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Corrosion studies in liquid Pb–Bi alloy at JAERI: R & D program and first experimental results

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Abstract

The program of corrosion study in liquid Pb–Bi at Japan Atomic Energy Research Institute (JAERI) is described. It was planned to clarify effects of parameters such as temperature, temperature difference between high-temperature and low-temperature parts, oxygen concentration in liquid Pb–Bi, flow rate, irradiation, stress and chemical composition of materials. The program contains the basic corrosion study in static Pb–Bi for elucidation of corrosion mechanism and effects of oxygen concentration in liquid Pb–Bi and ion irradiation on corrosion behavior. It also contains the corrosion study in flowing Pb–Bi using a corrosion testing loop. From the initial result of the static corrosion tests in oxygen saturated Pb–Bi at 550 °C for 500 h, it was shown that the thickness of the corrosion film decreases with increasing Cr content in steels. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Research and development for an accelerator driven system (ADS) have been carried out widely because it has possibility to transmute minor actinides and long-lived fission products in nuclear spent fuel [1–3]. In this system, liquid Pb alloys would be used as spallation targets and coolants.

Liquid Pb–Bi or Pb has been studied in the United States and Europe as nuclear reactor coolants and liquid metal fuel [4–7]. Liquid Pb–Bi and Pb are more corrosive than sodium because the solubility of Ni, Cr and Fe in them is high [5,6]. For this reason, employment of inhibitors such as Zr was proposed to use liquid Pb–Bi as liquid nuclear fuel [6]. However, the study on liquid Pb alloys was discontinued because of suspension of development of liquid metal fuel reactor.

On the other hand, the liquid Pb or Pb–Bi technology has been developed in Russia for nuclear submarine propulsion. In research and development of liquid Pb or Pb–Bi technology, it was made clear that corrosion behavior is controlled by oxygen concentration in liquid Pb alloys [8–10]. On this basis, the importance of controlling oxygen concentration is recognized and some corrosion resistant alloys in liquid Pb alloys have been developed [8,10].

Recently, liquid Pb alloys have attracted special interest as spallation targets and coolants of ADS on account of their excellent properties such as good neutron yield, low melting points, low vapor pressures and compatibility with water and air [1–3,11–13]. Since liquid Pb alloys are corrosive as described above, corrosion study in liquid Pb alloys has been carried out actively focussing development of ADS [14–16].

Corrosion tests using a liquid metal loop are necessary to estimate corrosion behavior in liquid Pb alloys since erosion and mass transfer caused by solution at high-temperature parts and precipitation at low-temperature parts are involved. However, static corrosion tests are useful to investigate corrosion properties and modes of various kinds of materials and to develop corrosion resistant materials in liquid Pb alloys [14–16]. In addition, it is essential to estimate effects of irradiation of high-energy protons and neutrons for beam

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window materials when liquid Pb alloys are used as spallation targets and coolants of ADS.

In this paper, the outline of a corrosion test program in liquid Pb–Bi at JAERI is firstly described focussing static corrosion tests, effects of oxygen concentration in liquid Pb–Bi, estimation of irradiation effects on corrosion resistance and loop tests. Furthermore, the initial result of static corrosion tests and the present status of loop tests are reported.

2. Outline of R & D plan

Liquid Pb–Bi was chosen at JAERI as spallation target/coolant from several reasons one of which was that low operation temperature would be possible because of its low melting point (125 °C). However, Pb–Bi is more corrosive than Pb because the solubility of Ni and Cr is high in liquid Pb–Bi. Therefore, corrosion tests in static Pb–Bi and tests using a Pb–Bi loop are carried out.

2.1. Corrosion in static Pb–Bi

Corrosion in liquid Pb alloys is principally caused by high solubility of main alloying elements [5,6]. However, the protective oxide film formed on metal surface in liquid Pb alloys prevent from leaching of alloy components according to experiences in Russia [8–10] and recent experimental results [14–16]. Therefore, the solubility of alloying elements is not the only key parameter to control corrosion in liquid Pb alloys [8,14,15]. Corrosion behavior in liquid Pb alloys is not fully understood because many parameters such as oxygen concentration, temperature and various alloying elements influence it. It is essential to carry out the well-designed experiment using the apparatus with care of controlling oxygen concentration in order to clarify effects of these parameters on corrosion behavior.

