



# Compatibility of ferritic steels with $\text{Li}_2\text{BeF}_4$ molten salt breeder

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## Abstract

The corrosion behavior of ferritic steels including JLF-1 (Fe–9Cr–2W) against Flibe ( $\text{LiF}$ – $\text{BeF}_2$  molten salt mixture) was investigated. Dipping experiments were carried out by (1) varying the dipping period and (2) varying the composition of the gas atmosphere. By the former experiment it was found that a protective scale of oxides was formed in about 3 days. By the latter, it was found that oxidization occurred prior to fluorination at 550 °C. From these results, it could be concluded in this stage that the compatibility of JLF-1 with Flibe is good in the first stage of the FFHR operation condition.

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## 1. Introduction

Flibe ( $\text{Li}_2\text{BeF}_4$ ; a 2:1 mixture of  $\text{LiF}$  and  $\text{BeF}_2$ ) is a candidate material for tritium breeding in a CTR liquid blanket, because of its low electric conductivity, its high chemical stability, and possibility of utilizing as coolant material. Actually, it is utilized in some conceptual designs for liquid blankets such as FFHR [1]. Flibe itself has higher chemical stability than the fluorides of ordinary metals and has almost no reactivity with structural materials. However, Flibe generates T, O, F, etc. under neutron irradiation, and some corrosive species such as TF have a strong influence. On the other hand, JLF-1 (Fe–9Cr–2W) and V–4Cr–4Ti are considered as candidate structural materials. However, almost no experimental data about the compatibility of such materials with Flibe containing some corrosive species are available. Therefore, its compatibility is a critical issue.

The behavior of JLF-1 was investigated in contact with molten Flibe under neutron irradiation by ther-

modynamic calculations, and it was proved that metal oxides such as  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{FeO}_4$  might be stable in Flibe and the corrosion by HF existing in Flibe might not occur if these oxides were formed as protective scales on the surface [2,3]. However, kinetic data on the stability of these oxide layers are required to judge whether they can survive in contact with molten Flibe or not. In this paper, the compatibility of JLF-1 with Flibe at elevated temperature is investigated in two ways: (1) dipping experiments varying the periods and (2) dipping experiments under corrosive atmosphere (Ar gas containing low concentrations of HF and  $\text{O}_2$ ).

## 2. Experimental

A schematic drawing of the experimental system is shown in Fig. 1. Dipping experiments were performed in a SUS316 container in flowing dry argon atmosphere. In a nickel crucible (10 mm in diameter  $\times$  30 mm in depth), each specimen was dipped in Flibe prepared by mixing  $\text{LiF}$  and  $\text{BeF}_2$  with the ratio of 2 to 1 at 550 °C.  $\text{BeF}_2$  is hygroscopic and deliquescent, HF is generated at elevated temperatures by the reaction:  $\text{BeF}_2 + \text{H}_2\text{O} \rightarrow \text{BeO} + 2\text{HF}$ . Therefore, initial Flibe contains small amounts of HF (in several ppm). After each specimen

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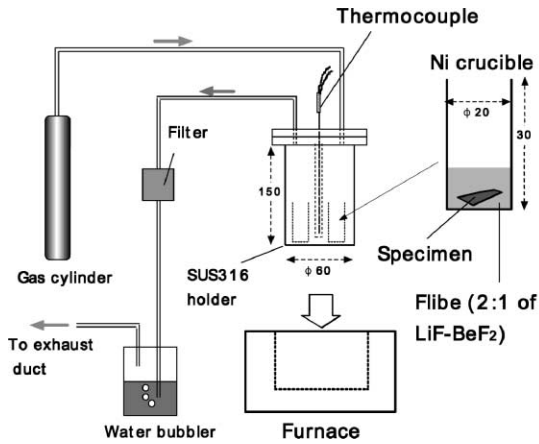


Fig. 1. Experimental system.

was picked up from Flibe and cooled down, it was cleansed in LiCl–KCl molten salt in order to remove the Flibe solidified on the specimen surface. Then, LiCl–KCl sticking to the specimen was removed by ultrasonic washing in water, and finally the surface of the specimen was wiped with alcohol. Though LiCl–KCl washing is a milder method than others (e.g. physically removing), it may remove non-adhesive compounds from the surface. In this experiment, however, we chose this method because we were concerned about strongly adhesive products.

