



Corrosion characteristics of low activation ferritic steel, JLF-1, in liquid lithium in static and thermal convection conditions

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ABSTRACT

The compatibility of JLF-1 (Fe–9Cr–2W–0.1C), a reduced activation ferrite/martensitic (RAFM) steel with static and flowing lithium (Li) was investigated. The corrosion characteristics were studied by means of measurement of weight losses and scanning electron microscope (SEM)/energy dispersive X-ray spectrometer (EDS) analysis on the surfaces and cross-sections of the specimens. The weight losses of JLF-1 specimens showed saturation at the temperature of 500 °C and 600 °C. This is possibly due to the saturation of Fe, Cr in bulk Li or formation of saturated layer of dissolved elements in liquid Li near the specimen surface. In the corrosion test in a thermal convection loop, the corrosion rate at 500 °C for 250 h was significantly larger than that obtained in the static test in an identical condition. After Li exposure, the phase transformation from martensite to ferrite was found on the specimens. The chemical analysis results and the loss of carbides suggested that the phase change was caused by the depletion of carbon. At the same time, selective depletion of alloy elements, such as Cr and W was detected by EDS on the surface. The result of Vickers hardness test showed that obvious softening occurred on the surface of the specimens after Li exposure and the depth of the softened region was consistent with that of the phase transformation. The flowing Li enhanced the weight loss, phase change and hardness reduction due to the mass transfer.

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1. Introduction

Fe–Cr–W-based reduced activation ferritic/martensitic (RAFM) steels are regarded as a candidate blanket structural material for liquid blanket system in fusion reactors [1]. Some liquid blanket concepts have been proposed to use RAFM as structural material and liquid lithium (Li) as coolant and tritium breeding materials [2]. For these systems, the compatibility between Fe–Cr–W steels and Li is one of the critical issues. However, since the previous research mainly focused on the conventional Fe–Cr–Mo steels [3,4] the data on RAFM (Fe–Cr–W steels) are still limited. Recently, the compatibility of RAFM steel EUROFER97 with Li–Pb has been investigated in Europe [5,6]. But the corrosion behavior of steels in Li–Pb and pure Li are dissimilar. The influence of non-metallic impurities, such as O, N, C, on the compatibility is limited in Li–Pb in

contrast to significant effects in Li. In Li–Pb, a layer of protective corrosion products can form on the surface of RAFM because of lower Li reactivity.

The corrosion behavior of the RAFM steel, JLF-1, in a static Li was investigated preliminarily in the previous study [7]. The corrosion of the JLF-1 was summarized as selective dissolution of C, Cr and W, and phase transformation from martensite to ferrite because of C depletion. The depth of the phase transformation was estimated to be 100 μm for JLF-1 exposed in Li for 100 h at 700 °C, while no phase change occurred at 600 °C for 100 h. The structure change was considered not to be the result of thermal history effects but the chemical effects, because no phase change was observed on the specimen after a vacuum anneal with the same temperature history. However, the corrosion and the depth of the phase change in the static experiment can be underestimated because saturation could be formed around the specimen, which might suppress further corrosion in the static test condition.

The purpose of the present study is to investigate further the corrosion characteristics and phase transformation phenomena of JLF-1 in blanket relevant conditions. Various static experiments

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were carried out at 500 °C and 600 °C for longer exposure time and a corrosion test for JLF-1 in flowing Li in a thermal convection loop was performed at 500 °C.

2. Experiment

The material, JLF-1, is Fe–Cr–W-based RAFM, with composition (wt% analyzed by chemical method): 8.93Cr, 1.96W, 0.64Mn, 0.49Ni, 0.21V, 0.10C, 0.015N, and Fe as balance. JLF-1 specimens were heat-treated at 1050 °C/3.6 ks/air cooled (normalizing) and 780 °C/3.6 ks/air cooled (tempering). The coupon specimens with the size of 26 mm × 5 mm × 0.25 mm were prepared from sheet. The surfaces of the specimens were mechanically polished before the experiment. Static exposure experiments to liquid Li were carried out in a Mo crucible with Mo specimen holders, which were placed in a stainless steel autoclave. The detail of the static test facility was introduced in the previous work [7]. In order to suppress the effect of impurities, especially N, in Li which was reported previously [8–10], high purity Li (99.9 wt% with the nominal N impurity level of 40 ppm) was used, and the preparation was carried out in a glove box filled with argon whose nitrogen level was less than 1 ppm. The content of N in Li during the experiment was estimated to be <100 ppm. For each experiment, 10 specimens were exposed in 100 ml Li, and the ratio of Li volume V_{Li} (cm³) to total surface area of specimens S (cm²) was around 4 cm.

