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Journal of Nuclear Materials 356 (2006) 203–212
journal of nuclear materials
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Corrosion resistance of Si- and Al-rich steels in flowing lead–bismuth

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Abstract

Corrosion resistance of Si- and Al-rich steels in lead–bismuth flow was studied experimentally. The specimens of SUH3 (10Cr–1Mo–2Si), NTK04L (18Cr–3Al) and Recloy10 (18Cr–1Al–1Si) were exposed to flowing lead–bismuth for 500–2000 h. After the exposure, metallurgical analysis of their surfaces and weight loss measurement of the specimens were carried out. The surface of the Si-rich steels, SUH3, was smooth with no liquid metal corrosion. Double-oxide layers were observed on the surface of SUH3 steel, where an inner layer might serve as a barrier for the liquid metal corrosion attack, while the outer layer could detach from the surface. An initial metallic luster of the surfaces remained on NTK04L and Recloy 10 steels after the exposure. An Al-rich single layer was formed and stuck on the steel surfaces. This layer protected the steel matrix from the corrosion. The weight losses of these Al-rich steels, NTK04L and Recloy10, in the exposure for the time up to 2000 h were negligibly small.

1. Introduction

The compatibility of core, structural and window materials with a liquid 45%lead–55%bismuth (Pb–Bi) at high temperature is one of the critical issues for the development of Pb–Bi-cooled fast reactors and the Pb–Bi target type accelerator driven system (ADS) [1–4].

The authors have investigated corrosion characteristics of steels in flowing Pb–Bi. In the previous studies, it was found that severe liquid metal corrosion (LMC) could be inhibited if a stable oxide layer was formed on the steel surface in flowing Pb–Bi [5,6]. It was also found that high content of Cr in the steels promoted the formation of a compact oxide layer, and consequently improved the corrosion resistance in the flowing Pb–Bi [6–8].

Barbier et al. [9] reported that Si content in steel (EP823: 12Cr–1.2W–1.8Si) improved oxidation corrosion resistance in flowing Pb–Bi. Ballinger et al. [7] also studied the corrosion of Fe–1.24%–3.82%Si alloys in a rotating electrode system and in a quasi-loop system. It has been found that Si is enriched in the form of SiO_2 in the surface region of material which is effective for corrosion resistance as a protection layer. Recently, Kurata et al. [10] reported that 5 wt% of Si in austenitic steel SX (17.6%Cr–19%Ni–4.8%Si) beneficially influenced

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doi:10.1016/j.jnucmat.2006.05.019

the corrosion resistance in stagnant Pb–Bi due to the formation of Si-oxide layer. This layer inhibited the LMC attack to austenitic steels in spite that high solubility of Ni in the liquid Pb–Bi generally caused the LMC on the austenitic steels [6,11]. In addition to Si, Al content in steels may also enhance oxidation corrosion resistance due to the formation of stable Al-enriched oxide layers in flowing Pb–Bi [12].

The purpose of the present study is to investigate the effect of Al content in steels on corrosion resistance in flowing Pb–Bi in addition to the investigation of corrosion characteristics of a Si-rich steel in flowing Pb–Bi circumstance.

2. Experimental

2.1. Pb–Bi corrosion test loop

The Pb–Bi initially contained the impurity of 1.4×10^{-3}Cu–8.8×10^{-4}Ag–2.2×10^{-4}Au–2.2×10^{-4}Sn–6.9×10^{-4}Zn–1.8×10^{-3}Fe (wt%).

The corrosion tests were carried out using a Pb–Bi forced convection loop reported in [5,6,13,14]. Fig. 1 shows a schematic diagram of the loop. The loop consists of a cold region made of 9Cr–1Mo steel and a hot region made of SS-316, where Pb–Bi flows from the electro-magnetic pump [15], through the electro-magnetic flow meter [15], and the air cooler in the cold region and then flows through the heater, the test section, the oxygen sensor [6] and the expansion tank in a hot region. The volume of the liquid Pb–Bi in the loop was 22 L.

For the corrosion test, cylindrical specimen holder made of molybdenum (Mo) was used. Fig. 2 shows a schematic of the specimen holder inserted in a corrosion test section. Rectangular plate-type specimens were mounted between top and bottom halves of the cylindrical specimen holder. Mo wires were wound around the holder at three axial positions to fix the specimens inside. Then, there were made two flow channels above and below the specimens.