### 2.1. Dipping experiment during several periods (experiment 1)

As a preliminary experiment, SUS430 ferritic steel (Fe–18Cr) consisting of two components was used as a model material for examination. The covering gas was pure Ar gas (99.9999%) flowing at about 10 ml/min. The periods of dipping were 1, 3 and 10 days. The corrosion behavior was investigated by X-ray diffractometry (XRD) and Rutherford backscattering spectrometry (RBS). The RBS analysis was carried out using 3 MeV  $^4\text{He}^{2+}$  ions ( $\theta_{\text{lab}}: 160^\circ$ ) with a tandem accelerator in the Research Center of Nuclear Science and Technology of the University of Tokyo. Conversion electron Mössbauer spectroscopy (CEMS) was also applied to SUS430 specimens.

### 2.2. Dipping experiment under corrosive atmosphere containing low concentration of HF and O<sub>2</sub> (experiment 2)

JLF-1 (Fe–9Cr–2W) was chosen as candidate material. In order to examine in severe conditions, not only pure Ar (99.9999%) but also Ar + 1%O<sub>2</sub> and Ar + 82 ppm HF were used as the cover gas. The dipping period

was 30 days (9 days in the case of Ar + 82 ppm HF). The characterization methods were the same as in experiment 1. The specimens were supplied from National Institute of Fusion Science (NIFS).

## 3. Results

### 3.1. Results of experiment 1

There was no significant change observed for each specimen with an optical microscope. It was observed that the surface of the specimen did not suffer from destructive corrosion. By XRD analysis, small peaks of Fe<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>, which cannot be distinguished from each other, and a peak of the spinel phase were observed besides those of  $\alpha$ -Fe phase at the specimen dipped after 3 days. The RBS spectra of the specimens before dipping and after 1, 3 and 10 days dipping are shown in Fig. 2. The horizontal axis corresponds to the energy of scattering ions times 2.8655 keV. The vertical axis is the value normalized by the total counts. By this analysis, the penetration depth of oxygen near the surface of each specimen was substantially the same. It was found to be 100 nm by considering the stopping power calculated by SRIM 2000, which is too small for detection by XRD analysis. The standing shoulder of Fe and Cr indicates that Cr is concentrated on the surface of the specimen rather than the other elements. By CEMS, the specimen after 3 days dipping shows the most similar structure to pure Fe near the surface and less similar after 1 day dipping. The similar structure to pure Fe indicates that the Cr-depleted phase grew under the oxide layer by diffusion of Cr to the surface. The ratio of six sextet Fe

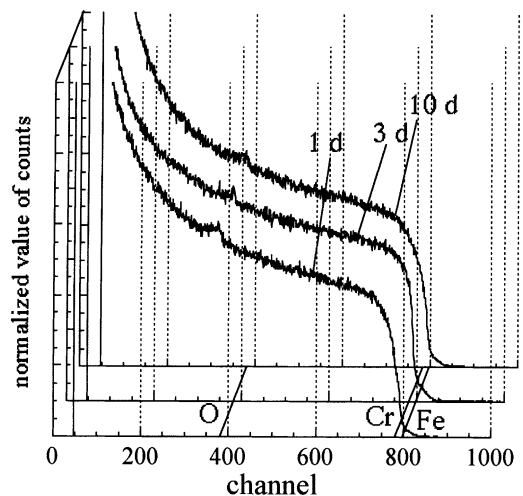


Fig. 2. Normalized RBS spectra of dipped SUS430 specimens (1, 3 and 10 days).

