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NSWC/WOL TR 77-67

LITHIUM-BORON ALLOY ANODES FOR MOLTEN SALT BATTERIES (I)

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RESEARCH AND TECHNOLOGY DEPARTMENT

11 JANUARY 1978

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. ~~REPORT NUMBER~~ (14) NSWC/WOL/TR-77-67
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER (9)
4. ~~TITLE (and Subtitle)~~ (6) LITHIUM-BORON ALLOY ANODES FOR MOLTEN SALT BATTERIES (I)
5. TYPE OF REPORT & PERIOD COVERED: Progress ~~Rep~~[illegible]t.
6. ~~PERFORMING ORG. REPORT NUMBER~~
7. ~~AUTHOR(s)~~ (10) S. Dallek, D. W. Ernst and B. F. Larrick
8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS

Naval Surface Weapons Center✓
White Oak Laboratory
White Oak, Silver Spring, Maryland 20910

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NIF;0;0;WR33JA(1);
11. CONTROLLING OFFICE NAME AND ADDRESS
12. ~~REPORT DATE~~ (11) 11 Jan[illegible]y [illegible]78
13. ~~NUMBER OF PAGES~~ 24
14. MONITORING ~~AGENCY NAME~~ & ADDRESS (if different from Controlling Office) (12) 28p.
15. SECURITY CLASS. (of this report) UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release.
Distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
18. SUPPLEMENTARY NOTES
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Lithium Alloys, Boron Alloys, Anodes, Batteries

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The current work is concerned with the development of a procedure for the preparation of a lithium-boron alloy suitable for use as an anode in thermal batteries. Metallography, thermal analysis, and X-ray diffraction techniques are being developed as tools for studying this multiphase material. A chemical analysis is planned to identify the composition of the various phases. Once the phase diagram for the system has been determined, we will be able to → over

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prepare material having optimum electrochemical properties for use as an anode material.

SUMMARY

This is the first of a series of progress reports on the development of a lithium-boron alloy for use as an anode in thermal batteries. A preparation procedure is being developed and the phase diagram for the alloy system is being determined. This alloy system, utilizing the electrochemical superiority of lithium as an anode material, will be used in the development of an improved thermal battery.

This work is being performed under Program Element NIF Task Area Number 0, work unit number WR335A (1).

, acting
J. R. Dixon
By direction

ACKNOWLEDGEMENTS

The authors wish to thank L. Kowalchik for assistance in the techniques of the alloy preparation and many valuable discussions on the system. The helpful advice of L. E. DeVries and F. M. Bowers is also gratefully acknowledged.

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I. INTRODUCTION

Most thermal batteries employ solid calcium metal anodes discharging in a molten lithium chloride-potassium chloride eutectic electrolyte. Thermal batteries typically deliver less than 30 percent of the available discharge capacity because the anode reaction product ($KCl \cdot CaCl_2$) forms a solid, non-conducting barrier between the anode and the molten salt electrolyte.

The electrochemical superiority of lithium as an anode material is well known. Its reaction product ($LiCl$) is soluble, and it is known that lithium could provide a twofold to threefold improvement in both the specific energy and specific power of thermal batteries. However, lithium melts at 453K (180°C), well below the 800K (527°C) operating temperature of thermal batteries. The escape of lithium during discharge and the difficulty of maintaining the physical integrity of a liquid metal anode have precluded the use of lithium in molten salt batteries. This problem may be solved by utilizing the lithium in the form of an alloy having a high melting point. Alloys of lithium with such metals as Al, Mg, Si, Zn, Cu, and Pb have been examined as high-temperature anode materials[1]. Their deficiencies include low melting points, severe polarization at high current, and poor lithium utilization.

The lithium-boron alloy system, which was first prepared at NSWC[2], does not have these deficiencies and has shown great promise for use as an anode material in molten salt batteries.

A large amount of information has been accumulated on this alloy system but has never been written down in one place. This report serves two purposes; first, it will attempt to describe the early

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[1] Selman, J. R., Steunenberg, R. K., Barghusen, J. J. and W. G. Howard (ED), Proceedings of the Symposium and Workshop on Advanced Battery Research and Design, Argonne National Laboratory, Report No. 76-8 (1976).

[2] Wang, F. A., Invention Disclosure, Navy Case #60,721, NSWC, Silver Spring, Maryland (1974).

work done on the Li-B system, and, second, it will summarize current progress and serve as the first in a series of progress reports.

