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Letter to the Editors

Excellent corrosion resistance of 18Cr–20Ni–5Si steel in liquid Pb–Bi

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Abstract

The corrosion properties of three austenitic steels with different Si contents were studied under oxygen-saturated liquid Pb–Bi condition for 3000 h. The three austenitic steels did not exhibit appreciable dissolution of Ni and Cr at 450 °C. At 550 °C, the thick ferrite layer produced by dissolution of Ni and Cr was found in JPCA and 316SS with low Si contents while the protective oxide film composed of Si and O was formed on 18Cr–20Ni–5Si steel and prevented dissolution of Ni and Cr.

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1. Introduction

Development of the accelerator driven system (ADS) for the purpose of treatment of nuclear wastes has been conducted vigorously in recent years [1,2]. The ADS is a very attractive system which enables us to incinerate long-life nuclear wastes such as minor actinides by combining a proton accelerator, spallation target and subcritical core. Liquid Pb–Bi eutectic is a potential candidate of the target and coolant. Although liquid Pb–Bi eutectic has the advantage of low melting point, low vapor pressure, good neutron yield, low neutron absorption and good heat removal, corrosion of structural materials is concerned due to high solubility [3,4] of main elements of structural materials in liquid Pb–Bi. Therefore, corrosion tests in liquid Pb–Bi have been actively performed recently [5–13]. According to the previous Russian studies [5,6], importance of oxygen control in liquid Pb–Bi was pointed out and development of martensitic steels containing Si was introduced from the viewpoint of formation of suitable protective oxide layers on steel surface against corrosion in Pb alloys.

The following phenomenon was often reported: ferritization of the austenitic steels owing to Ni dissolution caused by high solubility of Ni in liquid Pb–Bi [9,13]. Benamati et al. [9] showed that the ferritization of austenitic stainless steels, AISI 316L and Mannet II occurred during corrosion in a pot under oxygen-saturated Pb–Bi condition at 550 °C. Furthermore, Mueller et al. [13] indicated that AISI 316L exhibited dissolution of Ni and penetration of Pb and Bi into the ferrite layer during a loop test at 600 °C. It was also reported that Russian martensitic steel with 1.8% Si exhibited good corrosion resistance in flowing liquid Pb–Bi [7,9,12]. It is known that Si addition to steels produces SiO_2 layer and increases oxidation resistance drastically in a gas environment [14]. However, the effect and role of Si are not confirmed and understood sufficiently in liquid Pb–Bi environment. While Si addition above 0.7% to Fe–9%Cr steel produced a protective SiO_2 layer at the oxide–metal interface and significant improvement of oxidation

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resistance in a gas environment at 575–650 °C [14], there is a little data in liquid Pb–Bi for this kind of discussion.

The purpose of this study is to examine whether Ni and Cr in austenitic steels with different Si contents dissolve into liquid Pb–Bi at different temperatures and to elucidate whether Si addition to austenitic steels has the effect of preventing ferritization or not.

2. Experimental apparatus and procedure

Materials used in this study are austenitic steels, JPCA (Japan Prime Candidate Alloy), type 316SS and 18Cr–20Ni–5Si steel, SX (Trademark of the Sandvik Corporation), the chemical compositions of which are shown in Table 1. The SX steel is an alloy developed for use in a sulfuric acid environment and the high Si content is characteristic of the steel. The size of corrosion specimens was 15 mm × 30 mm × 2 mm. Corrosion specimens were polished using emery papers up to #600.

The corrosion equipment was described in detail elsewhere [10]. Components contacting liquid Pb–Bi were made of quartz in the corrosion equipment. Fresh eutectic Pb–Bi (45Pb–55Bi) of 7 kg was used in the present test. The Pb–Bi was melted in a pot under Ar gas environment. Ar gas of 99.9999% purity was used as a cover gas over the liquid Pb–Bi. Corrosion tests were conducted at 450 and 550 °C for 3000 h. PbO was formed on the surface of the liquid Pb–Bi and corrosion tests were made in oxygen-saturated liquid Pb–Bi. Oxygen saturation concentration was estimated to be 3.2×10^{-4} wt% at 450 °C and 1.2×10^{-3} wt% at 550 °C using the equation in the literature [3].