peaks was near 3:2:1:1:2:3 in all dipped specimens. This indicates that the boundary between the oxide and the metal layer became rough. The peaks of paramagnetic Fe(III) were observed for each specimen. Fe(III) can take the forms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, various FeOOH and Fe<sub>3</sub>O<sub>4</sub> (A site). Among these compounds,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and FeOOH are excluded considering the dipping temperature and the after treatment temperature. If Fe<sub>3</sub>O<sub>4</sub> was produced, the peaks of Fe(III) (A site) and the peaks which are averaged between Fe(III) (B site) and Fe(II) (B site) should be detected, and these peaks could not be detected. Therefore, it is appropriate that these Fe(III) peaks indicate  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. In case of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the peaks of Fe(III) should split to six sextet because of its antiferromagnetism. However, only doublet peaks were detected in the spectra. This is because the diameter of Fe<sub>2</sub>O<sub>3</sub> grains is less than 10 nm and its magnetization vibrates, and the peaks do not show magnetic split. This phenomenon is called superparamagnetism. From these results, it can be concluded that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> whose grains are very small is produced on the surface of the dipped specimens.

Based on these results, the mechanism of oxidation can be speculated. First of all, a layer of spinel type oxide is formed on the surface. Secondly, a layer containing Cr<sub>2</sub>O<sub>3</sub>, Fe(Fe,Cr)<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> grows, under which a Cr-depleted zone is formed. Finally, Cr atoms diffuse from the base material to the Cr-depleted zone. The fact that the degree of Cr-depletion was moderated after 3 days indicates that a stable oxide layer containing mainly Cr is formed in a few days and the formation of this oxide layer prevents a severe corrosion. The random boundary between the oxide layer and the metal layer seems to contribute to good adhesion of the oxide layer. Thus, it was found that SUS430 shows good compatibility with Flibe.

### 3.2. Result of experiment 2

By visual observation, no specimen suffered from severe corrosion. However, there were a lot of differences in color and surface phases among them. XRD spectra of the specimens before and after dipping under each atmosphere are illustrated in Fig. 3(a)–(c), RBS spectra in Fig. 4 and Mössbauer spectra in Fig. 5. Table 1 shows the value of the isomer shift (IS) of each specimen. The color of the specimen dipped under pure Ar atmosphere was gray brown, and the surface was smoother and optically more metallic than the other specimens. Only the peaks of the base metal ( $\alpha$ -Fe) were detected by XRD analysis. By RBS analysis, the peaks similar to those in experiment 1 were observed, which indicated the existence of a very thin oxide film and was expected to be about 100 nm thick by calculation using the stopping power. Near the surface, W was concentrated, though the phase could not be made clear.

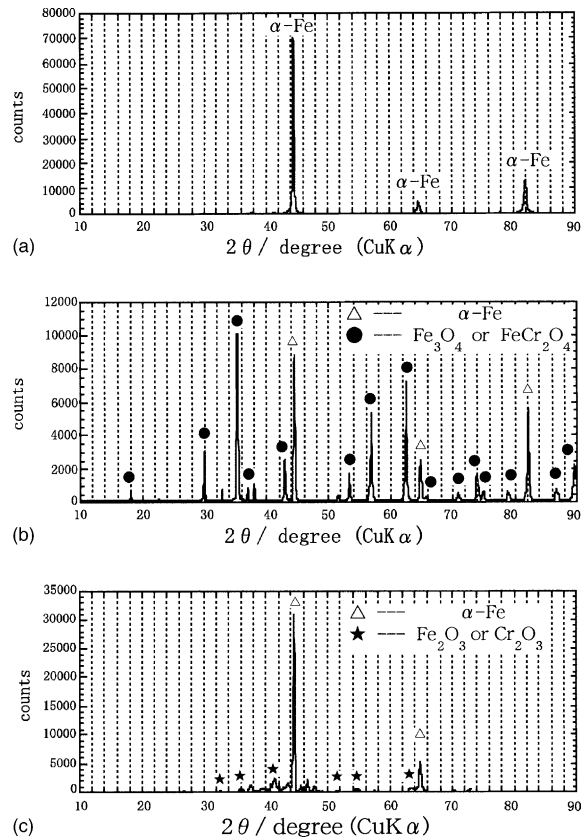


Fig. 3. XRD spectra of JLF-1: (a) before dipping and dipped under pure Ar atmosphere, (b) dipped under 1% oxygen atmosphere and (c) dipped under 82 ppm HF atmosphere.