Fig. 1 shows oxygen potential with PbO, Fe_3O_4, Cr_2O_3 and so on. According to experimental results of IPPE in Russia [8–10], recommendation for corrosion resistance in liquid Pb–Bi is the condition of oxygen potential where Fe_3O_4 forms without PbO precipitation:

$$0.5\Delta G^0\ (\mathrm{Fe_3O_4}) < RT\ln P_{\mathrm{O_2}} < 2\Delta G^0\ (\mathrm{PbO}), \tag{1}$$

where ΔG^0 is the Gibbs energy for formation of oxides [17], $P_{\mathrm{O_2}}$ oxygen partial pressure, R gas constant and T absolute temperature. Oxygen partial pressure for PbO formation is about 2×10^{-19} (MPa) at 550 °C and that for Fe_3O_4 is about 3.5×10^{-28} (MPa) at 550 °C. This low oxygen partial pressure can be obtained by using the constant ratio of H_2/H_2O.

$$\mathrm{H_2} + 1/2\mathrm{O_2} = \mathrm{H_2O}, \tag{2}$$

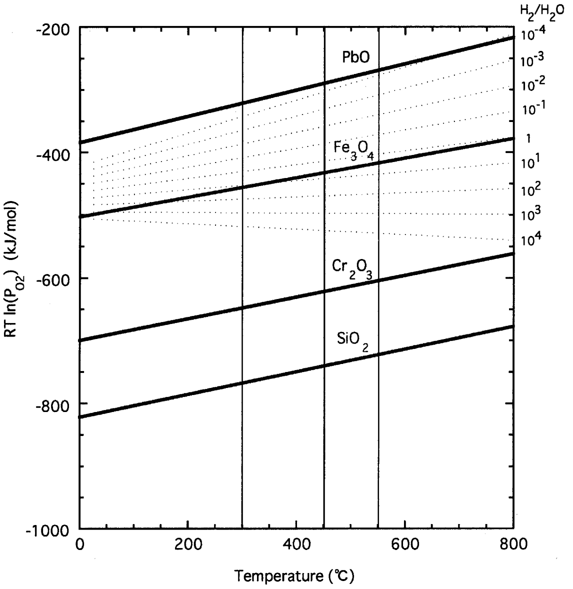


Fig. 1. Oxygen potential diagram of PbO, Fe_3O_4 and other oxides as a function of temperature. Dotted lines of constant H_2/H_2O ratio are also drawn.

$$P_{\mathrm{O_2}} = \frac{P_{\mathrm{H_2O}}^2}{P_{\mathrm{H_2}}^2} \exp\frac{2\Delta G^0(\mathrm{H_2O})}{RT}, \tag{3}$$

where $P_{\mathrm{H_2O}}$ and $P_{\mathrm{H_2}}$ are partial pressure of H_2O and H_2, respectively. Lines of the constant H_2/H_2O are also drawn in Fig. 1. When we choose a H_2/H_2O ratio of 0.1, we can get the condition of Fe_3O_4 formation without PbO precipitation. When we choose a H_2/H_2O ratio of 100, neither PbO nor Fe_3O_4 will be formed. Dissolution of oxygen in liquid Pb alloys follows Siverts' law.

$$C_{\mathrm{O}} = K(P_{\mathrm{O_2}})^{1/2}, \tag{4}$$

where C_{O} is oxygen concentration in liquid Pb alloys and K is the Siverts' constant. Solubility of oxygen in liquid Pb–Bi is expressed by the following equation [9].

$$\log C_{\mathrm{S}} = 1.2\text{–}3400/T \tag{5}$$

where C_{S} is saturation oxygen concentration (mass%). Saturation oxygen concentration in liquid Pb–Bi is about 1.2×10^{-3} mass% at 550 °C.

A schematic diagram of the static corrosion equipment in Pb–Bi is shown in Fig. 2. The retort contacting molten Pb–Bi is made of quartz. The specimens are pulled out from the molten Pb–Bi when the experiment is completed. Purging gas of a constant H_2/H_2O ratio is a good methodology to control oxygen concentration in liquid Pb–Bi. The test temperature will range between 350 °C and 600 °C. Development of an oxygen sensor used in liquid Pb alloys is also an important research item. Tests of oxygen sensors will be performed using

