

Corrosion Characteristics of RAFM Steels and Unalloyed Metals in Static Pb-17Li^{*)}

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The corrosion characteristics of reduced activation ferritic martensitic steels, JLF-1 (Fe-9Cr-1.94W-0.09C) and 9Cr-ODS (Fe-9Cr-1.97W-0.14C-0.29Y-0.23Ti), and unalloyed metals of Cr, W and Mo in liquid Pb-17Li were investigated by means of static corrosion tests at 600°C for 500 hours. The corrosion of the JLF-1 steel was based on the dissolution of Fe and Cr from the steel surfaces in the Pb-17Li. The dissolution type corrosion of the 9Cr-ODS steel was based on the strong depletion of Cr, W and O at the steel surface. The corrosion of the unalloyed Cr specimen in the Pb-17Li was much larger than that based on the Cr solubility in the Pb-17Li when a Mo crucible was used in the corrosion test. The corrosion was promoted under an unsaturated condition because the wetted surface of the Mo crucible trapped the dissolved Cr in the Pb-17Li by the alloying process. The dissolution of Mo in the Pb-17Li was also promoted by the alloying with the dissolved Cr though the solubility of Mo in the Pb-17Li was quite low. The weight loss of the unalloyed W specimen exposed in the Pb-17Li was larger than that estimated from the solubility in the Pb-17Li. Some oxide particles were detected on the surface of the W specimen. The reasonable mechanism on the large weight loss of the W specimen was the formation and detachment of the oxide particles in the Pb-17Li.

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1. Introduction

The liquid lead lithium alloy (Pb-17Li) is one of the candidates of the tritium breeders of fusion blanket systems. Compatibility of the Pb-17Li with structural materials is one of the critical issues. The reduced activation ferritic martensitic (RAFM) steel, JLF-1 [1], is one of the candidates of the structural materials. The oxide dispersion strengthened (ODS) steel is also one of the candidate structural materials for a high performance blanket, which can be operated at higher temperature. Corrosion characteristics of the JLF-1 steel in the Pb-17Li have been investigated under the collaboration work with national institute for fusion science and Tokai university, and the results were partially reported in the previous paper [2]. However, the detailed corrosion characteristics of the JLF-1 and 9Cr-ODS steels in the Pb-17Li were not made clear so far.

It is known that the solubility of chromium (Cr) in the Pb-17Li is low as less than 10 wppm [3]. The solubility of tungsten (W) is also low as less than 1 wppm in the Pb-17Li [4]. Therefore, these metal elements are foreseen to be the material as an anti-corrosion barrier in the Pb-17Li. Some previous studies on the corrosion of steels in the Pb-17Li indicated that some oxide layers such as Fe-Cr-O and Al₂O₃ formed and survived on the steel surface

in the Pb-17Li [5, 6]. If the unalloyed Cr is oxidized and forms a stable oxide layer such as Cr₂O₃, the oxide layer may work as an anti-corrosion barrier in the Pb-17Li. An unalloyed Cr can be plated on the steel surface [7]. The information on the corrosion of these unalloyed metals in the Pb-17Li was limited.

A series of corrosion tests on the RAFM steels and the unalloyed metals was performed in a static Pb-17Li. The purpose of the present study is to investigate the corrosion characteristics of these materials in the Pb-17Li.

2. Experimental Condition

2.1 Test material

The chemical compositions of the test materials are presented in Table 1. The JLF-1 steel was normalized at 1323 K for 3.5 ks, and then air cooled and tempered at 1053 K for 3.6 ks, and then air cooled. The 9Cr-ODS steel

Table 1 Chemical compositions of test materials (wt%).

	Fe	Cr	W	C	Others
JLF-1	Bal.	9	1.94	0.09	Mn: 0.49
9Cr-ODS	Bal.	9.08	1.97	0.14	Y: 0.29 Ti: 0.23 O:0.16

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was normalized at 1323 K for 60 min, and then air cooling, and tempered at 1073 K for 60 min, and then air cooling [8, 9]. The purity of the unalloyed metals Cr, W and Mo is 99.95%.

