Journal of Nuclear Materials 307–311 (2002) 743–748

journal of nuclear materials

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Fabrication and properties of a tin–lithium alloy

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Abstract

A Sn–25at.%Li alloy has been fabricated by starting with pure Sn and Li. The alloy was cast into various shapes and sent to researchers in several organizations in the United States and abroad for property measurements. The fabrication procedure involved gradual addition of Li from a separate vessel into a vessel that contained Sn; continuous stirring of the mixture during Li addition increased the Li content of the alloy gradually from 0 to the final value of 25 at.%. The melting temperature of the alloy was 334 °C; its density was 6.36 g/cm^3. Results are presented on microstructure, chemical composition, phase distribution, and microhardness of the alloy. Several experiments were conducted to evaluate the chemical reactivity of the alloy with air, water, and steam. Results showed that the alloy undergoes catastrophic oxidation when $T > 250$ °C in air and develops an oxide scale in water at temperatures up to 95 °C. Exposure in low-pressure steam at 200 °C caused significant swelling and cracking of the alloy.

1. Introduction

In the US Fusion Power Program, APEX (Advanced Power Extraction) and ALPS (Advanced Limiter-Divertor Plasma-Facing Systems) are being considered for the development of high-performance blanket and divertor schemes, respectively [1]. To accommodate the high heat flux and high neutron wall loading, the free-flow first wall and divertor are being examined. Because the coolant/breeding material directly faces the plasma chamber in these concepts, a coolant/breeding material with low vapor pressure is of significant interest. Tin–lithium alloys seem to have several attractive thermophysical properties, in particular thermal conductivity and heat capacity, when compared with those for another proposed coolant, Pb–17at.%Li. Furthermore, Sn–Li coolant exhibits low vapor pressure, a significant benefit in the design of the free-flow first wall and divertor. Even though, conceptually, Sn–Li is a potential coolant/breeding material, several technical issues, such as physical and chemical properties, materials compatibility, activation characteristics, and breeding potential, must be addressed. Fütterer et al. [2] assessed the use of Sn–Li alloys as breeder material for blanket application in fusion power plants. Table 1 lists the thermophysical properties of Sn, Pb, and Li.

Fig. 1 is a schematic illustration of the Sn–Li phase diagram, which shows several Li–Sn compounds (such as LiSn, Li_2Sn, Li_5Sn_2, Li_7Sn_2, and Li_4Sn) that exhibit melting temperatures of 485–783 °C. Because a Li concentration of at least 20 at.% is suggested for tritium breeding, a composition of Sn–25at.%Li was selected for fabrication. The liquidus temperature for this alloy will be ≈330 °C. However, if Sn and Li are mixed together and heated to the liquidus temperature, there is a danger that local regions in the mixture with a high Li concentration (due to lower melting temperature of pure Li) will lead to the formation of the high-melting compounds of Sn and Li mentioned above. If the high-melting compounds form during alloy fabrication, the mixed alloy must be heated to very high temperatures to melt these phases and to develop an alloy with a homogeneous composition. Therefore, it is essential that none of these high-temperature phases form during mixing of Sn and Li to make the alloy. This paper presents details of the procedure used to fabricate an Sn–Li alloy that contains 25 at.% Li for use by researchers from several institutions in the US and abroad to evaluate various properties of the material. In addition, results are presented on the

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PII: S0022-3115(02)01221-7

Table 1
Physical properties of Sn, Pb, and Li

Property	Sn	Pb	Li
Melting temperature (°C)	232	327	180
Temperature at $p = 14$ Pa (°C)	1492	987	745
Density (g/cm^3)	7.3	10.4	0.54
Specific heat capacity (J/K g)	0.23	0.13	3.6
Thermal conductivity (W/m K)	66	35	85
Vapor pressure at melting temperature (Pa)	5.8×10^{-21}	4.2×10^{-7}	1.6×10^{-8}
Electrical resistivity (μΩ cm)	11	21	9

chemical reactivity of the alloy when exposed to air, water, and steam.

