Thermochimica Acta, 133 (1988) 305–310
Elsevier Science Publishers B.V., Amsterdam

DSC ANALYSIS OF LITHIUM RICH Li-B ALLOYS

T.MARČAC, P.BUKOVEC and N.BUKOVEC
Department of Chemistry and Chemical Technology,
E.Kardelj University, 61000 Ljubljana, Yugoslavia

ABSTRACT

Lithium-boron alloys of approximate compositions Li_7B_6 have been studied by differential scanning calorimetry and X-ray powder diffraction. The results indicate that the alloy gives off lithium at temperatures above 800°C to approach the composition LiB. The initial alloy could therefore be formulated as LiB.xLi, with lithium trapped in a porous matrix of LiB.

INTRODUCTION

Thermal batteries have found a number of specialized applications |1|. As anode material lithium has advantages over the other metals, however due to low melting point of pure metal, lithium rich Li-B alloy is used |2|. There was more care given to the preparation of anode material as to the exact composition of the alloy. The stoichiometry seems to be near LiB, with two formulas, Li_7B_6 |3,4| and Li_5B_4 |5,6| respectively, proposed in the literature. The present work reports some preliminary results on the DSC analysis of lithium rich Li-B alloys.

EXPERIMENTAL

The samples of Li-B alloys were prepared in an argon atmosphere glove box equipped with a recirculating gas purification system. Boron (Merck, 99.9%) was puverized to give particles of less then 0.5 mm in diameter. Lithium foil (Foote Mineral Comp., 99.8%) and boron powder were pressed together to give Li-B-Li sandwiches (about 5g) which were rolled and weighted into stainless caps.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

The caps were hermetically sealed, put into a preheated furnace and heated for an hour at 450°C. The samples were then allowed to cool. Two phases separated within each sample. The upper one was porous, light brown and brittle, the lower one was light and ductile. The phases were analyzed for lithium.

DSC curves of both phases were recorded by means of a Mettler TA 2000C apparatus. Stainless steel crucibles which could be sealed electrically were designed specially for these measurements. The heating and cooling DSC runs were made at 5 and 10 $Kmin^{-1}$ heating/cooling rates. The upper temperature limit was 1050°C.

X-ray powder patterns were obtained with a Guinier-Simon camera, using CuKα radiation. The samples were prepared in a glove box.

RESULTS AND DISCUSSION

The main experimental results are summarized in Table 1. The elemental analysis gives no definitive answer on the stoichiometry of the phases. Inspection of X-ray powder patterns shows that all samples contain the same phase, designated by Ernst |3| as Li_7B_6, or by Wang |5| as Li_5B_4. The admixtures of Li_3N and LiOH have also been detected in the upper brittle parts of ingots, which means that surfaces of the samples were partly contaminated when handeled. X-ray powder patterns show Li_7B_6 to be the main phase of the ductile part. Additionally, the lines of unreacted lithium and in some cases weak lines of LiOH were observed. Wang et al.|6| stated there were at least two phases for lithium reach compositions. For an unidentified phase with 50 and 40 at% Li, two characteristic lines at 7.25 and 4.25 Å were found |6|. In most our specimens these additional lines were observed (see Table 1).

The DSC experiments in heating and cooling modes were carried out to elucidate the nature and reversibility of thermal events in the prepared alloys. The temperatures of DSC effects are summarized in Table 1 and the characteristic effects are shown in Figs. 1 , 2 and 3.

The samples containning between 50 and 60 at% Li exhibit similar DSC curves. The first endothermic peak on heating appeared at 581°C (sample A1) and at 588°C (sample A2, first cycle). As these two specimens contain some LiOH as proved by X-ray powder diffractometry, the DSC effect could possibly be ascribed to the decom-