The specimen was rectangular plate type, and the size was 15 mm × 10 mm × 2 mm. The JLF-1 and 9Cr-ODS specimens were cut from the ingot by a low speed cutter. After the cutting procedure, the specimen surface was mechanically polished to remove the oxide layer, which was preliminary existed on the surface. The surface roughness (Ra) must be 0-2 μm based on the previous study [10] though the surface roughness was not measured in the present study. Also, the change of the surface morphology by the mechanical cutting and polishing before the exposure to the liquid metal was investigated and it was already made clear that the cutting procedure did not influence on the surface morphology [2]. As for the specimens of the unalloyed metals, the surface of as-received specimens was mechanically polished by the same way to the specimens of the RAFM steels.

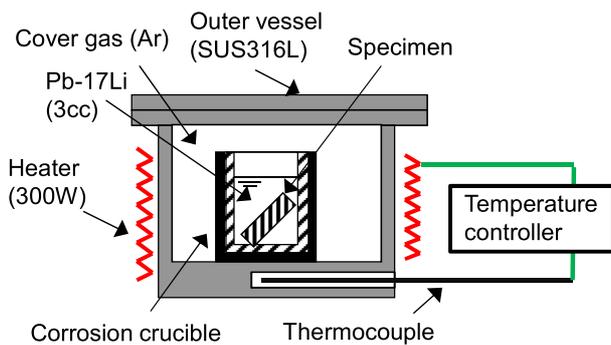


Fig. 1 Corrosion test apparatus.

Table 2 Experimental conditions.

	Temperature (K)	Crucible (material)	Time (hour)	Specimen number
JLF-1	873	JLF-1	500	1
			750 [2]	1
			3000 [2]	3
9Cr-ODS		JLF-1	500	1
W		Mo	500	1
Cr		Mo	500	1

2.2 Test conditions

The corrosion tests were performed at a static condition by the test apparatus shown in Fig. 1. The temperature of the outer vessel was measured and controlled by a thermocouple which was placed at the bottom of the vessel, and a heater which was placed on the outer vessel [2]. The specimen was placed in a small crucible which was filled with 3 cc of Pb-17Li. The outer diameter, the inner diameter and the height of the crucible was 20, 16 and 30 mm, respectively. One specimen was placed in one crucible. The crucible was placed in an outer vessel which was filled with high purity Ar. The corrosion tests' conditions are summarized in Table 2.

After the corrosion test duration, the heater was turned off. Then, the temperature of the vessel decreased to the room temperature without forced cooling. In the cooling down procedure, the vessel was cooled from the outside. The crucible was removed from the vessel at room temperature, and heated up to the melting point of the Pb-17Li in a glove box. Then, the specimen was removed from the liquid Pb-17Li. After the removal of the specimen, the small portions of the solidified Pb-17Li were collected by a drilling. The metal impurity was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, SII NanoTechnology, SPQ 8000 A1). The metal impurity of the Pb-17Li before and after the corrosion test was presented in Table 3 together with the solubility of the metal elements in the Pb-17Li.

After the removal of the specimen from the Pb-17Li, the specimen was rinsed in a liquid metal Li to remove the Pb-17Li adhered on the specimen surface. The weight loss of the specimen was measured using an electro reading balance with an accuracy of 0.1 mg. The metallurgical analysis on the surface and the cross section of the specimens and the crucibles was performed by Electron Probe Micro Analyzer (EPMA: SHIMADZU, EPMA-1610).

3. Results and Discussion

3.1 Corrosion of JLF-1 steel in Pb-17Li

Figure 2 shows the weight loss of the specimens tested in the Pb-17Li. The weight loss of the JLF-1 steel increased with the exposure time [2]. The concentration of the metal elements such as Fe, Cr and W in the Pb-17Li after the test was estimated from the weight loss of the

Table 3 Concentration of metal impurity in Pb-17Li and solubility data (unit: wppm).