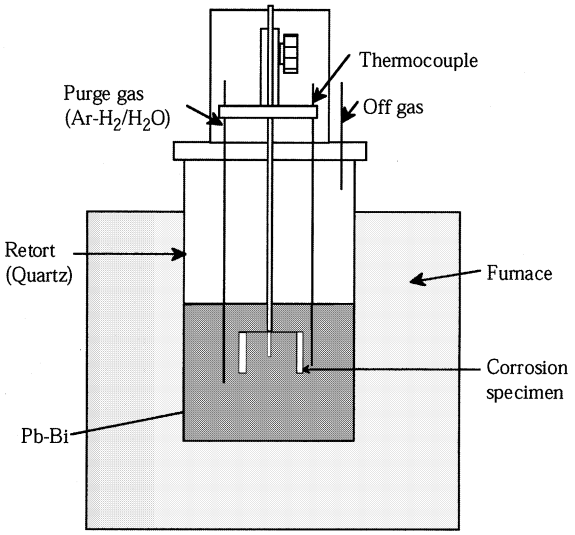


Fig. 2. Schematic diagram of the static corrosion equipment in liquid Pb–Bi.

the static corrosion equipment. At present, tests are planned for an oxygen sensor using ZrO_2 stabilized by Y_2O_3 as a solid electrolyte and Pt/air as a reference system. Oxygen sensors operating at lower temperatures will be developed.

Table 1 shows chemical composition of tested materials. Effects of Cr and Ni contents in steels on corrosion in liquid Pb–Bi are studied using 2.25Cr–1Mo steel, F82H, Mod.9Cr–1Mo steel, austenitic stainless steel, JPCA (14Cr–16Ni–2Mo), 410ss 430ss and pure iron. The F82H is a reduced activation martensitic steel developed for nuclear fusion reactor and the JPCA is also an austenitic stainless steel developed for nuclear fusion application in Japan. Tests of coating materials will be carried out because surface treated steels after alloying Al had excellent corrosion resistance in liquid Pb [14,15]. The size of corrosion specimens was 15 mm × 30 mm× 2 mm.

Furthermore, effects of irradiation on corrosion will be investigated using Takasaki ion accelerators for advanced radiation application (TIARA) apparatus at JAERI. Radiation damages in austenitic stainless steels for a high power spallation source have been studied using triple ion beam irradiation technique [18]. Fig. 3 shows a schematic diagram showing our procedure to study the irradiation effect on corrosion using ion irradiation. Displacement damage can be obtained by irradiation of Ni^{3+} or Fe^{2+}. Ions of He^{+} and H^{+} can be simultaneously implanted. The following ion irradiation is planned: An Fe^{2+} dose of 15 dpa will be used with or without injected helium of 1500 appm and hydrogen of 10 000 appm. Property change of surface films by ion irradiation and corrosion will be studied using indentation techniques [19].

2.2. Corrosion in flowing Pb–Bi

A liquid Pb–Bi loop is necessary to perform corrosion tests in flowing Pb–Bi and to investigate mass transfer and effects of flow rate on corrosion behavior. Fig. 4 shows a flow diagram of the Pb–Bi loop for materials test. This loop has a simple structure consisting of electromagnetic pump, heater, test section, cooler, expansion tank, electromagnetic flow meter, dump tank etc. Maximum temperature is 450 °C. Fluid volume is 0.015 m^3 and velocity at the test section is 1 m/s. Tube type test specimens are used at present. Higher velocity is possible by employing different size and shape of test pieces. Objectives of the liquid Pb–Bi loop are the following: estimation of corrosion property of candidate materials for a beam window in flowing liquid Pb–Bi and establishment of liquid Pb–Bi technology including oxygen control system and flow measurement. Oxygen sensors will be placed into the material testing Pb–Bi loop. Materials showing good corrosion resistance in stagnant corrosion tests will be tested in the Pb–Bi loop.

3. Experimental results and discussion

3.1. Results of corrosion in static Pb–Bi

Initially the static corrosion test was performed in oxygen saturated Pb–Bi at 550 °C for 500 h for mate-

Table 1
Chemical composition of materials tested in the static corrosion experiment (mass%)

