

Novel Cleaning Methodologies for Specimens Tested in Liquid Metals

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Liquid metals are excellent coolants of fission and fusion reactors. However, the chemical compatibility of structural materials is important issue. The mass losses of the high-temperature materials such as FeCrAl-ODS, SiC, and refractory metals by corrosion in liquid metals are essential information to obtain their corrosion rates. The specimens must be cleaned to remove liquid metals solidified and adhered on the specimens after the corrosion tests, though the damage of the specimens in the cleaning procedure must be minimized. Cleaning methodologies appropriate for the specimens tested in liquid metals are urgently required for further compatibility study. The cleaning methodology with 0.1 M sodium hydroxide (NaOH) solution was developed, in which Sn was selectively dissolved without any damage on the specimens of the high-temperature materials. The cleaning procedure to remove Pb, Bi, and these alloys (i.e., Pb-16Li and Pb-Bi) adhered on the specimens in the solution mixture of acetic acid, ethanol, and H₂O₂ were also studied.

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Liquid tin (Sn) is a candidate coolant of liquid surface divertor concepts [1]. The chemical compatibility of liquid Sn with structural materials is one of the important issues to be addressed. FeCrAl alloys and SiC are the candidate structural and functional materials. Alumina (Al₂O₃) protective layers formed on the surface of FeCrAl alloys were effective to mitigate the corrosion in liquid Sn [2]. US/Japan joint research project FRONTIER has started [3], and the corrosion resistance of FeCrAl alloys and other materials in liquid Sn under neutron irradiation is going to be studied.

The corrosion rate is one of the essential parameters not only for the investigations on corrosion behaviors but also for the design of liquid divertor systems. The corrosion rate can be obtained from the mass loss of the specimen due to its corrosion in the liquid metals. The corrosion tests of Mo and W were performed in liquid Sn, and the adherence of Sn on their specimens was removed by the cleaning process using liquid lithium (Li) [4]. However, this cleaning method cannot be applied for SiC and FeCrAl alloys protected by Al₂O₃ layer, since they are thermodynamically unstable and chemically corroded and damaged in liquid Li [5]. Liquid lithium lead alloy (Pb-16Li) is a promising liquid breeder of fusion reactors. Lead (Pb) and

Lead bismuth eutectic (Pb-Bi) are considered as a coolant of Generation four (GIF) fast reactors (FRs). The specimens tested in liquid Pb alloys were cleaned with the solution mixture of acetic acid, ethanol, and H₂O₂ solution (1 : 1 : 1) in the previous studies [6, 7]. However, the effect of the solution on the SiC and FeCrAl alloys has to be clarified.

Appropriate cleaning methodologies for the specimen tested in liquid metals are urgently required. The purpose of the present study is to develop the cleaning methodologies for further liquid metal compatibility studies.

Dissolving behaviors of solidified liquid metals (i.e., Sn, Pb, Bi, Pb-16Li, and Pb-Bi) in chemical solutions were investigated by means of dissolution tests. The solidified Sn specimen was immersed in 0.1 M NaOH solution (160 cc) at 60 °C. The specimens of high-temperature materials (i.e., Kanthal APMT (Fe-21Cr-5Al-3Mo), NF12 (Oxide dispersion strengthened alloys alloy (ODS), Fe-12Cr-6Al-0.4Zr-0.47Y₂O₃-0.24Ex.O), 430 (Fe-18Cr), and CVD-SiC (fabricated by Rohm&Haas Co, Purity: 99.9995% [8])) were also separately tested. The specimen size of solidified liquid metals were approximately $\phi 20 \times 2$ mm, that of APMT and SiC were 10 mm \times 15 mm \times 2 mm, and that of NF12 was 6 mm \times 17 mm \times 1 mm. The specimens of APMT and NF12 were pre-

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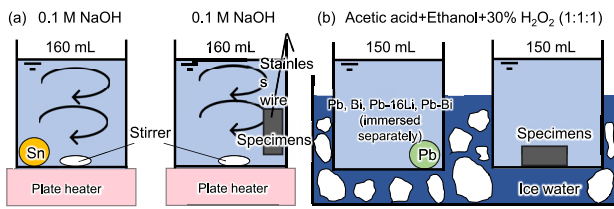


Fig. 1 (a) Immersion of Sn and high temperature materials in 0.1 M NaOH solution, (b) Immersion of Pb alloys in the solution of mixture of acetic acid, ethanol, and 30% H₂O₂ (1 : 1 : 1).

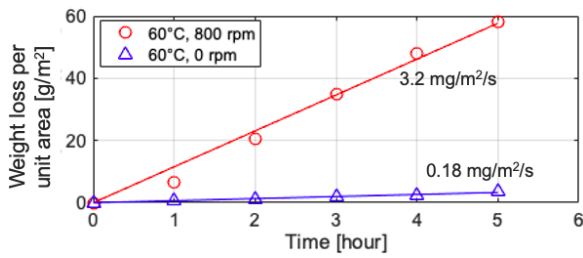


Fig. 2 Dissolution of Sn in 0.1 M NaOH at static and mixing flow conditions.

oxidized at 1000 °C for 10 hours before the immersion, and their surface were covered by α -Al₂O₃ oxide layer. The temperature of the solution was kept at 333 K using a plate heater. The dissolution tests were performed at a static and a mixing flow condition. The mixing flow was made by a rotating magnetic stirrer with the rotational speed of 800 rpm as shown in Fig. 1 (a). The specimens were taken out from the solution after the tests, and cleaned with ethanol. The mass losses of the Sn specimen in the solution are summarized in Fig. 2. Sn dissolved in the alkali solution and its rate was $1.8 \times 10^{-4} \text{ g/m}^2/\text{s}$ (0.090 $\mu\text{m}/\text{h}$) in the static condition. The dissolution rate of Sn in the mixing flow (800 rpm) was $0.0032 \text{ g/m}^2/\text{s}$ (1.57 $\mu\text{m}/\text{h}$). The dissolution of Sn in the solution is expressed as [9],



