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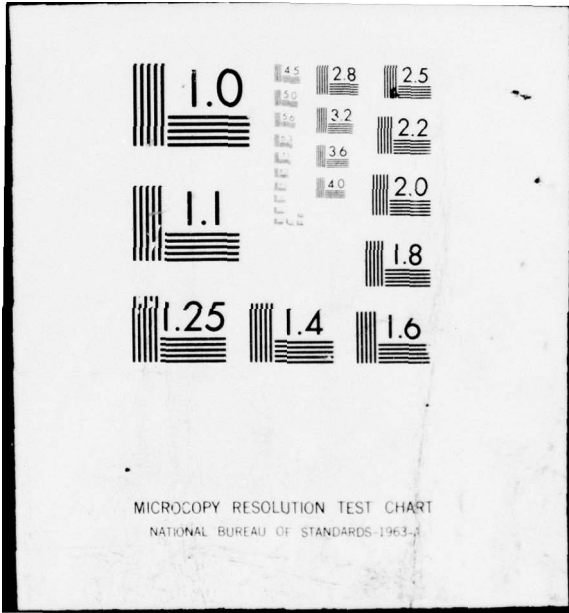
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# DETERMINATION OF FREE LITHIUM IN Li-B ALLOYS

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RESEARCH AND TECHNOLOGY DEPARTMENT

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SUMMARY

Lithium-Boron alloys are presently being studied as a potential replacement for lithium as an anode material for thermal batteries. This report describes part of an ongoing investigation of the lithium-boron phase systems in an effort to optimize the preparation and properties of the various alloys.

A new technological procedure has been developed for investigating lithium-metal alloys in which the free lithium phase is extracted and the composition of the remaining  $Li_xB_y$  compound determined.

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## DETERMINATION OF FREE LITHIUM IN LI-B ALLOYS

INTRODUCTION

This laboratory is presently investigating the potential of Li-B alloys as an anode material for thermal batteries and as a substitute for lithium in the lithium organic/inorganic electrolyte batteries.

Lithium, being the most electropositive and one of the lightest elements, is a prime anode material for thermal batteries as it does not react extensively with the LiCl-KCl melt. However, its low melting point, 180.6C, precludes its use as an anode material. This problem can be overcome by using a lithium alloy with a high melting point. Such an alloy, lithium-boron, was first prepared in this laboratory<sup>1</sup> and has shown promise for use as an anode material in molten salt batteries<sup>2</sup>.

In addition, replacement of the lithium anode in organic/inorganic electrolyte batteries by a high melting lithium-boron alloy might eliminate potential safety problems resulting from melting of the lithium anode due to high temperatures created during discharge.

One of the problems encountered with Li-B alloys is in the preparation of a suitable alloy for use as an anode material. One of the reasons contributing to this is that to date, the composition of the phases present in the alloy remains undetermined. A mixture of  $\text{Li}_x\text{B}_y$  type compounds cannot be chemically analyzed unless a method for distinguishing or separating each phase can be developed.

Voltammetric discharge curves of Li-B alloys containing 70 and 80 weight percent Li produced a potential break at a composition approximating  $\text{Li}_2\text{B}^2$ . Mitchell and Sutula suggest this could be a mixture of two phases  $\text{Li}_5\text{B}_4$  and  $\text{Li}_3\text{B}^3$ . X-ray, neutron diffraction

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<sup>1</sup>Wang, F. A., Invention Disclosure, Navy Case #60721, NSWC Silver Spring, Md. (1974).

<sup>2</sup>DeVries, L. E., and James, S. D., J. Electrochem. Soc. 123, 321 (1976).

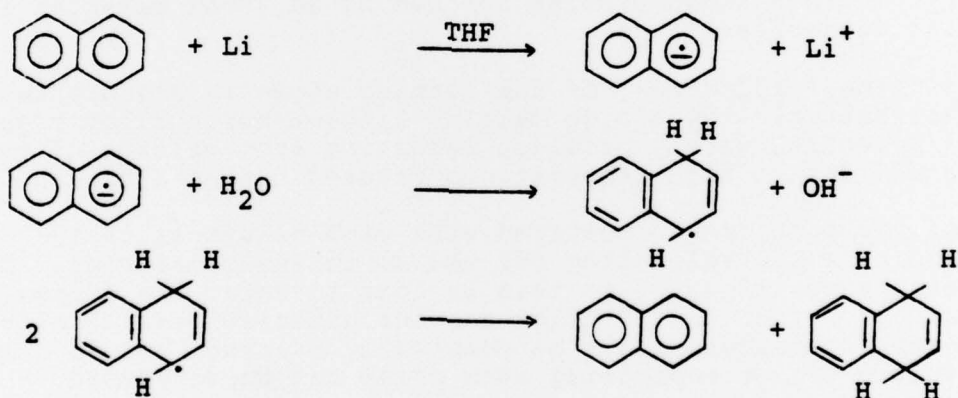
<sup>3</sup>Sutula, R. A., and Mitchell, M. A., Journal of Less Common Metals, Accepted 12 Jul 1977.