	C	Si	Mn	Cr	Ni	Mo	Fe	V	N	W	Ti	Al
F82H	0.095	0.10	0.01	7.72	<0.02	<0.01	Balance	0.18	0.010	1.95	0.005	<0.001
Mod.9Cr–1Mo steel	0.10	0.30	0.40	8.41	0.06	0.88	Balance	0.20	0.047	<0.0005	<0.01	0.033
14Cr–16Ni–2Mo (JPCA)	0.058	0.50	1.54	14.14	15.87	2.29	Balance	0.03	0.003	0.010	0.22	0.012
410ss	0.067	0.31	0.80	12.21	0.12	0.02	Balance	0.07	0.013	–	<0.01	0.002
430ss	0.080	0.52	0.23	16.24	0.15	0.02	Balance	0.10	0.024	–	<0.01	0.007
2.25Cr–1Mo steel	0.10	0.34	0.44	2.18	0.02	0.92	Balance	0.01	0.009	–	<0.01	0.002
Fe	0.002	–	–	–	–	–	Balance	–	0.001	–	–	–
Mo	0.014	–	–	–	–	Balance	–	–	–	0.016	–	–

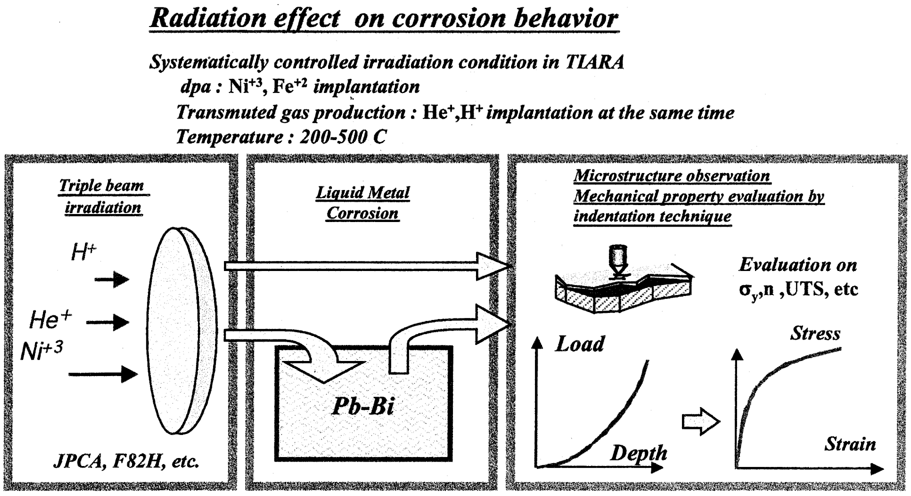


Fig. 3. Schematic diagram showing procedure to study radiation effect on corrosion behavior.

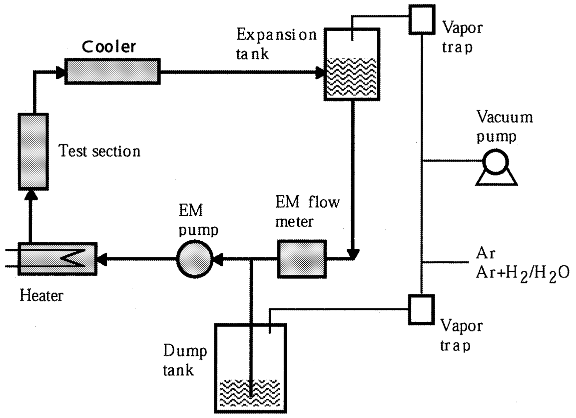
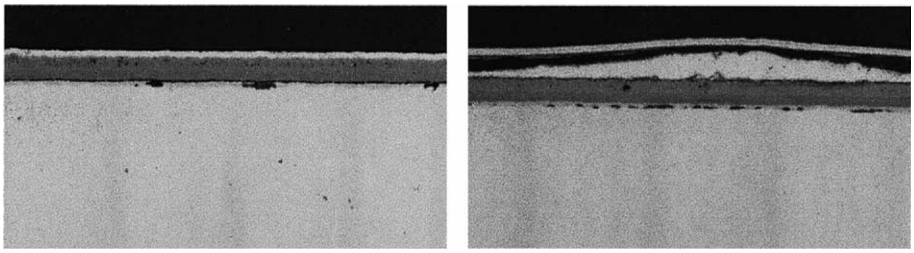


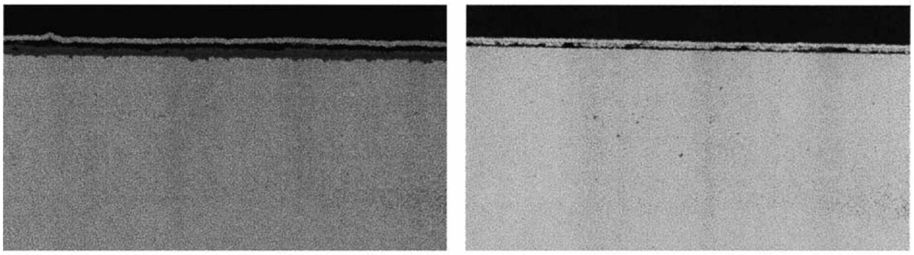
Fig. 4. Flow diagram of material testing Pb–Bi loop.