Test specimens were cleaned in silicone oil at about 170 °C after the corrosion tests to remove Pb–Bi stuck to the surface of the specimens. However, there was adherent Pb–Bi left on some parts of the specimen surface. Analyses were made using an optical microscope, a SEM (scanning electron microscope) with EDX (energy dispersion X-ray) for the specimen copper-plated to protect corrosion films during polishing. X-ray diffraction was also used to characterize corrosion products.

3. Results and discussion

Fig. 1 shows optical micrograhs of the cross sections of JPCA and SX specimens after corrosion in liquid Pb–Bi. There is a ferrite layer mentioned later near the surface region of JPCA after corrosion at 550 °C for 3000 h (Fig. 1(b)). Formation of the layer is not found in JPCA specimen after corrosion at 450 °C (Fig. 1(a)) and SX specimens after corrosion at 450 °C (Fig. 1(c)) and 550 °C (Fig. 1(d)). Fig. 2 shows SEM images of the cross sections of JPCA and SX specimens after corrosion at 550 °C. There seems to be a corrosion film under the Cu plating and the ferrite layer with thickness of 45 μm is formed under the corrosion film of JPCA (Fig. 2(a)). On the other hand, the ferrite layer is not observed in the SX specimen (Fig. 2(b)).

X-ray diffraction measurements were made on the surface of the tested specimen and EDX analyses were

Table 1
Chemical composition of materials tested (mass%)

	C	Si	Mn	Cr	Ni	Mo	Fe	Ti	Cu
JPCA	0.058	0.50	1.54	14.14	15.87	2.29	balance	0.22	–
316SS	0.04	0.69	1.22	16.83	10.79	2.06	balance	–	–
SX	0.010	4.80	0.60	17.58	19.08	0.356	balance	–	2.14

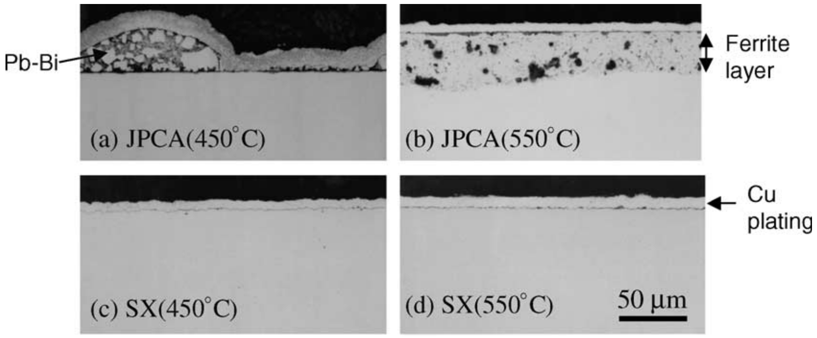

Fig. 1. Optical micrographs of cross sections of (a) JPCA (450 °C), (b) JPCA (550 °C), (c) SX (450 °C) and (d) SX (550 °C) after corrosion in liquid Pb–Bi.

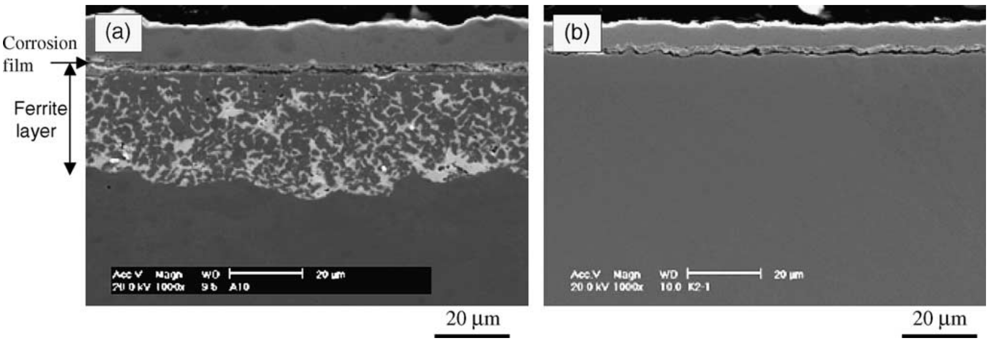

Fig. 2. SEM images of cross sections of (a) JPCA and (b) SX after corrosion at 550 °C in liquid Pb–Bi.