II. LITERATURE SURVEY OF INITIAL STUDIES

The first reported work (1932) on LiB alloys was by Andrieux and Barbetti[3] who electrolyzed fused borate solutions and obtained boron and lithium hexaboride as products. In 1959, two Russians, Markovskii and Kondrashev[4], reported that they prepared a black powder from the direct mixing of lithium and boron in a 1 to 6 ratio. An unidentified boride and free boron were found to be present in the X-ray patterns. Secrist[5], in 1962, studied the LiB system between 3 and 55 atomic percent Li and found a compound at 32 at.% Li. In 1967, he also reported the existence of a brownish colored phase[6] identified as $LiB_{10.85 \pm 0.35}$. In 1965, Casanova[7] reported the existence of LiB_4 in a French patent. His compounds were prepared by reduction of boron carbide with lithium metal between 973.3K (700°C) and 1273.3K (1000°C). In most of these early preparations, black or brownish colored powders were formed. It is generally believed that these powders were borides and not metallic alloys of lithium and boron.

Wang[2], in 1972, states that he prepared a metallic alloy instead of the borides made by previous investigators. In preparing the alloy, a solution of boron in liquid lithium was first prepared at a temperature below 670K (397°C); then, as the solution was gradually heated to about 823K (550°C), its viscosity spontaneously increased until the material solidified. On continued heating, an exothermic reaction occurred and the alloy changed from one having a metallic luster to one with a whitish non-metallic luster. It is important that the alloy be completely solidified before proceeding to the last step in order to produce an alloy stable above 823K (550°C).

Sutula, while working on a lithium/chlorine type battery which was being developed at NSWC as a future high rate primary battery, suggested that this alloy might be useful as an anode material

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3. Andrieux, L. and Barbetti, A., Compt. Rendu, 194, 1573 (1932).

4. Markovskii, L. Ya. and Kondrashev, Yu. D., Zh. Neorgan. Khim., 2, 34-41 (1957).

5. Secrist, D. R. and Childs, W. J., USAEC TID-17149/Secrist, D. R. USAEC KAPL-2182 (1962).

6. Secrist, D. R., J. Amer. Cer. Soc., 50, 520 (1967).

7. Casanova, J., French Patent No. 1461878 (1965).

Table 1. Density (kg m^{-3}) of Li-B Alloys

Atomic Percent Li	TEMP. (K) 293	373	473
70	935	926.3	915.3
78	795	783.8	769.8
78	805	788	780
87	1005	990	975

Table 2. Electrical Resistivity (10^8 Ωm) of Li-B Alloys

Atomic percent Li	TEMP.(K)												
	293	298	373	423	473	573	673	773	873	973	1073	1123	1173
70	168			218	160								
70	160			204	160	68	54	72	93	106	116		122
70	9.5		10.9		17.5	24.5	33.8	29.1	34.9	41.6	48.5	51.8	
78		8.2	10.3		14.5	18.2	23.8	29.1	34.9	41.6	48.5	51.8	
78	900		990	1030	500		200	250	340	390	420		450
78	11.0		14.0		18.8	26.5	38.0	49	67.5	98.0	122		
78	10.9		13.8		19.0	26.8	38.8	55.1	75.2	98.5	119		
87		10.1	13.4		18.4	26.0	32.8	39.2	44.4	49.5	54.8		
87		11.1	14.7		20.0	31.2	36.2	41.4	46.4	51.2			

Table 3. Thermal Conductivity ($W\ m^{-1}\ K^{-1}$) of Li-B Alloys

Atomic percent Li	TEMP.(K) 373	473	573	673	773	873	973	1073
70	72	62	51	38	35	30		28
70	78	65	56.5	48	39	28	25	25
78	75	63	55	45	38	33	30	
78	77	73	70	66	62	56		48
87	71	66	58	53	50	47		43

Table 4. Heat Capacity ($J\ kg^{-1}\ K^{-1}$) of Li-B Alloys

Atomic percent Li	TEMP.(K) 373	473	573	673	773	873	973	1073
70	3450	3550		3690		3750		3850
78	3650	3700		3800		3900		4000
78	3450	3500		3660		3700		3850
87	3700	3730		3840		3950		4000

JANAF TABLES

	TEMP.(K) 298	300	400	500	600	700	800	900	1000	1100
Li	3549	3555	3978	4341	4257	4177	4170	4163	4156	4148
B	1025	1031	1438	1736	1930	2057	2150	2227	2301	2367