The experimental conditions are summarized in Table 1. The specimens were exposed at 500 °C and 600 °C for 250 h and 750 h. Considering the serious phase transformation observed only after 100 h exposure at 700 °C in the previous experiment [7], exposure time of 250–750 h was considered to be sufficient for comparative study. The Li was refreshed in every exposure test. After the experiment, the Li remained on the specimens and the holder was dissolved in water. In this case, most of corrosion products on the specimens were removed during the cleaning. To reserve the products for analysis, ammonia was used for removing Li in limited cases. The results at 600 °C and 700 °C, which were presented in the previous paper, are also presented for comparison.

Flowing tests were carried out in a thermal convection Li loop facility, which was made of SS 316L stainless steel and consisted of the loop, a Li tank and a heating system. The detail of a loop was reported in reference [11]. A schematic diagram of the facility is shown in Fig. 1. The inventory of Li in the loop was 200 ml and the estimated flowing velocity was 0.05 m/s. During the corrosion tests, the operating temperatures for the loop system were divided as: hot-leg region 3 (500 °C); cold-leg region 1 (400 °C); transition temperature parts, regions 2 and 4. Specimens were fixed by Mo

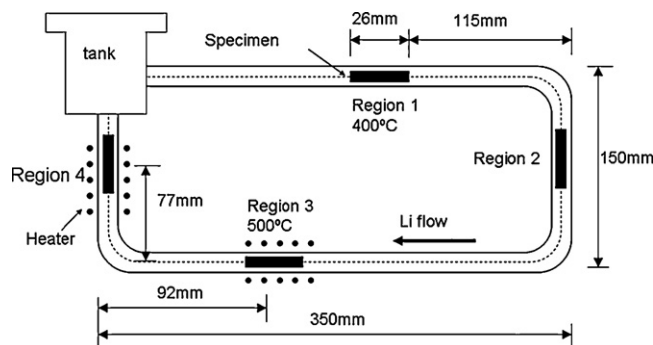


Fig. 1. Illustration of the Li convection loop.

wires in each position. The impurity concentration in the loop test was expected to be comparable with the static experiment because of the similar preparing procedure. The size and surface condition of the specimens were common to those for the static exposure. After Li exposure for 250 h, liquid Li drained away from the loop to the drain tank. The loop was disassembled and Li remained on surface of the specimens and the loop interior was cleaned by water.

The examinations of the specimens were carried out for weight loss measurements by electro-balance with the accuracy of 0.1 mg, surface morphology and composition by scanning electron microscope equipped with energy dispersive X-ray spectrometer, microstructure by transmission electron microscope (TEM), hardness by Vickers Hardness Testing Machine with the weight of 10 g.

3. Results

3.1. The corrosion rate

The corrosion rate was evaluated by measuring the change in the specimen weights before and after the exposure in static and flowing Li. The weight loss in static and flowing Li at 500 °C and 600 °C is shown in Fig. 2. Each symbol type in the figure represents weight loss for a specimen after various exposure conditions. The data of static tests at 600 °C and 700 °C for 100 h [7] were also presented. According to the figure, the weight loss became almost constant after exposure for ~250 h at 500 °C and 600 °C in static test as average of the data. The specimens suffered from a serious corrosion at 700 °C. In flowing Li, the weight loss of JLF-1 (hot-leg specimen) was one order of magnitude larger than that in static exposure.