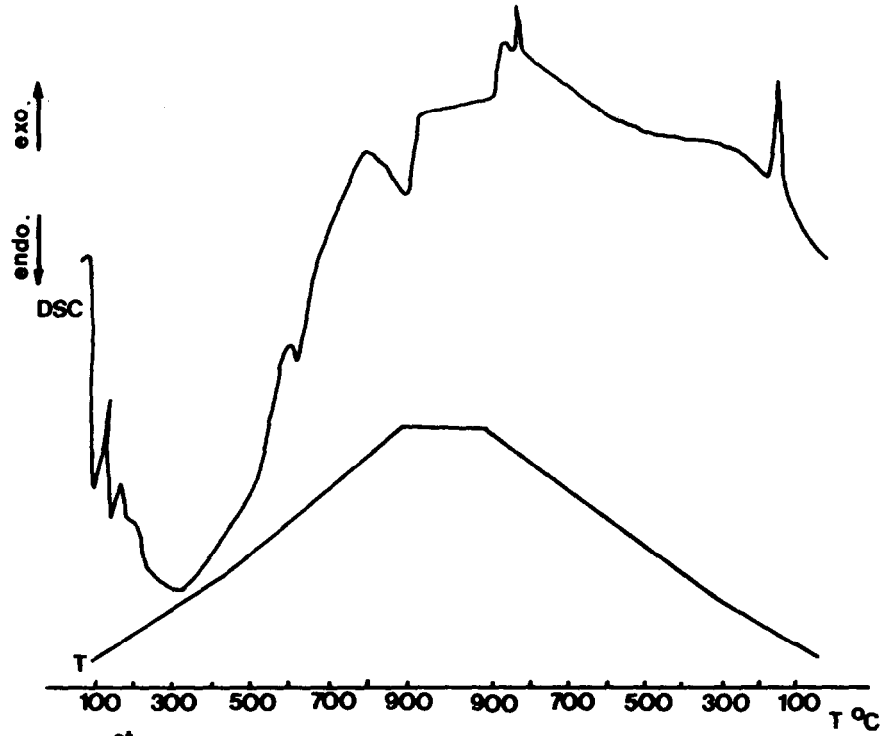

FIG.1. A2 1st cycle.

position of LiOH |7|. At higher temperatures (up to 950°C) one or two endothermic DSC peaks were observed. At least one of them is always sharp and appears exothermally on cooling (see Figs.), indicating reversible phase change.

The phases with 40-50 at% Li have no melting DSC peaks for lithium in the first heating cycles. On cooling however, exothermic crystallization of lithium at about 180°C can be seen on DSC. In the following cycles successive melting and crystallization of lithium take place. Examination of the enthalpies for the two processes as a function of the number of cycles shows the convergence toward a constant value. A possible explanation for these effects could be the formulation of Li_7B_6 and Li_5B_4 compositions as LiB.xLi with lithium traped in a porous matrix of LiB. On heating above 800°C lithium is set free until the composition becomes LiB.

The present state of knowledge should be considered preliminary. The DSC study of Li-B alloys in combination with other methods is continued in our laboratory.

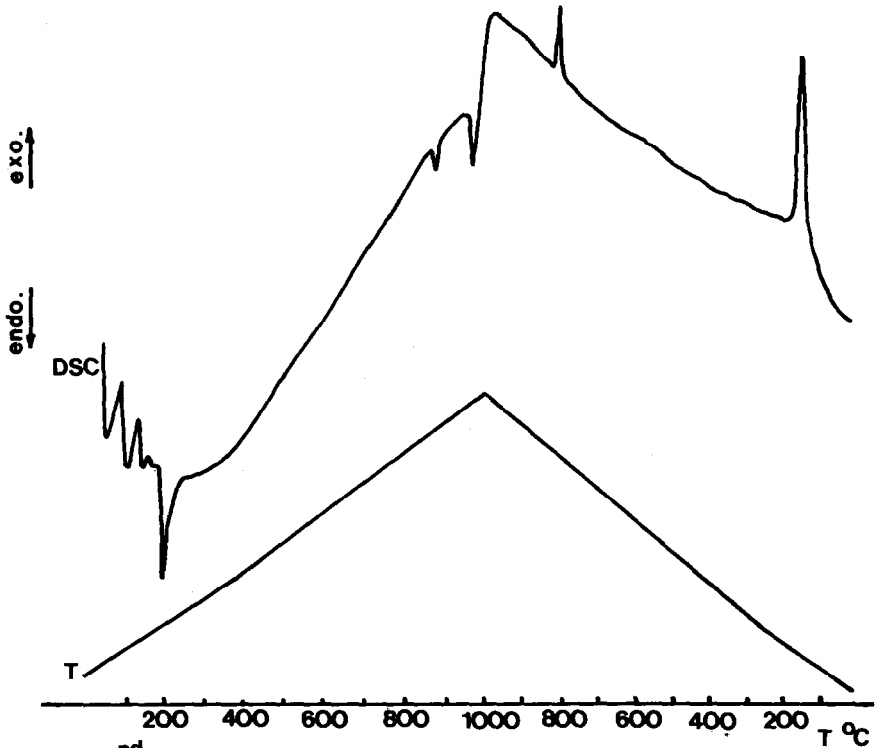

FIG. 2. A2 2nd cycle.