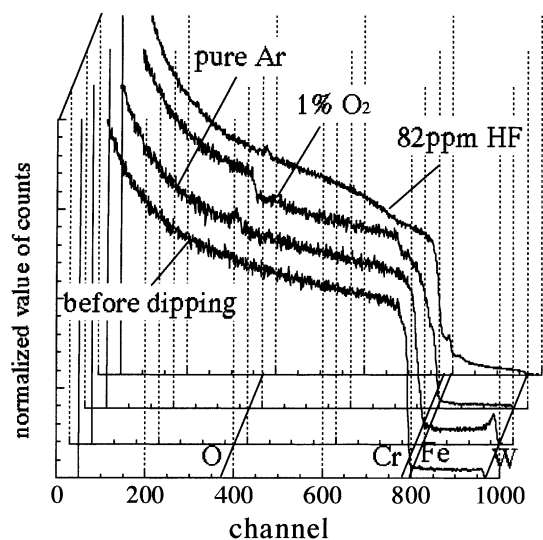


Fig. 4. Normalized RBS spectra of dipped JLF-1 specimens dipped under each atmosphere.

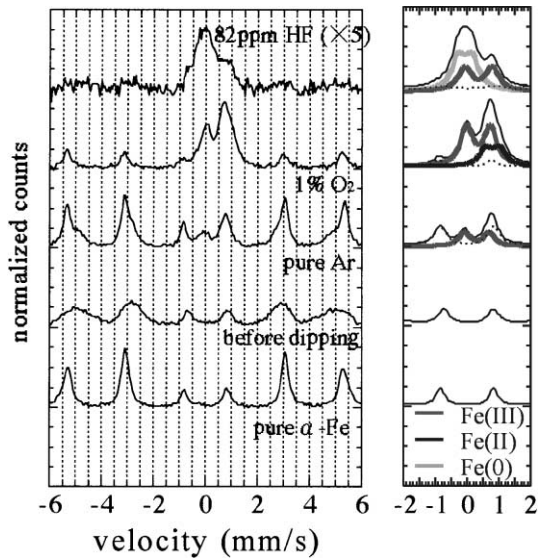


Fig. 5. CEMS spectra of pure  $\alpha$ -Fe and JLF-1 specimens before dipping and after dipping under each atmosphere.

Table 1  
IS value of peaks except for  $\alpha$ -Fe in CEMS spectra

Dipping condition	IS value (mm/s)
Before dipping	–
Pure Ar	0.31
Ar + 1%O <sub>2</sub>	0.41, 0.85
Ar + 82 ppm HF	0.12, 0.42

Doublet paramagnetic peaks with the IS value of 0.31 were detected by CEMS analysis. This indicates the existence of very fine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> grains of the size smaller than 10 nm, as in the case of SUS430. The sharpness of the sextet peaks of  $\alpha$ -Fe indicates that there is a Cr-depleted phase. The strength ratio of the peaks 3:4:1:1:4:3 means that the boundary between the oxide layer and the base metal is smooth. From these results, it can be concluded that the cross-section of this specimen is like Fig. 6(a).