The detail of the weight loss and the surface composition for the specimens exposed in the loop are presented in Table 2. From the table, only the specimen located in hot-leg (region 3) lost weight, while other specimens placed in lower temperature area

Table 1
Experimental condition

Static exposure	
700 °C	
100 h	√ ^a
600 °C	
100 h	√ ^a
250 h	√
750 h	√
500 °C	
250 h	√
750 h	√
Flowing exposure	
500 °C	
250 h	√

√, cleaned by water to remove the corrosion products; a, cleaned by ammonia to reserve the corrosion products for analysis.

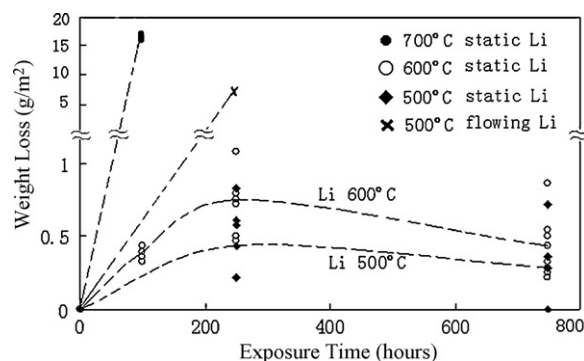


Fig. 2. Weight loss versus exposure time.

Table 2

Weight loss and EDS results after exposure to Li

	Weight change (g/m ² h)	Phase transformation	Surface EDS analysis			
			Cr	Fe	W	Ni
Before exposure	–	–	8.9	89.0	2.0	–
Region 1 (cold-leg 400 °C)	0.038	No	1.7	32.3	0.7	65.3
Region 2	0.014	No	2.6	40.3	0.9	55.4
Region 3 (hot-leg 500 °C)	–0.033	~10 μm	4.0	59.8	1.2	3.3
Region 4	0.001	No	2.3	39.5	0.8	56.5

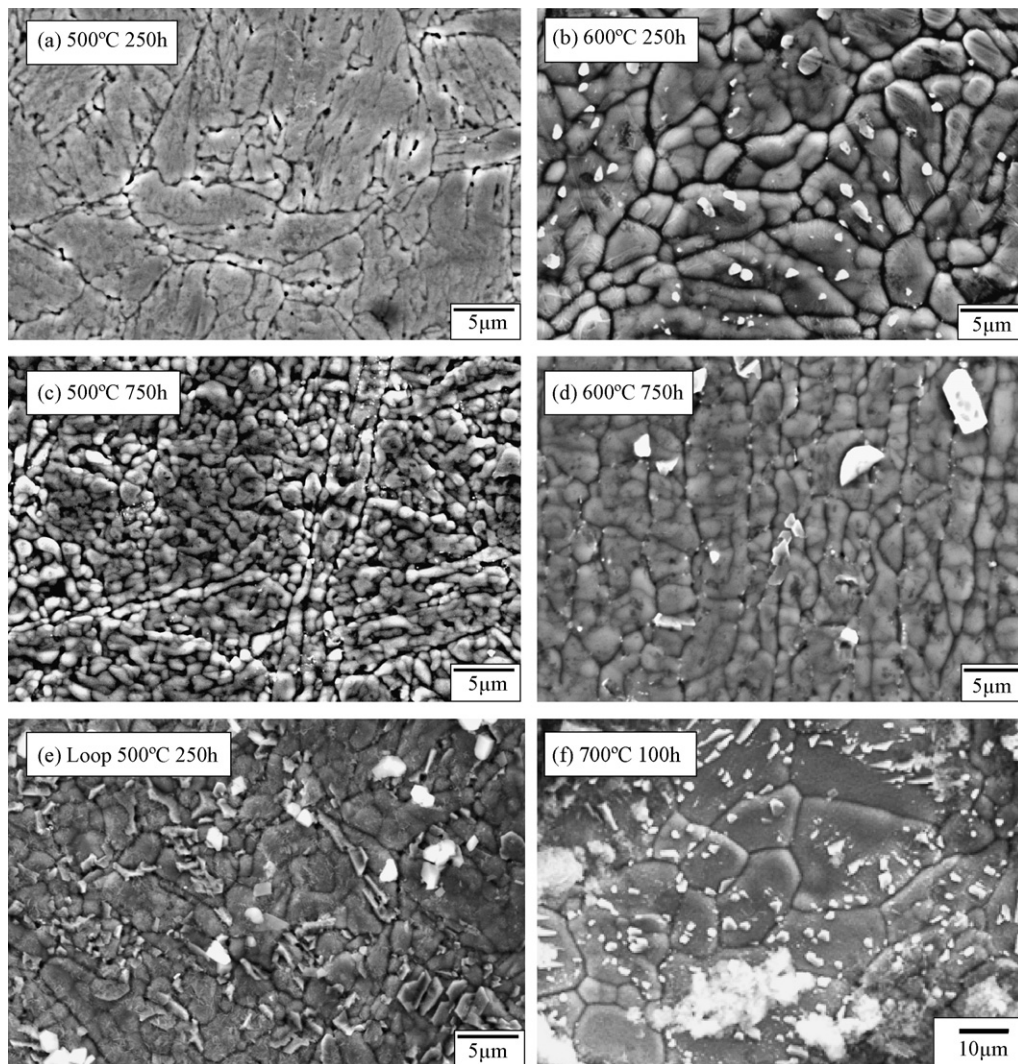
gained weight after the flowing Li exposure. The specimen located in cold-leg (region 1) gained weight most. The enrichment of Ni was detected by EDS on the surface of the specimens located in low temperature area, but almost no Ni was detected on the specimen exposed at hot-leg (region 3), as presented in Table 2. It is thought that the nickel was originated from the tube materials of SS316L.

