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Corrosion–erosion test of SS316 in flowing Pb–Bi

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Abstract

Corrosion tests of austenitic stainless tube were done under flowing Pb–Bi conditions for 3000 h at 450 °C. Specimens were 316SS produced as a tubing form with 13.8 mm outer diameter, 2 mm thickness and 40 cm length. During operation, maximum temperature, temperature difference and flow velocity of Pb–Bi at the specimen were kept at 450, 50 °C, and 1 m/s, respectively. After the test, specimen and components of the loop were cut and examined by optical microscope, SEM, EDX, WDX and X-ray diffraction. Pb–Bi adhered on the surface of the specimen even after Pb–Bi was drained out to the storage tank from the circulating loop. Results differed from a stagnant corrosion test in that the specimen surface became rough and the corrosion rate was maximally 0.1 mm/3000 h. Mass transfer from the high temperature to the lower temperature area was observed: crystals of Fe–Cr were found on the tube surface in the low-temperature region. The sizes of crystals varied from 0.1 to 0.2 mm. The depositing crystals were ferrite grains and the chemical composition ratio (mass%) of Fe to Cr was 9:1.

1. Introduction

Under the framework of the Japan Atomic Energy Research Institute/High Energy Accelerator Research Organization (JAERI/KEK) joint project [1] on high intensity proton accelerator program, a transmutation experimental facility (TEF) is planned for construction. The TEF consists of two buildings: the accelerator driven transmutation system (ADS) target test facility and the transmutation physics experimental facility. The ADS target test facility is an engineering-aided test facility where a Pb–Bi spallation target technology will be established [2].

In the present plan, a material irradiation examination is scheduled to be carried out with research and development relevant to the Pb–Bi target and containment material performance. The target will be bombarded by protons, which are accelerated by normal state conduction to 400 MeV and by the superconducting linear accelerator to 600 MeV. The incident proton cycle is 25 Hz with a long pulse of 500 μs. As a result of taking into consideration generation of heat produced in a spallation process both in Pb–Bi and in the target containment, the highest temperature of a target container was estimated to be around 450 °C at a flow velocity estimated as about 1 m/s.

Corrosion evaluation of the material in Pb–Bi under irradiation by protons and neutrons will be conducted when TEF is completed. Preliminary design information regarding the effects of flowing Pb–Bi on containment materials is required. Information regarding irradiation effects will be gathered by the examination of SINQ accelerator irradiation material at JAERI hot cell.

The results of the material corrosion-proof test are reported in order to evaluate the amount of corrosion under flowing Pb–Bi conditions during 3000 h operation.

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2. Experimental method

JAERI lead–bismuth loop for material corrosion (JLBL-I) was installed at JAERI in January of 2001 and has completed its first 3000 h continuous operation. A flow diagram is shown in Fig. 1. JLBL-I consists of an electro-magnetic pump, a heater, a specimen tube, a surge tank, a cooler, an electro-magnetic flow meter, a surface-level meter, an observation window, and a drain tank. The electro-magnetic pump is a linear inductive type with an annular channel. The electro-magnetic flow meter has electrodes, which contact with flowing lead bismuth in the flow channel. During operation, the maximum temperature, the temperature difference and the flow velocity of Pb–Bi at the specimen were 450, 50 °C, and about 1 m/s, respectively.

All of the materials for piping and tanks that contact lead–bismuth in the loop were made of type 316 austenitic stainless steel. One of the purposes of the loop test is to verify the durability of the material in flowing high temperature lead–bismuth, including mass transfer.

Testing used is a cold drawn seamless type 316SS, which was produced as a tubing form with 13.8 mm outer diameter, 2 mm thickness and 40 cm length (Fig. 2). Chemical composition is Cr16.61/Ni11.28/Mo2.08/Mn1.55/Fe Bal. (wt%). The tube was solution-heat treated at 1080 °C for 1.5 m and then cooled rapidly. The manufacturing process consisted of making a tube shell by forging after melting an ingot, then cold-drawing and hot working. Acid washing was performed to remove the oxide layer after every heat treatment in the furnace.