	Fe	Cr	W	Mo	Ni
Initial impurity	2.2	0.17	0.52	-	1.3
After JLF-1 test	4.6	3.1	<0.1	-	1.9
After 9Cr-ODS test	1.1	0.21	<0.1	<0.1	-
After Cr test	1.3	1.3	0.1	0.3	-
After W test	2.4	0.3	<0.1	<0.1	-
Solubility	30 (723 K) [3] ~47 (773 K) [11] ~109.7 (873 K) [12]	<<10 (723 K) [3] 8 (773 K) [12]	<1 (873 K) [4]	0.3 (873 K) [4]	3851 (773 K) [12] ~5406 (873 K) [12]

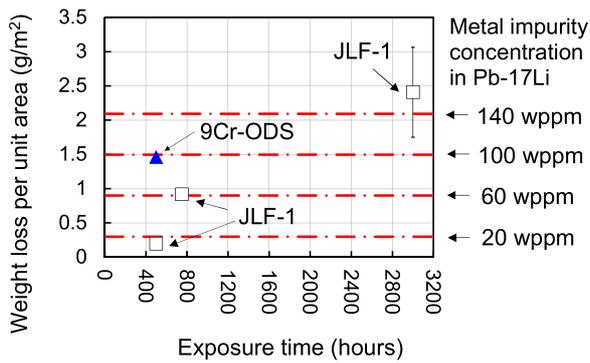


Fig. 2 Weight loss of JLF-1 steel and ODS steel by corrosion test.

specimen, and was summarized in Fig. 2. The corrosion loss of the crucible’s inner surface was taken into account for this estimation. The weight loss of the steels and the unalloyed metals at an isothermal condition must be smaller than that estimated from the total solubility of all the chemical compositions in the Pb-17Li (Table 3), if the corrosion was caused only by the simple dissolution of the metal elements in the Pb-17Li. The solubility of Cr and W in the Pb-17Li was small as reported in [3,4]. Therefore, the solubility of Fe may determine the weight loss of the steels in an isothermal Pb-17Li.

The concentration of metal elements in the Pb-17Li used was presented in Table 3. The increase of the concentration was due to the corrosion of the specimen and the crucible. Some parts of the metal elements must be precipitated in the cooling down procedure (Fig. 3). Therefore, these precipitated portions were not collected for the ICP-MS analysis. The increase of the concentration in the Pb-17Li was much smaller than that estimated from the weight loss as shown in Fig. 2 and Table 3. The Ni concentration in the Pb-17Li used was slightly larger than the initial Pb-17Li. However, the difference was within the error range of the analysis because the nickel content in the JLF-1 was negligibly small [13].

The surface of the JLF-1 specimen, which was exposed to the Pb-17Li for 500 hours, had a granular like morphology. The phase transformation which was observed after the immersion to a static Li [2] was not detected. The surface had some small pits [2].

Figure 3 shows the results of EPMA analysis on the surface cross section. The results indicated Cr depletion on the surface in the Pb-17Li, and the depth of the Cr depleted region was approximately 6 μm (Fig. 3, Area (a) and line (b)). In the region, Fe and W were slightly enriched. The enrichment of Fe on the surface could be low dissolution ratio [2] in spite of the large solubility (Table 3). The enrichment of W was possibly due to the low solubility and the low dissolution ratio. The diffusion of Pb into the steel matrix, which was detected when the steels were exposed into the Pb-Bi [8], was not detected. The small par-

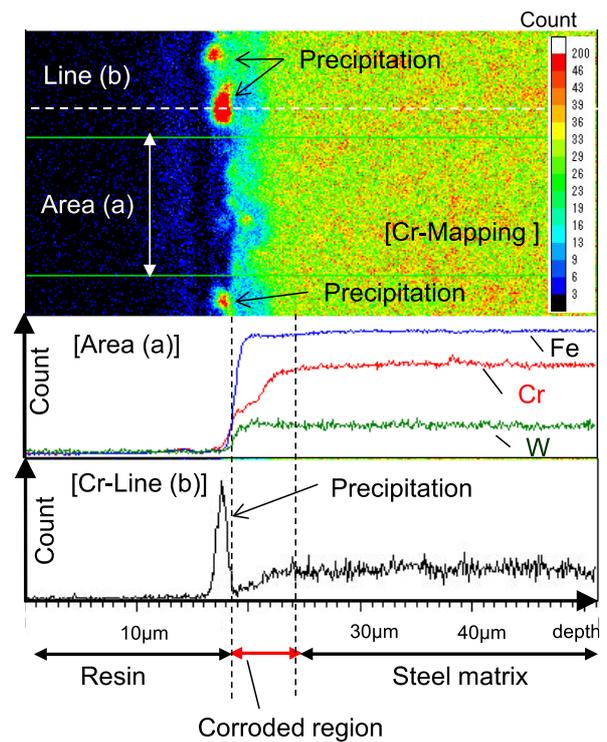


Fig. 3 Result of cross sectional EPMA analysis on JLF-1 surface after 500-hr corrosion test in Pb-17Li.