Table 5. Heat Evolved During Exothermic Transition

ATOMIC PERCENTAGES Li	B	HEAT EVOLVED cal/g	cal/mole of alloy
90.3	9.7	1.56	11.4
82.4	17.6	2.46	18.8
75.7	24.3	4.70	37.0
67.5	32.5	8.37	22.4
66.3	33.7	7.47	61.6
60.9	39.1	11.4	96.4
57.7	42.3	14.3	122.6
57.2	42.8	13.2	113.4
54.8	45.2	15.9	138.0
53.9	46.1	15.4	134.3
51.0	49.0	16.0	141.5
48.3	51.7	15.2	135.8
44.8	55.2	14.3	129.6
41.8	58.2	14.9	136.8

(Electronol). James and DeVries[8] reported on the anodic discharge behavior of Electronol alloys in LiCl-KCl eutectic melts. They showed that current densities up to 8 A/cm^2 could be sustained without any detectable diffusional limitations at temperatures between 750K (477°C) and 870K (597°C). They also concluded that the end discharge product was Li_2B and that the Li_2B matrix solid held the molten lithium in place during the discharge. Figure 1 is a plot of their data. More recently, Mitchell and Sutula[9] have reported on the density, Hall coefficient, and electrical resistivity of alloys containing up to 60 atomic percent boron. Wang et al.[10] have also reported on the crystal structure of the Li_5B_4 compound.

Over the years, other properties of the Li-B system have been determined. As part of the lithium/chlorine battery development program, the electrical resistivity, thermal conductivity, heat capacity, and density of several Electronol alloys were measured. These data are summarized in Tables 1-4. Wang[2], in his patent, gives heat of reaction data. These data and the heat of reaction per mole are tabulated in Table 5 with a plot of the data given in Figure 2.

III. REPORT OF CURRENT WORK

A major goal of the current work is the preparation of a suitable Li-B alloy for use as an anode in thermal batteries. One of the problems is that there is a lack of information on how to make the material. Wang's patent gives a general procedure with no information concerning phases or phase boundaries. One objective of this work is to determine the phases present in the system and their electrochemical and physical properties. Further electrochemical measurements are needed to identify the lithium transport mechanism within the alloy structure during discharge. It is especially important to know whether loss of lithium can be avoided in molten salt electrolytes at high temperatures. Knowledge of the physical properties is necessary to guide in the design, fabrication, and use of these alloys as battery anodes. Among the measurements needed are strength, ductility, and electrical resistance at both high and low temperatures. The second objective of the work is to set up specifications on how best to make the anode.

A. ALLOY PREPARATION. Sutula, using essentially Wang's[2] method, made the first Electronol anodes by dissolving the boron in molten lithium, stirring until the grittiness in the crucible

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[8] James, S. D. and DeVries, L. E., J. Electrochem. Soc., 123, 321-27 (1976).

[9] Mitchell, M. A. and Sutula, R. A., The Density, Electrical Resistivity, and Hall Coefficient of LiB Alloys. To be published in J. Less Common Metals.

[10] Wang, F. A., Mitchell, M. A., Sutula, R. A., Holden, J. R., and Bennett, L. H., Li_5B_4: The Structure Study Of. To be published in Acta Cryst.

was gone, raising the temperature until the solution thickened, and then increasing the temperature until a visible exothermic reaction was observed. The crucible was then removed from the furnace and allowed to cool. This was the type of Electronol supplied to James and DeVries[8] and used in their work. Analysis showed that this material was inhomogeneous, with the lithium content varying by 6 to 8% from one part of the ingot to another. The process was refined to create a more homogeneous material by stirring more thoroughly and using a smaller particle size boron. Subsequent analysis on this material showed improved homogeneity with only a 1 to 1.5% variation and indicated that Fe, Ni, Cr, and Mn were also present up to a total of 0.14%[11].

Since the behavior of this system is unknown and complex, preparation procedures were varied from one composition to the next in order to obtain an overall understanding of the system. A list of equipment used and the method of preparation of ingots of 80 atomic percent lithium are presented in the appendix. (This composition was chosen for development of a battery anode material because its theoretical coulombic capacity, as shown in Table 6, is about the same as that of calcium.) Due to the unusual nature of the alloy system, and until a phase diagram can be determined, the best way to present the data is to describe the general facts gathered so far.

1. Boron is wetted by lithium at around 623K (350°C). At lower temperatures, lithium forms a ball in the crucible; the meniscus of the molten lithium is tightly curved.