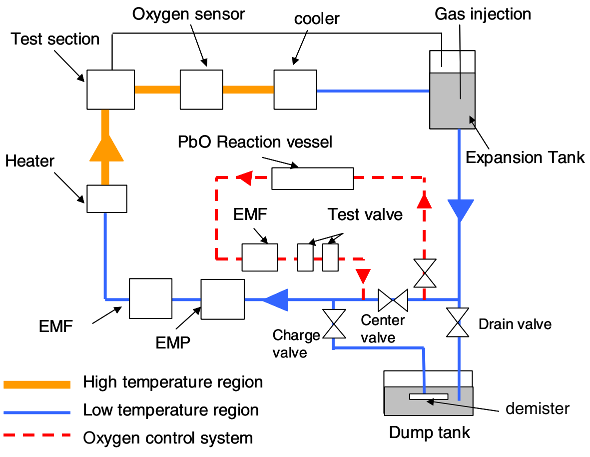


Fig. 1. Schematic of corrosion test loop.

Oxygen concentration in the flowing Pb–Bi was measured by a solid electrolyte type oxygen sensor which was made of a solid electrolyte conductor of ZrO_2–Y_2O_3 with a reference fluid of oxygen-saturated Bi [16]. The oxygen concentration in the Pb–Bi was controlled by a mass exchanger type oxygen control system filled with solid Pb oxide particles [16].

2.2. Test steels

In dry corrosion system of steels in general, the Al and Si in the steels have been effective for the oxidation corrosion inhibition [12]. Then, Al and Si-rich steels were chosen as test steels.

The chemical compositions of test steels are given in Tables 1 and 2. As-received materials were machined to specimen plates and the surfaces of the specimens were mechanically polished to remove the pre-oxidation layers. That was because the effect of pre-oxidation on the corrosion characteristics in the flowing Pb–Bi that had been already investigated in the previous study [17] was not the scope of the present study. The arithmetic mean surface roughness *Ra* was decreased to 1.5 μm to remove the effect of the surface roughness on corrosion behavior that had been reported in Ref. [18]. The sizes of the specimens were given in Table 3. Then, they were mounted in the specimen holder to be immersed in the flowing Pb–Bi. In each corrosion test, one specimen for each steel was mounted in the holder.

2.3. Test conditions

The corrosion tests were carried out at the conditions given in Table 4. The electromotive force (EMF) of 0.43 V, that was measured by the oxygen sensor in the 500-h test and 1000-h test, indicated that the oxygen content in the alloy was 1.7×10^{-8} wt%. The EMF of 0.30 V in the 2000-h test indicated the oxygen content of 1×10^{-6} wt%, where the oxygen concentration was made higher than the former tests by the oxygen control using

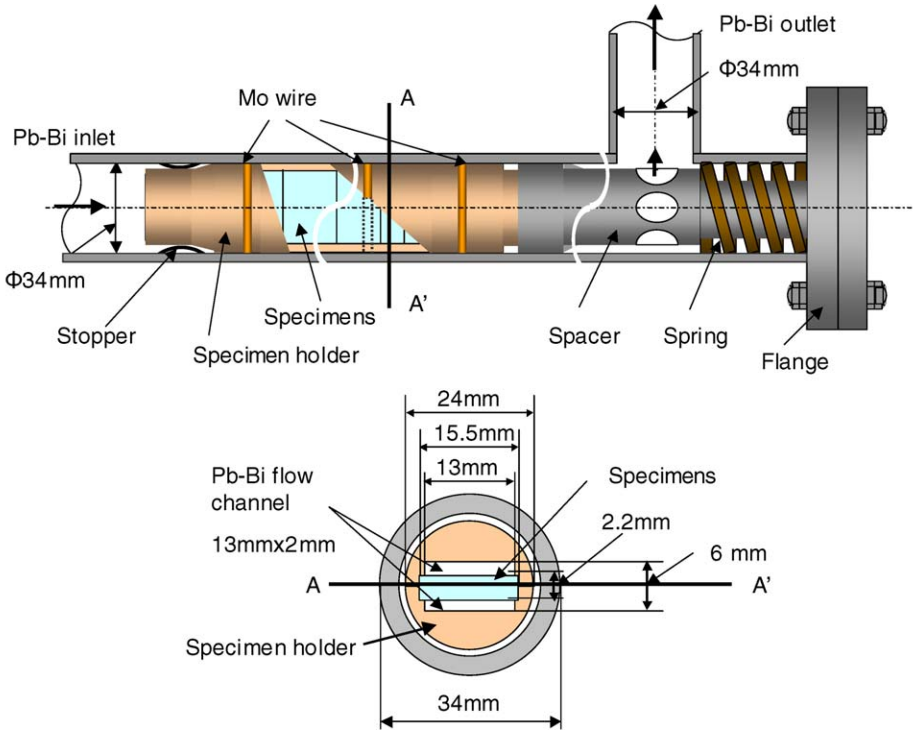


Fig. 2. Schematic of specimen holder inserted in corrosion test section.