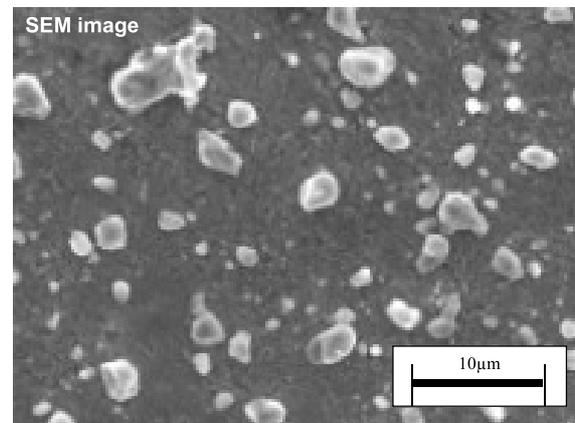


Fig. 4 Surface SEM image of the 9Cr-ODS steel after 500-hr test in Pb-17Li.

ticles of Cr were detected on the surface (Fig. 3, Line (b)). The small particles might be the precipitations which were precipitated in the cooling down procedure from 600°C to room temperature after the corrosion test [9].

3.2 Corrosion of 9Cr-ODS steel in Pb-17Li

Figure 4 shows the results of SEM observation on the surface of the 9Cr-ODS steel after the corrosion test. The surface morphology was similar to that of the JLF-1 though there were a lot of particles on the surface. The particles were metallic compound of Fe-Cr-Pb. These particles

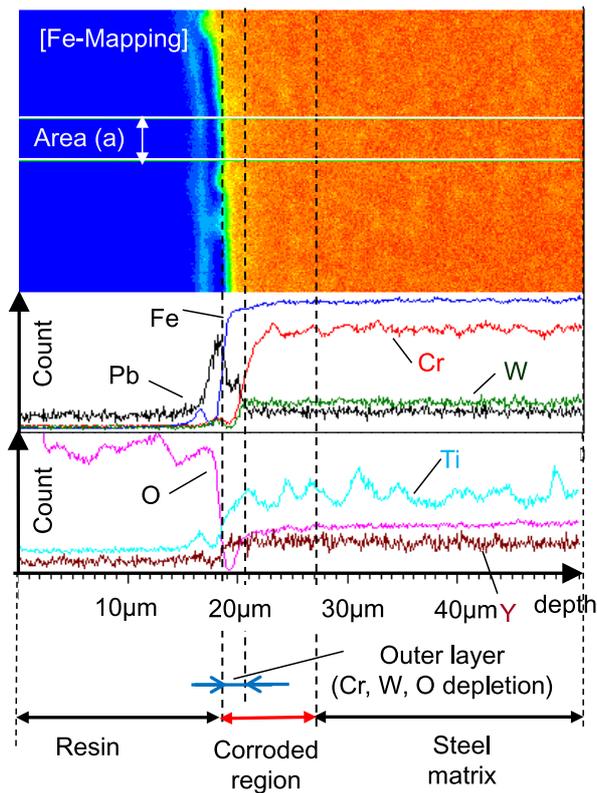


Fig. 5 Results of cross sectional EPMA analysis (Area (a)) on 9Cr-ODS surface after 500-hr test in Pb-17Li.

might be the precipitates. The weight loss of the 9Cr-ODS steel was shown in Fig. 2. The weight loss of the 9Cr-ODS steel was larger than that of the JLF-1 steel (Fig. 3). However, the weight loss of the specimen must be an underestimation because of the precipitates.