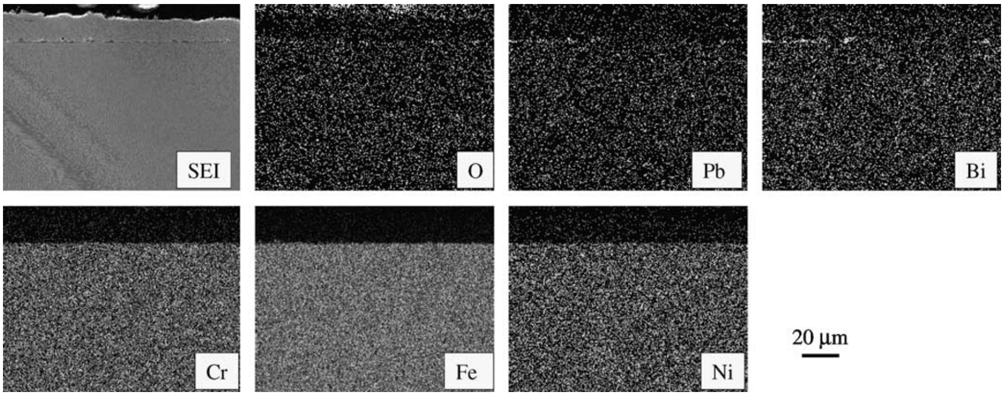

Fig. 3. EDX analysis of the cross section of JPCA specimen after corrosion at 450 °C for 3000 h in liquid Pb–Bi.

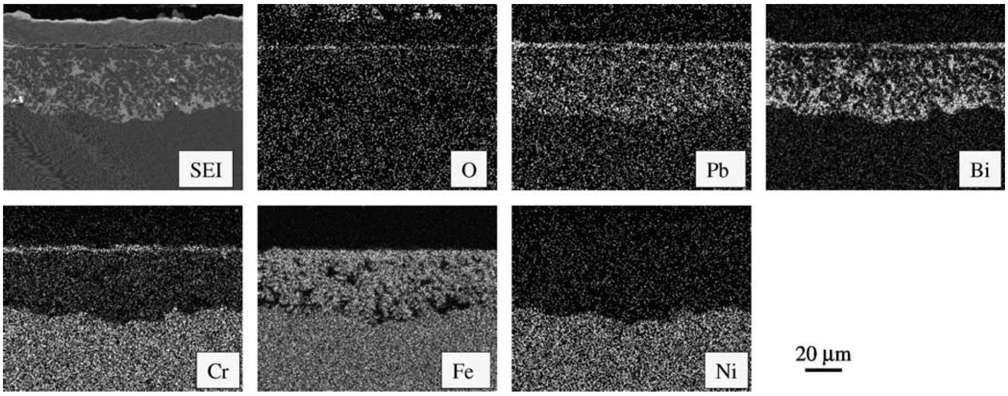

Fig. 4. EDX analysis of the cross section of JPCA specimen after corrosion at 550 °C for 3000 h in liquid Pb–Bi.

made on the cross section to examine corrosion products on the specimen surface after corrosion at 450 and 550 °C. Fig. 3 shows the results of EDX analysis for JPCA specimen after corrosion at 450 °C. Since decrease in Cr, Ni and Fe concentrations is not observed near the surface region, it is considered that appreciable dissolution of these elements has not occurred. Thin oxide films were formed on the surface under oxygen-saturated Pb–Bi condition at 450 °C although it is not clear in Fig. 3. In contrast with the result in Fig. 3, the layer

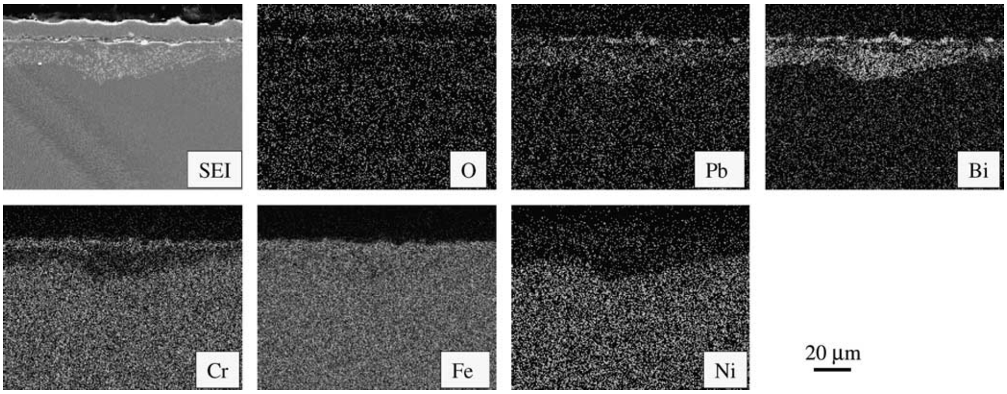

Fig. 5. EDX analysis of the cross section of 316SS specimen after corrosion at 550 °C for 3000 h in liquid Pb–Bi.