2. Fabrication procedure

The Sn, obtained from Ames Metal Products, was in the form of 25 × 12.5 × 250 mm^3 bars with a purity of 99.95 wt% Sn. Lithium was obtained from Cypress Foote Mineral in the form of rods 12.5 mm in diameter × 275 mm long. To avoid forming Sn–Li compounds with high-melting temperatures, an apparatus was assembled in which Li is gradually added to Sn so that the Li concentration increased monotonically from 0 to 25 at.%, with an associated increase in melting temperature from 250 to 350 °C. The equipment used to mix Li into Sn was assembled with components made of austenitic stainless steel. The mixing chamber was a vessel 0.4 m in diameter × 0.5 m high and was equipped with a viewing port, thermowell, drain, and two insertion ports at the top. One of these insertion ports was used to assemble a stirrer mechanism, the other was used as a line (12.5-mm-diameter tubing) to transfer Li into the Sn-containing vessel. Li was contained in another vessel (0.15 m in diameter × 0.35 m high) above the Sn vessel. Resistance heaters and thermal insulation were applied to both Li and Sn vessels, as well as to the Li transfer line. The gas phase of the two vessels was independently connected to a source of vacuum and purified Ar gas. To improve the homogeneity of the final Sn–Li alloy composition, a stainless steel stirrer was used to stir the liquid while Li was continuously added to the Sn.

The requirements for Sn and Li were calculated to produce ≈15 L of the Sn–25at.%Li alloy. Using the density values of 0.54 and 7.3 g/cm^3 for pure Li and Sn, respectively, we calculated the density of Sn–25at.%Li alloy as 6.36 g/cm^3. To produce 15 L of the Sn–Li alloy, the initial amounts of Sn and Li needed were 93.5 and 1.81 kg of Sn and Li, respectively. The initial step was to melt the slender bars of pure Sn in the lower vessel. Inasmuch as many bars were available, as many as possible were inserted into the vessel through the view port, and the system was then closed, evacuated, and back-filled with Ar. The evacuation/refill operations were repeated three times before the vessel that contained Sn was heated. The bars were then melted and cooled. Two loadings of Sn and melting were required to

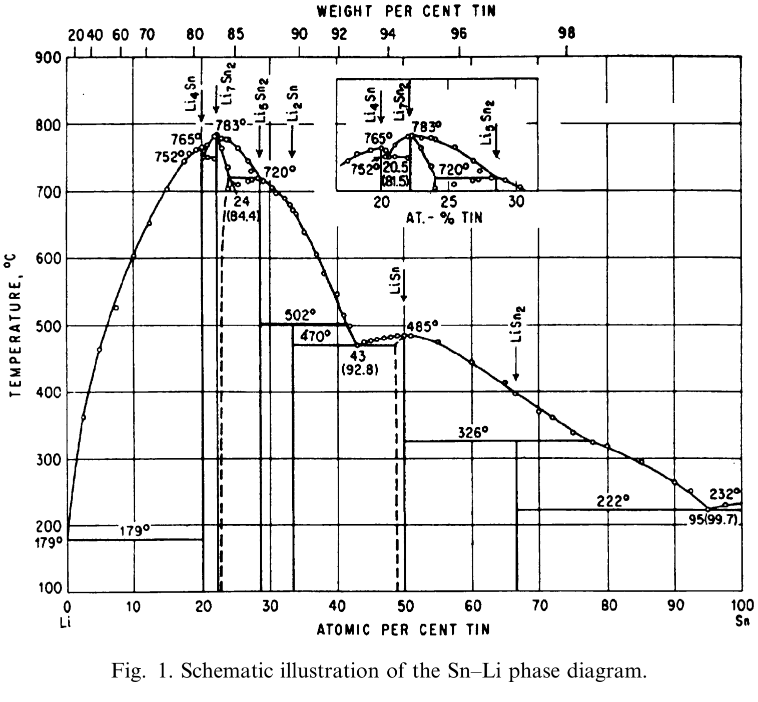

Fig. 1. Schematic illustration of the Sn–Li phase diagram.