The color of the specimen dipped under 1%O<sub>2</sub> atmosphere was brown, and the surface was very rough. Very strong peaks of a spinel type oxide were detected by XRD analysis. The peak heights were roughly the same as those of the base metal, and the oxide layer was found to be very thick. The RBS spectra of this specimen indicate that the metal density became higher with the depth from the surface. The boundary between the oxide layer and the base metal was clearly separated because the shoulder of the metal signal was gently sloping and the signal stood up suddenly at 710 in channel. The energy difference between the shoulder and the standing

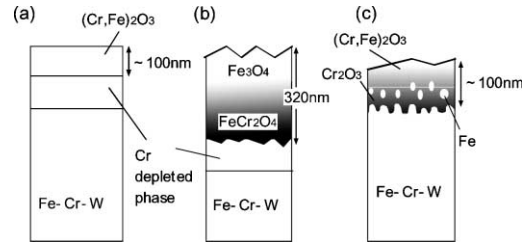


Fig. 6. Mechanism of JLF-1 oxidation under each atmosphere: (a) very small amount of both HF and O<sub>2</sub> are contained, (b) mainly O<sub>2</sub> is contained and (c) mainly HF is contained.

point indicates that the thickness of oxide layer is approximately 320 nm. It was found by CEMS analysis that the boundary between the oxide layer and the metal phase is rough, and the paramagnetic peaks of Fe(II) and Fe(III) were detected. Fe(III) can form  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. Because these peaks were very strong and the high peaks of spinel type oxides were detected by XRD, it is proper to think that Fe<sub>3</sub>O<sub>4</sub> was produced. Fe<sub>3</sub>O<sub>4</sub> should be detected as the two sets of peaks. However, if Fe(II) in the B site is oxidized with a stoichiometry change, the spectra also change. In this case, the compound is written as (Fe<sup>3+</sup>)<sub>A</sub>(Fe<sup>2+</sup><sub>1-3x</sub>Fe<sup>3+</sup><sub>1+2x</sub>V<sub>x</sub>)<sub>B</sub>O<sub>4</sub>. V means a cation vacancy and  $x$  can range from 0 to 0.33. The strength of the internal magnetic field of Fe(III) (B site) is almost the same as that of Fe(III) (A site), and the peak of each Fe(III) is detected almost at the same energy. In this work, such a situation should take place. The IS value of Fe(II) is 0.85 mm/s, which agrees well with the IS value [4] of FeCr<sub>2</sub>O<sub>4</sub>,  $0.91 \pm 0.06$ . This indicates the existence of FeCr<sub>2</sub>O<sub>4</sub>. The peaks of both Fe<sub>3</sub>O<sub>4</sub> and FeCr<sub>2</sub>O<sub>4</sub> were detected as paramagnetic peaks. This also indicates that these compounds show superparamagnetism and the grain size is less than 10 nm. The peak ratio of the sextet of Fe also indicates that the boundary between the base metal phase and the oxide layer are rough. Judging from these results, it can be concluded that a model drawing of the cross-section of the specimen dipped under 1%O<sub>2</sub> atmosphere is shown in Fig. 6(b).

A specimen dipped under 82 ppm HF atmosphere was gray brown. Broad peaks of Cr<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> were detected by XRD analysis. Some peaks are still unknown and were not identified as FeO, Fe<sub>3</sub>O<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub>, FeF<sub>2</sub>, CrF<sub>2</sub>, CrF<sub>3</sub>, etc. It was found by RBS results that the near surface region was lacking in Fe and the Cr to Fe ratio became about 2. This indicates that the surface region consisted mainly of Cr compounds. Judging from the O peak, the depth of O penetration was about 100 nm. Peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> whose grain size is less than 10 nm were detected by CEMS analysis. Peaks with the IS value of 0.12 mm/s showing superparamagnetism were also detected. It is reasonable that Fe originating from the base metal was left in island shape because the

charge number is zero. The size of these grains is very small, which shows no peak split. From these results, it can be concluded that the compound layers near the surface are shown in Fig. 6(c).