The chemical composition of the lead bismuth is Bi-55.60/Sb0.0009/Cu0.0002/Zn0.0001/Fe0.0005/As0.0007/Cd0.0005/Sn0.0001/Bal Pb (wt%). When charging lead bismuth into the test loop, we used a melting tank separate from the loop. Argon gas was added after inserting lead–bismuth bars in the melting tank. The tank was heated to 150 °C and the bars were melted. Then liquid lead bismuth was pumped out into the test loop through the connected pipe by the pressure of argon gas.

Oxygen concentration at saturation, Cs, in Pb–Bi was generally given by

$$\log(\mathrm{Cs}) = A - B/T, \tag{1}$$

where T is absolute temperature. According to research in Russia at IPPE [3], $A = 1.2$ and $B = 3400$ are the constants for lead–bismuth. The oxygen content in Pb–Bi at room temperature after 3000 h operation was 1.0×10^{-3} mass%. The saturation concentration of the oxygen in lead bismuth at the operation temperature of 450 °C is calculated as 3.2×10^{-4} mass%. Oxygen was not actively controlled. The argon gas of 99.95 mass% purity covered the surge tank, which has a free surface,

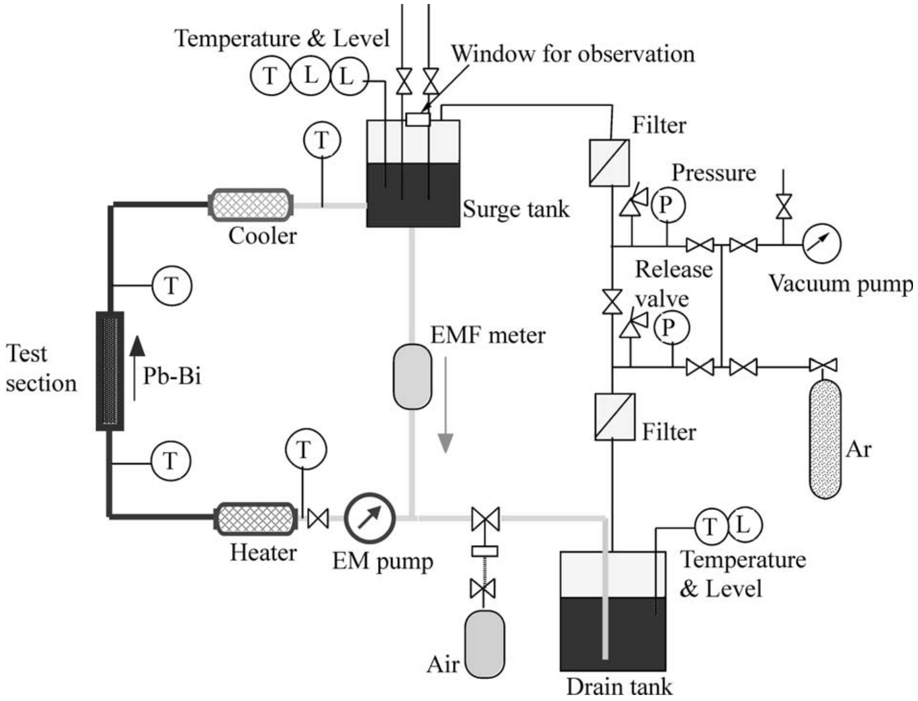

Fig. 1. JAERI lead–bismuth flow loop for material corrosion (JLBL-I).

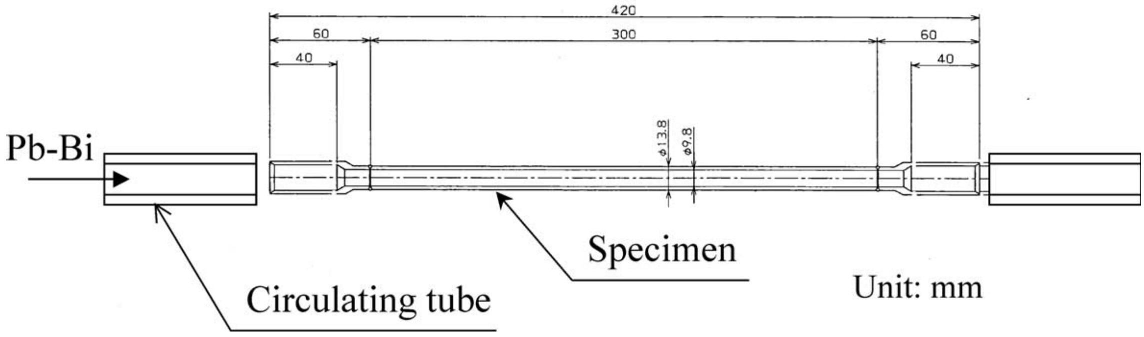

Fig. 2. Geometry of tubing specimen.

during operation. An oxygen sensor and gas controlling system will be used in the next coming experiment.