Figure 5 shows the results of EPMA surface cross sectional analysis on the 9Cr-ODS steel after the corrosion test. It was found that the corroded region was formed by the corrosion and the depth was app. $8\ \mu\text{m}$ on the surface of the 9Cr-ODS steel. The depth of the region was almost the same with that in the JLF-1 steel (see Fig. 3). However, the region consisted of two layers. In the outer layer, Cr, W and O were completely lost. The depth of the layer was app. $2\text{--}3\ \mu\text{m}$ depth. When the depth of the layer was assumed as $2\ \mu\text{m}$ on all the specimen surface, the weight loss was theoretically estimated as app. $1.78\ \text{g}/\text{m}^2$ according to the depletion of metal elements of 11.21 wt% (Cr (9.08 wt%), W (1.97 wt%) and O (0.14 wt%)) in the layer. This value agreed with that obtained in the corrosion test when the underestimation of the weight loss was taken into account. Therefore, the depletion of Cr, W and O on the surface in the Pb-17Li made large weight loss in the 9Cr-ODS steel. This type of the depletion layer was not detected on the JLF-1 specimen, since the Cr content in the corroded layer of the JLF-1 steel had a gradual slope as shown in Fig. 3.

The corrosion characteristics of the 11.7Cr-ODS steel

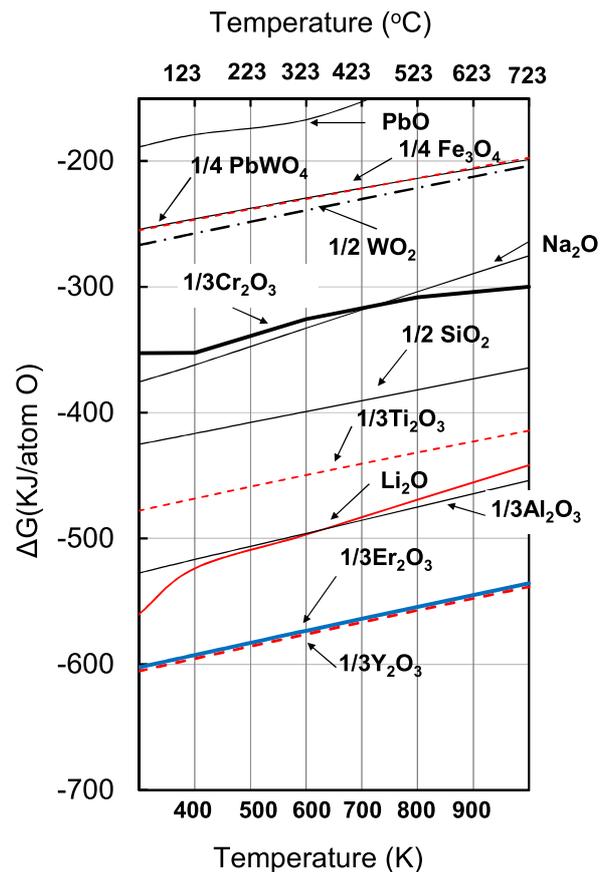


Fig. 6 Gibbs free energy for formation of oxides.

(11.7Cr-2W) in the Pb-Bi at low oxygen concentration was investigated and the characteristics were compared with those of the other ferritic steels [14]. The weight loss of the 11.7Cr-ODS steel was larger than that of 9Cr ferritic steel. The larger Cr content in the steel affected on the large corrosion in Pb-Bi, since the dissolution ratio of Cr was large in the Pb-Bi. The corrosion of 9Cr-ODS (9Cr-2W) steel in the Pb-Bi at high oxygen concentration was also investigated, and the weight loss was larger than that of P122 steel (12Cr-2W) [15]. Though the oxides dispersed in the steel matrix can promote the nucleation of the other oxides, which are capable of forming a protective oxide layer in the liquid metal at the concentration adequately controlled, the corrosion characteristics of the ODS steel is not always better than that of normal RAFM steel. The corrosion tests for 9Cr-ODS in the Pb-17Li were performed in the previous study [9]. The results indicated that the weight loss of ODS steel was larger than that of the reduced activation ferritic steel JLF-1 though the immersion time was shorter than the current study. Therefore, the results in the present study had the consistency with the previous study.