2. Boron reacts completely with molten lithium at 673K (400°C). If lower temperatures are used, a longer time is required for complete reaction. The nature of this reaction process is not yet understood. It apparently involves both a slightly exothermic chemical reaction and a physical mixing of the reaction product with excess lithium. Whether the mixing also includes the formation of solid or liquid solutions is not yet known.

3. At 773K (500°C), the melt becomes extremely fluid, and the meniscus starts to creep up the container walls. No solid particles are present that are large enough to be detected by ordinary stirring of the fluid mixture.

4. Between 803K (530°C) and 853K (580°C), the melt gradually thickens. At approximately 853K (580°C), an exothermic transition occurs, during which the melt solidifies and contracts from the walls of the crucible. The heat liberated is enough to cause the crucible

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[11] DeVries, L. E. and Gubner, E., Analytical Procedure For Main Components and Major Impurities in Lithium-Boron Alloys. To be published in Analytical Chemistry.

temperature to be visibly increased above that of the furnace. Wang[2] and Sutula both report seeing the exotherm in samples of 80 atomic percent lithium. Our studies indicate that the exotherm is not observed if the lithium content is high or if the heating is done slowly.

5. The observations described above apply principally to alloys made with more than about 50 atomic percent lithium. The behavior of alloys made with less than about 50 atomic percent lithium is different. For example, great difficulty in achieving complete reaction of the boron is one significant difference. Alloy ingots with high boron content and of uniform composition have not been successfully prepared. Because they contain relatively less lithium, such alloys would be of little interest as battery anode materials.

B. METALLOGRAPHIC STUDIES. Metallographic studies were conducted on ingot samples in an effort to determine the presence of various phases in the alloy. The alloy, being a reactive material, posed some problems in its handling, and it was first thought that the actual work would have to be carried out in an inert atmosphere glove box. However, if one works fast (10-15 minutes), photomicrographs taken with a metallurgical microscope can be made before the alloy deteriorates.

Mounting the specimen was the first problem to overcome. It is not possible to use mounting compounds which have a liquid as one of the ingredients. The reaction of the alloy with the liquid creates bubbles before the mounting compound hardens, resulting in a poorly adherent mount. A series of Epoxy-Patch kits (white, blue, clear) were tried. The white and blue were found to be satisfactory, the clear less so because of its long set-up time (1 hour) and reaction of the alloy during this time. The blue is hard to work with because of its fast set-up time (4 minutes) but gave very good mounts. The white is also very good because it sets up in 1/2 hour and can be heated to set up faster, but with some alloys a slight reaction was observed.

Another type of epoxy system (Biggs Epoxy Putty), in which two solids are mixed together like dough until a uniform color is obtained, offered a convenient and satisfactory method for mounting the alloy and is currently being used.

The second problem involved finding a lubricant for use on the silicon carbide grinding paper. A number of organic fluids were tried, including alcohols, glycols, mineral oil, and Kel F polymer oil. Mineral oil was found not to react with the alloy, but its viscosity makes grinding difficult. However, mineral oil is used with the 600 grit paper and is also put on the specimen after it has been etched to slow down the reaction with air. Kel F polymer oil was the best lubricant used but is dangerous because of the reaction of halogenated hydrocarbons with lithium, which leads to a reaction product that can explode when shocked. Propylene carbonate, a commonly used solvent in lithium batteries, was finally chosen as the lubricant in the polishing stages down to 600 grit.

The next problem solved was what to use for an etchant. Again, a number of organic solvents were tried. Three, with different reaction rates, were found to be suitable. They were methanol, ethanol, and ethylene glycol, and their reactivity decreased in that order. A water etch was found to be much more reactive than methanol and not suitable for alloys containing 66 atomic percent or more lithium.

Since we are still in the early investigation stages, we have not identified phases as to their composition and under what conditions they are formed, but can only give a description of what we have observed. Compositions below 50 atomic percent lithium are not covered because of uncertainties in their preparation. All of the alloys discussed have been taken high enough in temperature to have gone through the exothermic reaction but have not been allowed to remain at high temperatures long enough to ensure equilibrium conditions. However, we are now in the process of carrying out that experiment.