3. Experimental results

Lead–bismuth was removed from the flowing loop 10 or more times into the drain tank during 3000 h operation because of calibration of flow meter and system control events. The lead–bismuth in the drain tank and the circulation loop were always covered by high purity argon gas as mentioned above. However, floating oxide was observed on the surface of Pb–Bi in the surge tank during operation through the observing window. It is thought that the oxygen concentration under operation had reached the saturation concentration, that is, 3.2×10^{-4} mass%. After operation a solid portion of lead bismuth was sampled from the circulation loop, which adhered to the specimen tube and oxygen concentration in the portion was measured by an infrared spectroscopic analysis. The concentration was 1.0×10^{-3} mass%. Lead bismuth did not leak from the test loop, and no crack was found in the test tube.

The test tube removed from JLBL-I was cut as shown in Fig. 3 and macroscopic observation was carried out. Fig. 4 shows the comparison of cross-sectional photos parallel to the flow direction: the left photo is a part of upstream (D) and the right photo is a part of downstream (G), respectively in Fig. 3. A thin lead bismuth layer adheres to the inside of test tube, and original tube surface is not visible as shown in D part. where Pb–Bi flew from the left to the right. When the upstream (D) test tube was compared with the downstream tube (G), it was clearly found that the corrosion depth in the down stream (G) was deeper than the upstream (D). The corrosion depth was not uniform. It reached in depth of a maximum of 0.1 mm at (G) part.

Fig. 5 shows that the surface roughness in the unused tube of the same lot material is about 10 μm. Surface geometry clearly changed from somewhat flat to rugged in the right photo which was taken at the center part (E) of the tube in Fig. 4. It looks like hollows and lead bismuth fills there. Fig. 6 shows the SEM observation of one of the hollows. It is recognized that the third layer with a thickness of 20 μm existed in the 316SS/lead–bismuth specimen on the right-hand side. However, this third layer was seen only in the bottom of the hollow. It was not seen at the surface facing the flowing Pb–Bi.

Elemental analysis was done by EPMA for detecting Ni, Cr, Fe, Pb and Bi; those are the main elements of both 316SS and lead bismuth. Elements from both the original material and Pb–Bi are mixed together in points 2, 3 and 4 as shown in Fig. 7. WDX, wavelength-dispersed X-ray, analysis was done to detect oxygen.

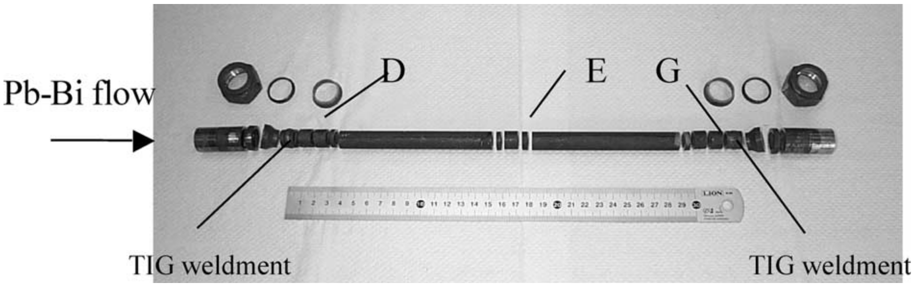

Fig. 3. Test tube after 3000 h operation at 450 °C.