and NMR measurements indicates two or more phases present in addition to the free lithium phase, one of the phases appears to have the stoichiometry  $\text{Li}_5\text{B}_4$ <sup>4</sup>.

It was the aim of this investigation to develop a method for the removal of the free lithium phase from the Li-B alloy and quantitatively determine its concentration. Since it appears, that only the free lithium in a Li-B alloy is available to undergo oxidation and perform useful work as an anode<sup>2</sup>, a method to measure the available lithium in an alloy of known weight percent, enables one to predict the maximum energy output from a given alloy.

### THEORY

Alkali metals react with unsaturated aromatic compounds, such as naphthalene, in the more polar ethereal solvents, such as dimethyl ether or tetrahydrofuran, to produce aromatic radical anions<sup>5</sup>. These aromatic radical anions function as reducing agents in their reactions with other compounds. The mechanism by which they trigger chemical reaction is through transfer of an electron to the reacting partner with regeneration of neutral aromatic hydrocarbon. The following mechanism illustrates the reaction pattern:



The gram equivalents of hydroxide generated is equal to the number of equivalents of lithium reacted.

### EXPERIMENTAL

**ALLOY PREPARATION.** Li-B alloys, containing from 90 to 50 atomic percent lithium, were prepared under dry helium in the following manner<sup>1</sup>. Finely ground boron is placed in the bottom of the reaction vessel, lithium is added, the vessel is placed in a furnace preheated

<sup>4</sup>Wang, F. A., et. al., NSWC/WOL TR 77-84.

<sup>5</sup>Garst, J. F., Accounts of Chem. Res., 4, 400 (1971).

to about 500°C and the melt is stirred with a stainless steel rod when the lithium has melted. The temperature is raised slowly and the melt is occasionally thoroughly stirred to facilitate the dissolution of boron. Boron is assumed to be completely dissolved when the grittiness of the boron disappears at about 570°C. At a temperature about 597°C a solid phase appears which redissolves with stirring. The melt is stirred frequently as the temperature is raised slowly until solidification occurs at about 680°C. The alloy is cooled and stored under Helium.

EXTRACTION MEDIA. Reagent grade tetrahydrofuran (THF) was distilled over sodium and collected over molecular sieves. Reagent grade naphthalene was dried over desiccant under vacuum. All storage bottles, caps and reaction vessels were heated approximately three hours at about 120°C to remove any traces of water.

#### PROCEDURE

The Li-B alloys were cut and weighed under dry helium, stored in dry glass vials with helium and sealed. These in turn were placed in a Helium filled desiccator and transported to a "dry room" where the relative humidity was maintained at 2 percent.

Solutions of approximately 8.0g of the dried naphthalene in about 100 ml of dry THF were prepared in the dry room and stored in 250 ml dry screw cap Erlenmeyer flasks. It is essential that water be removed from these solutions.

The pre-weighed Li-B alloy was added to the naphthalene-THF leaching solution and sealed as quickly as possible. The start of the extraction begins upon addition of the alloy and the leaching process was allowed to continue in the dry room. The alloy that remains after the lithium has been extracted will be referred to as the residue. After a specified time, the extraction process was discontinued by filtering the solid residue from the leaching solution. The residue was rinsed with dry THF and the washings added to the leached solution. Distilled water was then added to the leaching solution in an amount sufficient to separate the THF-naphthalene from the aqueous lithium hydroxide. Under these conditions (approximately equal volumes of water and leaching solution), the naphthalene remains dissolved in the upper THF layer. After separation in a separatory funnel, the lower aqueous solution containing LiOH is titrated with standard HCl using phenolphthalein as an indicator. The THF layer is also titrated but if separation is effective, only a minimum of titrant (0.1 ml) is required. Depending on the composition of the alloy, the end point color varies, so in addition to the indicator, the titrations were followed potentiometrically.