The results of our metallographic study suggest that four phases may exist between 50 and 80 atomic percent lithium. There is a creamy-white, lithium-rich phase, a steel-gray phase, a black-gray phase, and a brownish color phase. Between 50 and 66 atomic percent lithium, the steel-gray and black-gray phases coexist. From 66 to 69 atomic percent lithium, the black-gray and brownish phases coexist. Above 69 atomic percent lithium, the creamy-white, lithium-rich phase coexists with the black-gray and brownish phases. It has not been possible to determine the relative amounts of the two phases that are present from the photomicrographs of the alloys. The lever arm rule does not seem to apply; one would expect more of the black-gray phase to be present at 66 atomic percent lithium than at 55 atomic percent lithium, or vice versa, but this does not appear to be the case. Instead, the two phases always seem to be present in the same proportions. The same situation exists for the two phases between 66 and 69 atomic percent lithium. However, above 69 atomic percent lithium, it is possible to see the difference in relative amounts of the lithium rich phase and the coexisting black and brownish phases. The possibility has been considered that the material is a single phase of variable composition. However, this does not fit in with the different colored phases observed.

A typical photomicrograph of an 80 atomic percent Li(B) alloy is presented in Figure 3.

C. THERMAL ANALYSIS. Initial thermal analysis work using the DuPont 990 Modular Thermal Analysis System has included differential thermal analysis (DTA) and differential scanning calorimetry (DSC) studies. These techniques will be used as a tool for constructing the phase diagram. A major difficulty in working with this system is the extreme reactivity of lithium. Lithium reacts with the platinum and aluminum sample cups and alumina cup liners supplied with the instrument, and so sample cups of other materials have to be constructed. We are now on the process of having Armco iron cups made for the DSC apparatus.

An observation made in the metallographic work was that one of the phases was more reactive than the others, and if the specimens were over-etched, hills and valleys appeared. This led us to think that, maybe, if the material were dissolved in the etchant, one of the phases would be dissolved away from the other. Water and methanol were the primary reagents (etchant) used in our separation techniques. Ethanol was also tried but was much slower in its reaction than methanol, and no benefit was derived from its use. The alloy phase that is most reactive is the black-gray phase followed by the creamy-white lithium-rich phase. After reaction with the reagent, two different materials remained, a black compound obtained from the alloys between 50 and 66 atomic percent lithium and a brownish compound obtained from alloys containing more than 66 atomic percent lithium. A centrifuge was used to separate the material from the reagent. Transitions characteristic of these hase-separated materials have been obtained using DTA and DSC methods but have not yet been identified.

D. X-RAY ANALYSIS. X-ray diffraction techniques are frequently used in the determination of phase diagrams, and we planned to make extensive use of this method. The samples X-rayed were the same ones used in the metallographic work. The diffractometer shield was enclosed in Saran Wrap and Drierite placed in the sample area to remove water vapor. The combination of Saran Wrap shield and mineral oil on the sample permitted X-ray exposure up to 3 hours without deterioration of sample surface. However, metallographic examination revealed that the material is multiphase, and therefore it is not possible to tell which peaks belong to which phase. X-ray patterns taken on the phase-separated material have not been ideal for several reasons. The powders are finely divided material which does not give well-defined diffraction peaks. Both lithium and boron are fairly transparent to X-rays and most of the beam passes through the material rather than being diffracted. The Debye-Scherrer film method gave more satisfactory results due to integration of the peak intensities. At present, all of the separated compounds have not been X-rayed, but it is noted that there are at least three different patterns present. It is necessary to improve X-ray techniques used before the peaks can be indexed or the lattice parameters determined.

IV. FUTURE WORK

The goal of the present research is the development of a lithium-boron alloy suitable for use as an anode in thermal batteries. By varying the preparation procedure, we will be able to better understand the reactions occurring in the formation of the alloy. Thus, the use of different amounts of starting materials and different temperatures during the preparation should result in the formation of different phases in varying proportions. We plan to identify these various phases using metallography, thermal analysis, and X-ray diffraction techniques. A chemical analysis will be performed on phase-separated material. We also plan to anneal alloy samples at

700°C for several weeks to see if an equilibrium can be achieved among the various phases we have seen. A comparison will then be made between this material and newly prepared material using the techniques mentioned above. Studies are also planned on material which has not undergone the exothermic transition. Valuable information will be obtained by comparing phases present before and after this exothermic reaction.

General Electric Neutron Devices (GEND), under contract to this Center, has made thermal battery cells using the Li-B alloy system as an anode. Correlations will be made between the alloys we prepare and GEND results on cell fabrication and testing.

V. SUMMARY

The procedure for the preparation of lithium-boron alloys is being studied and the phase diagram for the system is being determined using metallography, X-ray, and thermal analysis techniques.

Metallographic results indicate that as many as four phases may exist in the composition range 50-80 atomic percent lithium. These phases are probably formed under non-equilibrium conditions since the phase rule is not obeyed.