Table 1
Chemical composition of SUH3 steel (unit: wt%)

	C	Si	Mn	P	S	Cr	Mo
SUH3	0.42	1.90	0.49	0.023	0.002	10.39	0.72

Table 2
Chemical composition of Recloy10 and NTK04L steels (unit: wt%)

	C	Si	Mn	P	S	Cr	Al
Recloy10	0.01	0.99	0.68	0.24	0.003	17.69	0.89
NTK04L	0.002	0.41	0.14	0.022	0.001	17.84	3.34

Table 3
Sizes of specimens (unit: mm)

Steels (test time)	Width	Length	Thickness
SUH3 (500)	15	10	2.3
SUH3 (1000)	15	30	2.3
SUH3 (2000)	15	30	2.3
Recloy10 (500)	15	30	2.3
Recloy10 (2000)	15	30	2.3
NTK04L (500)	15	30	2.3
NTK04L (2000)	15	30	2.3

Table 4
Test conditions

Exposure time (h)	500	1000	2000
Flow velocity (m/s)	1	1	1
Temperature of Pb–Bi (°C)	550	550	550
Oxygen concentration (wt%)	1.7×10^{-8}	1.7×10^{-8}	1×10^{-6}
Test steel	SUH3 NTK04L Recloy10	SUH3	SUH3 NTK04L Recloy10

the mass exchanger. The reason why the high oxygen concentration condition was chosen was that the purpose in the 2000-h test was to compare clearly the oxidation corrosion resistance of the Al-rich steels with that of the Si-rich steel.

The conditions of oxygen potential are plotted in Fig. 3 for comparison with Gibbs free energy of metal oxides. It is found that the oxygen potentials were higher than the curve of Al_2O_3, SiO_2 and Fe_3O_4 formation potential.

2.4. Corrosion examination

After exposed in the Pb–Bi flow, the specimen holder was demounted from the test loop. Then, the holder with the specimens immersed in a glycerin

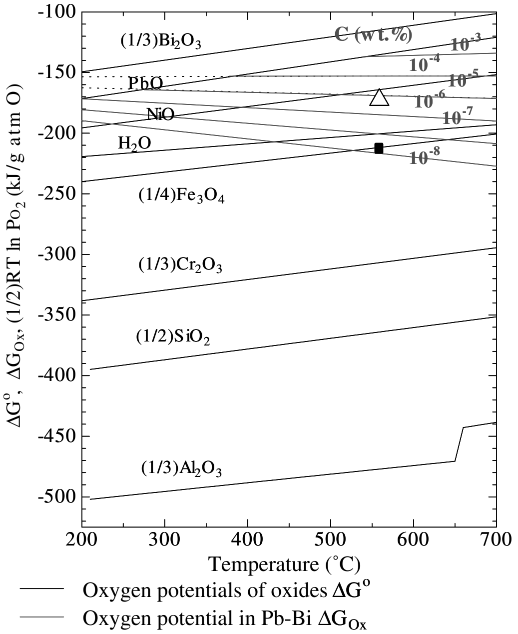


Fig. 3. Diagram of oxygen potential; oxygen condition in 500-h and 1000-h test was shown in black square; oxygen condition in 2000-h test was shown in vacant triangle.

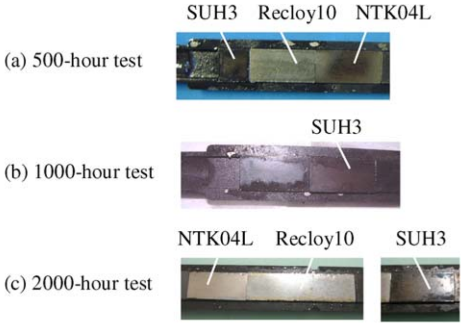
pool at the temperature of 180 °C for 10 min to remove adherent Pb–Bi from the outside and inside of the holder. Then, the holder was opened and the specimens were taken out of the holder, and rinsed again in glycerin pool at the temperature of 180 °C for 10 min to remove adherent Pb–Bi from the specimen surfaces without removal of the oxide layers. Finally, glycerin on the specimen surface was removed in water at the temperature of 70 °C.

The surfaces of the specimens were observed before and after the exposure to inspect the occurrence of erosion [5]. In order to determine the corrosion rate, weight losses of the specimens were measured using an electro reading balance with an accuracy of 0.1 mg. The specimens were cut at the span wise center and the cross sections were polished, and then observed by a scanning electron microscope (SEM) and analyzed by an energy-dispersive X-ray spectrometer (EDX).

3. Results and discussion

3.1. SUH 3

After the 500 h-exposure to the flowing Pb–Bi, the surface of the Si-rich steel SUH3 was smooth without appreciable traces of erosion as shown in Fig. 4(a). The surface color changed from metallic luster before the exposure to black. This indicates that the oxide layer or corrosion products were formed on the surface. The surface colors of the SUH3 after the 1000-h and 2000 h-exposure (Fig. 4(b) and (c)) were similar to that after 500 h-exposure (Fig. 4(a)). The weight of SUH3 specimen decreased due to the corrosion in the flowing Pb–Bi as given in Table 5. The weight losses in 500- and 1000-h test were small, although that in 2000-h test was large.



