Progress in Flibe Corrosion Study toward Material Research Loop and Advanced Liquid Breeder Blanket

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Abstract. High purity Flibe was prepared for corrosion study. Fundamental corrosion experiments in static condition were performed on the structural material for Flibe blanket and Material Research Loop, which is non-isothermal forced convection loop simulating the blanket condition. Corrosion rate for the structural materials in static condition was estimated as small as 0.83-5.4 μm/yr in the high purity Flibe. The corrosion rate is acceptable for the structural materials. Main corrosion process was identified as formation of oxide corrosion products and their dissolution into Flibe, therefore oxygen impurity control will reduce corrosion weight loss further. The good compatibility between the fabricated Flibe and the structural materials, and progress in other related R&D indicate feasibility for Material Research Loop and the Flibe blanket.

1. Introduction

Liquid breeder blanket is promising for DEMO and commercial fusion reactors. Flibe molten salt (BeF_2 + LiF) is a very attractive liquid breeder material because of (1) non-reactivity with the air and water, (2) low vapor pressure leading to low operation pressure, (3) low tritium inventory and (4) low MHD resistance, compared with the other liquid metal breeders (Li and Li-Pb). Flibe blanket has been designed for Force-Free-like Helical Reactor (FFHR)[1]. The blanket structural material is low activation ferritic steel. Operation temperature is 723 K and 823 K for inlet and outlet of the Flibe blanket, respectively. Critical issues, on the other hand, for Flibe blanket system are (1) corrosion of structural materials by HF (TF from tritium breeding) in Flibe, (2) enhancement of heat transfer, and (3) reduction of tritium permeation from Flibe to the structural materials. JUPITER-II (Japan USA Program for Irradiation/Integration TEst for fusion Research-II) and inter-university collaboration programs have exhibited progress in various research fields on the critical issues[2][3][4]. In the JUPITER-II program, the reduction of the corrosion agent, HF, in static Flibe has been successfully demonstrated[2] by the REDOX (REDuction and Oxidation) control with the following reaction.

$$2HF + Be \rightarrow H_2 + BeF_2 \qquad (1)$$

The next milestone to the blanket development is material corrosion research with convection loop to predict corrosion rate in the blanket condition.

Generally, static corrosion test is preferred to evaluate fundamental corrosion resistance of the materials. However, corrosion rate is usually enhanced under the flowing condition with temperature difference, compared with static condition, due to un-saturation of dissolution and removal of the corrosion products. Natural convection loop is used to examine the effect of un-saturation of dissolution under small flow velocity (< 0.1 m/s), while non-isothermal forced convection loop can widely control flow velocity (0.1 ~ 10 m/s) and operation temperature, and leads to systematic corrosion tests under the Flibe blanket condition.

In the present study, purification technique for Flibe has been developed for the corrosion experiments, and also its scale-up has been demonstrated for application to the non-isothermal forced convection loop (material research loop). Fundamental corrosion experiments have been performed for the blanket structural material (JLF-1: Fe-9Cr-2W-0.1C) and the loop structural material (316L stainless steel: Fe-18Cr-8Ni-2Mo). From the progress in the fundamental researches and other related R&D, feasibility of the material research loop is verified.

2. High Purity Flibe Production

High purity Flibe is required for materials corrosion test, because HF, O and metal impurities heavily affect corrosion rate in Flibe. In addition, the impurity levels for constituent elements of the samples, such as Fe, Cr, W, Ni, should be reduced for corrosion research to detect small dissolution of these elements by chemical analysis on Flibe. The goal for the first purification was set to obtain the same or higher purity compared with the conventional Flibe in the previous research[2].