obtain the required 93.5 kg of pure Sn in the vessel. The smaller Li vessel also required two loadings to obtain 1.81 kg of Li. Rods of Li were removed from their secondary protective plastic containment near the vessel intended for the Li and inserted with minimal exposure to ambient air. In addition, flowing Ar from the vessel mitigated the potential for unwanted oxygen contamination during the transfer. At the end of each loading, the Li was melted and slowly added to the molten Sn in the mixing chamber. An attempt was made to video tape the first addition of Li to Sn, but the viewing window did not allow a clear view of the stream of Li striking the molten Sn, the lighting was poor, and after the initial exothermic reaction, the window became clouded. The results were less than desirable but a VHS tape of the operation does exist.

In the first mixing operation, Sn and Li vessels were maintained at 240 and 200 °C, respectively. Upon adding Li to Sn, the temperature of the mixing chamber increased to 419 °C. When the second batch of Li was added to the mixing chamber, the temperature of the Li was maintained at 320 °C. The temperature of the mixing chamber rose to 512 °C after addition of the second batch of Li. The Sn–Li alloy was maintained at this temperature for 15 min while the stirrer was operating at high speed. A sample of the alloy was taken by casting it under vacuum in a heated stainless steel tube (≈0.5 m long × 12.5 mm in diameter) attached to the mixer vessel drain. The initial analysis indicated an Li content of 0.83 wt%, which was significantly lower than the additions made to the vessel, probably because of the inhomogeneity of the melt. The mixture was held at 400–500 °C with vigorous stirring approximately eight times a day for three days to dissolve any high-temperature compounds and to homogenize the melt. A second sample, taken in the same manner as before, showed a Li content of 1.96 wt%, based on an analysis of duplicate samples. This value corresponds to an alloy composition of Sn–25at.%Li. Table 2 lists the concentration of several substitutional and interstitial elements in the alloy.

Table 2
Chemical composition of Sn–Li alloy fabricated in current project

Element	Concentration (wt%)
Ag	0.017
Al	<0.01
Ba	0.002
Be	<0.001
Ca	<0.001
Cd	<0.001
Co	<0.01
Cr	0.03
Cu	<0.005
Fe	0.08
K	0.011
Li	1.96
Mg	<0.001
Mn	0.017
Na	<0.001
Ni	0.02
Pb	0.02
Si	<0.05
Sr	<0.001
Ti	<0.005
V	<0.005
Zn	<0.001
Zr	<0.005
O	0.091
N	<0.0002
C	0.085
S	<0.0035
Sn	Balance

Fig. 2 shows scanning electron microscopy (SEM) photomicrographs of the alloy in two magnifications. The two-phase solidified structure consists of Sn and $SnLi_2$ at room temperature. Vickers hardness measurements with a 100 g load indicated average values of ≈HV20 and HV85 for the light and dark phases, respectively. Fig. 3 shows the temperature-vs.-time cooling curve generated for the alloy. The point where the slope

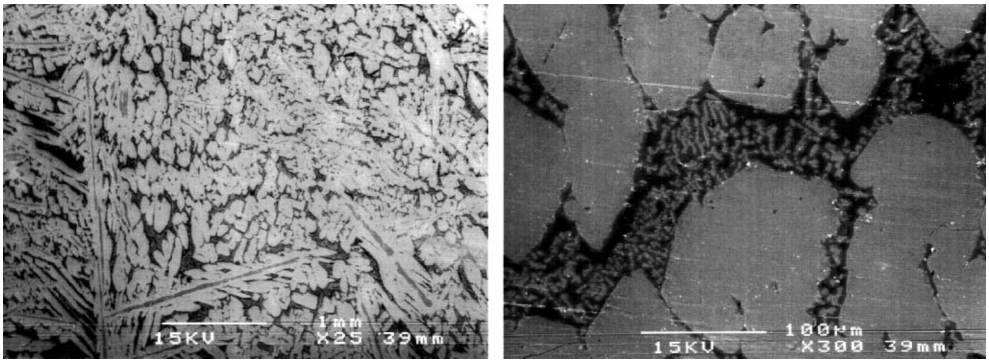

Fig. 2. SEM photomicrographs of Sn–25at.%Li alloy fabricated at Argonne National Laboratory.