The X-ray patterns of the alloy have been difficult to interpret since the material is multiphase and relatively transparent to X-rays. However, several good patterns have been obtained on phase-separated material.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are being developed as tools for characterizing the material and developing the phase diagram.

The combination of a chemical analysis on phase-separated material with metallography, X-ray and thermal analysis is planned for characterizing the alloy for use as an anode in thermal batteries.

Table 6. Electrochemical Equivalents of Some Metals and Li-B Alloys

Metal or Alloy	Equivalent Weight, grams*
66.7 at % Li	∞
70	81.00
75	31.63
80	19.28
85	13.67
90	10.47
100	6.939
Al	8.99
Mg	12.16
Ca	20.04
Na	22.99
Fe	27.92
Zn	32.68
Cd	56.20
Pb	103.60

*Equivalent weight of alloy based on the reaction $Li_nB \rightarrow Li_2B + (n-2)Li^+ + (n-2)e^-$.

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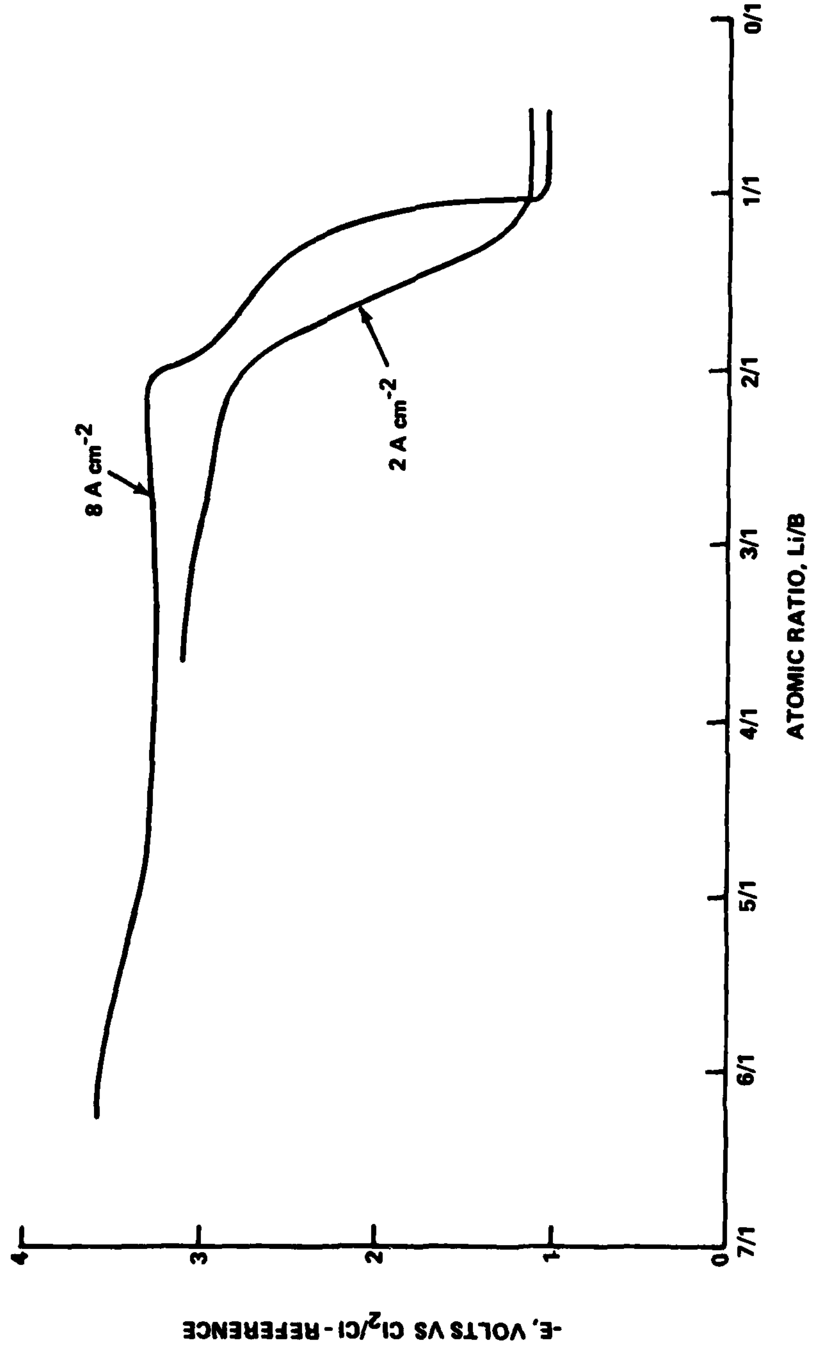