3.2. SEM/EDS observation

The surface configuration of the specimens exposed at 500 °C and 600 °C is shown in Fig. 3. Because of the cleaning with water, there was almost no corrosion products adhered on the surface. The possible corrosion products, such as Li₂O, Li₉CrN₅, etc., would

have dissolved into the water. As shown in Fig. 3a–d, phase transformation from martensite to ferrite was observed on the surface of almost all specimens exposed in liquid Li, except the specimen exposed at 500 °C for 250 h, where the martensite lath structure was observed. However, the phase change was found after exposure to flowing Li for 250 h at 500 °C, as shown in Fig. 3e.

After the loss of the martensite structure, grain boundaries can be seen on the surface of the specimens. The grain size of the ferrite phase observed after exposure at 500 °C and 600 °C was much smaller than the original austenitic grain boundary (10 μm), but close to martensitic lath size. On the other hand, after 700 °C exposure for 100 h, the surface of the specimens displayed large grains, whose size was close to those of austenitic boundary.

**Fig. 3.** Surface of JLF-1 exposed in static Li.

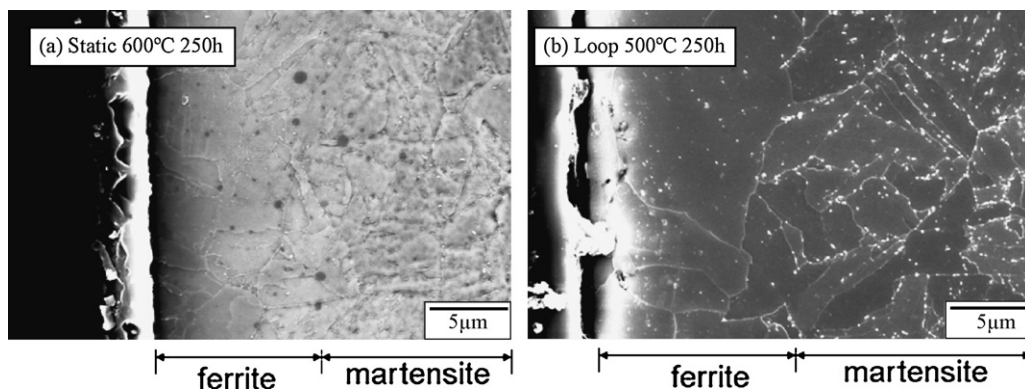


Fig. 4. Phase change on cross-section of JLF-1.

