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DSC analysis of the reaction between lithium and boron

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Abstract

The reaction between lithium and boron has been followed by differential scanning calorimetry and X-ray powder diffraction in the temperature range 25–1050 °C. After melting of lithium at 180 °C, the exothermal solvation of boron in liquid lithium at about 350 °C was observed. At approximately 450 °C, the exothermal reaction begins, giving $LiB \cdot xLi$ which decomposes above 900 °C to yield LiB.

INTRODUCTION

In studies on lithium-rich Li–B alloys, the stoichiometries Li_7B_6 [1,2] and Li_5B_4 [3,4] have been proposed. It was recently shown that the two phases have the same X-ray powder pattern [5]. DSC analysis of the alloy of approximate composition Li_7B_6 indicates that the initial alloy could be formulated as $LiB \cdot xLi$, with lithium trapped in a porous matrix of LiB [5]. The alloy gives off lithium at temperatures above 800 °C, approaching the composition LiB. In the present work, the reaction between lithium and boron was studied in order to elucidate the formation of $LiB \cdot xLi$.

EXPERIMENTAL

The physical mixtures of lithium (Foote Mineral Comp., 99.8%) and boron (Merck, 99.9%) were prepared in a glove box equipped with a recirculating argon purification system. Boron was pulverised to give particles between 0.5 and 1 mm in diameter. The samples were weighed into stainless steel caps, which were hermetically sealed.

DSC curves were recorded by means of a Mettler TA 2000C apparatus. The stainless steel crucibles used were designed specially for these measurements and could be sealed electrically. Heating and cooling DSC curves were run at 2, 5 and 10 K min^{-1}.

X-ray powder patterns were obtained with a Guinier–Simon camera, using Cu-K_α radiation. All sample handling was in a glove box.

RESULTS AND DISCUSSION

A number of samples containing more than 50 at.% of Li were cycled between 25 °C and various higher temperatures. The main experimental conditions are given in Table 1. In addition to the melting of lithium at about 180 °C, there are two exothermal effects at approximately 350 and 450 °C on the DSC heating curves of each sample. To elucidate the nature of the first reaction, the sample (S1 in Table 2) was heated up to 350 °C, left at that temperature for two hours, and then cooled down to room temperature. The melting and the solidification enthalpy of lithium are the same (Table 2), which means that the first exothermal effect cannot be ascribed to a chemical reaction, such as the formation LiB_3 [2]. Re-heating the sample (S2) between 25 and 440 °C gave the same result (Table 2); the exothermal effect at 341 °C, however, only appeared in the first heating. This effect may be explained by the solvation of boron in liquid lithium [3]. This idea is supported by the X-ray powder pattern of the sample S2 after DSC cycling, where strong lines of lithium appeared at *d* values of 2.48, 1.75 and 1.43 Å (ASTM file 15-401). In addition, weak lines of Li_3N, Li_2O and LiOH were also found, due to partial contamination on handling. The reaction of lithium with traces of air, or possibly with the wall of the crucible has been examined by analysing pure lithium. In the first heating period, a few weak effects were found (Table 2). In the successive cooling and heating curves, only the effects due to melting and solidification of lithium were found. The respective enthalpies remained constant throughout the cycling.

The next sample (S3) (see Fig. 1) was heated up to 700 °C and cooled down to room temperature. The second exothermal effect begins at 467 °C. There are no DSC effects on cooling, proving that all the lithium was used in the reaction. According to the initial mole ratio, the composition is approximately Li_7B_6. This phase has also been confirmed by X-ray powder pattern, with the *d* values being 3.46 and 2.02 Å [2]. According to the latest results [5], the formulation should be $LiB \cdot 0.167Li$.

TABLE 1

Experimental conditions in DSC analysis

Sample	Composition (at. %)		Heating rate ($K\ min^{-1}$)	Heating–cooling interval (°C)
	Li	B		
S1	54	46	2	25–350–25
S2	54	46	2	25–440–25
S3	54	46	2	25–700–25
S4	54	46	10	25–900–25
			5	25–1050–25
Li	100		5	25–950–25

TABLE 2

Experimental results of DSC analysis

Sample	Cycle	Temp. interval (°C)	T_{peak} (°C)	Thermal effect	ΔH_m (J)
S1	1	25– 350	180	endo	7.3
			344	exo	
		350– 25	182	exo	7.1
S2	1	25– 440	181	endo	11.7
			341	exo	
		440– 25	181	exo	12.9
	2	25– 440	178	endo	10.7
		440– 25	179	exo	10.9
S3	1	25– 700	185	endo	
			335	exo	
			467	exo	
		700– 25	–		
S4	1	25– 900	180	endo	11.0
			410	3 peaks	
		900– 25	–		
	2	25– 900	–		
		900– 25	–		
	3	25–1050	934	endo	
		1050– 25	854	exo	
			178	exo	1.2
	4	25–1050	180	endo	1.1
			911	endo	
		1050– 25	853	exo	
			177	exo	1.4
	5	25–1050	180	endo	1.4
			913	endo	
		1050– 25	851	exo	
			178	exo	1.5
	6	25–1050	179	endo	1.6
			913	endo	
		1050– 25	852	exo	
			177	exo	1.6
Li	1	25– 950	185	endo	9.3
			289	exo, w	
			345	exo, vw	
			373	exo, vw	
			621	sh	
		950– 25	196	exo	9.3
	2	25– 950	183	endo	9.5
		950– 25	193	exo	9.3
	3	25– 950	182	endo	9.2
		959– 25	186	exo	9.1

Key: w, weak; vw, very weak; sh, shoulder.