with excessive decrease in Ni and Cr is observed in JPCA and 316SS specimens after corrosion at 550 °C as shown in Figs. 4 and 5, respectively. It was confirmed that the layer was a ferrite phase because peaks of Fe–Cr ferrite phase with bcc structure were detected in X-ray diffraction measurements on JPCA and 316SS specimens. Lead and Bismuth penetrate into the ferrite layer as indicated in Figs. 4 and 5. According to EDX analysis and X-ray diffraction results, it was found that the oxide film was formed on JPCA and 316SS specimens under oxygen-saturated Pb–Bi condition at 550 °C. Nickel and Chromium in JPCA and 316SS dissolved into Pb–Bi in spite of the formation of Fe–Cr oxide. There is a question whether the dissolution of Ni and Cr occurred at the early stage before the formation of the oxide film or not. The ferrite layer with penetration of Pb and Bi was not observed in JPCA specimen after corrosion at 550 °C for 500 h in the previous study [10]. Furthermore, the Fe–Cr oxide seems to be porous in Figs. 2(a), 4 and 5. From these results, it is considered that the dissolution of Ni and Cr occurred due to an imperfect performance of the Fe–Cr oxide at 550 °C as a diffusion barrier of Ni and Cr.

As described in the paragraph of Section 1, the ferritization of AISI 316L and Mannet II occurred at 550 °C [9], and AISI 316L exhibited the dissolution of Ni and penetration of Pb and Bi into the ferrite layer at 600 °C [13]. These results are consistent with those obtained for JPCA and 316SS at 550 °C in this study. In contrast with the results of Figs. 4 and 5, Fig. 6 shows

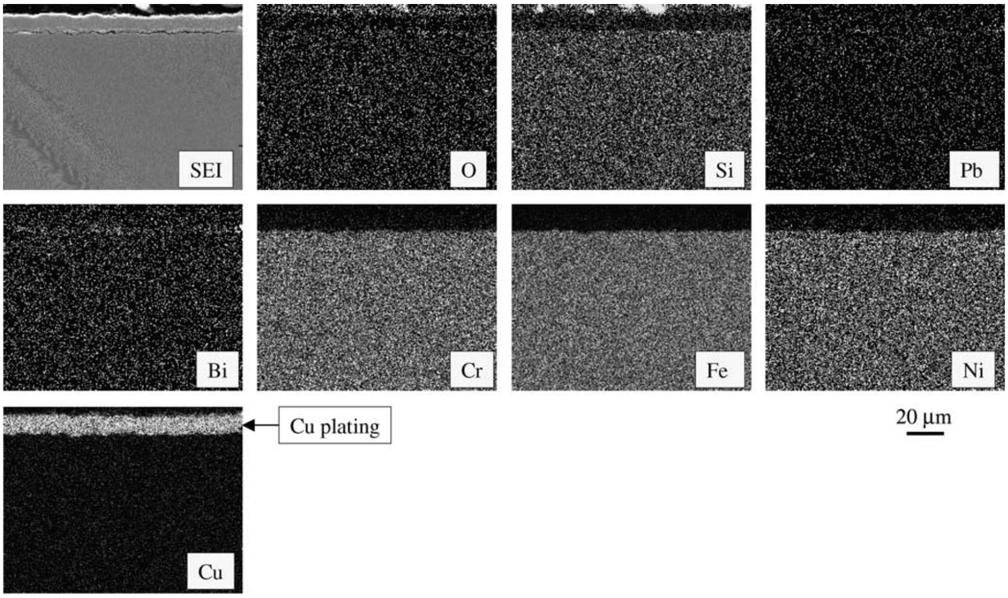

Fig. 6. EDX analysis of the cross section of SX specimen after corrosion at 550 °C for 3000 h in liquid Pb–Bi.