Oxygen in air atmosphere dissolved into the solution mixture, and might contribute the chemical reaction in Eq. (1). Finally, HSnO_2^- was dissolved in the solution. The mass losses of the APMT, NF12, and SiC specimens by the immersion to the solution for 6 hours were in the range between 0.27 g/m² and -1.08 g/m² (mass gain). These values were negligibly small rather than the mass losses of the specimens by the corrosion in liquid Sn [10].

Figure 3 shows the cleaning procedures of the 430 specimen immersed in liquid Sn at 773 k for 250 hours. Solid Sn adhered on the specimen dissolved little by little in the 0.1 M NaOH solution at 333 K and 800 rpm as indicated with solid line in Fig. 3. The dissolution rate of Sn adhered on the 430 specimen was 7.5 mg/m²/s and it was larger than that obtained for the solidified Sn specimen

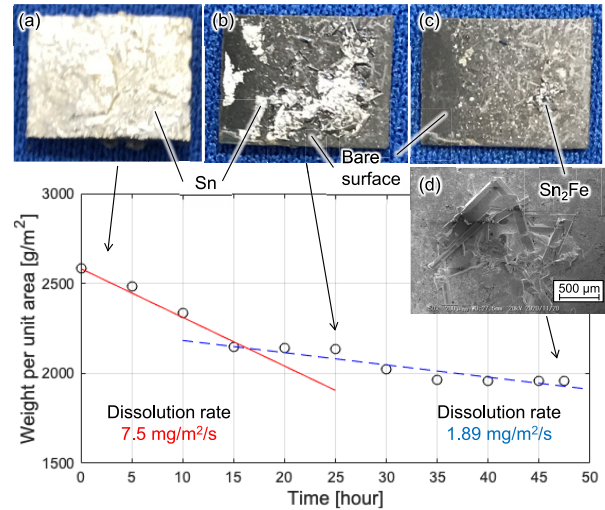
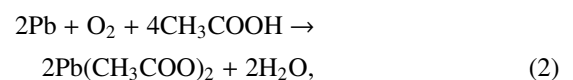


Fig. 3 Cleaning process of 430 specimen in 0.1 M NaOH solution at 333 K and 800 rpm, (a) after test in liquid Sn at 773 K for 250 hours, (b) after immersion in solution for 25 hours, (c) after immersion in solution 50 hours, and (d) SEM image of Sn₂Fe needle-like substance on specimen surface.

described above (3.2 mg/m²/s). The dissolution of Sn adhered on the 430 specimen was promoted due to its rough and large surface area. The intermetallic compounds of FeSn and FeSn₂ [9] formed on the specimen surface. The dissolution rate of these compounds was lower than that of pure Sn as indicated by dotted line in Fig. 3. The specimen was totally cleaned in two days, though few needle-like substances of FeSn₂ remained on the specimen. The thickness of solid Sn adhered on steels after the corrosion tests is typically 50 μm , though the adherence on the high temperature materials are much less than that on the steels. Therefore, the cleaning of specimens can be completed within a few days.

Figure 1 (b) shows the experimental set up for the dissolution tests with the specimens of Pb alloys and the composition elements in the solution of mixture of acetic acid, ethanol, and 30% H₂O₂ (1 : 1 : 1). This solution has been used to dissolve Pb-16Li [6] and Pb-Bi [7] adhered on the specimens. The solution was installed in an ice water bath. The test duration was in the range between 5 and 20 minutes. The temperature of the tests with Pb-Bi and Bi samples was 5 °C. The solution temperature in the tests performed with of Pb, Sn, and Pb-17Li specimens was 15 °C because of the heat generation of the chemical reactions. The specimens were taken out from the solution and cleaned with ethanol.

Figure 4 shows the mass losses of Pb, Bi, Sn, Pb-16Li, and Pb-Bi in the solution. In this acetic acid mixture solution, Pb and Bi dissolved as,



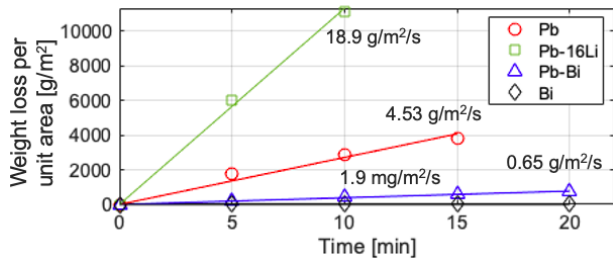
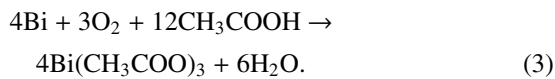


Fig. 4 Mass loss of Pb, Pb-16Li, Pb-Bi, and Bi in acetic acid mixture solution.



The dissolution rate of Pb, Pb-16Li, Pb-Bi, and Bi

were 4.53 g/m²s (1437 μm/hr), 18.9 g/m²s (6670 μm/hr), 0.65 g/m²s (230 μm/hr), and 0.0019 g/m²s (0.69 μm/hr), respectively. Sn did not dissolve in the mixture solution. The mass losses of the APMT, NF12, and SiC specimens by the immersion to the solution were negligibly small.

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