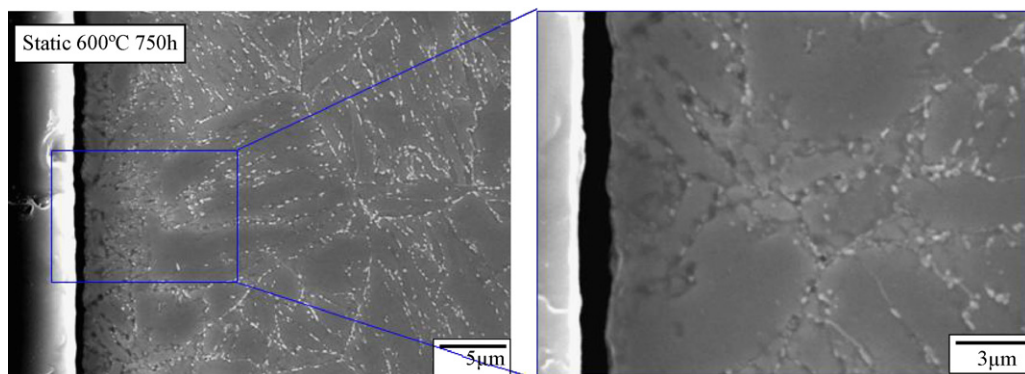


Fig. 5. Disappearance of carbide precipitates after exposure at 600 °C for 750 h.

Phase transformation was also observed in depth of JLF-1 specimens. Fig. 4 shows the cross-sections SEM micrographs of the specimens exposed at 600 °C for 250 h in static Li and at 500 °C for 250 h in flowing Li. The figures show that the depth of the phase change on JLF-1 specimens is about 10 μm in both cases. In the phase transformation zone, the density of carbide precipitates decreased drastically. In Fig. 5, local depletion of carbide was clearly observed on the specimens exposed at 600 °C for 750 h. The dissolution of carbides into liquid Li resulted in holes near the surface. Neither phase change nor C depletion was observed by cross-section SEM in the case of static exposure at 500 °C.

The phase transformation phenomenon was found under different exposure conditions. The relationship of phase change with temperature and exposure time is shown in Fig. 6. The figure shows

that the phase transformation depends on exposure time, temperature and flowing condition. In the static exposure, the phase transformation appeared when the temperature exceeded 600 °C and the exposure time was relatively long. At 700 °C, deeper phase transformation was observed. In the flowing test, however, phase change in 10 μm depth was already found on the specimens after exposure at 500 °C for 250 h.

To determine the composition of the corroded region, EDS surface analysis and line scan of the cross-section were performed. The results of line scan of the cross-section were presented in Fig. 7. The figures revealed a slight depletion of Cr and W near the surface after exposure at 500 °C and 600 °C. In the flowing test, on the other hand, the significant selective dissolution of Cr was found in depth (Fig. 7e).

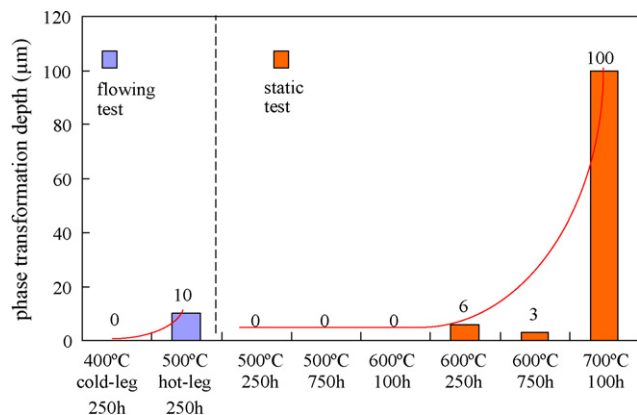


Fig. 6. The phase transformation depth in different conditions.