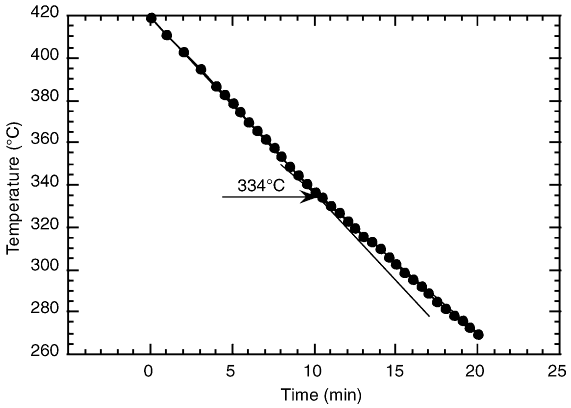

Fig. 3. Temperature-vs.-time cooling curve for Sn–25at.%Li, indicating a melting temperature of 334 °C.

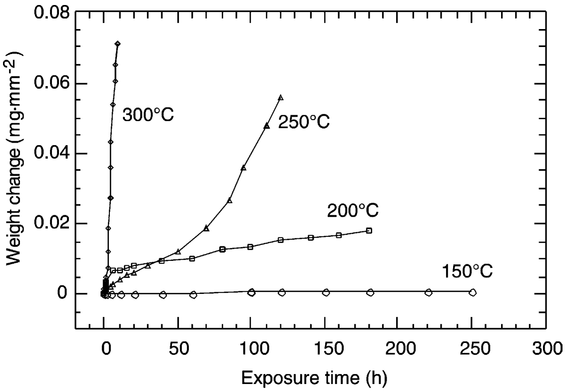

Fig. 4. Weight-change data for oxidation of the Sn–25at.%Li alloy in air.

of the line changes (334 °C) indicates the melting temperature of the alloy, which agrees well with the temperature depicted in the Li–Sn phase diagram (see Fig. 1) for an alloy with a composition of Sn–25at.%Li.

3. Chemical reactivity

One of the safety concerns with any liquid metal is its chemical reactivity with the exposure environment. As a first step to determine chemical reactivity, solid samples of Sn–25at.%Li alloy were examined in air, water, and steam environments over a wide temperature range and for extended time periods. Disks 12.7-mm in diameter and 2–3 mm thick were fabricated from as-cast ingots of the alloy.

3.1. Oxidation in air

Oxidation tests were conducted in a thermogravimetric setup at 150–300 °C in a flowing ultrapure air environment. Weight change in the specimens was continuously monitored during exposure. Fig. 4 shows the weight-change data for oxidation of the alloy at 150, 200, 250, and 300 °C. The alloy exhibited low oxidation rates at 150 and 200 °C and, based on our tests, seemed to follow parabolic kinetics. The parabolic rate constants derived from the data are 5.1×10^{-5} and 1.4×10^{-3} mg mm^{-2} h$^{-0.5}$ at 150 and 200 °C, respectively. At 250 °C, the alloy exhibited protective, parabolic kinetics for up to ≈50 h but, beyond 50 h, the rate accelerated. At 300 °C, the alloy showed accelerated oxidation from the beginning of exposure and the catastrophic nature of oxidation was evident from the weight-change data shown in Fig. 4. The surfaces and fracture cross sections of the specimens after oxidation were examined by SEM. Fig. 5 shows the SEM photomicrographs of a specimen oxidized at 200 °C, whereas Fig. 6 shows the X-ray diffraction (XRD) data for the oxidized specimen. The results indicated the presence of Li_2CO_3 and traces of Li_2O and SnO_2. The oxide layer was so thin that Sn in the base alloy was dominant in the XRD pattern.