A purification system for Flibe has been developed in TNF (The University of Tokyo-National Institute for Fusion Science Flibe Grove box) facility[5]. Flibe was fabricated from 99.5 %-grade BeF_2 and 99.9 %-grade LiF by melting in Ni crucible under He gas at 873 K. The composition was 33.3 mol % BeF_2 + 66.7 mol % LiF. The melted Flibe was purified by He- 2 vol. % HF gas bubbling at 873 K and He – 5 vol. % H_2 gas flowing at 873 K[6]. HF reduces oxygen impurity by the following reaction,

$$2HF + BeO \rightarrow H_2O + BeF_2 \qquad (2)$$

where H_2 removes metal impurity by reduction as the following reaction.

$$\frac{x}{2}\ H_2 + MF_x \rightarrow x\ HF + M \qquad (3)$$

M: Fe, Cr etc.

Improvements in the present study were (1) to use the high purity LiF and BeF_2, (2) to flow

H_2 gas to the surface of melted Flibe instead of bubbling to inside, and (3) to keep low cooling rate after purification melting. (2) is expected to limit the reduction reaction at the surface of the melted Flibe, and (3) avoids convection mixture for the reduced metal (M) and the purified Flibe. Purified volume for Flibe 1 and 2 was 50 g, and then it was increased to 150 g for Flibe 3. Table I lists impurity levels of the starting materials (LiF and BeF_2), purified Flibe (Flibe 1-3) and the conventional Flibe[2]. Purified volume for Flibe 1 and 2 was 50 g, and then it was increased to 150 g for Flibe 3. According to Table 1, especially Fe impurity level (4-70 mass ppm for Flibe 1-3) was successfully reduced compared with the conventional Flibe (260 mass ppm). Concentrations of Cr and W, the alloying elements to JLF-1 steel, were kept to 3-11 mass ppm and < 1 mass ppm. The low impurity levels are suitable to detect transfer of the constituent elements for JLF-1 steel in Flibe at ppm level.

TABLE I: IMPURITY LEVEL FOR THE STARTING MATERIALS AND FLIBE FABLICATED (unit: mass ppm).

	Fe	Cr	W	Ni	Mo	Cu	Na	Mg	Al	K	Ca
LiF	14	2	<1	1		1	160	68	15	66	220
BeF_2	25	7	<1	7		2	1800	210	12	4200	190
Flibe 1 (50 g)	4	3		<1			890	180	33		
Flibe 2 (50 g)	5	11	<1	27		1	830	170	31	1900	210
Flibe 3 (150 g)	70	5	<1	16	<1	<1					
Conventional	260	16		15							

TABLE II: CHEMICAL COMPOSITION OF JLF-1 STEEL AND 316L STAINLESS STEEL (unit: mass %).

	Fe	C	Si	Cr	W	Ni	Mo	V	Ta	Mn
JLF-1	balance	0.09	0.05	9.00	1.98			0.20	0.083	0.49
316L SS	balance	0.009	0.56	17.26		12.66	2.05			1.64

3. Corrosion Test for JLF-1 Low Activation Ferritic Steel and 316L Stainless Steel

3. 1. Test Procedure

JLF-1 steel and 316L stainless steel (316L SS) were exposed to the purified Flibe at 773-873 K for up to 2003 hr in static condition, to evaluate basic compatibility with Flibe and corrosion characteristics[7][8]. JLF-1 steel used in the present study was a 1 inch-thick plate of JLF-1 JOYO-II heat (JLF-1 LN) ferritic steel[9]. Table II shows the chemical composition of the JLF-1 steel and 316L SS. The final annealing for JLF-1 was normalizing at 1323 K for 1 hr and tempering at 1053 K for 1 hr. 316L SS was cold-rolled state. The specimen size was 15 x 10 x 1 mm for JLF-1 and 15 x 10 x 0.5 mm for 316L SS. Crucibles made from the JLF-1 and 316L SS were prepared. The size of the crucibles was 20 mm in outer diameter, 30 mm in height and 2 mm in wall thickness. 1 specimen and 3-4 g of the Flibe was set into crucible made from the same material as the specimen. Flibe 2 and 3 were used for JLF-1 test and 316L SS test, respectively. The crucibles containing the specimen and the Flibe were sealed in a stainless steel (SS304) capsule filled with high purity helium. The capsule with JLF-1 was heated up to 823 K for 2003 hr, while the one with 316L SS was heated at 773 and 873 K for 1000 hr. After exposures, the crucibles were heated again to melt and separate the Flibe from the specimens and crucible. The extracted Flibe was chemically analyzed by inductively coupled plasma (ICP) - atomic emission spectroscopy (AES) or ICP- mass spectroscopy (MS). The remaining Flibe on the specimen surface was dissolved and removed by a LiCl-KCl mixture.