3.3. Hardness measurement

To investigate the influence of Li corrosion on mechanical properties, Vickers hardness test was carried out before and after the Li exposure. The hardness was measured on the cross-section of the specimens. Fig. 8 shows hardness change as a function of depth after exposure to Li for 250 h at different temperatures. The hardness before and after exposure at 700 °C for 100 h is presented as well. As reported in the previous paper [7], the hardness of JLF-1 drastically reduced from 250 Hv to 140 Hv when specimens were exposed at 700 °C for 100 h. The softened range was around 100 μm, which was consistent with the phase transformation range. In the case of 600 °C for 250 h in static condition and 500 °C for 250 h in flowing condition, the area where the hardness largely decreased also corresponded with the area where martensite changed to ferrite.

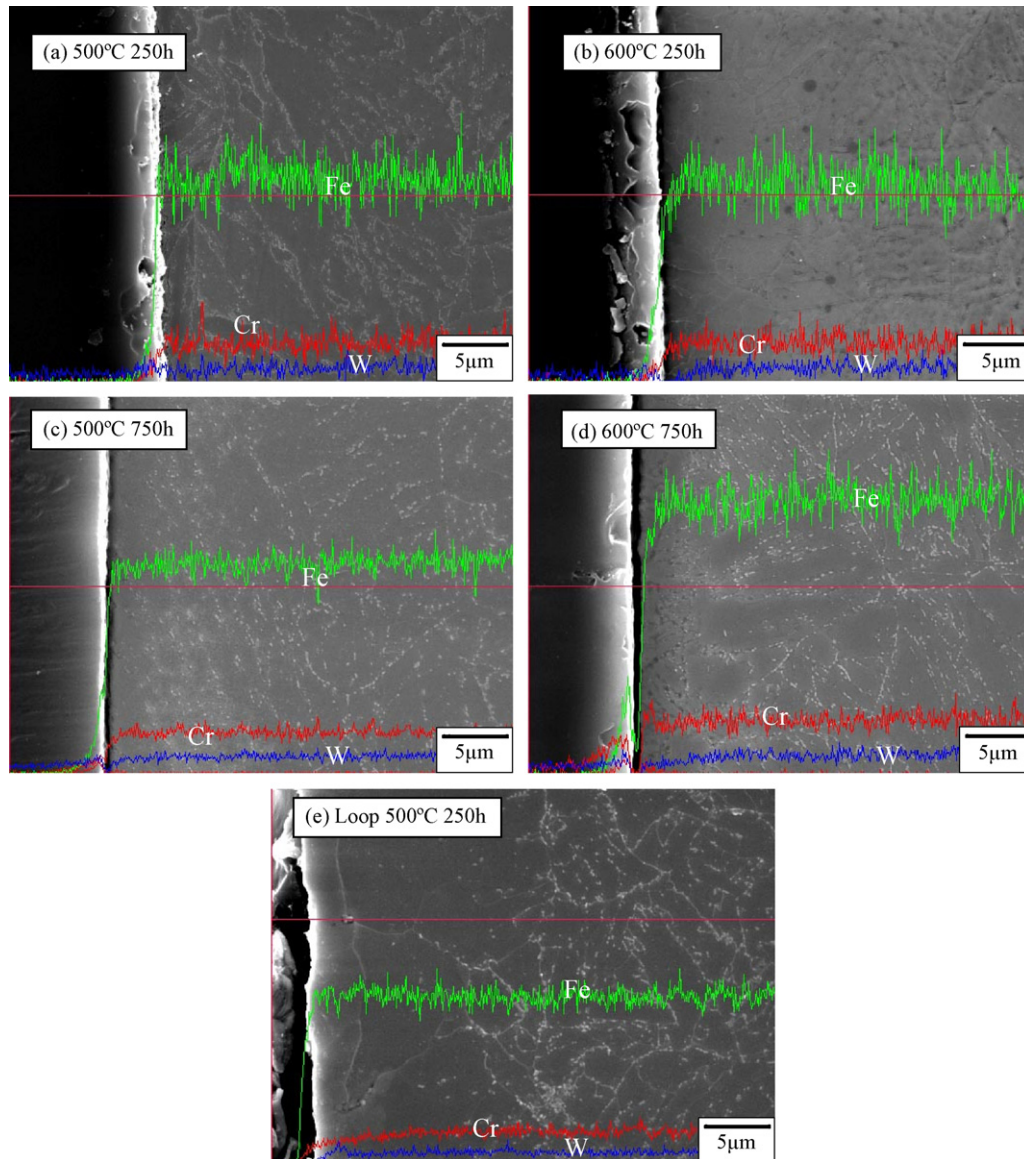


Fig. 7. EDS line scan on cross-section.