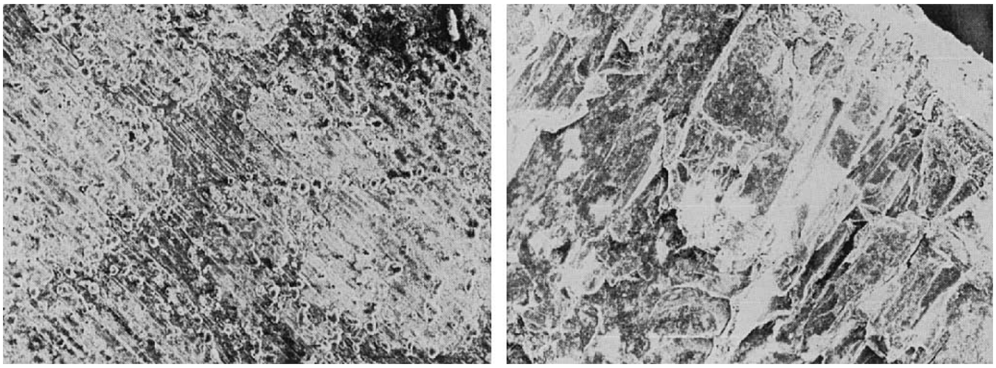

Fig. 5. SEM photomicrographs of (left) surface and (right) fracture cross section of Sn–25at.%Li alloy after oxidation in air at 200 °C.

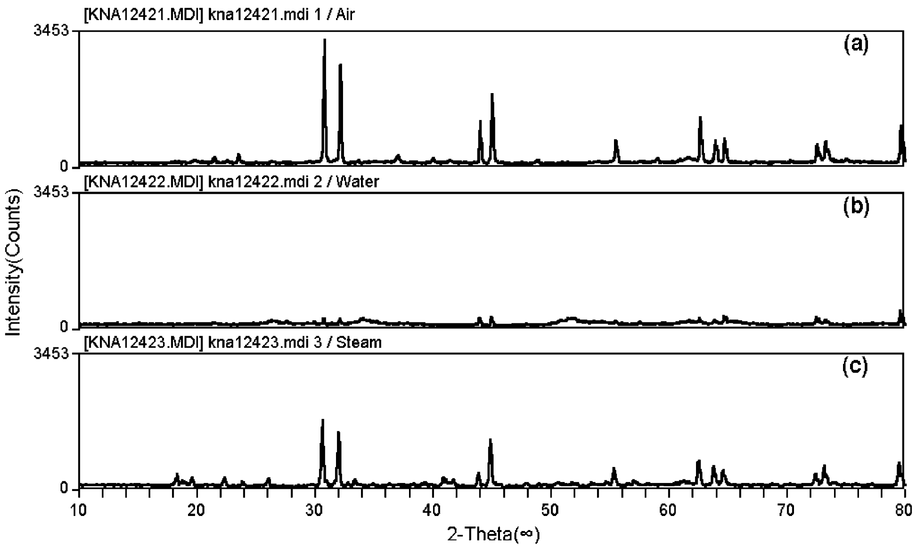

Fig. 6. XRD patterns for the Sn–25at.%Li alloy after (a) oxidation in air at 200 °C, (b) 320 h exposure to water at 95 °C, and (c) 72 h exposure in 0.8 MPa steam at 200 °C.

3.2. Exposure in water and steam

Disk specimens of the alloy were exposed in deionoized water at room temperature, 65, and 95 °C. The water was stirred with a magnetic stirrer to establish uniformity in impurity concentration (if any) and temperature during the test. The weight gain of the specimens during these tests was a result of scaling and development of layers of oxidation-products. The weight gains at room temperature, 65, and 95 °C were 0.0011, 0.0014, and 0.0004 $\mathrm{mg\,mm^{-2}\,h^{-1}}$, respectively. After exposure in tests at room temperature and 65 °C, the samples were rough, and contained significant, visually observable spalled areas. In contrast, the specimen tested at 95 °C showed a low corrosion rate and exhibited a smooth appearance, indicating that the corrosion product layer was adherent. Additional experiments are needed to evaluate if passivation of the alloy surface is possible at the higher temperature. The XRD analysis of the specimen (see pattern (b) in Fig. 6) showed peaks with significant broadening, indicating that the corrosion product layers may be closer to the amorphous than crystalline state. In one of the tests a specimen was exposed to alternately dry and aqueous environments at 95 °C. After a 320 h exposure, the specimen exhibited weight loss at a rate of 0.0006 $\mathrm{mg\,mm^{-2}\,h^{-1}}$, indicating that the oxide that developed in the dry environment was less resistant to spallation/erosion in the aqueous medium.

