66/72

473

UCRL-51463

COMPATIBILITY OF BORON NITRIDE IN LITHIUM SYSTEMS

A. E. Morris

October 9, 1973

Prepared for U.S. Atomic Energy Commission under contract No. W-7405-Eng-48

**LAWRENCE
LIVERMORE
LABORATORY**

University of California/Livermore

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

MASTER

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ *; Microfiche \$0.95

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

TiD-4500, UC-4
Chemistry

LAWRENCE LIVERMORE LABORATORY

University of California, Livermore, California, 94550

UCRL-51463

COMPATIBILITY OF BORON NITRIDE IN LITHIUM SYSTEMS

A. E. Morris

MS. date: October 8, 1973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

fy

COMPATIBILITY OF BORON NITRIDE IN LITHIUM SYSTEMS

Abstract

A compatibility test procedure was developed to study the reactions between lithium, refractory metals, and insulating ceramics. In the first series of tests, boron nitride was found to be completely

dissolved by lithium in 600 hr. at 1270K. The refractory metals were borided, and the nitrogen went into solution in the lithium. The results are interpreted from a thermochemical standpoint.

Introduction

In some fusion reactor designs, it is desirable to electrically insulate the flowing lithium from the pipe to minimize the MHD loss. Such an insulator must be a material which is compatible with lithium and the refractory metal pipe. Because of the reactive nature of lithium, only the most stable compounds are expected to chemically resist reduction by lithium. A comparison between the free energy of formation of the insulator and the corresponding lithium compound may serve as a guide to predicting which insulators might be stable in contact with lithium. However, the presence of a refractory metal such as molybdenum, tungsten, niobium or tantalum may complicate this simple picture. If the refractory metal forms stable compounds with any of the constituents of the insulator, the stability of the insulator will be reduced.

Several insulating nitrides are more

stable than the corresponding lithium compound; boron and aluminum form the most stable. Their ΔG_f° is 33 and 43 kcal/atom of nitrogen more negative respectively than the ΔG_f° of Li_3N at 1200K.¹ However, the formation of refractory metal borides or aluminides will make this difference less favorable. In addition, the large solubility of nitrogen in lithium above the melting point of Li_3N ² is another unfavorable factor.

Calcium and yttria are probably the most stable oxides. Their ΔG_f° values are about 15 kcal/atom of oxygen more negative than the ΔG_f° of Li_2O at 1200K.³ Although this difference is not as large as that for the nitrides, neither calcium nor yttrium form stable compounds with the refractory metals. Also, the solubility of oxygen in lithium is much lower than the solubility of nitrogen — probably about 1.4 wt% oxygen at 1200K.⁴

Purpose of Test

One of the main purposes of the compatibility tests was to study the amount of attack on the ceramic by the lithium. Of almost equal importance was to determine the chemical reactions that took place, so as to understand the mechanism of attack. In addition, the test procedure

itself was to be studied, so that the test could be made as representative as possible. To begin with, boron nitride was chosen as the first ceramic to be studied. Subsequent tests will be made on aluminum nitride, calcium oxide, yttrium oxide, and various yttrium oxide-based materials.

Starting Materials

Pyrolytic-grade boron nitride ("Bor-alloy") was obtained from the Union Carbide Corporation* as 25-mm by 13-mm plates, of two different thicknesses (2.4 mm or 1.7 mm). The purity was stated to be 99.99% boron + nitrogen. Boron was -325 mesh crystalline powder, 99.99% pure, from United Minerals and Chemicals Corporation.

The lithium was obtained in the form of 13-mm-diam sticks from D. F. Goldsmith Corporation, sealed in metal cans.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

The purity is apparently greater than 99.95%, with less than 0.005% Na. The lithium nitride was obtained from Research Organic/Inorganic Chemical Corporation in the form of 96% Li_3N powder.

The refractory metal samples were tungsten, molybdenum, tantalum and niobium foils 0.13-mm thick, tungsten foil 0.025-mm thick and tungsten discs 2.14-mm thick. The 0.13-mm foils were obtained from Materials Research Corporation as their MARZ or VP grade. The 0.025-mm tungsten foil was 99.95% pure, from Rembar Corporation. The tungsten discs and crucibles were machined from high-density sintered bar stock.

Sample Preparation and Experimental Procedure

The metal foils and crucibles were washed in hot detergent water and rinsed in water and acetone. Pieces of boron nitride were cut from the original plates and used without further treatment. The boron and Li_3N were used directly from the bottle.

Weighed samples of the refractory metals, boron and boron nitride were loaded into an argon glove box, along with the supply of crucibles and lids, lithium, and Li_3N . The cleaned lithium sticks and the Li_3N were weighed in the glove box.