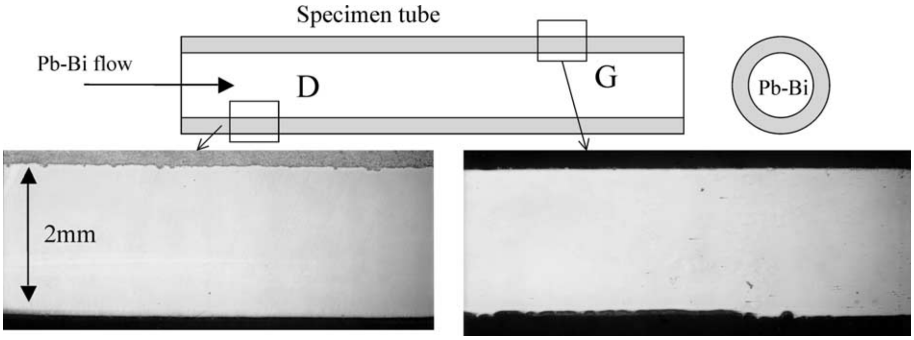

Fig. 4. Cross section to the axial direction observed by microscope: left is a location at upstream (D) and right is a location of downstream (G). Arrows indicate the flow direction of Pb–Bi in flowing channel.

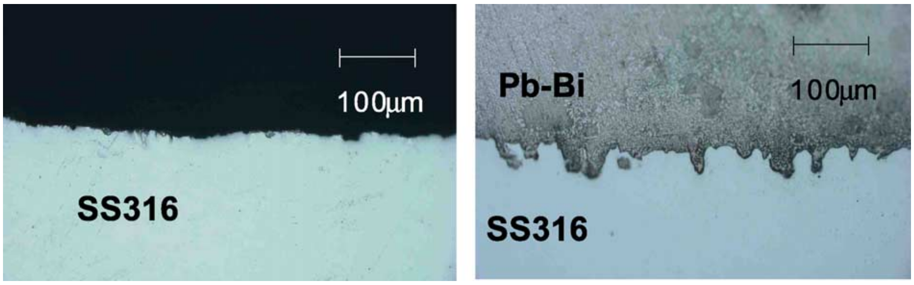

Fig. 5. Cross section of the center part (E) to the circumferential direction. Two photos were compared; the right is after 3000 h test and the left is unused.

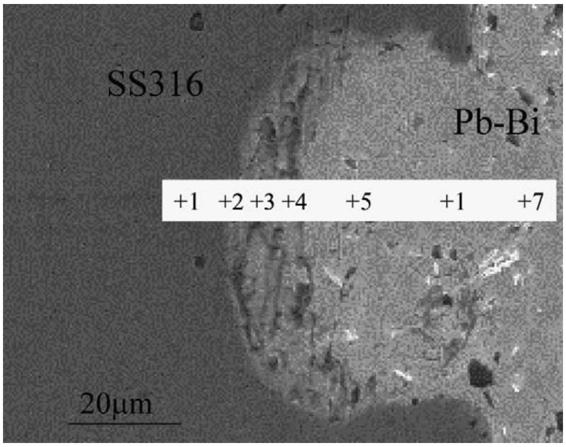

Fig. 6. SEM observation of cross section in the circumferential direction at specimen part (E). Sign '+' with the number indicates the location of point analysis.

Fig. 8 shows that the oxygen exits in the third layer at least. The oxygen, which was soluble in lead bismuth, is considered to be a source of supply. There are two TIG welding parts at both tube ends. Remarkable corrosion was not found as compared with the un-welded parts.

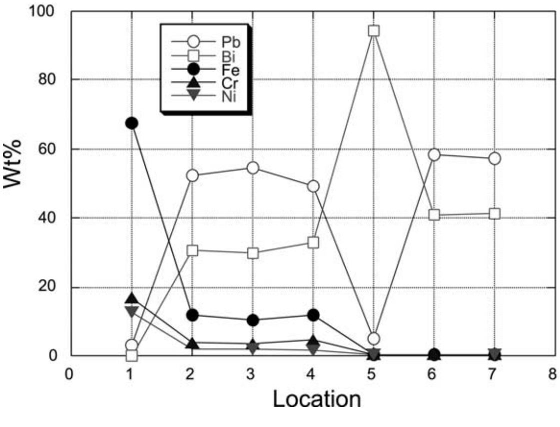

Fig. 7. Point analysis of Ni, Cr, Fe, Pb and Bi by EPMA. Location indicates the point number in Fig. 6.