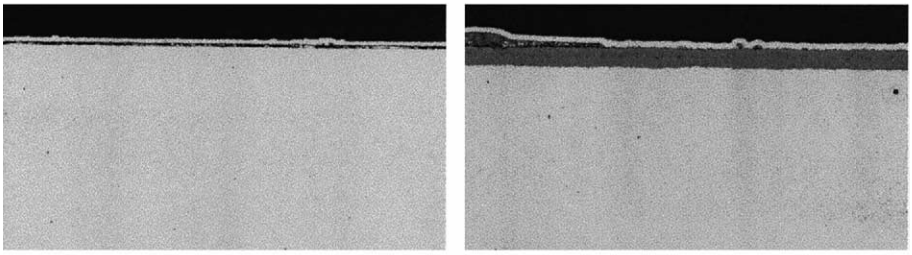
rials shown in Table 1. In this experiment, Ar gas containing several percentage of O_2 was used as cover gas over liquid Pb–Bi. PbO with about 1 mm thickness formed on the surface of the molten Pb–Bi during the corrosion test. Test specimens were pulled out from the molten Pb–Bi and cooled in the cover gas. Although test specimens were washed in silicon oil at about 170 °C, adherent Pb–Bi could not be removed from the specimen surface completely.

The cross-section of the tested specimen was observed using optical microscope, laser microscope and EPMA after cutting corrosion specimens. Fig. 5 shows optical micrographs of the cross-section of materials after corrosion in oxygen saturated Pb–Bi at 550 °C for 500 h. Nickel was plated on the specimen surface to protect corrosion films. The lead–bismuth stuck to the specimen surface during pulling out from the molten Pb–Bi was found in several samples (Fig. 5(b), (d), (f) etc.). Thickness of the corrosion film changes depending on materials. The corrosion film of pure iron is the thickest as shown in Fig. 5(g). The corrosion film of F82H, Mod9.Cr–1Mo steel and 2.25Cr–1Mo steel is thicker than that of austenitic stainless steel, JPCA. Type 410ss, type 430ss and Mo have thin corrosion films. Pores are observed beneath the corrosion film in Fig. 5(a) and (b). It is also observed that corrosion proceeds along grain boundaries in JPCA as shown in Fig. 5(c). Fig. 6 shows the relationship between thickness of corrosion film and Cr content in steels. From this figure, there seem to be four groups of steels which have different corrosion properties in oxygen saturated Pb–Bi at 550 °C: pure iron with the thickest corrosion film, steels containing 2.25–9%Cr with about 20 μm thickness corrosion film, JPCA and martensitic/ferritic stainless steel containing 14–16%Cr with very thin corrosion film.

Fig. 7 shows the result of EPMA observation of the cross-section of F82H specimen immersed in oxygen saturated Pb–Bi at 550 °C for 500 h. There are three zones formed by corrosion. Outer corrosion film consists of magnetite without appreciable Cr. Inner corrosion film is considered to be Cr–Fe spinel. In addition, aggregates of pores are observed beneath the inner corrosion film. The result of EPMA observation of the cross-section of JPCA specimen is shown in Fig. 8. Corrosion films of the JPCA are also composed of the outer magnetite and the inner Fe–Cr spinel. High concentration of Ni is observed in the Fe–Cr spinel. Furthermore, Pb is found in the magnetite formed on JPCA. As shown in Fig. 6, thickness of the corrosion film decreases with increasing Cr content in steel. From the EPMA analysis, it is considered that the inner Cr–Fe spinel lowers the growth rate of the oxide film. However, it was also reported that the corrosion rate increased in liquid Pb at 600 °C with increasing Cr content in the