RESULTS AND DISCUSSION

Lithium-boron alloys were prepared with initial compositions corresponding to 90, 80, 75, 69, 67, 50 atomic percent lithium. Only Li-B alloys prepared by heating beyond the second exotherm (see footnote 1) were subjected to the extraction studies.

An estimate of the time required to completely remove free lithium from the Li-B alloy was determined by plotting weight percent lithium remaining in the residue as a function of time. Figure 1 represents curves of weight percent Li in the residue vs. time for alloys of 75 and 67 atomic percent lithium. The data in Figure 1 represents an average weight percent lithium obtained from approximately 0.50 gm Li-B alloy samples. As the plateau in the curves indicate, the extraction nears completion in about six days for both the 75 and 67 atomic percent lithium alloys. The rate of extraction of the lithium is dependent on both the composition of the alloy and the mass of the alloy. The extraction of lithium from samples of larger mass will be slower due to diffusion processes. Alloys containing larger percentages of lithium, will require somewhat less extraction time due to larger voids created in the sample when large amounts of lithium react. Excess lithium from a 0.5 gm sample of 90 atomic percent lithium alloy appears to be completely removed in about three days time. It should be noted that the residue remaining after extraction of excess lithium from the 90 atomic percent lithium alloy behaves somewhat differently from the residues obtained from the lower atomic percent lithium alloys. First, the 90 atomic percent lithium residue invariably becomes a powder whereas the other lower atomic percent lithium residues remain intact. Secondly, the 90 atomic percent residue is very pyrophoric.

In order to insure complete removal of lithium by the extraction process, smaller samples of alloy, approximately 0.30 gm were used. In addition, the alloys were allowed to react with the THF-naphthalene solution for a period of eighteen days. After this period of time, the solutions were analyzed and the percentage of lithium extracted and the percentage lithium remaining in the residue were calculated using the following equations:

$$\text{gm Li in ALLOY} = \text{gm ALLOY} \times \text{wt. \%Li} \quad (1)$$

$$\text{gm Li extracted} = N_{\text{HCl}} \times \text{VOL. HCl (LITERS)} \times \text{gm Equiv. Wt. Li} \quad (2)$$

$$\% \text{Li in residue} = \frac{(\text{Gm Li in ALLOY}) - (\text{Gm Li EXTRACTED})}{(\text{total grams ALLOY}) - (\text{Gm. Li EXTRACTED})} \times 100 \quad (3)$$

