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Fabrication of lithium lead alloy and impurity control by temperature‐programmed desorption

鉛リチウム合金の合成と昇温脱離法による純度管理に関する研究

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The experimental studies on fabrication methods of a lithium lead alloy (Pb-Li) and desorption of non-metal impurities dissolved in the alloys were carried out. The alloys having various Li concentrations were fabricated from small metal grains of Pb and Li. The desorption behavior of gases dissoved in Pb, Pb-Bi and Pb-Li was investigated by the temperature programmed desorption (TPD) analysis. Pb and Pb-Bi contained H_2O and CO_2, and these chemical compounds were desorbed from the alloys below 700K. Desorption of H_2 from Pb-17Li was detected. These behaviors were based on their thermodynamic stability in the alloys. It was found that the non-metal impurities in the alloys could be removed by the TPD method.

1. Background

Liquid lithium lead alloy (Pb-Li) is one of the promising candidates of the tritium breeders for fusion DEMO reactors. Its tritium breeding performance and thermo properties were determined by Li concentration in the alloy. The fabrication of Pb-Li alloy at targeted Li concentration is important issue. The Li in the alloy has relatively large chemical reactivity, and reacts with oxygen and water. If Li in the alloy is preferentially oxidized and does not work as the alloying element, above-mentioned performance must be degraded. Therefore, the oxygen concentration in the alloy must be kept as low as possible. The impurity control of the fabricated alloy is essential technology. In the present work, the experimental studies on the fabrication of Pb-Li and the control of the non-metal impurities in the alloy were carried out.

2. Experimental conditions

2.1 Fabrication of Pb-Li alloy

Pb-Li alloys having various Li concentrations were fabricated from small metal grains of Li and Pb. The diameter of these grains is approximately 2.5mm. The purity of Pb grains used was 99.999%. The purity of Li grains was 99.9%. These grains were mixed well to be targeted composition at room temperature in a grove box, which was filled with Ar having a purity of 99.999%. Then, Pb-Li alloy was fabricated as the grains mixed were heated, melted and stirred in the glove box. The experimental conditions are presented in Table 1. After the fabrication procedure, the alloy was naturally cooled while its temperature was monitored by a thermocouple inserted into the melt. The Li concentration in the alloy was determined by the line change of the temperature cooling curve obtained by the temperature measurement. The concentration of Li in the solidified Pb-Li alloy was measured by ICP-AES. However, the Li concentration in the alloy fabricated was lower than that expected from the mass of Li used. The loss of Li was caused by the selective oxidation reaction of Li with lead oxides on the surface of Pb grains during the melting procedure. Then, the Li concentration of the alloy was adjusted to be targeted concentration by mixing with a Li rich alloy.

2.2 Non-metal impurity analysis by TPD experiment

The temperature‐programmed desorption (TPD) experiments were performed with the alloys to investigate the desorption behavior of the non-metal impurities dissolved in the alloy. The test materials of Pb, Pb-17Li and Pb-28Li were used to investigate the effect of Li on the desorption behavior of the gases from the metals. Figure 1 shows the test section connected to the Temperature Programmed Desorption and Mass Spectrometer (TPD-MS). The metal or the alloy of 100g was installed in the test cylinder. The test cylinder was connected through some tubes, the cold trap and valves into the TPD-MS.

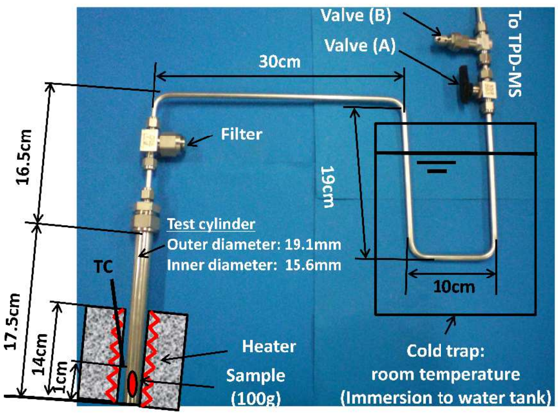

Fig. 1 Test section of TPD experiment

Table 1 presents the experimental conditions. A baking procedure for the test samples was not performed before the TPD experiments in order to detect the non-metal impurity adsorbed on the sample surfaces by the TPD experiments. First, all the part of the test section was evacuated by a turbo molecular pump at a room temperature and the pressure reached 10^{-4} Pa. The valve (A) was used for the evacuation of the TPD-MS system. The valve (B) was opened and the temperature of the test cylinder was raised at a temperature rising rate of 2.5K/min, starting at 308.5 K and finishing at 774.5 K. After the experiment, the heater was turned off, and the cylinder was naturally cooled. The TPD experiments with Pb-Bi sample, that is one of the candidates of fast reactor coolant, were carried out for the comparison.