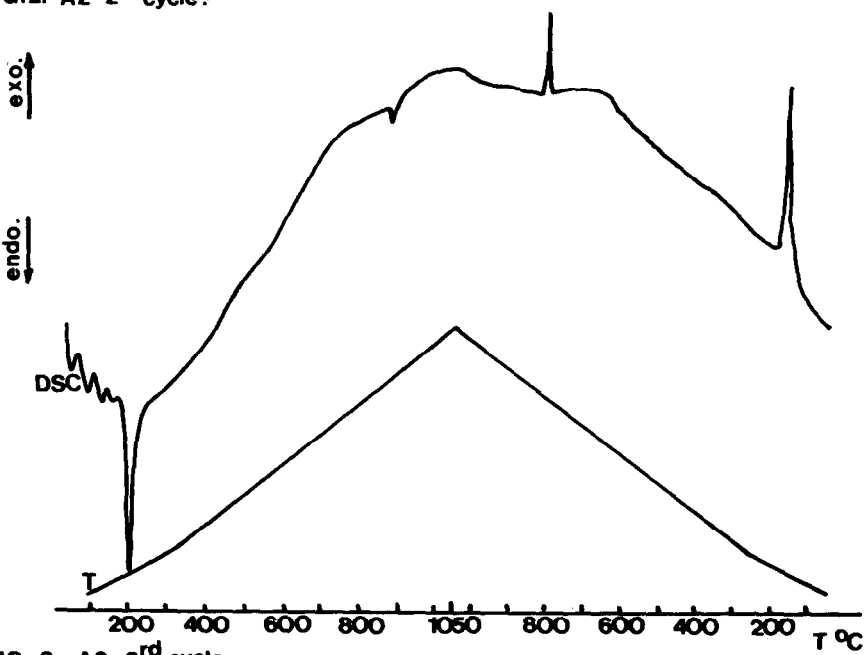

FIG. 3. A2 3rd cycle.

TABLE 1

Some experimental data on Li-B alloys

Alloy	Composition (at %)	Part of alloy taken for DSC	X-ray pattern	DSC effects (^{o}C)
A 1	Li 56.0 B 44.0	brittle part	Li_7B_6,Li_3N LiOH, 7.18	*H:581, 638 C:823, 178
A 2	Li 54.0 B 46.0	ductile part	Li_7B_6,LiOH Li, 7.18, 4.18, 3.56	H:588, 800 C:853, 180 H:182, 850, 958 C:813, 181 H:182, 780, 876 C:814, 183
A 3	Li 88.4 B 11.6	ductile part	Li_7B_6,Li	H:181, 795 C:802, 177
A 4	Li 65.3 B 34.7	brittle part	Li_7B_6,Li_3N, Li, LiOH	H:182, 766 C:863, 791, 175
A 5	Li 66.5 B 33.5	brittle part	Li_7B_6,Li_3N	H:814, 903 C:836, 825, 184 H:181, 823 C:833, 183
A 6	Li 66.5 B 33.5	brittle part	Li_7B_6,Li	H:181, 822 C:830, 183
A 7	Li 94.0 B 6.0	ductile part	Li_7B_6,Li, Li_3N, 7.14, 4.15, 3.56	H:182,700-900 C:800-750, 184

*H: Heating
C: Cooling

REFERENCES

1 C.W. Jennings, in The Preliminary Battery, N.C. Cahoon and G.W. Heise, Editors, John Wiley, New York, 1976, p. 263.
2 R. Szwarc, R.D. Walton, S. Dallek and B.F. Larrick, J. Electrochim. Soc., 129 (1982) 1163.
3 D. Ernst, J. Electrochim. Soc., 129 (1982) 1513.
4 S. Dallek, D.W. Ernst and B.F. Larrick, J. Electrochem. Soc., 126 (1979) 866.
5 F.E. Wang, Metallurgical Transactions A, 10A (1979) 343.
6 F.E. Wang, M.A. Mitchell, R.A. Sutula and J.R. Holden, Journal of Less-Common Metals, 61 (1978) 237.
7 F.A. Cotton and Wilkinson, Advanced Inorganic Chemistry, Interscience Pub., 1972, p.191.