(a) F82H (b) Mod.9Cr-1Mo steel


(c) JPCA(14Cr-16Ni-2Mo) (d) 410ss


(e) 430ss (f) 2.25Cr-1Mo steel

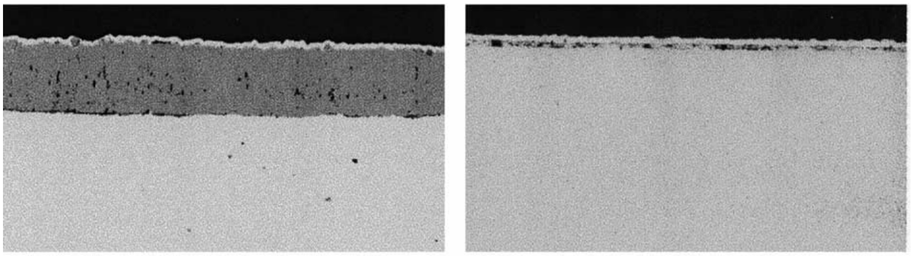

(g) Fe (h) Mo

Fig. 5. Optical micrographs of the cross-section of (a) F82H, (b) Mod.9Cr–1Mo steel, (c) JPCA(14Cr–16Ni–2Mo), (d) 410ss, (e) 430ss, (f) 2.25Cr–1Mo steel, (g) Fe and (h) Mo. The corrosion test was carried out in oxygen saturated Pb–Bi at 550 °C for 500 h.

alloy [20]. Tests with much longer immersion times in liquid Pb–Bi and loop tests will be necessary to confirm the role of Fe–Cr spinel.

3.2. Present status of corrosion tests in flowing Pb–Bi

The corrosion test using the Pb–Bi loop was performed under the condition of 450 °C at high-temperature parts and 400 °C at low-temperature parts. The test section was a tube with inner diameter of 9.8 mm and outer diameter of 13.8 mm, and made of type 316ss. Before starting the corrosion test, the Pb–Bi loop was fully evacuated and degassed. High purity Ar (99.995% purity) was used as the cover gas in a expansion tank and a dump tank. According to observation from a view-port, it was found that a little oxidation occurred on the surface of molten Pb–Bi of the expansion tank. Velocity of liquid Pb–Bi at test section was 1 m/s. Initially the electromagnetic flow meter was calibrated. We measured the output of the electromagnetic flow meter

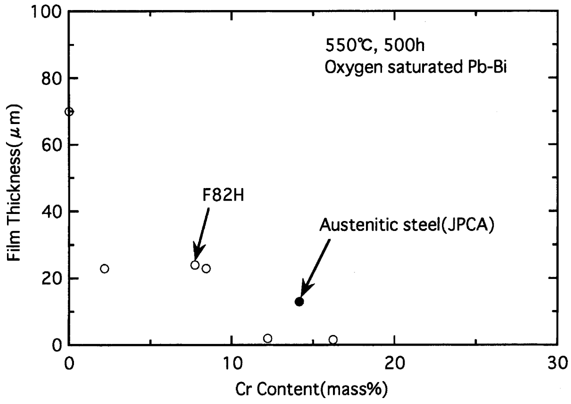


Fig. 6. Relationship between thickness of the corrosion film and Cr content in steels. The corrosion test was carried out in oxygen saturated Pb–Bi at 550 °C for 500 h.

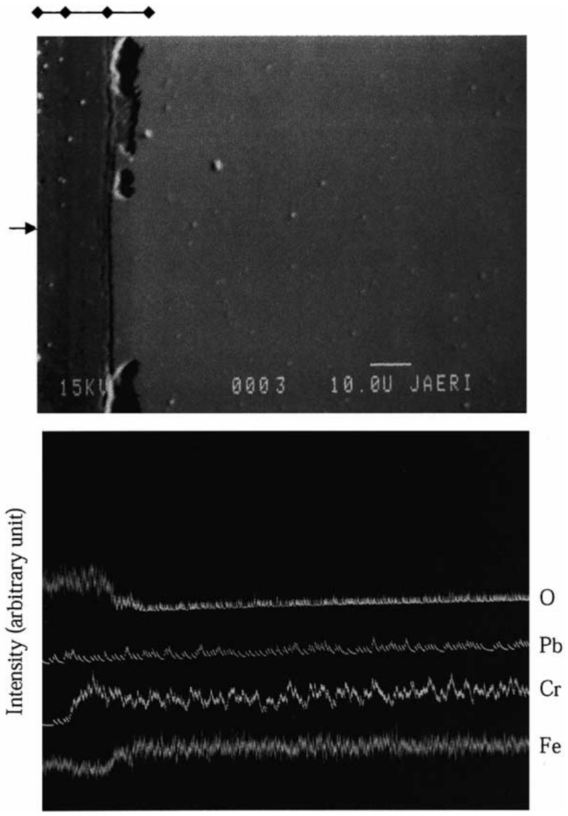


Fig. 7. EPMA of the cross-section of F82H specimen. The corrosion test was carried out in oxygen saturated Pb–Bi at 550 °C for 500 h. Line analysis was performed at the arrow position.