3. Results and discussions

The results of TPD experiments were summarized in Fig. 2 and Table 1. Desorption of various gases was detected by the TPD-MS. Large desorption of CO_2, O, C and H_2O from the solid Pb below the melting point as shown in Fig.2 (a). The result for Pb-Bi test indicated that the desorption behavior was close to that from Pb. The standard Gibbs free energies for the formation of H_2O and CO_2 were smaller than that of PbO as shown in Fig. 3. Pb does not react with carbon, and does not form its carbide. H_2O and CO_2 were thermodynamically stable more than PbO, and these were attached on the surface and/or dissolved in the metal or the alloy in the state of molecule. Then, H_2O and CO_2 were desorbed from the metals. Desorption of atomic oxygen and hydrogen was also detected. These results indicated the degassing effect may be obtained by a baking procedure.

The results for Pb-Li tests were shown in Figs. 2 (c) and (d). The desorption ratio of H_2O and CO_2 from Pb-Li alloy was much smaller than that from Pb and Pb-Bi. This was because LiOH is thermodynamically stable rather than H_2O and CO_2. The adsorption of these molecules on Pb-Li alloy must cause the formation of LiOH as expressed by following equation.

$$H_2O\,(g) + 2Li \rightarrow LiOH\,(sl) + LiH\,(sl) \qquad (1).$$

This reaction indicated the formation of LiOH and lithium hydride (LiH). The results of TPD analysis indicated H_2O and CO_2 were not desorbed from the Pb-Li alloys. LiH is not so chemically stable. Therefore, atomic hydrogen could be desorbed according to the chemical decomposition of LiH at higher temperature. LiH could be generated in the fabrication procedure since Pb grains which contained H_2O were used without a baking procedure.

4. Conclusions

The experimental studies on the fabrication of Pb-Li alloy and desorption of non-metal impurities from the alloys were carried out. The alloys having various Li concentrations were fabricated from small grains of Pb and Li. Desorption behavior of various gases dissoved as non-metal impurities in the alloy was investigated by the temperature programmed desorption (TPD) analysis. Pb and Pb-Bi contained H_2O and CO_2, and these chemical compounds were desorbed from the alloys below 700K. Desorption of hydrogen from Pb-17Li was detected. These behaviors were determined by their thermodynamic stability in the alloy. Non-metal impurities in the alloys could be removed by the TPD method.

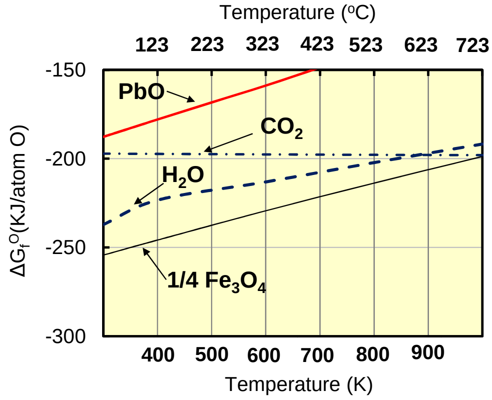

Fig. 3 Standard Gibbs free energy for formation of PbO, CO_2 and H_2O

Table 1 Experimental conditions and results of TPD experiment

ID		Purity (%)	Melting point [K]	Non-metal impurity desorbed from alloys
(a)	Pb	99.9	601	C, O, **CO_2, H_2O,** (N)
(b)	Pb-Bi	-	397	C, **CO_2**, **H_2O,** (N)
(c)	Pb-17Li	Pb: 99.999	508	**H**, O, (N)
(d)	Pb-28Li	Li: 99.999	617	**H**, O, (N)

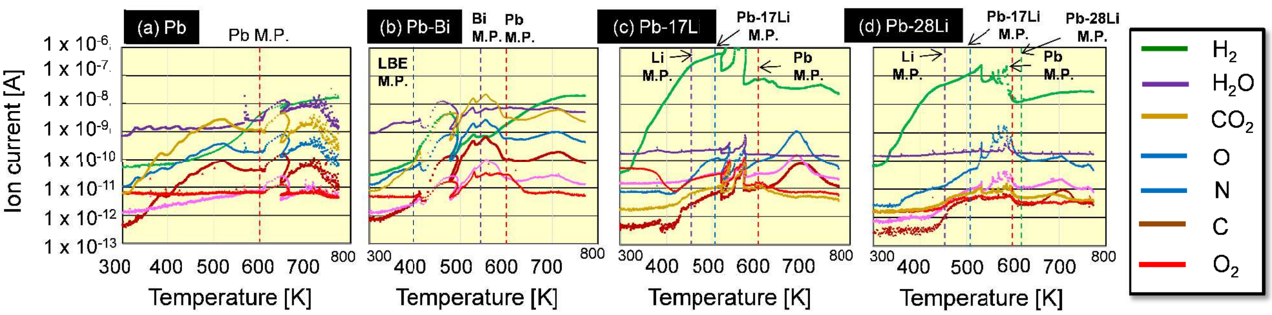

Fig.2 Results of TPD analysis (a) Pb, (b) Pb-Bi, (c) Pb-17Li, (d) Pb-28Li