was applied in our earlier studies [29-32] was used. The only difference concerned the construction of the crucible in which the dissolution of the metals or compounds was conducted. In the case of the reaction calorimetric method, the contact surface of the thermopile with the reaction crucible was sustained and the reaction volume of the crucible was limited to ensure the contact of the boron with the lithium after its melting and in order to decrease both the amount of metals and the reaction heat effect.

Directly before the measurement, the calorimeter was tested with the use of boron samples and the proper calibration constant was determined. The samples of boron used in the measurements weighed about 50 mg. The lithium samples in the form of sticks were introduced from room temperature into the reaction zone by the calorimeter delivery device, tipped with a valve cutting off the calorimeter from the air (environment). The delivery of Li from the glove-box into the calorimeter was performed with the use of a glass tube with two valves on its ends. The latter was filled with Li in the glove-box, and after closing the valves, it was drawn out of the glove-box and connected with the delivery device of the calorimeter.

The volume between the delivery device and the closed glass tube with Li (containing air) was evacuated three times and filled with high purity Ar. Next, the lithium sample was introduced into the reaction zone of the calorimeter by the opening of the valves of the delivery device and the stainless steel tube 3. The reaction time observed equaled about  $3/4 \div 1$  hour. The experiment was carried out three times and the obtained values of heat effects and the formation enthalpy at 752°C (1025 K) are shown in Table 2. The comparison of the data in Table 1 on crystal boron (column 7) with those on the direct synthesis in Table 2 (column 5) shows excellent agreement of the two. This can mean that the formation enthalpy of the BLi phase is independent of temperature and also that the water reaction calorimetric method is suitable for the measurement of the formation enthalpy of compounds or phases, in the case when it is easy to dissolve at least one of the phase components of a two component phase.

The X-ray analysis of the BLi sample after the direct synthesis (Fig. 3), beside the BLi ( $B_4Li_5$ ,  $B_6Li_7$ ) phase, also showed a small amount of  $Li_2N_2O_3$  (~3 wt. %),  $Li(NO_3)$  (~2 wt. %), and  $Li_3N$  (~1 wt. %). The estimated amounts of compounds consisting of lithium, oxygen and nitrogen could not considerably influence the measurement of the formation enthalpy of the BLi phase by the direct reaction calorimetric technique. It is also possible that they were formed during the structural study which was conducted in the air or in the course of demounting the calorimeter, removing the crucible with the reaction product from the calorimeter and also transporting it into the glove-box. Taking into account the standard error of calibration from [24] and of this study one can state that the

measurement error of  $\Delta_f H$  is  $\pm 2$  kJ/mol at. Comparing the experimental results obtained by the two different methods (Table 1 and 2), one can notice the excellent agreement of the formation enthalpy data of the BLi phase.

TABLE 2  
Heat effects and formation enthalpy of BLi phase at 752°C (1025 K) obtained by direct synthesis calorimetric method

Phase	T [K]	No of sample	Heat effect $\Delta H^{ef}$ [kJ/mol at.]	Enthalpy of formation $\Delta_f H$ [kJ/mol at.]
BLi	1025	1	-19,0	-29,6
		2	-17,9	-28,7
		3	-19,1	-29,9
		Average value	<b>-18,6</b>	<b>-29,4</b>
		Standard error	<b>0,7</b>	<b>0,6</b>

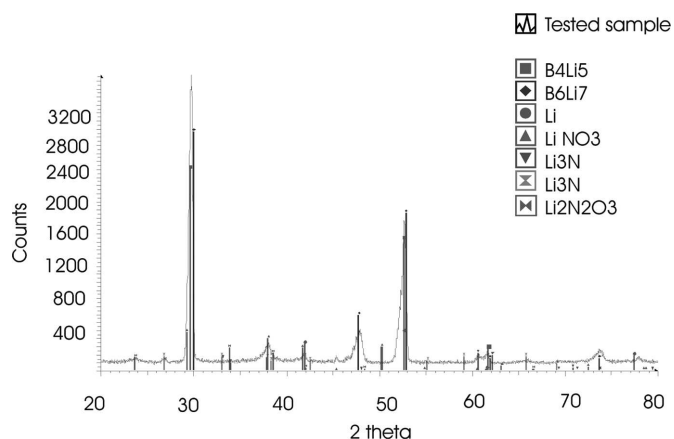


Fig. 3. Diffraction pattern of the BLi alloy after the reaction of B and Li in the measurement of the formation enthalpy by the direct synthesis calorimetric technique

Although the Miedema model [33] is not recommended for the systems with B, the calculation of the formation enthalpy was conducted and the obtained value for the BLi phase equaled -30.1 kJ/mol at. Such excellent agreement of the calculated value with the values obtained in this experimental study by both of the used methods was an astonishment for the authors, as the modeled values of the formation enthalpy [33] in the case of the  $B_3Li$ ,  $B_{13}Li$  and  $B_{14}Li_3$  phases, presented in [24], differed from the experimental data even by 5 kJ/mol at.

#### 4. Conclusions

Taking into account the comparable values of the formation enthalpy of the BLi phase measured by both the water reaction and the direct synthesis calorimetric method one can suppose that these experimental methods were suitable for the calorimetric examinations of lithium contained intermediate phases. This fine agreement of experimental data was the most probably to the effect of the fast reaction of the B with Li to the BLi in the case of direct synthesis calorimetric method (this



supposition was confirmed by the structural study of reaction products).

The comparable values of the formation enthalpy obtained at room and elevated temperature (752°C (1025 K)) can point at its slight dependence on or independence of temperature.

The study showed excellent agreement of the BLi formation enthalpy measured in this study by two different methods with that calculated by the Miedema model. However, it should be noted, that such good agreement between modeled and measured values of the formation enthalpy is not often observed.

One can suppose that the water reaction calorimetric method may also be suitable in the future examinations of the solution energetic effects of those phases which contain other alkali metals, too, and which are almost impossible to study by means of other calorimetric methods, because of the great difficulties caused by the low melting and vaporization temperatures as well as the reactivity of the alkali metals with the elements of the apparatus and the impurities of the protective atmosphere.

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