

ANL/CMT/CP-96844

SYNTHESIS AND CASTING OF A LITHIUM-BISMUTH COMPOUND FOR AN ION-REPLACEMENT ELECTROREFINER

Sean M. McDeavitt

Chemical Technology Division
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
Email: mcdeavitt@cmt.anl.gov

RECEIVED
SEP 28 1999
OSTI

Abstract

The intermetallic compound Li_3Bi played an integral part in the demonstration of an ion replacement electrorefining method developed at Argonne National Laboratory. The Li_3Bi compound was generated in a tilt-pour casting furnace using high-purity lithium and bismuth metals as the initial charge. At first, small-scale (~20 g) experiments were conducted to determine the materials synthesis parameters. In the end, four larger-scale castings (500 g to 1250 g) were completed in a tantalum crucible. The metals were heated slowly to melt the charge, and the formation reaction proceeded vigorously above the melting point of bismuth (~270°C). For the large-scale melts, the furnace power was temporarily turned off at this point. After several minutes, the tantalum crucible stopped glowing, and the furnace power was turned on. The temperature was then increased to ~1200°C to melt and homogenize the compound, and liquid Li_3Bi was cast into cold stainless steel molds. Approximately 3.7 kg of Li_3Bi was generated by this method.

Introduction

The Chemical Technology Division at Argonne National Laboratory (ANL) has a long history of developing new and varied applications for the electrometallurgical processing of metals and molten salts. Recently, a pyrochemical process was developed and demonstrated at the laboratory scale for the treatment of the radioactive salt waste from the Molten Salt Reactor Experiment (MSRE) that operated from June 1, 1965 to December 12, 1969 at Oak Ridge National Laboratory (ORNL) [1-3]. This paper describes a small subset of the process development effort involving the synthesis and casting of the Li_3Bi intermetallic anode material used to supply lithium to the electrochemical cell.

Background: MSRE Salt Treatment Process

The Molten Salt Reactor Experiment was a nuclear reactor concept designed to produce power using a homogeneous

liquid core [3]. The reactor fuel was uranium tetrafluoride [initially (^{235}U) F_4 and later (^{233}U) F_4] dissolved in a molten fluoride salt with the composition 65 mol % LiF -30 mol % BeF_2 -5 mol % ZrF_4 . Upon reactor shutdown, the system was drained, and the radioactive salt was stored at ORNL. In the early 1990s, a task force was formed at ORNL to evaluate methods for the cleanup and disposal of the MSRE salt [1-2].

An electrometallurgical process developed at ANL is one of several methods considered for the treatment of the MSRE waste [1-2]. The key step in this treatment process is an electrochemical ion-replacement method that introduces lithium into the salt as other metals are extracted. The reduction of non-lithium salt constituents is accomplished using a lithium-bearing compound at the anode and various types of "collection" cathodes. Two candidate anode materials, Li_3Bi and Li_3Sb , were considered for this process, but only the Li_3Bi compound has been demonstrated.

The process operates at temperatures between 530°C and 650°C and includes four extraction steps. In the first step, zirconium and the noble metal fission-product fluorides are electrochemically reduced and collected at a solid cathode as the Li_3Bi anode is converted to lithium fluoride (LiF). As lithium is extracted from the Li_3Bi anode, bismuth is left behind as a liquid and collected in a catch basin below the anode. Calculations indicate that up to 90% of the zirconium must be removed before uranium extraction becomes favorable.

In the second reduction step, uranium and other actinides in the salt are reduced along with the rare earth fission products and any leftover zirconium. The reduced metals are deposited in a liquid bismuth cathode. At this stage, the bismuth cathode is removed and placed in a different electrorefiner, which contains a LiCl-KCl-UCl_3 electrolyte to extract the uranium from the bismuth alloy. This chloride salt electrorefining method is a well-developed technology being applied to the treatment of spent nuclear fuels [4].