The reasonable mechanism of oxygen depletion on the surface of the 9Cr-ODS steel in the Pb-17Li is considered as follows; The chemical stability of the complex oxides of Ti-Y-O dispersed in the 9Cr-ODS steel for the Pb-17Li is not known. In the same time, the oxygen potential in the

Pb-17Li is not known. However, the oxygen potential in the Pb-17Li must be quite low because it was reported that only few types of the oxides, e.g. Al_2O_3 [16] and Er_2O_3 [2], could stably exist in the Pb-17Li. The Gibbs free energy of these oxides was quite low as shown in Fig. 6. Though the free energy formation of Y_2O_3 is quite low, that of Ti_2O_3 is relatively high. The results of the present study indicated that the complex oxide of Ti-Y-O might have relatively high free energy for formation, and was unstable in the Pb-17Li. The oxide was reduced in the Pb-17Li and the oxygen was dissolved into the Pb-17Li.

The contents of Fe and Cr in the Pb-17Li after the 9Cr-ODS test was much smaller than those after JLF-1 as presented in Table 3. The reason was possibly due to the precipitated portions of metallic compound (Fe-Cr-Pb), which were shown in Fig. 4, could not be collected for the ICP-MS analysis.

3.3 Corrosion of unalloyed Cr in Pb-17Li

The weight loss of the unalloyed Cr specimen was 103.53 g/m^2 , and this corresponds to Cr concentration of 1273.8 wppm in the Pb-17Li. The concentration was much higher than that expected from the solubility (Table 3). The results indicated that the protective oxide layer such as Cr_2O_3 , which could work as the anti-corrosion barrier in the Pb-Bi, was not formed in the Pb-17Li. The corrosion was promoted by the mass transfer in the dissimilar material system of Mo (crucible)- Cr (specimen) as explained in chapter 3.5.

3.4 Corrosion of unalloyed W in Pb-17Li

The weight loss of the W specimen was 5.8857 g/m^2 , and corresponded to content of 72.416 wppm in the Pb-17Li. The concentration was larger than that expected by the solubility presented in Table 3. Figure 7 shows the back scattered electron (BSE) image together with the mapping image of O, W and Pb on the unalloyed W surface after the test. A lot of small particles are adhered on the surface. The particles were identified as oxides since the particles appeared in dark contrast in BSE image and oxygen was enriched in the small particles as shown in Fig. 6. The concentration of W in the particles was not high. The Gibbs standard free energy for formation of PbWO_4 , which was calculated by Molt 2 code, was smaller than that of PbO as shown in Fig. 6. The particles might be Pb-(Li)-W-O. The surface of the W was also slightly oxidized.

The weight loss of the specimen was much larger than that expected from the solubility. Though the formation of these oxide particles could cause weight gain of the specimen, the detachment of the particles could cause the weight loss of the specimen. The detachment must be caused in the cleaning procedure by the liquid Li.

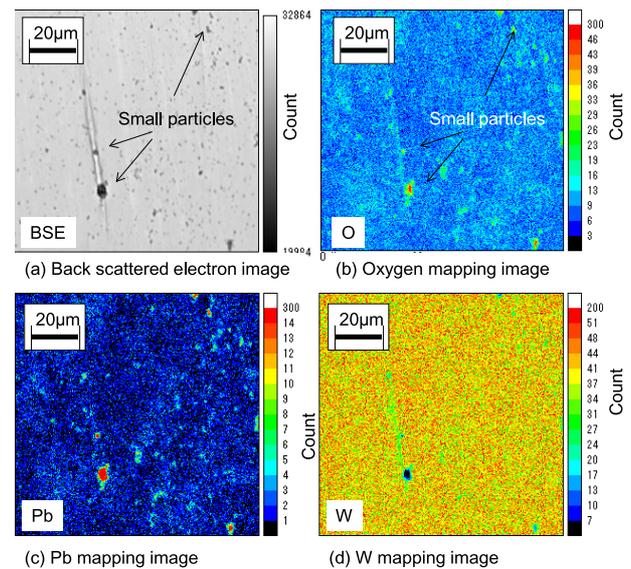


Fig. 7 Results of EPMA analysis on pure W surface after 500-hr test in Pb-17Li (a) BSE image, (b) Oxygen mapping, (c) Pb mapping, (d) W mapping.