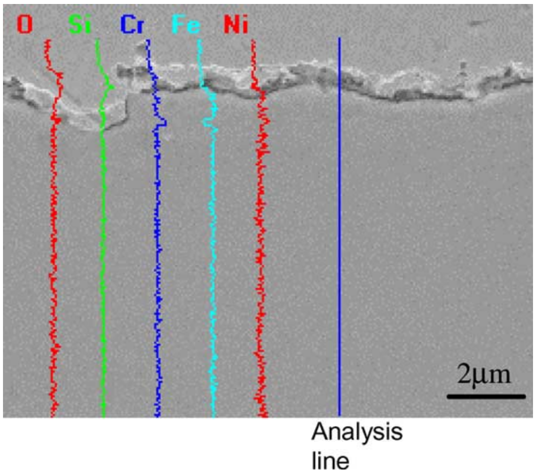

Fig. 7. Line analysis of the cross section of SX specimen after corrosion at 550 °C for 3000 h in liquid Pb–Bi.

that Ni and Cr concentrations did not decrease near the surface region of the SX specimen after corrosion at 550 °C for 3000 h. In addition, only peaks of Fe–Ni–Cr austenitic steel with fcc structure were observed on the SX specimen after corrosion at 550 °C. The SX steel contains ≈2% Cu. Since Cu concentration does not decrease near the surface region as shown in Fig. 6, it is considered that Cu in the SX steel does not dissolve into Pb–Bi. Although a very thin oxide film seems to exist on the SX specimen, the detail of the film is not clear in Fig. 6. In order to examine the film on the SX specimen, EDX analysis was made with higher magnification (×8000) and lower accelerating voltage (12 keV). Fig. 7 shows the result of line analysis for the cross section of the SX specimen after corrosion at 550 °C. A thin continuous film with the thickness of 200–400 nm was formed on the surface of the SX specimen. As shown in Fig. 7, this film is an oxide composed of Si and O. Enrichment of Cr, Fe and Ni cannot be observed in the oxide film. It is found that the thin oxide film prevents ferritization of the austenitic steel because Ni and Cr concentrations keep constant beneath the oxide film. The thin protective oxide film acts as a diffusion barrier.

In the present study, it was made clear that Si oxide without Fe and Cr was formed as a result of the corrosion test of SX in a pot at 550 °C for 3000 h. The oxide formed on SX specimen seems to be different from the Fe–Cr oxide containing 3% Si formed in a loop test of EP823 at 550 °C for 700 h [9]. It is considered that a continuous Si oxide film has been formed at the early stage of the corrosion because of the high Si content in SX although the process of Si oxide formation on SX in liquid Pb–Bi has not been understood fully yet. Since the oxygen potential of Si oxide is lower than that of Fe_3O_4 and Cr_2O_3, Si can produce a continuous silica layer below the main oxide scale. In this study, it is thought that Fe and Cr were also oxidized on SX at the first stage during the corrosion. However, oxides of Fe and Cr were not observed on SX specimen. This result might be caused by the following: the formation of Si oxide film before the formation of dense and continuous Fe–Cr oxide film and/or peeling of the porous Fe–Cr oxide. As shown in Fig. 7, Si oxide formed on SX was dense and prevented dissolution of Ni and Cr. Improvement in corrosion resistance of an austenitic steel containing 4.8% Si is associated with the formation of a thin continuous protective layer of Si oxide. Therefore, it is considered that Si addition to steels is very effective on improvement of corrosion resistance in liquid Pb–Bi. However, Si is one of elements giving harmful influence on weldability and creep properties of steels. Furthermore, Si in steels may affect irradiation properties such as swelling, radiation induced segregation and embrittlement. It is necessary to estimate the applicability of Si added steels to ADS components from the viewpoints of corrosion resistance in liquid Pb–Bi, weldability and irradiation properties.

4. Conclusions

Corrosion tests of three austenitic steels, JPCA, 316SS and SX(18Cr–20Ni–5Si steel) in a pot were conducted in oxygen-saturated liquid Pb–Bi at 450 and 550 °C for 3000 h. The following conclusions are drawn:

(1) Appreciable dissolution of Ni and Cr does not occur in the three austenitic steels at 450 °C. Thin oxide films are formed during exposure to liquid Pb–Bi.
(2) Nickel and Chromium in JPCA and 316SS dissolve into Pb–Bi at 550 °C in spite of formation of Fe–Cr oxide. The thick ferrite layer is produced under the oxide film.
(3) A protective oxide film composed of Si and O is formed on the surface of SX containing 4.8% Si during corrosion in liquid Pb–Bi at 550 °C. The thin oxide film prevents dissolution of Ni and Cr into Pb–Bi. The Si added austenitic steel exhibits excellent corrosion resistance in liquid Pb–Bi.

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