We cut the circulation tubes to inspect them after 3000 h. Fig. 9 shows the tubes on the floor: tube a–b between the surge tank and EMF, tubes c–d and e–f–g between EMF and EMP, tubes h–i and j–k between the main flow and the drain tank, and tubes m–n and o–p between EMP and heater. All tubes were the section in the low temperature. Temperatures measured in the circulation loop were 400 °C at a heater inlet, 450 °C at

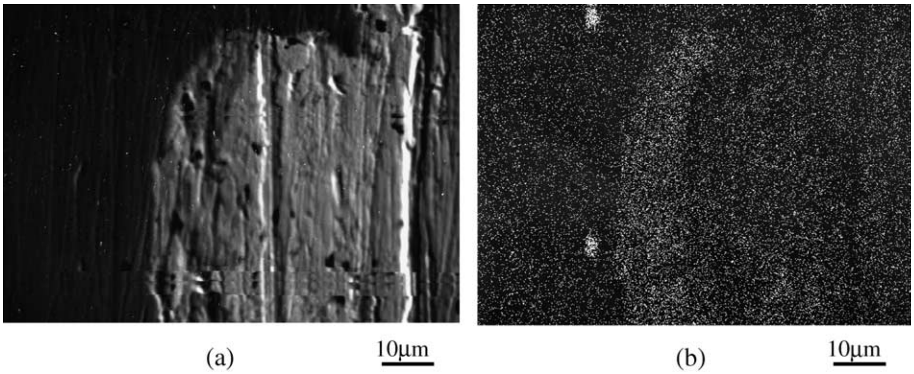

Fig. 8. Oxygen mapping by WDX: (a) SEM image and (b) Oxygen.

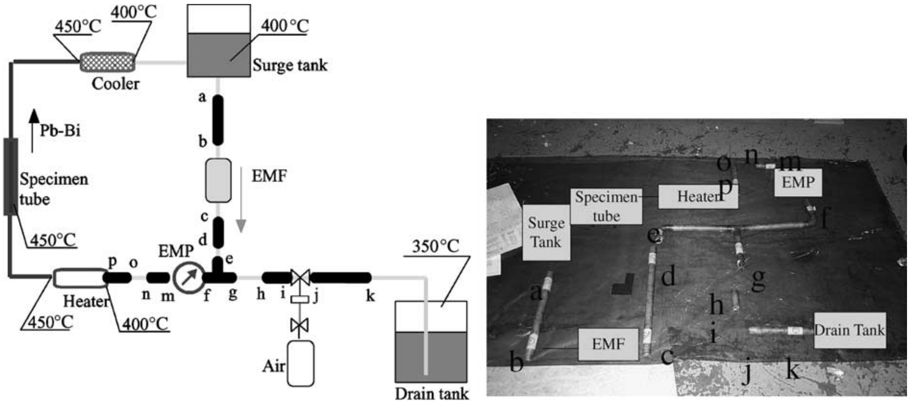

Fig. 9. Tubes after cutting for inspection after 3000 h test.

heater outlet, 450 °C at specimen tube, 450 °C at a cooler inlet, 400 °C at a cooler outlet and 400 °C at a surge tank, respectively. Temperature of Pb–Bi in a drain tank was 350 °C. Air-driven valve located near the drain tank was closed during operation. So Pb–Bi did not flow in tubes h–i and j–k. In EMP Pb–Bi was heated by induction coils and temperature at outlet EMP might be a couples of tens degree higher than that at inlet.

Eye inspection was done for flaws and deposits of Pb–Bi. Flaws were not found on the surface of the circulation tubes. Bright substances were observed in the internal surfaces at the ends of a, b, c, d, e and f, but at the ends of m, n, o, p, g, h, i, j and k. Conclusively the bright substances were noticed in the flow line at the minimum temperature 400 °C. Fig. 10 shows SEM image of an internal surface near the point f in Fig. 9. Polycrystal structure was found there and surrounded by solidified Pb–Bi. The size of crystals was about 0.1–0.2 mm roughly.

As a result of the quantitative analysis of deposit crystal at the point c in Fig. 9 by X-rays, Fe and Cr were detected and the weight concentration ratio was roughly Fe:Cr = 9:1. Nickel does not exist in the polycrystals as shown in Fig. 11. They were precipitations from the lead–bismuth including impurities dissolved from 316SS. It is found that they are ferrite steels.