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

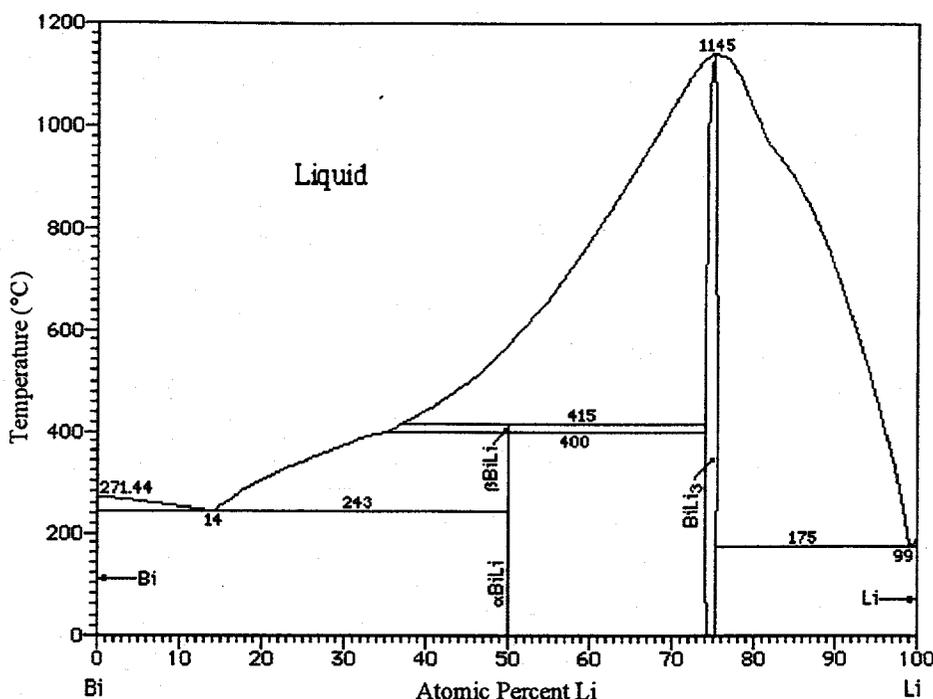


Figure 1. Phase Diagram of Bismuth-Lithium Binary System [6].

The third and fourth extraction steps are designed to continue the purification of the MSRE salt by extracting the more active fission product elements from the salt. The third step again uses a bismuth collection cathode to extract some cesium and barium while removing rhenium and daughter products from thorium decay. The fourth step uses a nitride bed in liquid bismuth that scavenges strontium, yttrium, and the remaining cesium and barium. After the fourth step, the waste salt will only contain LiF-BeF₂ with trace amounts of radioactive fission products and may be classified as low-level waste.

The first two steps were demonstrated successfully in the laboratory using ~8 kg of simulated MSRE fuel salt and ~3.7 kg of Li₃Bi [2]. A set of incremental electrotransport experiments was carried out in an inert atmosphere glovebox. The experiments successfully extracted zirconium and uranium from the simulated salt and demonstrated that the Li₃Bi anode material performed as anticipated [2]. Therefore, this treatment technology has been established and demonstrated. However, no decision has been reached regarding its application to the MSRE salt at this time.

Background: The Formation of Li₃Bi

An evaluation of the Bi-Li phase system was presented by Sangster and Pelton [5]. The binary phase diagram (Figure 1) shows two intermetallic compounds in this

system, LiBi and Li₃Bi. The LiBi compound disassociates to Li₃Bi plus liquid above ~415°C and is, therefore, not relevant to the ~600°C electrorefining process described above. The Li₃Bi compound is very stable with a relatively high melting temperature of 1145±20°C, as compared with 180.6±0.5°C for lithium and 271.4±0.5°C for bismuth [5].

The formation of Li₃Bi is an exothermic reaction represented by the following formula:



The enthalpy of formation for Li₃Bi at room temperature is -251.3 kJ/mol [5]. As an extreme illustration of the significance of this value, a "worst case" temperature rise may be estimated by assuming that all the released energy is deposited into the product. The specific heat of Li₃Bi at ~300°C is ~115 J/mol·K [6], which implies a temperature rise of more than 2000°C ($\Delta T \approx -\Delta H/C_p$). Obviously, in real systems, energy is lost to the crucible and other furnace materials, making the true temperature rise much lower. However, this simple calculation highlights the need for caution during the synthesis of kilograms of Li₃Bi.