TABLE III: COMPOSITION OF HE- HF GAS MIXTURE. Ratio of the number of F atom and O atom (F/O) in the gas mixture is also shown.

Nominal composition	H_2O %	O_2 %	HF %	F/O
He	0.0027	0.0089	-	0
He- 0.1% HF	0.055	0.0016	0.14	2.4
He- 1% HF	0.055	0.0016	0.96	16

In order to investigate fundamental process for corrosion products formation by oxidation and fluoridation, the JLF-1 specimens were exposed to He- (0~1%) HF gas mixture at 823 K for 2.5~100 hr. The base He gas contained moisture (H_2O) and O_2 as impurities. The H_2O and O_2 concentrations were measured with Dewpoint transmitter XDT-PM-PB, Xentaur and Oxygen Analyzer DF-150, Delta F Co., respectively. HF gas was generated by reaction between H_2 gas and NiF_2 at 873 K. HF concentration was determined by titration. Table III lists He- HF gas compositions. Concentration of H_2O and O_2 in He- 0.1%HF and He- 1%HF were evaluated by the one before HF generation, since the gas analyzers are not applicable to corrosive gas.

Weight change during the exposures was measured. The corrosion products on the specimen surface were analyzed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

3.2. Results and Discussion

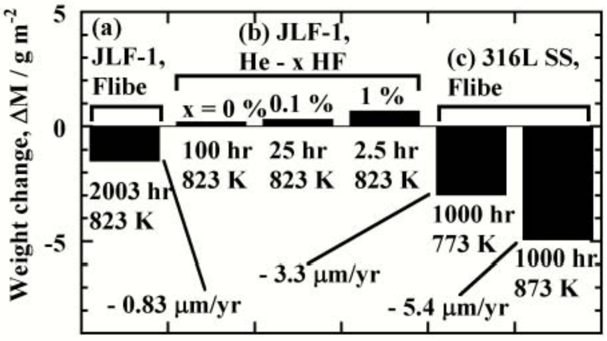


FIG.1. Weight Change after Corrosion Tests. Corrosion conditions were (a) 823 K x 20003 hr in Flibe for JLF-1, (b) 823 K x 100 hr for He, 25 hr for He- 0.1% HF, 2.5 hr for He- 1% HF for JLF-1, and (c) 773 K and 873 K x 1000 hr for 316L SS.

Figure 1 shows weight change during the exposure test. In this figure, exposure atmosphere, time and temperature are indicated. For Flibe exposure tests, equivalent corrosion rates calculated from the weight loss are also given in μm/yr for specimen thickness. The weight loss of JLF-1 at 823 K was 1.5 g m^{-2} for 2003 hr, which is multiplied to 0.83 μm/yr in corrosion rate. On the other hand, JLF-1 showed weight gain in the He or He- HF gas conditions. In the gas conditions, all the corrosion products were remained on the specimen surface, while the products were lost by dissolution in Flibe condition. The fundamental process for weight loss in Flibe is considered as formation of corrosion products shown in the He or He- HF gas, and their dissolution into Flibe. In the same way, corrosion rate for 316L SS at 773 K and 873 K was evaluated as 3.3 and 5.4 μm/yr, respectively. The corrosion rates for both JLF-1 and 316L SS were considered as acceptable level for the structural materials.

Table IV is the results of the chemical analysis on the Flibe after exposure tests. The exposed specimen and exposure temperature are also shown in the table. From comparison between Table I and IV, dissolution of the constitute elements, Fe, Cr and W, into Flibe was indicated by increase in their element concentration in Flibe 2 after exposure test for JLF-1. Cr dissolution was larger than Fe, while W dissolution is much smaller than Fe and Cr.