#### 4. Discussion

In both cases of experimental 1 using SUS430 (Fe–18Cr) specimens under Ar and experiment 2 using JLF-1 (Fe–9Cr–2W) specimens under pure Ar, a  $(\text{Cr,Fe})_2\text{O}_3$  layer was formed on each specimen which can be considered as  $\text{Cr}_2\text{O}_3$  because the product in each condition contained mainly Cr. The  $\text{Cr}_2\text{O}_3$  layer is generally considered to be retained just under the condition of  $J_{\text{Cr}}^{\text{M}} > J_{\text{Cr}}^{\text{O}}$  at the boundary between the metal phase and the oxide phase, where  $J_{\text{Cr}}^{\text{M}}$  is the Cr flux in the metal phase toward the surface and  $J_{\text{Cr}}^{\text{O}}$  is that in the oxide phase. In the case of air oxidation at high temperatures, the concentration of Cr in the Fe–Cr alloy should be above 20% to form a  $\text{Cr}_2\text{O}_3$  layer. In the system of this work, the oxidization species such as  $\text{O}_2$  or  $\text{H}_2\text{O}$  (<0.5 ppm) should have infiltrated as impurities from the gas cylinder. By this work, it was clarified that JLF-1 contains a high concentration of Cr to form a  $\text{Cr}_2\text{O}_3$  layer and retain it in 30 days. In case of an Ar + 1% $\text{O}_2$  atmosphere,  $J_{\text{Cr}}^{\text{O}}$  became larger than  $J_{\text{Cr}}^{\text{M}}$  and the oxide species changed to  $\text{FeCr}_2\text{O}_4$ . It was expected by thermodynamic calculations that the minimum amount of the oxidization species was  $10^4$  ppm [2]. The results in this work meet the results of thermodynamic calculation.

The implications of these results are considered from the viewpoint of the FFHR-1 operating condition. This reactor is designed to have 3 GW fusion power with 500 t Flibe as tritium breeder and coolant. This means that 500 g of tritium will be consumed per day. If this amount of tritium should be supplied from the Flibe transmutation, 30 ppm of TF must be produced for conversion into tritium. On the other hand, 30 ppm of TF is piled up in the blanket system per day if the TF reducing system is stopped. The case of the atmosphere containing 82 ppm HF corresponds to the situation that TF reducing system is stopped for 3 days. Therefore, the results of this work indicate that the structural materials would not suffer from severe corrosion if the TF reducing system would be stopped during 3 days. In the case of oxidization species, the concentration of oxygen generated by transmutation is very few. The generation rate of the oxidization species seems to be from 0.02 to 0.1 of that of TF [3]. It could not be considered that the oxygen concentration became above  $10^4$  ppm in conditions of normal operation. Therefore, it is reasonable to

suppose that the oxide layer formed in conceivable conditions of operation is  $\text{Cr}_2\text{O}_3$ .

#### 5. Conclusion

SUS430 (Fe–18Cr) specimens were dipped in Flibe during several periods. It was observed that the oxide layer mainly containing Cr was formed in about 3 days and became stable. It could be concluded that Cr, which is component of the steel due to corrosion resistance, works well in Flibe.

JLF-1 was dipped in Flibe under several atmospheres such as (1) very small amounts of HF and  $\text{O}_2$  were added to Ar, (2) mainly  $\text{O}_2$  was added to Ar (Ar + 1% $\text{O}_2$ ) and (3) mainly HF was added to Ar (Ar + 82 ppm HF). It was confirmed by this experiment that the kind of the oxide product did not depend on HF but on  $\text{O}_2$ . When the  $\text{O}_2$  concentration was very low, a dense film of  $\text{Cr}_2\text{O}_3$  was formed and the specimens showed good compatibility with Flibe for 9–30 days. When the  $\text{O}_2$  concentration was high, a spinel type oxide was formed. This would also work as a protective scale against corrosion, but  $\text{Cr}_2\text{O}_3$  is more effective.

Considering all results, the compatibility of JLF-1 with Flibe was found to be good for the first 30 days. For the judgement on whether JLF-1 can be utilized as the structural material of a blanket system or not, further experiments are required: (1) corrosion behavior in longer term dipping, (2) corrosion behavior under neutron irradiation and (3) adhesion of oxide protective scale in flowing Flibe.

#### Acknowledgements

We thank Professor K. Nomura (Department of Applied Chemistry, University of Tokyo) for CEMS analysis and Dr A. Suzuki (NIFS) and Professor T. Muroga (NIFS) for supplying the JLF-1 specimens.

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