(a) 500-hour test

(b) 1000-hour test

(c) 2000-hour test

Fig. 4. Appearance of SUH3, Recloy10 and NTK04L steels after exposure to flowing Pb–Bi for 500 (a), 1000 (b) and 2000 h (c).

The results of SEM/EDX analysis show the existing of the single oxide layer on the surface of SUH3 specimen exposed to the Pb–Bi flow for 500 h as shown in Fig. 5. No penetration of the Pb–Bi was detected beneath the layer. The thickness of the layer can be estimated as 2–4 μm, and this is much thinner than the layer formed on the other Fe–Cr steels as reported in Ref. [6]. In the layer, Si and Cr were enriched while Fe content was decreased. Also, bared place without the oxide layer can be detected.

After the 1000 h-exposure, double layers were formed on the SUH3 steel as shown in Fig. 6. The double layers consisted of outer layer (Fig. 6 layer [O]) and inner layer (Fig. 6 layer [I]). The outer layer detached from the substrate, and the thickness was 5–7 μm. The inner layer was compact, and the thickness was 1–2 μm. Si was enriched in the inner layer,

Table 5
Weight changes of test steels

Exposure time (h)		500	1000	2000
Oxygen concentration (wt%)		1.7×10^{-8}		1×10^{-6}
Weight change (g/m^2)	SUH3	−12.7	−4.1	−54.07
	Recloy10	+12.2	–	+6.4
	NTK04L	+1.5	–	−8.5

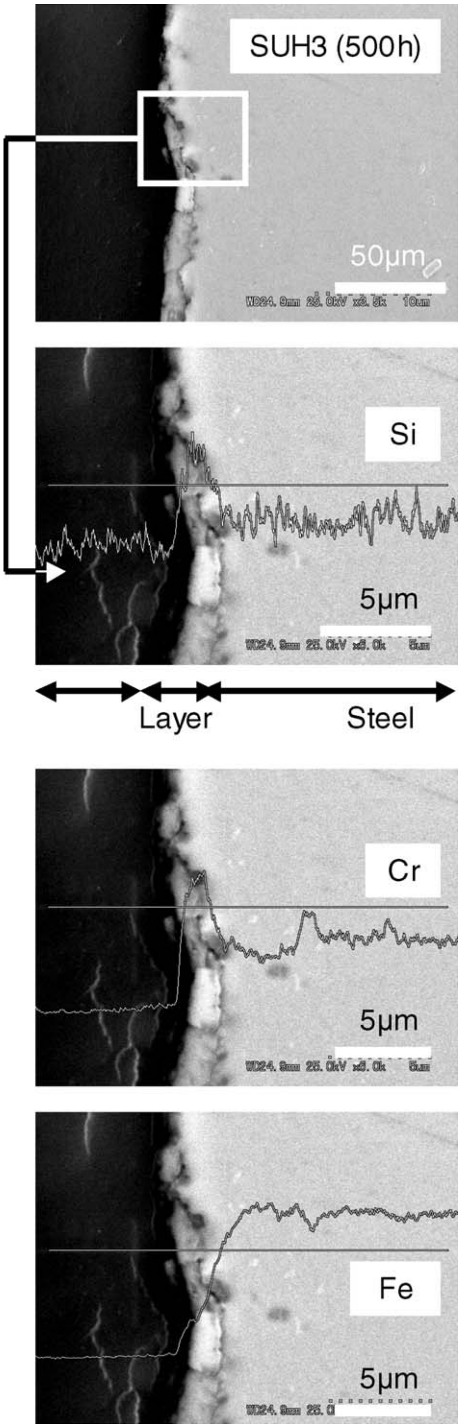


Fig. 5. Si-enrich single oxide layer formed on SUH3 surface in 500 h-exposure to flowing Pb–Bi.