and time required for flow of constant quantity of liquid Pb–Bi in the expansion tank down to the damp tank. As shown in Fig. 9, a linear relationship between the output and actual flow rate of liquid Pb–Bi was obtained. The corrosion test in the Pb–Bi loop will be continued until 3000 h. After the corrosion test up to 3000 h, we will carry out the inspection of the test section, electromagnetic flow meter and electromagnetic pump.

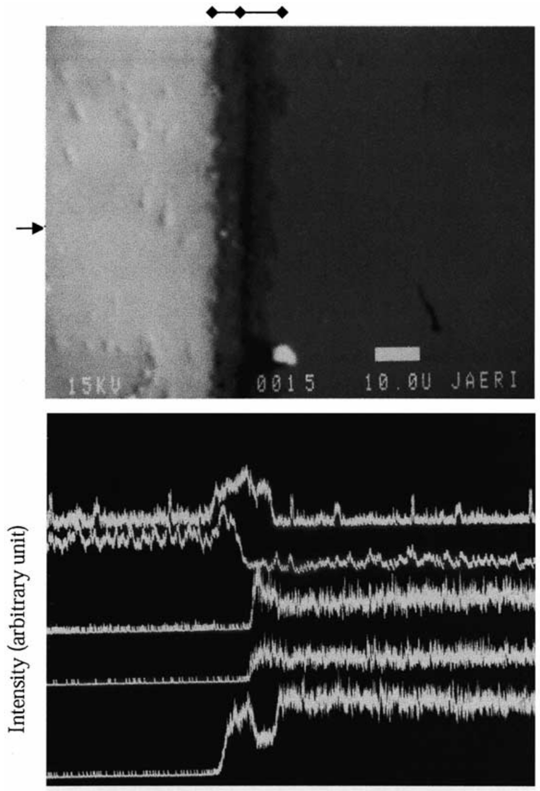


Fig. 8. EPMA of the cross-section of JPCA(14Cr–16Ni–2Mo) specimen. The corrosion test was carried out in oxygen saturated Pb–Bi at 550 °C for 500 h. Line analysis was performed at the arrow position.

4. Concluding remarks

Corrosion in liquid lead alloys as well as irradiation under a spallation condition are important issues for development of ADS. Since corrosion behavior in liquid Pb–Bi alloy is influenced by temperature, temperature difference between hot and cold parts, oxygen concentration in liquid Pb–Bi alloy, flow rate, irradiation, stress and chemical composition of materials, a research and development program was planned to clarify effects of these parameters on corrosion behavior. This program contains the basic corrosion study in static Pb–Bi and the corrosion study in flowing Pb–Bi.

In the study in static Pb–Bi, corrosion tests are performed using 2.25Cr–1Mo steel, Mod.9Cr–1Mo steel, JPCA(14Cr–16Ni–2Mo), type 410ss, type 430ss, pure

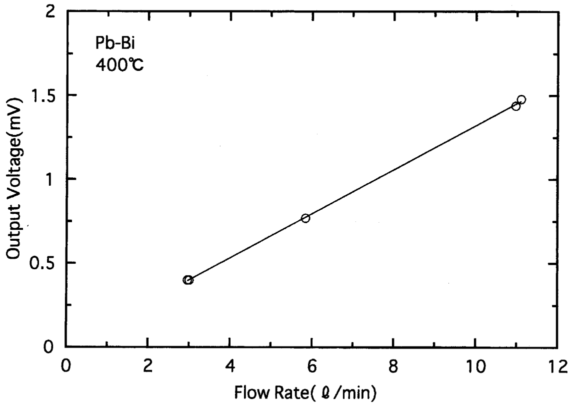


Fig. 9. Relationship between flow rate of liquid Pb–Bi and output of the electromagnetic flow meter. The temperature of liquid Pb–Bi was 400 °C.

metals and coated alloys for elucidation of corrosion mechanism. Effects of alloying elements, oxygen concentration in Pb–Bi and radiation using ion irradiation will be studied. From the initial results of the static corrosion test in oxygen saturated Pb–Bi at 550 °C for 500 h, it was shown that the thickness of corrosion films decreases with increasing Cr content in steels. A Pb–Bi loop was constructed to carry out the corrosion test in flowing Pb–Bi. Purposes of the Pb–Bi loop are the estimation of corrosion property of candidate materials of a beam window and the establishment of liquid Pb–Bi technology. The corrosion test up to 3000 h is being continued using the Pb–Bi loop at present. It is essential to conduct tests with longer immersion times and loop tests in order to estimate corrosion property in liquid Pb–Bi for materials of ADS.