Experimental: Li₃Bi Synthesis and Casting

The Li₃Bi synthesis experiments proceeded in two stages. First, a small-scale experiment (~40 g) was carried out to evaluate the true severity of the formation reaction. Large-

scale synthesis and casting runs (500 g to 1250 g) were then carried out. All experiments were done using tantalum crucibles in a tilt-pour induction casting furnace connected to an inert atmosphere glovebox described by McDeavitt et al. [7]. The lithium-to-bismuth composition was controlled to achieve a 3:1 molar ratio, which translates to ~91.0 wt % bismuth and ~9 wt % lithium.

In the small-scale test, 37.7 g of bismuth and 3.6 g of lithium were charged into a small tantalum crucible and placed in the furnace. The furnace was heated slowly, and the materials were monitored using a video camera. The lithium melted first without initiating a noticeable reaction, but when the bismuth melted, a rapid and violent reaction began. A significant amount of vapor and splattered liquid came out of the small crucible, but the tantalum maintained its integrity. The reaction product did wet the walls of the crucible, indicating that pouring is necessary for efficient recovery of Li_3Bi . The experiment was terminated after the initial vigorous reaction was concluded. In a second test, the product material was heated to 1200°C to melt and homogenize the Li_3Bi product. This step proved relatively uneventful and successful. Some of the Li_3Bi distilled away during melting; the remaining material was dark blue (previous reports on Li_3Bi noted a "steel blue" or "dark green" tint [5]).

Four large-scale experiments were carried out in a large tantalum crucible, ~10 cm in diameter and ~20 cm tall. A zirconia felt lid was used to contain the vapors expected from the observation in the small-scale results. A summary of the charge and product masses is shown in Table I. In the first experiment, lithium additions were made in small increments, from ~4 g initially up to the final addition of ~19 g, to minimize the energy release. This procedure proved unnecessary and time consuming because the expected temperature rise from the heat of reaction was never observed and because the furnace had to be shut down and opened for each incremental loading. After the final lithium addition, the product was heated to 1200°C for 30 minutes, and the liquid Li_3Bi was cast into a cold, stainless steel mold.

Table I. Summary of Charge and Product Masses (g).

Experiment Number.	Bismuth Charge	Lithium Charge	Li_3Bi Product
1	489.2	48.8	531.6
2	660.8	66.1	725.1
3	1,145.9	110.7	1200.6
4	1179.9	115.0	1250.6

In the second, third, and fourth experiments, the entire lithium charge was placed into the crucible with the bismuth at the onset. In all three experiments, a very significant temperature increase was observed shortly after



Figure 2. Photograph of Cast Li_3Bi Ingot (~11.4 cm dia.).

the furnace temperature exceeded the bismuth melting point. The tantalum crucible would glow bright red, indicating that the crucible temperature had risen from ~300°C to nearly ~1000°C. The furnace power was temporarily turned off at this time in the experiments. (The furnace is rated for temperatures up to 2200°C, so these experiments were not stressing the safe operating limits of the system.) After the reaction had consumed the charge material and the furnace had cooled down, the power was turned back on. The product was heated to 1200°C for 30 minutes, and the liquid Li_3Bi was cast into a cold, stainless steel mold.

The casting procedure was the same in all four experiments. A stainless steel casting mold and funnel were loaded into the tilt-pour furnace chamber prior to the synthesis experiment. Once the product had been held at 1200°C for 30 minutes, the zirconia lid was removed for pouring. A thick cloud of vapor then filled the furnace chamber, reducing visibility for the video camera and the optical pyrometer used to control the furnace. The liquid was quickly poured from the crucible and the furnace was cooled. A thick skull of Li_3Bi was always left behind in the tantalum crucible after each pour, but the same crucible was used for all four melt-pour experiments.