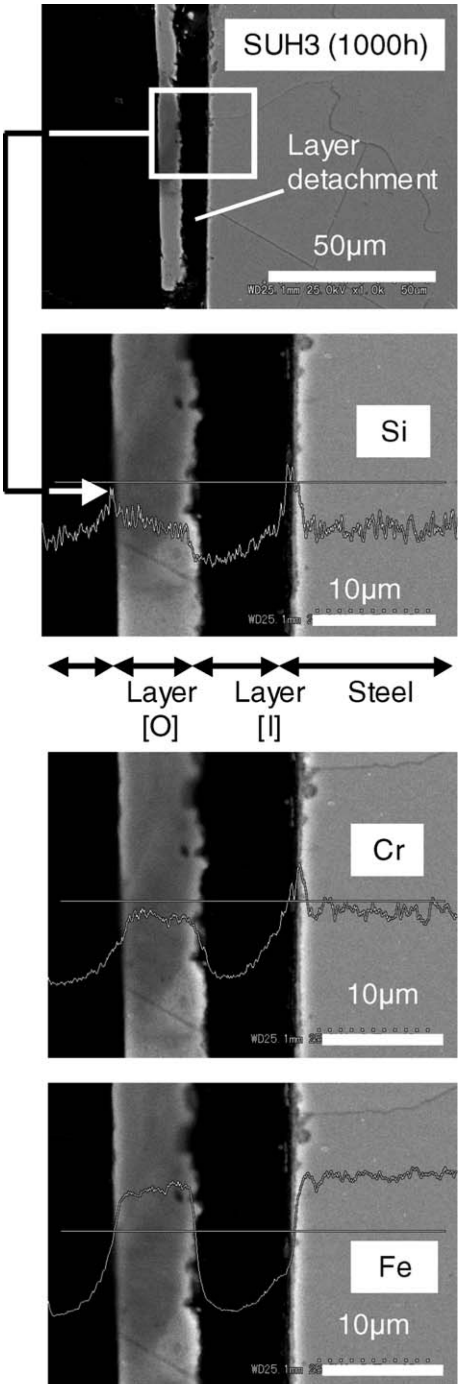


Fig. 6. Double-oxide layer consists of outer [O] layer and inner [I] layer formed on SUH3 surface in 1000 h-exposure to flowing Pb–Bi.

and the layer was stuck to the steel matrix stably. This means that the outer layer was unstable, and could be easily taken out by high density fluid flow after the layer detached from the substrate. In other words, the inner layer may protect the steel matrix from the LMC, while oxidation corrosion is caused by the detachment of the outer layer in the flowing Pb–Bi.

In the 2000 h-exposure, oxidation corrosion occurred in the SUH3 steel. The results of the weight loss measurement for the SUH3 steel are shown in Fig. 4. It was found that the weight loss in the 2000-h test was much different from the results of 500-h and 1000-h tests, even though the weight losses in the 500-h and 1000-h test were almost the same. This was because oxidation corrosion occurred due to the detachment of cracked layer as shown in Fig. 7. The reasons for the high weight loss after 2000-h exposure can be formation of a thick oxide layer with a poor adherence surface. The cracked layer was single layer and the thickness was 5–7 μm. Although Si and Cr were enriched in the layer, the layer was cracked and detached from the substrate in some places. The oxidation corrosion occurred in the 2000-h test due to higher oxygen concentration than that in the 500- and 1000-h tests.

3.2. NTK04L

Initial metallic luster was kept on the surface of the NTK04L steel in the 500 h-exposure to the Pb–Bi flow (Fig. 4(a)). The weight loss of NTK04L was very small and single Al-enriched oxide layer 1 μm in thickness was formed on the surface in 500 h-test (Fig. 8). The oxide layer on NTK04L was thinner than that formed on the SUH3 steel (Fig. 5).

Also in the 2000 h-exposure, corrosion did not occur in the NTK04L specimen. Weight loss was low. Metallic luster was kept on the surface (Fig. 4(c)), and the color of the surface was the same as that after 500 h-exposure (Fig. 4(a)). Single oxide layer was formed on the surface (Fig. 9). The thickness and property of the layer was similar to those of the layer formed in 500 h-exposure. The layer had no cracks.

Therefore, it is concluded that the Al-enriched oxide layer is formed on the surface of Al-rich NTK04L, and it inhibited the LMC. Since the formed layer was very thin and stable, neither cracks nor detachment occurred in spite of strong stress of high density Pb–Bi flow. The Al-enriched layer inhibited development of the oxide layer and consequently suppressed the oxidation corrosion.

3.3. Recloy10

In the Al- and Si-rich steel, Recloy10, shiny surface condition before the exposure was kept in 500 h-exposure (Fig. 4(a)). This was similar to that observed in the Al-rich NTK04L. The weight loss