3.5 Corrosion of unalloyed Mo in Pb-17Li and mass transfer promoted in dissimilar material system

The inner surface of the Mo crucible, which was used for the Cr test, was analyzed by EPMA. The results were shown in Fig. 8. Some Pb-17Li was adhered on the inner surface and Cr precipitated in the Pb-17Li. The precipitated Cr was mainly detected at the interface between the adhered Pb-17Li and the inner surface of Mo crucible. The Cr transported from the specimen surface into the Mo crucible and precipitated at the inner wall surface. Then, the corrosion of the Cr specimen was promoted at the unsaturated condition in the Pb-17Li.

Some carbon rich particles were widely distributed in the Pb-17Li adhered on the inner surface of the Mo crucible. The diameter was approximately 5-10 μm . The particles must be the carbides, and the carbon for the formation of the carbides must be the dissolved carbon originally in the Pb-17Li. The carbide particles were not Mo carbides or Cr carbides because the content of Mo and Cr in the particles was quite low. The carbides might be lithium carbides (Li_2C_2), though the molybdenum carbide ($\text{MoC}_{0.5}$) was chemically more stable than the lithium carbide [17]. However, the inner surface of the Mo crucible was covered by dissolved Cr according to the Cr precipitation, and the dissolved carbon could not stick to the Mo crucible. Then, the lithium carbides were preferentially formed since the Gibbs free energy for formation of the carbide had the relation of $\Delta G_{\text{MoC}_{0.5}} < \Delta G_{\text{Li}_2\text{C}_2} < \Delta G_{\text{Cr}_{23}\text{C}_6}$ [17].

The depletion of Mo on the inner surface of the Mo crucible was found by the EPMA analysis. The Mo was detected in the adhered Pb-17Li. These facts indicated that