4. Discussion

4.1. Mass change

In the static exposure, the average weight losses of JLF-1 specimens became constant for 250 h exposure at the temperature of 500 °C and 600 °C as shown in Fig. 2. This was probably caused by the saturation of Fe, Cr in bulk Li during the static exposure. Furthermore, the saturated layer of dissolution elements near the surface of specimen might also contribute to the reduction of the weight loss. However, Fig. 2 also showed that the weight loss is very different with specimens in the case of static exposure. This suggests that the situation was different with specimens because of the variation of local flow in static test condition.

According to Table 2, the specimens lost weight in hot-leg, but gained weight in cold-leg after the exposure to flowing Li. This is thought to be caused by mass transfer during the loop operation. The elements which dissolved from specimen surfaces and the tube interior in high temperature area deposited on the specimens in lower temperature area following temperature gradient.

This is supported by EDS measurement, in which Ni enrichment was detected on the surface of specimens exposed in lower temperature area, but not in the highest temperature area. Because of the mass transfer effect, the elements would not saturate in high temperature area. Thus the specimens in hot-leg continuously lost elements. The continued dissolution of the elements resulted in a significant corrosion compared with the static exposure. From Figs. 2, 6 and 8, the specimens exposed in flowing Li (hot-leg) showed more serious weight loss, phase change and softening than the specimens exposed in static Li at the same temperature and exposure time. The results clearly suggest the need for systematic loop experiments with temperature gradient to evaluate the corrosion performance in the blanket condition. On the other hand, the specimen in cold-leg (region 1) gained weight after loop exposure. This was mainly due to the precipitation of Ni originated from the loop materials of SS316L. According to the lectures [12–14], the solubility of Ni is an order magnification larger than Cr and Fe at Li in high temperature. Thus, during the exposure, significant amount of Ni was expected to have dissolved into Li from SS316L tube. Because of mass transfer effect, large amount

Ni precipitated on the surface of specimens in cold-leg during the operation.

The major process for the weight loss of JLF-1 steel in the liquid Li seems to be dissolution of Cr, Fe and W in the alloy and the corrosion rate depends on the solution rate of Cr, Fe and W in the liquid Li. C has much high solubility than Cr and W in Li at the same temperature. However, since the concentration and mass of C in JLF-1 are much lower than those of Fe, Cr and W, the contribution of C depletion on the mass loss was small. On the other hand, the depletion of C played an important role in phase transformation and hardness reduction.

4.2. Phase transformation

The loss of C seems to be the driving force to phase transformation. Because of chemical interaction between C and Li, the solubility of C in Li is much higher than Fe and Cr, and decarburization of JLF-1 in liquid Li is possible, as reported by Natesan [15]. According to the chemical analysis results, 2/3 of C in JLF-1 dissolved in Li after 100 h exposure at 700 °C. This agreed with the SEM result that more than 2/3 volume of JLF-1 specimen transformed from martensite to ferrite [7]. Because of loss of interstitial element, C, the phase transformation from bct to bcc could happen at 600 °C or 700 °C. Additionally the depletion of carbides was observed on the cross-section of JLF-1 specimens as shown in Fig. 5. After carbide depletion, small hole remained near the edge of cross-section. Fig. 4 shows that the area where the precipitates disappeared was consistent with that of the phase change.

The process of C depletion would be diffusion across the alloy to the surface facing the liquid Li. The experimental temperature, C concentration in the alloy (especially its gradients at the boundary), solubility of C in the liquid Li and the diffusibility of C in the alloy can affect the growth of the phase transformation region. Furthermore, the reaction between Mo and C could enhance the dissolution of C. Fig. 9 shows the Gibbs-free formation energy of carbide involved in this experiment. It is clear that the Mo is a C-trapper. The Gibbs formation energy of Mo_xC is lower than Li_2C_2 , but higher than Cr carbide. It suggested that Mo could get C from Li and reduce the C concentration in bulk Li. This will break the equilibrium of C in Li and enhance the depletion of C in the specimens.