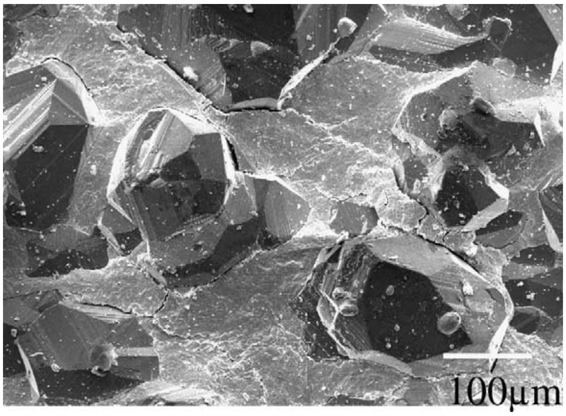

Fig. 10. Polycrystal in the solidified Pb–Bi at the internal surface.

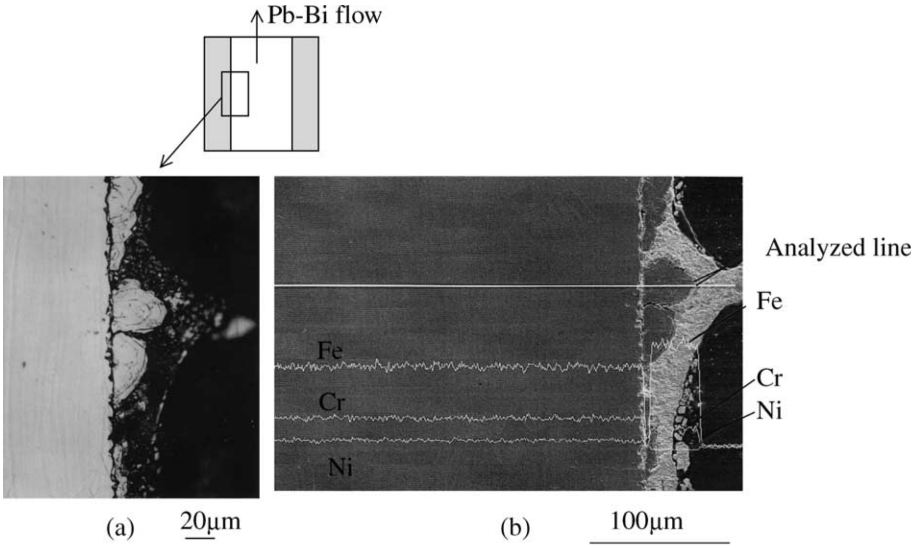

Fig. 11. X-ray analysis of polycrystal in the internal surface of tube in the low temperature; (a) is etched by 10% oxalic acid and (b) is unetched.

4. Discussion

As a result of conducting a corrosion test of 316SS austenitic stainless steel under flowing lead–bismuth, a maximum of 0.1 mm corrosion arose under the conditions of 450 °C maximum temperature, 50 °C temperature difference and 1 m/s of flow velocity during 3000 h. Corrosion was not uniform in the test specimen: the corrosion–eroded depth was deeper in the downstream portion than the upstream and the section showed concave–convex form. The Reynolds number in the test tube is nearly 78 000, and a flow is turbulent. As far as a main flow in the tube was concerned there is not any factor, which will affect the surface condition of specimen tube from points of views of fluid condition. To understand this tendency further considerations will be needed.

We showed the cross section views of unused tube in comparison with used one in Fig. 5. The surface of intact material had about a maximum of 10 μm roughness. Fig. 12 showed SEM observation on the internal surface of unused tube. What we saw is the crevis, apparently, along the grain boundaries. The tested tube was heat treated in an air environment in manufacturing process, and then acid washed. Specimen used in our test had not a special surface treatment. It suggests that the influence of the acid washing remained.

In a stagnant corrosion test carried under the saturation oxygen concentration condition [4], Pb–Bi was melted in the retort and the test pieces were suspended in the melt. During the test a uniform corrosion layer was formed several μm in thickness, but surface roughness was not observed. The flowing test results were different from the static corrosion results. The difference must be understood by corrosion-erosion. Moreover, according to the report of CEA [5], for example, cylindrical specimen was exposed in Pb–Bi flow with an oxygen concentration of 1–2 × 10^{-6} wt%. An oxide film with a thickness of 1 μm or less formed on austenitic steel 1.4970 equivalent to SS316 under the condition of 1.9 m/s flow velocity and 470 °C in the hot test section and 300 °C in the cold test section during 3116 h, and surface roughness was not reported. Those results were not the same with ours. Another corrosion test has been carried for examining the effect of surface treatment under the same condition with reported one.