TABLE IV: IMPURITY LEVEL AFTER EPOSURE TESTS (unit: mass ppm).

	Fe	Cr	W	Ni	Mo	Cu	Na	Mg	Al	K	Ca
Flibe 2 JLF-1, 823K	270	340	2	45		2	900	180	45	2200	190
Flibe 3 316L SS, 873 K	170	54	<1	34	1						
Flibe 3 316L SS, 973 K	160	530	<1	12	<1						

Figure 2 shows SEM images of the surface of the specimens before and after the exposure tests. Particles of corrosion products with various size under 1 μm were observed after exposure tests. The composition of the corrosion products on the surface was analyzed by XPS with Ar sputtering. Fig. 3 shows the typical depth profiles for the surface composition before and after Flibe exposure. Sputtering rate was 4.87 nm/min in SiO_2 and is not significantly different from other materials, so that 30 min sputtering should be equivalent to about 150 nm in depth from the surface. Intensity of O and F near the specimen surface was increased during exposure to Flibe, compared with the specimen before exposure. The main compounds of the corrosion products are thought to be oxide and fluoride. Figure 4 shows the results of detailed XPS analysis on the chemical state of Fe and Cr in the pure materials (pure Fe, Fe_2O_3, FeF_3, Cr, Cr_2O_3, CrF_3), and corrosion products at the position indicated by the dashed line in Fig. 3. In the measurement for the pure materials (Figs. (a) and (b)), peak energies of 2p orbit electrons were determined for the metal, oxide and fluoride of Fe and Cr. Peak profiles were also determined by Gauss-Lorentz fitting with the profile for metal Pt, which is used as the standard material with only metal state, because Pt is never oxidized even in the air. For the photoelectron intensity curves for the corrosion products (Figs. (c) and (d)),

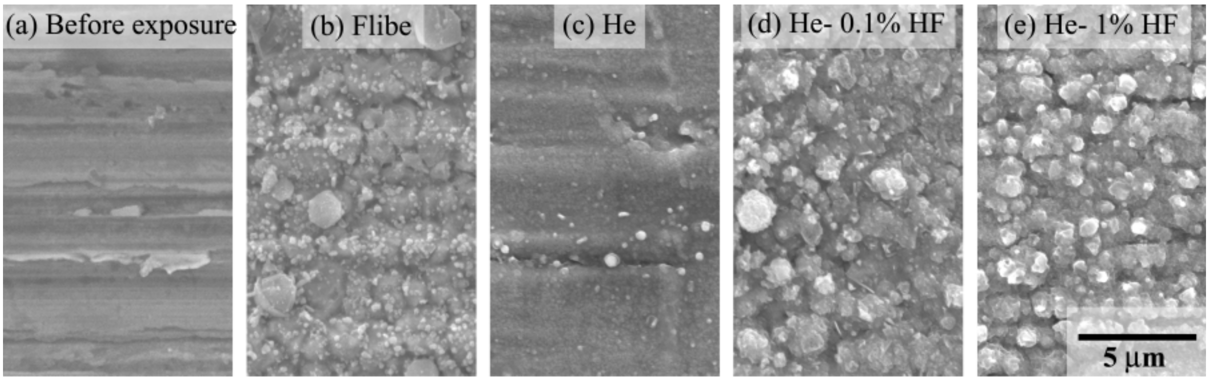


FIG.2. Surface Morphology (a) before the Exposure Tests, (b) after Flibe Exposure for 2003 hr, (c) He Gas for 100 hr, (d) He- 0.1% HF Gas for 25 hr and (e) He- 1% HF Gas for 2.5 hr. Exposure temperature was 823 K for all the tests.

peak separation was conducted by using the peak energy and the peak profile obtained in Figs. (a) and (b). Table V lists the ratio of the cross section enclosed by the separated peak for $2p_{3/2}$ electron in Fig. (c) and (d), which is considered as the ratio of chemical state in the corrosion products. Metal state Fe, however, is thought to be in the steel matrix because the Flibe exposure specimen surface was not fully covered with the corrosion products, though the one of He- 1%HF specimen was completely covered. The ratio of Fe_2O_3 and FeF_3 state in the corrosion products on the Flibe exposure specimen may be larger than the estimation in Table V.