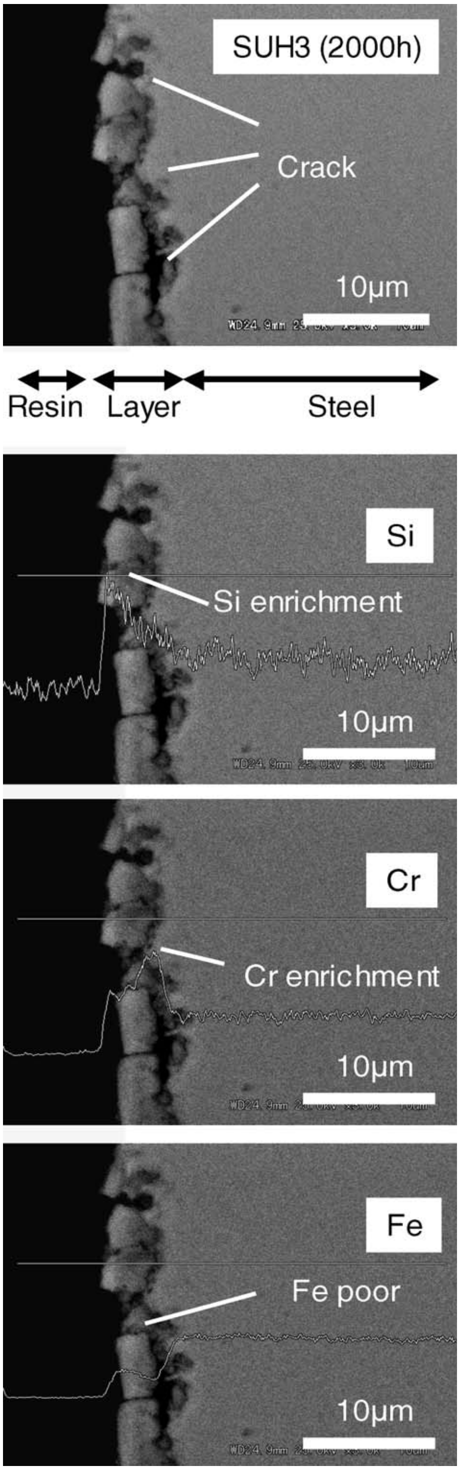


Fig. 7. Cracked oxide layer formed on SUH3 surface in 2000 h-exposure to flowing Pb–Bi.

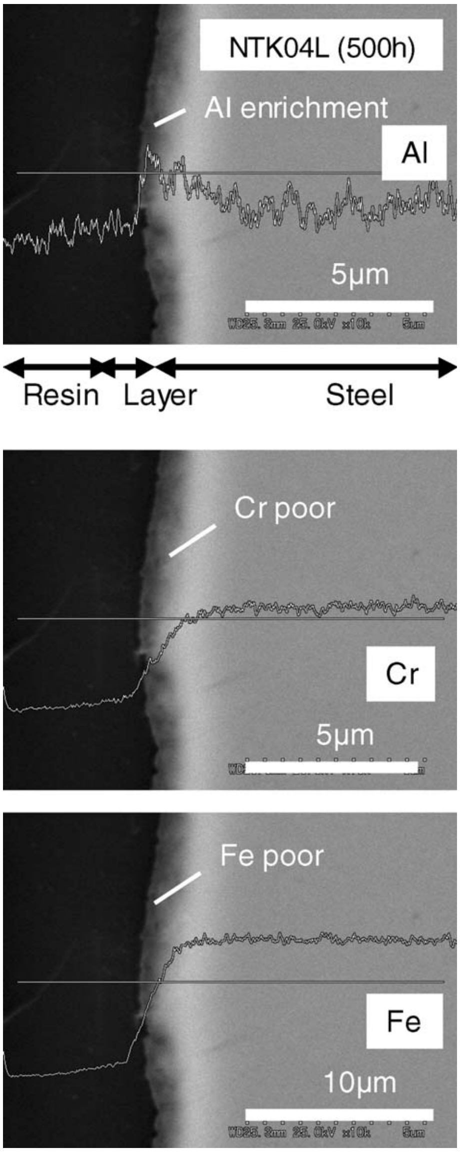


Fig. 8. Al-enriched oxide layer formed on NTK04L steel in 500-h test.

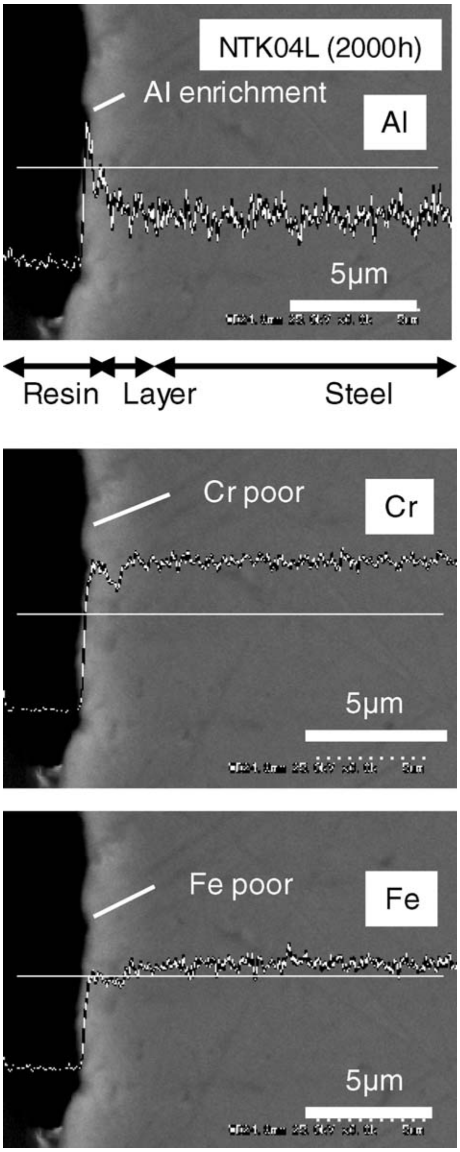


Fig. 9. Al-enriched layer formed on NTK04L steel in 2000-h test.

in the flowing Pb–Bi was negligibly small (Fig. 4). Most of the Recloy10 steel surface was covered with very thin Al- and Si-enriched layer of 1 μm in thickness (Fig. 10). The Pb–Bi did not penetrate into the steel beneath the oxide layer.