Figure 2 shows a photograph of a typical Li_3Bi ingot from this project. The large-scale ingots were typically bright and shiny with a light metallic blue color. This is slightly different from the "steel blue" and "green" reported previously [5] and the dark blue observed in the small-scale test. However, when the ingots sat for several days in an inert atmosphere glovebox with ~2 ppm water vapor and less than 5 ppm oxygen, the light blue of the fresh Li_3Bi

ingots darkened slightly. This observation indicates that the color of this material may be sensitive to minor impurity contamination. In a related observation, the underside of the zirconia lid was coated with a purple-blue material. This indicates that the vapors released from the high-temperature melt prior to pouring may have been Li_3Bi . Thus, this compound, apparently, has a high partial pressure at 1200°C .

The cast ingots did not react with the stainless steel molds and shrank away from the mold wall because of thermal contraction. As a result, the ingots were all easily removed from the molds. One notable exception came with the second ingot, which was slightly lithium-rich with ~ 9.1 wt % Li in the charge (see Table I). As a result, there was excess lithium metal in the Li_3Bi product wet and stuck to the casting mold and the stainless steel funnel. The ingot fell right out of the mold, but the excess lithium remained behind.

The Li_3Bi intermetallic is very brittle. The cast ingots were broken into chunks for the MSRE salt treatment experiments. All 3.7 kg of the material produced in this study was consumed in the electrorefiner as zirconium and uranium were extracted from the fluoride salt used to simulate the MSRE waste.

Summary and Conclusions

The intermetallic compound Li_3Bi was successfully synthesized from pure lithium and bismuth metals. The product was used in demonstration experiments for a novel fluoride-salt electrorefining method developed to treat waste salt from the Molten Salt Reactor Experiment. The following observations come from the synthesis and casting experiments described in this paper:

- The Li_3Bi formation reaction proceeds vigorously after the lithium and bismuth have melted, and the compound apparently has a high partial pressure at 1200°C .
- The Li_3Bi synthesis and 1200°C casting operations may be carried out safely in a tantalum crucible.
- Stainless steel is adequate as a cold casting mold for Li_3Bi , but there may be complications if too much lithium is present.
- The Li_3Bi compound is very brittle and its color is apparently dependent on impurity content.
- Based on the experience gained from generating the Li_3Bi compound and using it in electrorefining experiments, it is evident that recycling bismuth from spent process anodes to make new Li_3Bi is feasible within a remotely controlled process as required for

processing MSRE salt. This enables the minimization of the process waste volume.

Acknowledgments

The author wishes to acknowledge W. E. Miller, Z. Tomczuk, and J. J. Heiberger for developing the MSRE salt treatment process and for their help in planning this work. In addition, L. Leibowitz, J. K. Basco, and L. Putty contributed to this project. The U.S. Department of Energy supported this work under contract W-31-109-Eng-38.

References

- 1) J. J. Laidler et al., "Chemical Technology Division Annual Technical Report 1996," (Report ANL-97/13, Argonne National Laboratory, 1997) 98-101.
- 2) J. J. Laidler et al., "Chemical Technology Division Annual Technical Report 1997," (Report ANL-98/13, Argonne National Laboratory, 1998) 103-106.
- 3) S. Glasstone and A. Sesonske, Nuclear Reactor Engineering, 3rd Edition (New York, NY: Van Nostrand Reinhold Company, 1980) 771-773.
- 4) C. C. McPheeters et al., "Electrometallurgically Treating Metal, Oxide, and Al Alloy Spent Nuclear Fuel Types," JOM, 49 (7) (1997), 22-25.
- 5) J. Sangster and A. D. Pelton, "The Bi-Li (Bismuth-Lithium) System," Journal of Phase Equilibria, 12 (4) (1991), 447-450.
- 6) TAPP: Thermophysical and Physical Properties (Electronic Database: Hamilton, OH: E S Microwave, Inc., 1994).
- 7) S. M. McDevitt et al., "Stainless Steel-Zirconium Waste Forms from the Treatment of Spent Nuclear Fuel," JOM, 49 (7) (1997) 29-32.