The materials were loaded into the crucible according to the following sequence: First, a strip of thin tungsten foil was inserted around the inner circumference of the crucible so that it acted as a liner. Next the lithium was placed in the crucible, the crucible lid was put on, and the crucible was covered by a plastic cap. The crucibles were then placed in O-ring sealed metal containers and removed from the glove box. At the welding shop they were quickly transferred to the welding chamber which was immediately evacuated, and the lids were electron-beam welded.

Table 1 gives the sequence of sample placement, and Fig. 1 shows a sketch of the sample position during the compatibility test. Table 1 also gives the nitrogen and boron content in the lithium that was contributed by the added Li_3N or boron. Each crucible contained about 1 g of lithium (± 0.2 g), and from 0.7 to 0.9 g of boron nitride.

After the crucibles were welded shut and leak-checked, they were placed inside lidded stainless steel capsules which were then welded shut. Three tungsten crucibles were placed in each stainless steel capsule. The two stainless capsules were then placed inside a tungsten mesh vacuum furnace, the furnace

was pumped down, and the samples were heated to 1270K. The temperature of the samples was read by means of a Leeds and Northrup optical pyrometer which earlier had been found to be within 5K of a Standard lamp. Based on past experience, a sightglass correction of 20K was made. The actual sample temperature was not checked with a thermocouple. During the run, the sample temperature varied by $\pm 5\text{K}$. The furnace power was

Fig. 1. Sketch of sample placement in compatibility crucible.

Table 1. Sample placement in compatibility experiments.

Sample	Placement sequence (top to bottom).	All foils 0.13 mm.
A1	Li, W disc, Mo foil, BN, Mo foil, W foil, BN, W foil	
A2	Li_3N , Li, W disc, Mo foil, BN, W foil.	1.6 at.% N
A3	Li_3N , Li, W disc, Mo foil, BN, W foil.	2.9 at.% N
A4	B, Li, W disc, Mo foil, BN, W foil.	3.5 at.% B
B1	Li, W disc, Nb foil, BN, Nb foil, Ta foil, BN, Ta foil, 0.025 mm W foil	

shut off after the samples had been in the furnace 600 hours.

To accelerate the reactions between the contents of the crucibles, the test was conducted at a temperature about 300K higher than the lithium temperature in a demonstration fusion reactor.

After removal from the furnace, the tungsten crucibles were taken from the

stainless steel capsules and cracked open by tapping on the end with a hammer. The lithium was leached out with methanol for 12 hr, followed by a 4-hr water leach. Then the crucible and contents were rinsed carefully and dried in a glass beaker. An attempt to vacuum-distill the lithium out of the crucibles was not successful.

Results

The most striking result was that no boron nitride remained in any of the crucibles. Practically all of the metal foils had broken up into small flakes or powder. Generally, the tungsten disc was intact except for some reaction product around the rim, and the tungsten crucibles were generally unaffected. A summary of the test results is shown in Table 2.

During dissolution of the lithium in methanol or water, a strong ammonia smell was noted. This is indicative of the presence of Li_3N in the cooled sample.

As mentioned earlier, the tungsten disc emerged from the test with only surface discoloration and a small amount of granular reaction product around the rim. The condition of the disc was studied in

Table 2. Condition of samples after compatibility run at 1270K for 600 hr.

Sample	Foil condition	Disc condition
A1	All disintegrated to flakes or powder, except one round piece which curled up and cracked.	Discolored surface, and some reaction product around rim.
A2	About the same as A1, except the one intact round piece was not curled up, but broken in half.	Discolored surface, and some reaction product around rim.
A3	Foils generally cracked and broken, but not much powder. One round foil intact.	Same as A1, except possibly a bit less reaction product on rim.
A4	Foils generally broken, cracked, etc., but not much powder formed. Some foils in curled pieces.	Less apparent reaction product than A1.
B1	Foils generally cracked and broken, some powder formed. One round piece nearly intact.	About the same as A4.

Fig. 2. Sketch of sectioned tungsten disc.

some detail by x-ray diffraction analysis and metallography.

The disc from sample A1 was submitted to G. Smith for x-ray diffraction analysis of the disc surface, and analysis of the reaction product from the disc rim. In both cases, the only compound detected was tungsten boride (WB). Memos from G. Smith (dated 7/2/73 and 7/10/73) report the results of the x-ray diffraction analysis.

The disc from sample A2 was cut in half along the diameter, and mounted and polished for metallographic examination. Figure 2 shows the portion of the disc selected for a photomicrograph, and Fig. 3 is the photomicrograph of the sample at 50X. Figure 3 shows clearly

the film of WB on the surface and sides of the disc. The thickness of the film varies from about 0.10 mm to 0.18 mm. The thickness is definitely greater on one side than the other, which was probably caused by one side of the disc being in closer contact with boron nitride than the other. The WB film did not adhere tightly to the substrate, and could be chipped off with stainless steel tweezers.