FIGURE 1 DISCHARGE POTENTIALS OF LITHIUM-BORON ALLOY ANODES IN MOLTEN LiCl-KCl EUTECTIC AT 773 K (500°C)

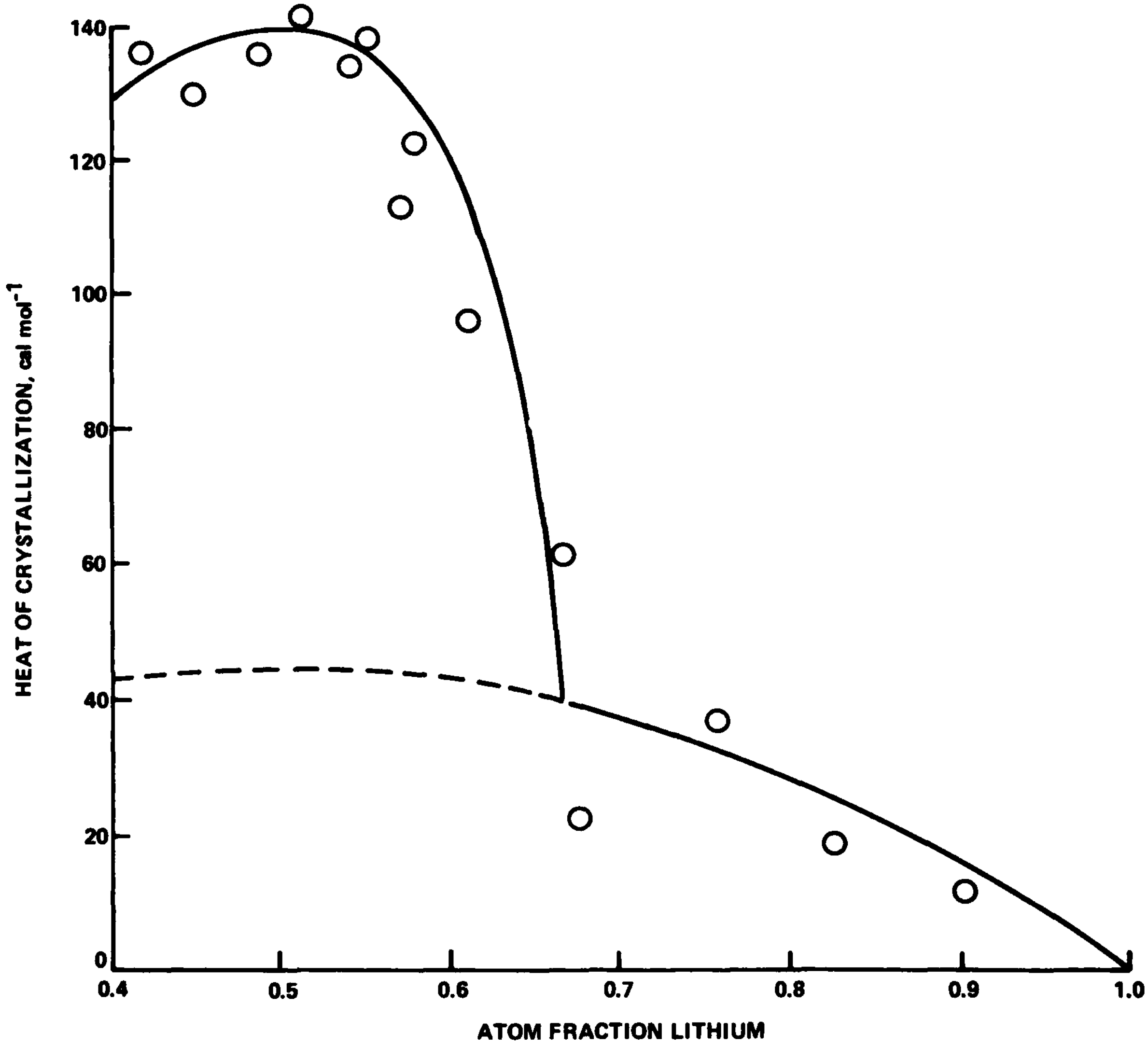

FIGURE 2 HEAT OF CRYSTALLIZATION OF LITHIUM-BORON ALLOYS

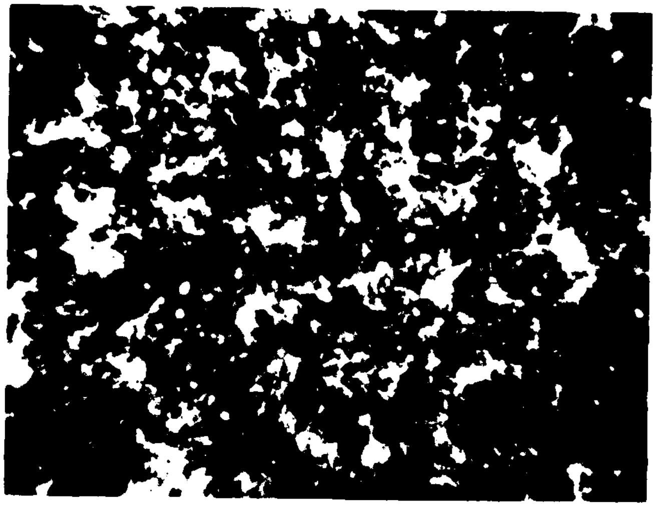

FIGURE 3 80 ATOMIC PERCENT Li (B) ALLOY (150X)

Appendix A

Preparation Method used at NSWC for Lithium-Boron Alloy Ingots (80 atomic percent Li)

I. Equipment and Apparatus

  A. Inert atmosphere glove box

    1. Vacuum Atmosphere Company - model HE 553-2 DRI-LAB

    2. He atmosphere vacuum 3×10^{-10} cc/sec or better

  B. Furnace

    1. Sybron Corporation, Thermolyne type 1300

    2. 0-1200°C, temperature control knob (percent time on)

  C. Reaction Vessel

    1. 318 Stainless Steel tube with screw-on bottom cap
       inner diameter 3.90 cm
       inside depth 3.49 cm
       outer diameter 4.13 cm
       cap outer diameter 4.45 cm

  D. Balance

    1. Mettler - model P163N

    2. Capacity, 160 g

    3. Accuracy, 1 mg

II. Materials

  A. Lithium, 99.9%

    1. Foote Mineral Company, standard grade

    2. 113 g - ingot or ribbon

II. Materials (Cont.)

B. Boron

1. Atomergic Chemetals Corporation
2. Boron, crystalline lump, 99.9%

III. Procedure for Alloy Preparation

1. Because the volume of the reaction vessel is only about 40 cm^3, the amount of starting material which can be conveniently used is generally in the range of 15-18 g. Thus, to prepare an ingot of 80 atomic percent lithium, 11.102 g of lithium and 4.324 g of boron are weighed out and placed in the reaction vessel. The boron, which had been ground into small chunks or powder, is placed in the crucible first, and then the lithium is added.

2. The reaction vessel is placed in the furnace, and the temperature is raised to approximately 623K (350°C). After the lithium is molten, the mixture is stirred with a stainless steel stirring rod.