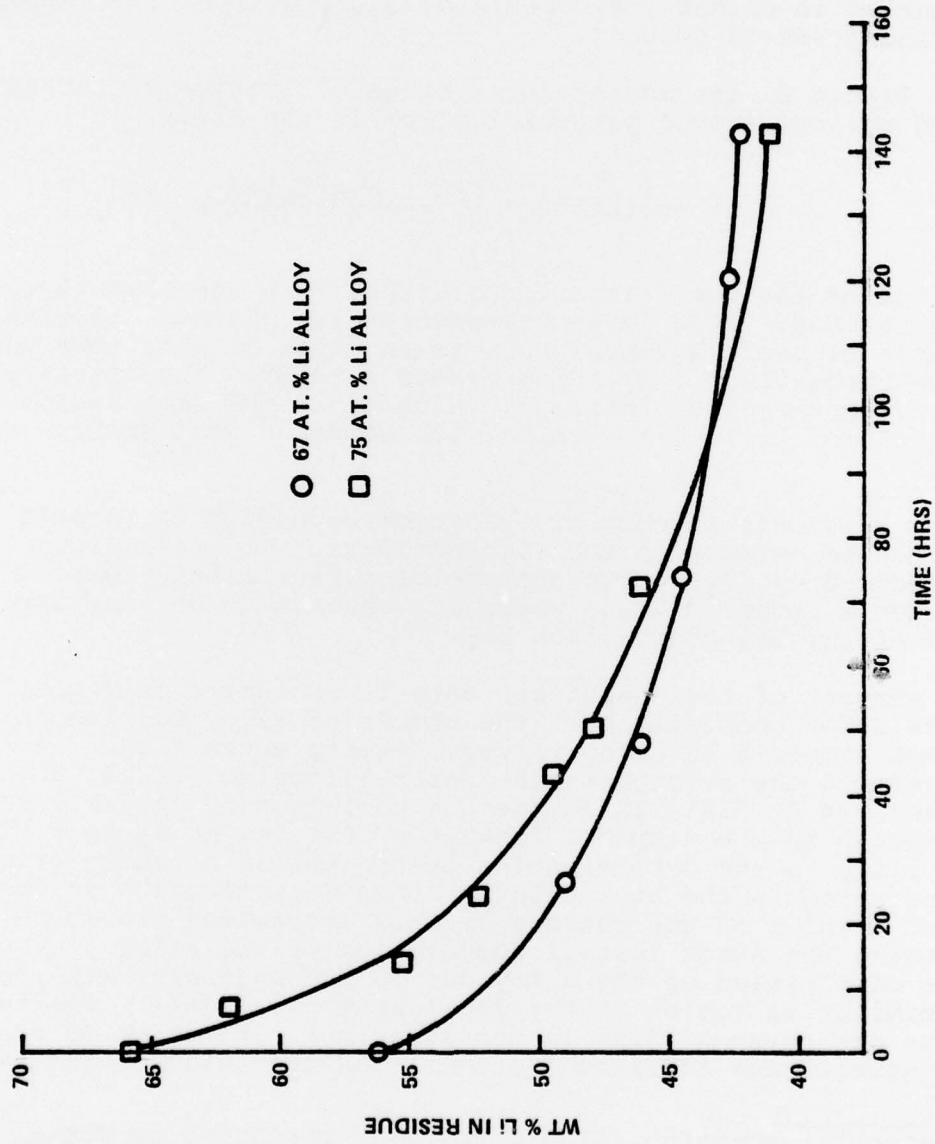


FIG. 1 WT % LI REMAINING IN THE RESIDUE OF LI-B ALLOYS AS A FUNCTION OF EXTRACTION TIME.

Since the mass of the residue was calculated from the difference between the mass of original alloy and the mass of lithium extracted, correct calculation of the percent lithium remaining in the residue is based upon the assumption that all the boron present has reacted with the excess lithium during the preparation of the alloy. The THF-naphthalene and aqueous portions of the solutions used in the extraction process were analyzed for boron. Since no boron could be detected in either the organic or aqueous layers, it appears that this assumption is correct.

In Figure 2, the average percentage of lithium extracted is plotted against atomic percent lithium in the alloy.

$$\% \text{ Li extracted} = \frac{\text{gm Li extracted}}{\text{gm Li in alloy}} \times 100 \quad (4)$$

A portion of the curve is extrapolated to the approximate composition of the residue. This curve represents the "maximum" lithium available to perform useful work as an anode in a battery using a lithium-boron alloy containing excess lithium. The actual useful work may approach the "maximum" value since the data indicates that extraction of Li from a lithium rich compound such as  $\text{Li}_2\text{B}$  appears unlikely.

The 50 atomic percent Li alloy corresponding to formula  $\text{LiB}$  was subjected to extraction for eighteen days. No green radical anion was produced verifying the absence of a free lithium phase. This indicates a compound  $\text{Li}_x\text{B}_y$  where  $y > x$  appears to be nonexistent in alloys of initial composition  $\text{LiB}$ .

A summary of the analytical data is presented in Table 1 for various alloy compositions. The number of alloy samples analyzed for each atomic % Li alloy varied. Twenty seven alloys were analyzed and the average weight percent lithium for all the residues was 42.51% with an average deviation of  $\pm 1.09\%$ . This corresponds to the simplest formula of  $\text{Li}_{1.15 \pm 0.05} \text{B}_{1.00}$ .\* The high variability in the determination of the %Li is a result of the heterogeneity in the Li-B alloy. Since determination of the weight percent lithium in the residue by this extraction procedure depends on knowing the exact initial composition of the alloy, any variation in the composition of the alloy due to inhomogeneity will result in a similar variation in the final analytical data. The relative average deviation of 2.5% in the data is a reflection of both the heterogeneity and analytical error. The precision of the analysis

\*Differential scanning calorimetry data presented by Steven Dallek at the September 1977 Electrochemistry Branch Technical Review at NSWC reveals a lithium endotherm at  $180.6^\circ\text{C}$  and two irreversible exotherms starting at about  $350^\circ\text{C}$  and  $530^\circ\text{C}$  and reaching a maximum at  $380^\circ\text{C}$  and  $580^\circ\text{C}$  respectively. Thermal analyses on the alloy produced at the second exotherm gave rise to the same empirical formula.