A disk specimen of the alloy exposed to steam at 200 °C and 0.8 MPa exhibited significant swelling and cracking. Fig. 7 shows the SEM photomicrographs (in

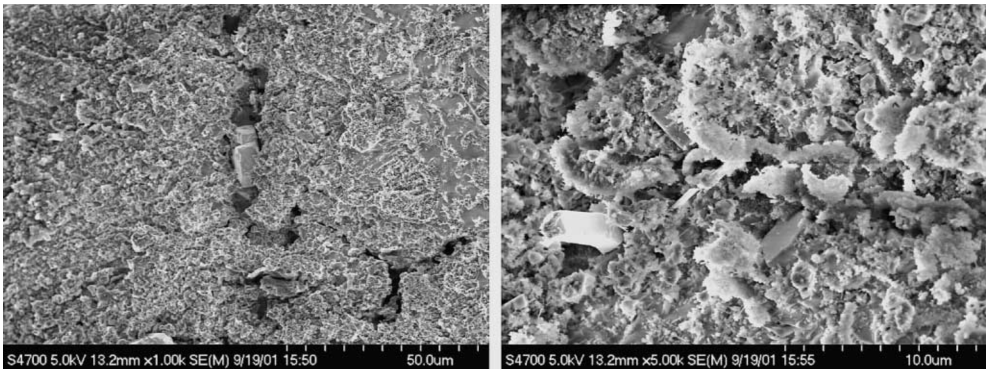

Fig. 7. SEM photomicrographs (in low and high magnifications) of the surface of the Sn–25at.%Li alloy after 72 h exposure in 0.8 MPa steam at 200 °C.

low and high magnifications) of the surface of the oxidized sample. Two large cracks and several smaller cracks can be seen. At high magnification, the photomicrograph shows a light phase growing outward from these cracked regions. The XRD pattern (see pattern (c) in Fig. 6) of this specimen indicated the presence of Li_2O and Li_2SnO_3. Additional effort that involves long-time exposure is needed to quantitatively assess the influence of steam on the corrosion performance and mechanical integrity of the fabricated material.

4. Summary

An Sn–25at.%Li alloy for application in high-performance blanket and divertor schemes has been fabricated from pure Sn and Li. The procedure involved gradual addition of Li from a separate vessel into a vessel that contained Sn; continuous stirring of the mixture during Li addition increased the Li content of the alloy gradually from 0 to a final value of 25 at.%. The alloy was a two-phase mixture of Sn and $SnLi_2$ at room temperature, with Vickers hardness values of $\approx$HV20 and HV85, respectively, for the two phases. Several experiments were conducted to evaluate the chemical reactivity of the alloy with air, water, and steam. Thermogravimetric test data showed that the alloy undergoes catastrophic oxidation in air at temperatures above 250 °C. The alloy develops oxide scales when tested in water at temperatures up to 95 °C. Results indicated that the reaction rate in water at 95 °C was lower and the surface scale was smoother than at lower temperatures, indicating a potential for the alloy to passivate at higher water temperatures. Exposure in steam at 200 °C and 0.8 MPa caused significant swelling and cracking of the alloy. Additional long-time exposures are needed to assess these reactions quantitatively, and further studies are needed to examine these reactions above 350 °C when the alloy is in liquid form.

Acknowledgements

This work was supported by the US Department of Energy, Office of Fusion Science, under Contract W-31-109-Eng-38. D.L. Rink assisted in the experiments on chemical reactivity, R.H. Lee assisted in the microstructural analysis of the tested specimens, and P. Johnson performed XRD analysis of the exposed specimens.

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