References

[1] C. Rubbia, J.A. Rubio, S. Buono, F. Carminati, Conceptual design of a fast neutron operated high power energy amplifier, CERN/AT/95-44(ET), 29 September, 1995.

[2] T. Mukaiyama, T. Takizuka, M. Mizumoto, Y. Ikeda, T. Ogawa, A. Hasegawa, H. Takada, H. Takano, Prog. Nucl. Energy 38 (2001) 107.

[3] DOE, A Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology DOE/RW-0519, October 1999.

[4] A.J. Romano, C.J Klamut, D.H. Gurinsky, BNL 811 (T-303) (1963).

[5] J.R. Weeks, A.J. Romano, Corrosion 25 (1969) 131.

[6] J.R. Weeks, Nucl. Eng. Design 15 (1971) 363.

[7] J.A. James, J. Trotman, J. Iron Steel Inst. 194 (1960) 319.

[8] I.V. Gorynin, G.P. Karzov, V.G. Markov, V.S. Lavrukihin, V.A. Yakovlev, Proceedings of Heavy Liquid Metal Coolants in Nuclear Technology, HLMC'98, 5–9 October 1998, Obninsk, Russia, 1999, p. 120.

[9] B.F. Gromov, Y.I. Orlov, P.N. Martynov, V.A. Gulevsky, Proceedings of Heavy Liquid Metal Coolants in Nuclear Technology, HLMC'98, 5–9 October 1998, Obninsk, Russia, 1999, p. 87.

[10] G.S. Yachmenyov, A.Ye. Rusanov, B.F. Gromov, Yu.S. Belomytsev, N.S. Skvortsov, A.P. Demishonkov, Proceedings of Heavy Liquid Metal Coolants in Nuclear Technology, HLMC'98, 5–9 October 1998, Obninsk, Russia, 1999, p. 133.

[11] M. Salvatores, G.S. Bauer, G. Heusener, The MEGAPIE Initiative—Executive Outline and Status per November 1999, internal document MPO-1-GB-6/0_GB, PSI, CEA and FZK, 1999.

[12] T. Takizuka, K. Tsujimoto, T. Sasa, H. Takano, K. Hirota, Y. Kamishima, Proceedings of Heavy Liquid Metal Coolants in Nuclear Technology, HLMC'98, 5–9 October 1998, Obninsk, Russia, 1999, p. 143.

[13] J.U. Knebel, X. Cheng, G. Mueller, G. Schumacher, J. Konys, H. Glasbrenner, Proceedings of Third International Topical Meeting on Nuclear Applications of Accelerator Technology AccApp'99, 14–18 November, Long Beach, CA, USA, 1999, p. 367.

[14] G. Mueller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.

[15] G. Benamati, P. Buttol, V. Imbeni, C. Martini, G. Palombarini, J. Nucl. Mater. 279 (2000) 308.

[16] Ed.J. Konys, Minutes of the Workshop on Heavy Liquid Metal Technology, 16–17 September, Karlsruhe, Germany, 1999.

[17] O. Kubaschewski, C.B. Alock, P.J. Spencer, Materials Thermochemistry, 6th Ed., Pergamon, Oxford, 1993.

[18] E.H. Lee, G.R. Rao, J.D. Hunn, P.M. Rice, M.B. Lewis, S.W. Cook, K. Farrel, L.K. Mansur, in: M.S. Wechsler (Ed.), Proceedings of the TMS Symposium On Materials for Spallation Neutron Sources, Orlando, FL, February 1997, p. 57.

[19] M. Futakawa, T. Wakui, I. Ioka, M. Eto, J. Eur. Ceram. Soc. 20 (2000) 1135.

[20] H.G. Glasbrenner, J. Konys, Z. Voß, O. Wedemeyer, Minutes of the Workshop on Heavy Liquid Metal Technology, 16–17 September, Karlsruhe, Germany, 1999, p. 43.