As shown in Fig. 8, liquid Li exposure has a strong effect on the mechanical properties of JLF-1. The softened area is consistent with the phase transformation area. According to the figure, the hardness decreases from center to edge gradually. This implies there was a transitional region where martensite and ferrite phase were mixed. This was verified by TEM observation [7].

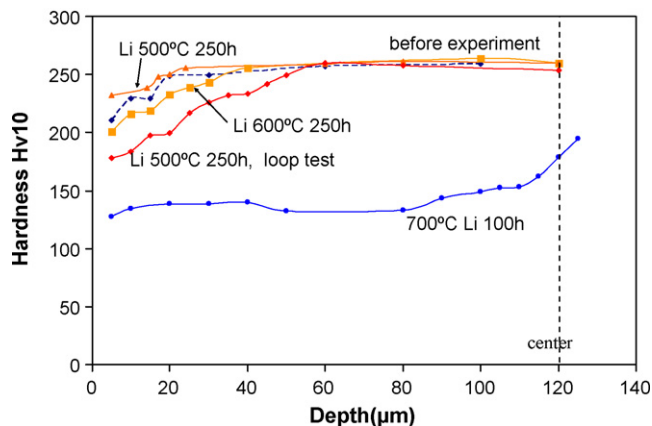


Fig. 8. Hardness change on cross-section of JLF-1 under various exposure conditions.

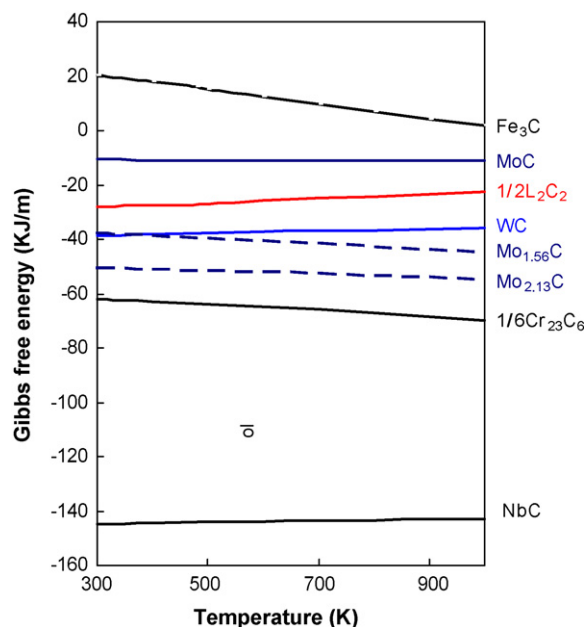


Fig. 9. Thermodynamic data of several carbides [16].

According to the above results, two consequences will be caused by the corrosion of JLF-1 in liquid Li: the general weight loss and reduction of mechanical properties. These need to be taken into consideration when RAFM is used facing Li. Further research into the mechanism of the corrosion in liquid Li will be carried out, including the interaction between specimen, Li and crucible (loop) materials, the solution and transfer of alloy elements and possible formation of chemical compounds, especially nitrides, in Li. The present results also suggest the need for long time flowing experiments with temperature gradient for evaluation the corrosion performance in the blanket condition.

5. Conclusions

The compatibility of RAFM steel, JLF-1, with static and flowing Li was investigated. The main conclusions are

- (1) In static exposure, the weight loss became constant after 250 h exposure, because of the saturated elements in liquid Li.
- (2) The phase transformation from martensite to ferrite was caused by C depletion.
- (3) The drastical softening of the surface area of JLF-1 by exposure to Li was due to the phase transformation.
- (4) The flowing Li accelerated the weight loss, phase change and hardness reduction due to the mass transfer. The results clearly suggest the need for systematic loop experiments with temperature gradient for evaluation the corrosion performance in the blanket condition.

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