The inside of the tungsten crucibles also appeared discolored, but no effort was made to study the phenomena. The powder and flakes remaining after each test were also not studied.

Fig. 3. Photomicrograph of tungsten disc. 50X

Discussion of Results

The complete absence of boron nitride after the tests came as somewhat of a surprise. From thermochemical considerations, BN appears to be far more stable than Li_3N , and somewhat more stable than tungsten boride. However, since the BN completely reacted, we should examine the available thermochemical data in light of this fact, and see if there can be an explanation.

The first interesting observation is that WB is not the lowest boride of tungsten. According to the phase diagram² for the W-B system, W_2B is the phase in equilibrium with pure tungsten. However, it is possible that a thin layer of W_2B actually exists between the tungsten disc and the WB layer, but it is so thin that it was not detected in the x-ray diffraction pattern, or in metallographic examination.

Unfortunately, no accurate thermochemical data exist for WB. However, a recent study⁵ of the equilibria between W_2B , W, BN, and N_2 provides good data for W_2B , and it is instructive to use these data to compare with the Li_3N data. The equilibrium between W, W_2B , and BN is:

$$\text{Log} (p_{\text{N}_2})_{\text{atm}} = \frac{-16,000}{T} + 9.40 \quad (1)$$

Use of the above equation gives a log (p_{N_2}) at 1270K of -3.16. Since WB has a higher boron activity than W_2B , the equilibria involving the WB phase would require a lower p_{N_2} than calculated above.

Since sample A1 contained no metals that form stable nitrides, the nitrogen from the reacted BN certainly went into

solution into the molten lithium. This conclusion is verified by the evolution of ammonia fumes during dissolution of the lithium after test. In sample A1, the amount of BN put in is equivalent to about 25 at. % nitrogen dissolved in the lithium, or a solution of composition near Li_3N . There are no published data on lithium-nitrogen solution thermodynamics at the temperature of interest to this work, so the best we can do is to use the extrapolated published data for solid Li_3N at 1270K, as tabulated by JANAF.¹ At 1270K, the tables predict the p_{N_2} in equilibrium with Li_3N to be greater than 1 atm. If we take into account the free energy of fusion of Li_3N , the calculated p_{N_2} would be higher. As mentioned earlier, the equilibrium expressed as Eq. (1) predicts that the p_{N_2} is less than about $10^{-3.2}$ atm. There is thus a discrepancy of about 3-1/2 orders of magnitude between the predicted p_{N_2} required for the formation of WB from BN, and the p_{N_2} that should exist over the resultant Li-N solution.

The most suspect thermochemical data for the above calculations appears to be the JANAF tabulation of data for Li_3N . The ΔH_{f298}° for Li_3N appears reliable, but ΔG_{f298}° was determined by an estimated entropy. The high temperature ΔG_f° data for Li_3N were estimated by extrapolating C_p data above 578K, and the C_p data is 34 years old. The most probable conclusion is that the tabulated ΔG_f° data for Li_3N is seriously in error at elevated temperatures.

Another explanation might be that nitrogen behaves much differently in

lithium solutions that contain boron than in otherwise pure lithium solutions. Another way of saying this is that boron might act to greatly decrease the activity coefficient of nitrogen in lithium solutions. Unfortunately, it is not possible to determine the amount of boron left in solution in the lithium at the end of the test. If the amount was very small, the explanation just mentioned would not be valid. Perhaps a combination of both explanations is the most accurate.

In any event, BN is not expected to be stable in Li systems with any metal that forms stable borides. Aluminum nitride (AlN), which is 10 kcal more stable than BN, might be suitable if stable metal aluminides are not formed. However, the thermochemical data on refractory metal aluminides is very scarce, so predictions are hard to make. We must therefore await the results of the next series of compatibility tests to determine the stability of AlN.

Summary and Conclusions

Boron nitride is incompatible with molten lithium at elevated temperatures in the presence of refractory metals. The decomposition of boron nitride takes place with the formation of refractory metal borides and lithium-nitrogen solu-

tions. The results illustrate that compatibility tests between lithium and ceramics must always take into account possible reactions between the ceramic components and the refractory metal used as the container.

References

1. D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd Ed., National Bureau of Standards, NSRDS-NBS 37 (1971).
2. R. P. Elliott, Constitution of Binary Alloys, 1st Supplement, (McGraw-Hill, New York, 1965).
3. C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides," Bull. 605, U.S. Bureau of Mines (1963).
4. E. E. Hoffman, Corrosion of Materials by Lithium at Elevated Temperatures, Oak Ridge National Lab. Rept. ORNL-2924, (1960).
5. F. D. Baehren and D. Vollath, "Determination of Thermodynamic Data of the Borides Mo_2B , W_2B , and Re_3B ," Planseeber. Pulvermet., 17, 180 (1969).