3. As the temperature is slowly raised, the reaction vessel is occasionally removed from the furnace, and the melt is thoroughly stirred to facilitate reaction of the boron with lithium and to insure homogeneity.

4. Gradually, the boron is wetted by the lithium and begins to react. It is assumed that the boron is completely reacted when the grittiness felt during stirring is gone at about 673K (400°C).

5. Coinciding with the reaction of the boron is the appearance of a new solid phase at the bottom of the reaction vessel. With stirring, this phase is dispersed in the remainder of the melt, and a smooth, syrupy material results.

6. The temperature is slowly raised, and the melt is thoroughly stirred until it becomes extremely viscous. Then, at approximately 853K (580°C), solidification occurs, and the ingot contracts away from the walls of the reaction vessel. When the melt first solidifies, the solid has a silvery, metallic appearance. This changes to a non-metallic, grey-violet appearance during the contraction.

7. After the contraction, the reaction vessel is removed from the furnace, the bottom of the container is unscrewed with pliers, and the ingot is removed and allowed to cool. When cool, the alloy is placed in a plastic zip-lock bag for removal from the glove box.

IV. Notes

1. The furnace temperature and crucible temperature are assumed to be identical.

2. The heating and stirring procedure is designed to produce a homogeneous mixture, formed under near-equilibrium conditions. Thus, no definite length of time is specified for the process. (After the boron dissolves, the remaining procedure takes approximately one hour.)

3. Coinciding with, or slightly above, the solidification temperature is the appearance of an exothermic transition in the system if the alloy is formed too quickly.

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