Also in the 2000 h-exposure, initial metallic luster was kept on the surface as shown in Fig. 4(c). The weight loss in the 2000-h test was nearly equal to zero. A 1 μm-thick Al-enriched layer was formed on the surface (Fig. 11). The layer was well stuck to the steel surface. This indicated that the different composition of the oxide layer formed under the different oxygen concentration or exposure time.

It is found that the Recloy10 steel has good corrosion resistance for the high temperature Pb–Bi flow as the NTK04L steel. The thin Al-enriched layer inhibited not only the LMC but also the oxidation corrosion.

3.4. *Effect of Al and Si in steels on corrosion resistance in Pb–Bi*

The formation process of the Al- and Si-rich oxide layers on the steels in the flowing Pb–Bi is

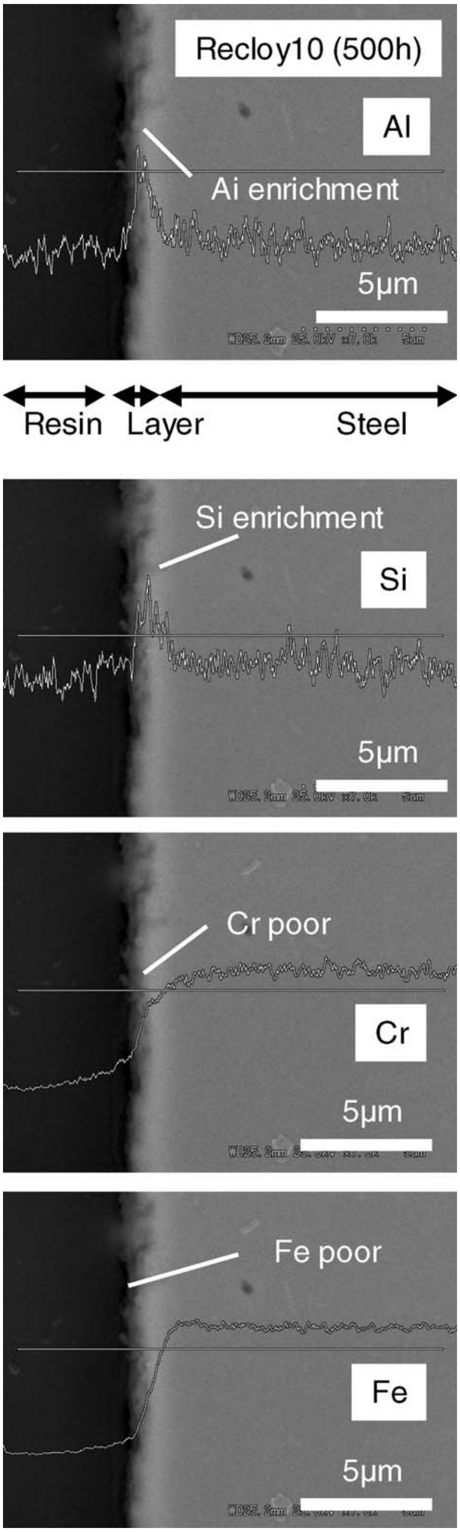


Fig. 10. Al-enriched thin layer formed on Recloy10 steel in 500 h-exposure to flowing Pb–Bi.