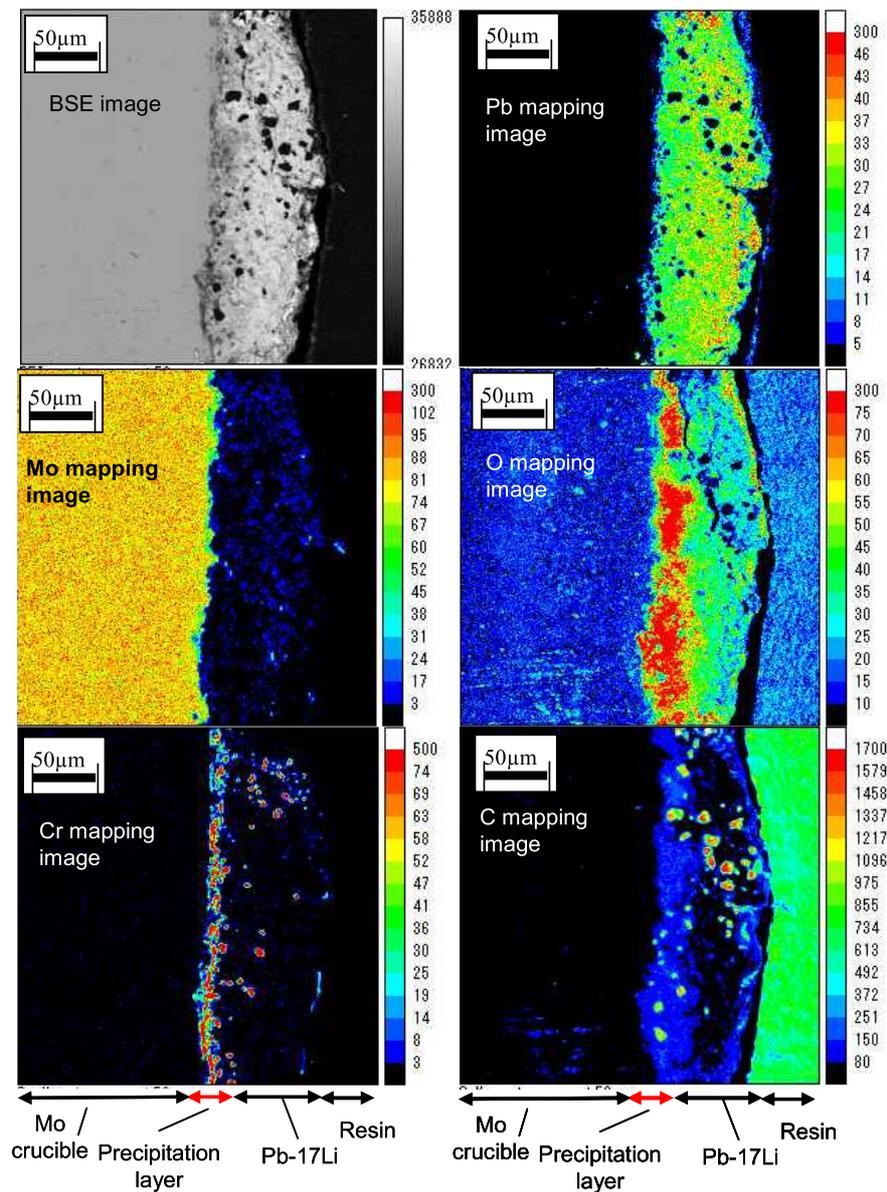


Fig. 8 Results of EPMA analysis on inner surface of Mo crucible after 500-hr test with pure Cr specimen.

not only the dissolution of Mo in the Pb-17Li but also the alloying of Mo with Cr. The dissolution of Mo in the Pb-17Li might not be based on the simple dissolution since the solubility in the Pb-17Li was quite low as reported in ref. [4]. The dissolution of Mo was possibly caused in the Pb-17Li, in which the concentration of Cr was high around the inner surface of the Mo due to the precipitation. In the same way to the Cr transport in the Pb-17Li, Mo might transport to the surface of the Cr specimen in the Pb-17Li, and might react with the Cr on the specimen surface. This phenomenon also could promote the dissolution of Cr in the Pb-17Li. The layer of the Mo-Cr alloy on the Cr specimen surface was removed in the cleaning procedure of the specimen by a liquid Li. It was found that the dissolution of Cr and Mo could be promoted at an unsaturated condition

such as present experiment condition, though the solubility of Cr in the Pb-17Li is quite low (Table 3).

It is known that the Galvanic corrosion was caused by the difference of the electrical potential in the corrosion system. In the present experiment, a lot of free electrons exist in the liquid metals. The potential difference in the corrosion system must be negligibly small. Therefore, the galvanic effect on the corrosion in the Pb-17Li must be negligibly small.

The segregation of Pb in the adhered Pb-17Li was detected, and indicated that the segregation of the Li, though the segregation of Li was not analyzed. These segregations could be caused by the enrichment of Cr and C, which had the large chemical affinity with Li. The dissolved oxygen in the Pb-17Li was enriched in the region near the inner

surface of the Mo crucible. The oxide layer [18] was not clearly detected in the region. The oxygen enrichment was possibly caused by the segregation of the Li in the Pb-17Li, since the chemical affinity of the oxygen with the Li was higher than that with Pb.

4. Conclusion

The corrosion tests on the JLF-1 steel, 9Cr-ODS steel and the unalloyed metals Cr, W and Mo were performed in the Pb-17Li. Major conclusions are follows;

(1) The corrosion of the JLF-1 steel was based on the depletion of Fe and Cr at the steel surfaces in the Pb-17Li. The test results indicated that Cr had larger dissolution ratio than that of Fe in the Pb-17Li. The metal elements of W in the steel had lower dissolution ratio in the Pb-17Li than that of Fe and Cr. The particles, which were precipitates of Cr, were detected on the specimen surface.

(2) The corrosion of the 9Cr-ODS steel was based on the depletion of Fe and Cr at the steel surfaces in the Pb-17Li. The weight loss of the 9Cr-ODS steel was larger than that of JLF-1 steel. The corroded region on the surface consisted of two layers. In the outer layer, the metal elements of Cr, O and W was strongly depleted by the corrosion. The precipitates, which contained Pb, Cr and O, were detected on the surface.

(3) The weight loss of the unalloyed Cr specimen in the Pb-17Li was much larger than that estimated from the solubility data for the liquid Pb-17Li. The corrosion was promoted at an unsaturated condition made by dissimilar material system of Mo (crucible) - Cr (specimen). The inner surface of the Mo crucible captured the dissolved Cr by the metal alloying reaction.

(4) The weight loss of the unalloyed W specimen in the Pb-17Li was larger than that estimated from the solubility data for the Pb-17Li. Some oxide particles were detected on the W surface. The reasonable mechanism on the large weight loss was the detachment of the oxide particles formed in the Pb-17Li.

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