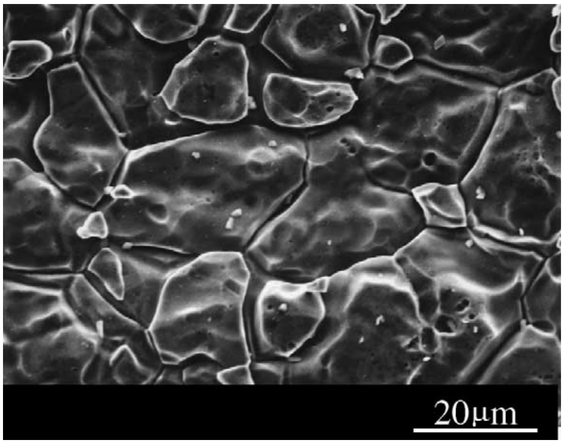

Fig. 12. SEM observation of the internal surface of unused tube.

At JLBL-I the material in contact with lead–bismuth was 316SS in order to investigate mass transfer. During the test of 3000 h, a temperature difference of 50 °C was maintained in the flowing loop. This is the value for consideration in design for a spallation target planned in our facility [2].

Consequently, the ferrite crystal of Fe–Cr appeared in the low-temperature section of the circulation channel. No ferrite of the loop was found in the high temperature part. There are two mechanisms considered for this process.

1. The crystal, which was separated from the tube at high temperature, precipitated in the low-temperature part.
2. Fe, Cr and Ni dissolved into lead–bismuth in the high temperature part and/or dissolved as grains separated from the tube, these crystals circulated in the loop, then precipitated in the low-temperature part according to the difference in solubility.

It is considered that the mechanism 2 is most likely to occur since that crystal contains only Fe and Cr but not Ni. The mass % ratio in crystal was Cr:Fe = 1:9. According to the report of Russia IPPE [3], the saturation solubility of Cr and Fe is calculated with 6.7×10^{-4} and 1.1×10^{-4} mass% at 450 °C, whereas the values are 3.9×10^{-4} and 3.9×10^{-5} mass% at 400 °C, respectively. Therefore, the solubility difference 50 °C in temperature becomes 2.8×10^{-4} and 7.1×10^{-5} mass%. Although it is expected that the Cr increases more than Fe in the crystal, it differs from the measurement. Solubility of nickel into lead–bismuth is large so that most of Ni still considered to be dissolved into lead bismuth.

The evaluation of the amount of solubility of each element will be needed. In a flowing lead–bismuth system we need to be cautious about deposit of a crystal resulting from the difference of saturation solubility. Actually the channel of electromagnetic pump was narrowed by the deposit crystal in our case and the resistance to flow increased. As a result the efficiency of pump decreased. We expanded the gap of flow channel double.

Internal deposit of Pb–Bi depend on inclined geometry of different size of tubes. The layer was so thin that potential plugging might be ignored as far as the gap of flow channel was kept. One problem we experienced was that seat-and-rod in the valve to the drain tank was not closed completely because of lead oxide adhesion.

5. Conclusions

Austenitic stainless steel was tested in flowing lead bismuth during 3000 h and the corrosion of material was investigated.

Maximum temperature was 450 °C, the difference of temperature was 50 °C, the flow velocity was 1m/s, and 99.95 wt% argon gas was used to cover liquid lead bismuth. The material evaluated was SS316, which receives a usual heat treatment in the manufacturing process.

Consequently,

- The amounts of corrosion under the flowing lead bismuth were 0.1 mm/3000 h.
- Crystals of Fe–Cr were found on the tube surface in low-temperature part. The size of crystal is 100–200 μm. The depositing crystal was ferrite and the chemical composition ratio (mass%) of Fe and Cr was 9:1.
- Fe and Cr that were melted into lead bismuth from SS316 in the high temperature part deposited in the low-temperature part according to the difference of solubility.

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