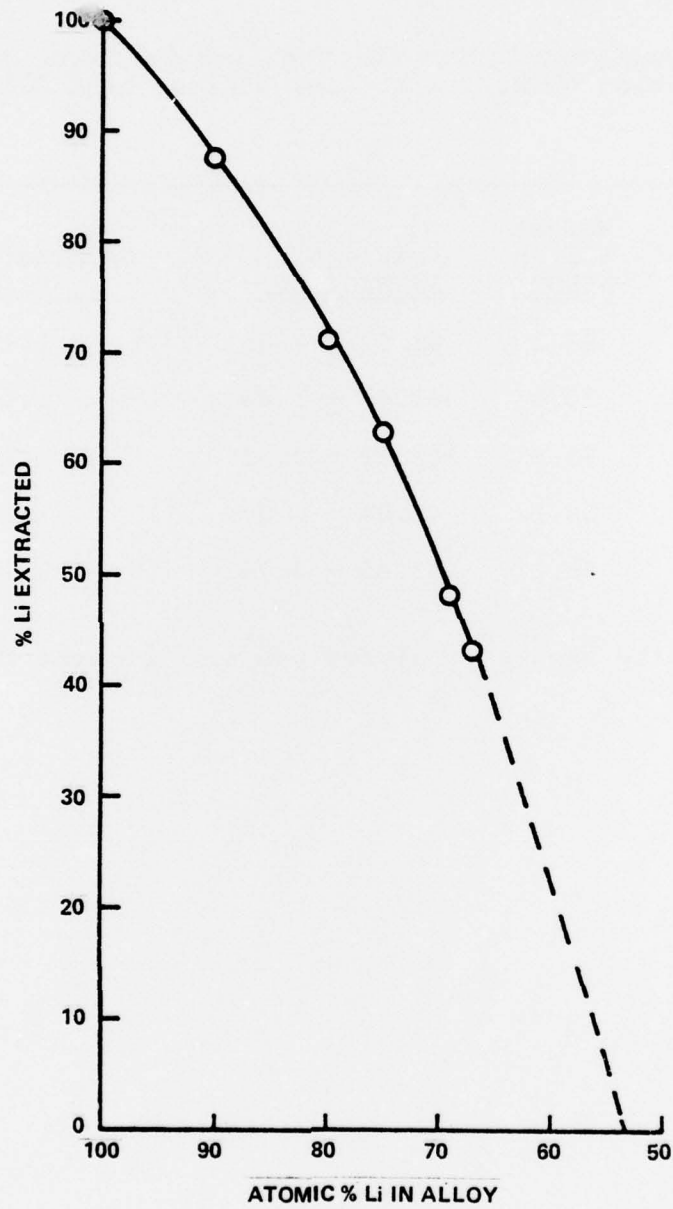


FIG. 2 % Li EXTRACTED VS ATOMIC % Li IN Li-B ALLOY

Table 1. Analytical Data for the Li-B Compound Formed On Extraction of Excess Li from Various Li-B Alloys

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<u>Atomic % Li in ALLOY</u>	<u>Weight %Li in ALLOY</u>	<u>Wt % Li in RESIDUE*</u>	<u>Gm Atomic RATIO Li/B</u>
90	85.2	42.62 $\pm$ 1.06	1.15
80	72.0	42.48 $\pm$ 1.44	1.15
75	65.8	42.12 $\pm$ 0.53	1.13
69	59.1	42.84 $\pm$ 1.07	1.17
67	56.2	42.45 $\pm$ 0.79	1.15

\*The number of alloy samples analyzed was not the same for each atomic % Li alloy.

indicates assignment of a molecular formula to the Li-B compound is not warranted until a more homogeneous alloy can be prepared.

CONCLUSION

We have shown one may completely remove the free lithium phase from lithium rich Li-B alloys of varying composition. This process should be adaptable to various lithium alloys as an aid in determination of metallic phase diagrams.

The empirical formula  $\text{Li}_{1.15 \pm 0.05} \text{B}_{1.00}$  is the compound that results whenever the free lithium phase is extracted from Li-B alloys containing excess lithium. This has been verified by thermal analysis. Assignment of a molecular formula awaits the preparation of a more homogeneous alloy.

Direct analysis of the residue that remains after extraction of the lithium is in progress. A procedure for dissolving the residue is being developed and analysis should confirm the "extraction" analysis.

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