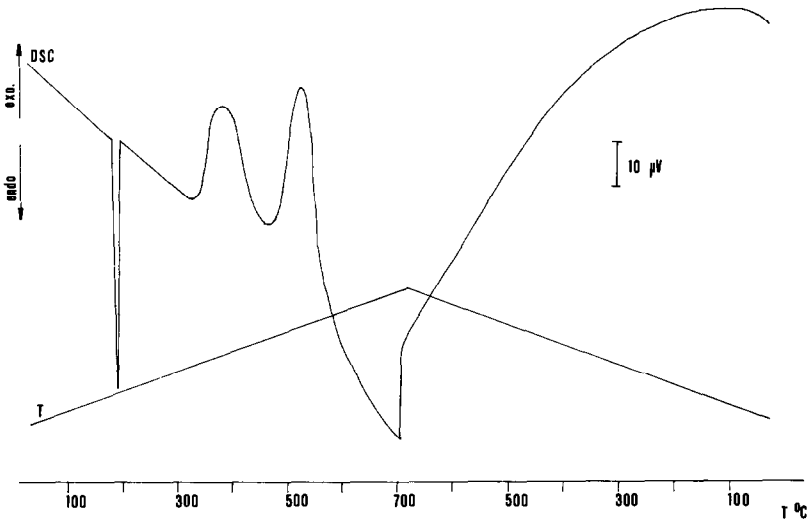

Fig. 1. Heating and cooling DSC curves of sample S3.

Increasing the heating rate resulted in a splitting of the solvation peak in the next sample (S4) in the temperature range 400–500 °C (Fig. 2). This splitting could also be brought about by different sizes of boron particles.

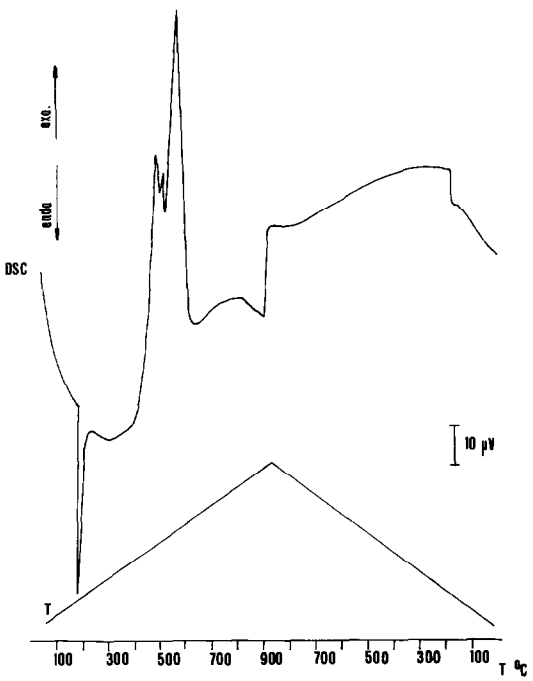

Fig. 2. Heating and cooling DSC curves of sample S4, cycle 1.

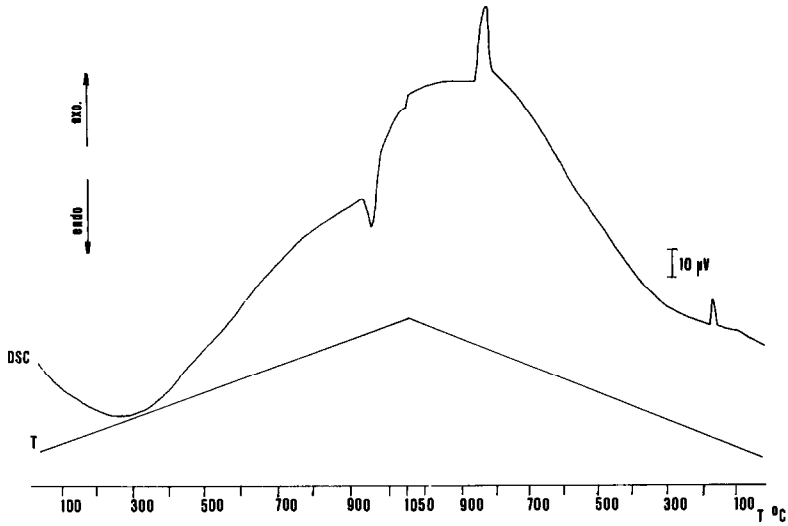

Fig. 3. Heating and cooling DSC curves of sample S4, cycle 3.

When the next cycles were run up to 900 °C, no effects were observed. At higher temperatures, the sample started to decompose at about 930 °C, releasing lithium which solidified on cooling. After several cycles, the amount of lithium released became constant, indicating that the decomposition was finished, giving the composition LiB. As well as the constant amount of lithium, a reversible phase change was observed (913 °C on heating and 852 °C on cooling) in the last cycles (see Fig. 3).

REFERENCES

1 D.W. Ernst, J. Electrochem. Soc., 129 (1982) 1513.
2 S. Dallek, D.W. Ernst and B.F. Larrick, J. Electrochem. Soc., 126 (1979) 866.
3 F.E. Wang, Metall. Trans. A, 10A (1979) 343.
4 F.E. Wang, M.A. Mitchell, R.A. Sutula and J.R. Holden, J. Less-Common Met., 61 (1978) 237.
5 T. Marčac, P. Bukovec and N. Bukovec, Thermochim. Acta, 133 (1988) 305.