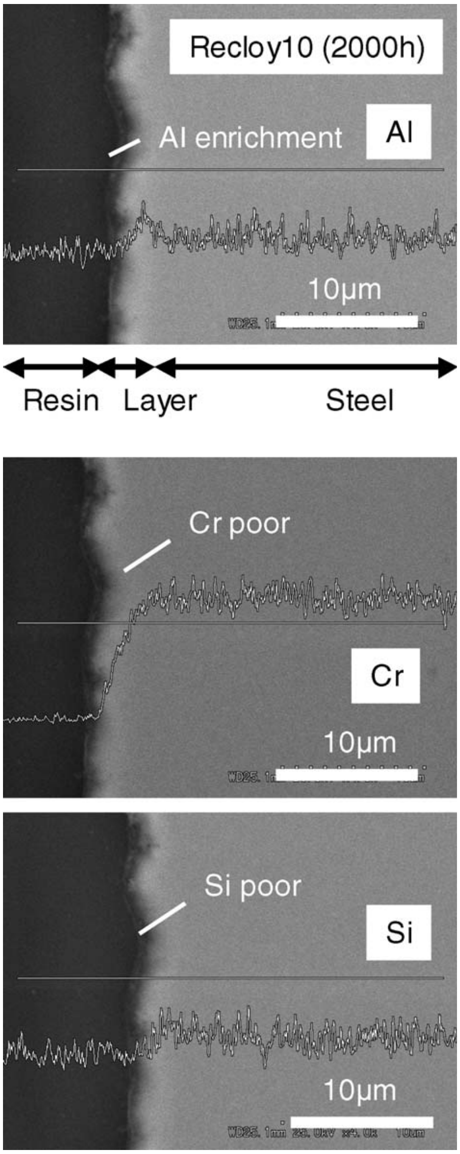


Fig. 11. Al-enriched thin layer formed on Recloy10 steel in 2000 h-exposure to flowing Pb–Bi.

possibly explained as shown in Fig. 12. The Fe–Cr oxide layers were formed on the steel surfaces due to the elements of Fe and Cr on the steel surfaces selectively reacted with the oxygen in the liquid Pb–Bi. Then, the Al or Si on the surfaces were condensed. The oxygen diffused through the Fe–Cr oxide layer reacted in the Al- and/or Si-condensed region. Then, the Al and/or Si-rich oxide layers were formed on the steel surfaces. Then, the dissolution of the Al and/or Si due to the direct contact with

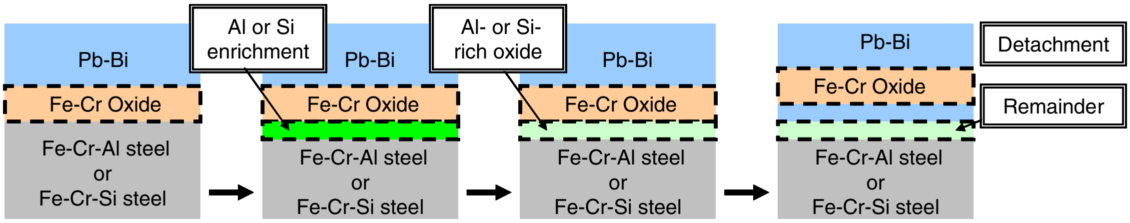


Fig. 12. Al- and Si-rich layer formation.

corrosive liquid Pb–Bi was not caused by the protection of the outer layer [19].

Pilling–Bedworth ratio (PB ratio) of the Si oxide formation on Si is 2.1, and this is almost the same with that of Fe–Cr oxide formation [20]. The PB ratio of the Al oxide formation is much less than those of Fe–Cr or Si oxide formation. This indicated that the Al oxide layer or Al-rich oxide layer was a compact layer, which did not cause the crack easily in the layer even if flow stress acted on the surface.

Thus, Al in steel promoted the formation of the stable oxide layer. The influence of radiation of Al_{13} with the half-life of 2.3 min formed in neutron irradiation may not be critical problem, since the amount of Al in steel is small enough and the half-life is short.

4. Conclusion

For the development of corrosion-resistant materials for Pb–Bi-cooled fast reactor and Pb–Bi target type accelerator driven system, corrosion resistance of Si- and Al-rich steels in flowing Pb–Bi was investigated by means of the exposure of the SUH3 steel (10Cr–2Si), the NTK04L steel (18Cr–3Al) and the Recloy10 steel (18Cr–1Si–1Al) to the Pb–Bi flow at the temperature of 550 °C for 500, 1000 with an oxygen concentration of 1.7×10^{-8} wt% and 2000 h with an oxygen concentration of 1×10^{-6} wt%. Conclusions are as follows:

(1) Si- and Cr-enriched 1 μm-thick oxide layer was formed on the surface of the SUH3 steel that had 2 wt% of Si in the Pb–Bi flow. No LMC occurred beneath the layer. The SUH3 steel exhibited excellent corrosion resistance in the Pb–Bi flow at low oxygen concentration. Oxidation corrosion occurred at high oxygen concentration due to the growth, destruction and detachment of Si-enriched layer.

(2) An initial metallic luster was kept on the surface of the Al-rich steel, NTK04L in the Pb–Bi flow. Al-enriched single layer stuck to the matrix was formed on the surface. This layer protected the matrix from not only the LMC but also the oxidation corrosion since this layer had oxidation resistance in the Pb–Bi flow at high oxygen concentration. The weight of the NTK04L steel decreased slightly with exposure time due to corrosion.

(3) Initial surface state was kept on the surface of the Al- and Si-rich Recloy10 steel in the exposure to the Pb–Bi flow. A single Al- and Si-enriched layer was formed on the surface. The property of the layer was similar to that in the NTK04L steel. By the exposure to the Pb–Bi flow for 2000 h, the weight of the Recloy10 steel did not decrease due to no corrosion.

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