It is said that oxidation was more dominant than fluoridation for both Fe and Cr even in He- 1%HF gas, where F atom concentration was 16 times larger than O atom in the atmosphere. Most of weight gain shown in Fig. 1 might be caused by oxide formation, and then weight gain attributed to its dissolution into Flibe. Especially, only oxide was detected for Cr state in Fig. 4 (d) in both Flibe and He- 1%HF gas condition. Selective dissolution of Cr into Flibe indicated in Table IV might be induced by such strong oxidation of Cr. Unfortunately, oxygen impurity concentration in Flibe is not available, however the level should be around 560 mass ppm, which is the one in conventional Flibe produced by the same HF purification process as shown by Eq. (2). Possible impurity source is contamination of H_2O and O_2 from the atmosphere. Oxygen impurity control will be important in Flibe blanket system, in addition to REDOX control (Eq. (1)) reducing HF impurity concentration.

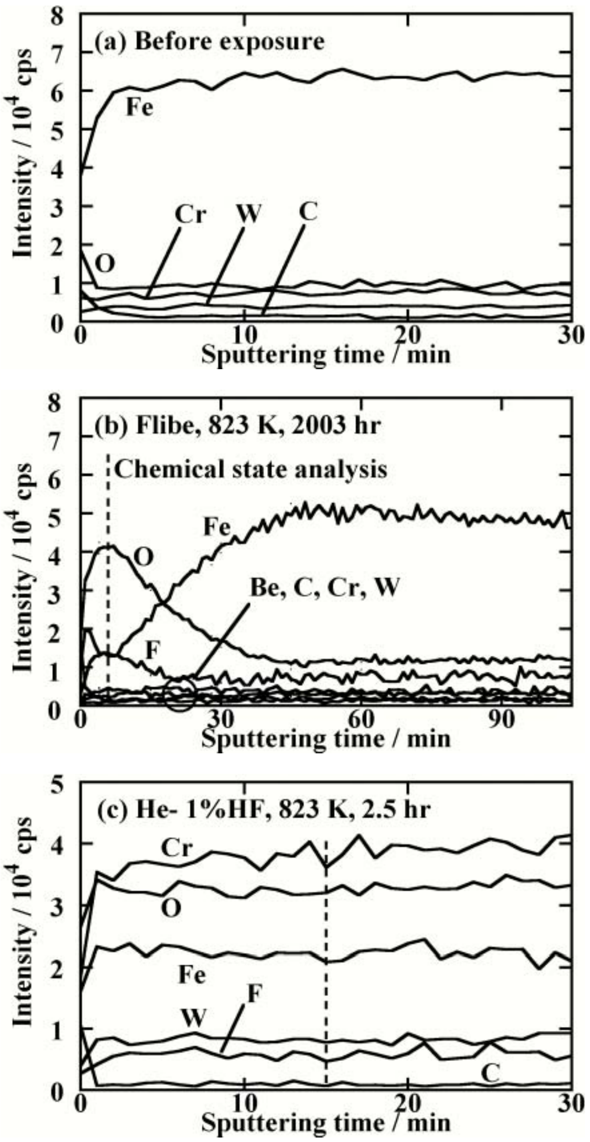


FIG.3. Depth Profile of the Intensity of Photoelectron. Sputtering rate was 4.87 nm in SiO_2.

4. Material Research Loop Design and Related R&D

Non-isothermal forced convection loop, Material Research Loop, was designed to investigate the effect of flow velocity (3~10 m/s) and temperature difference (100 K) in the blanket condition. Figure 5 show a bird-eye view of Material Research Loop and its specifications. Key issues for the loop construction were identified as (1) development of components, such as valve, flow meter and impurity censor for HF and O, which can work in Flibe, (2)

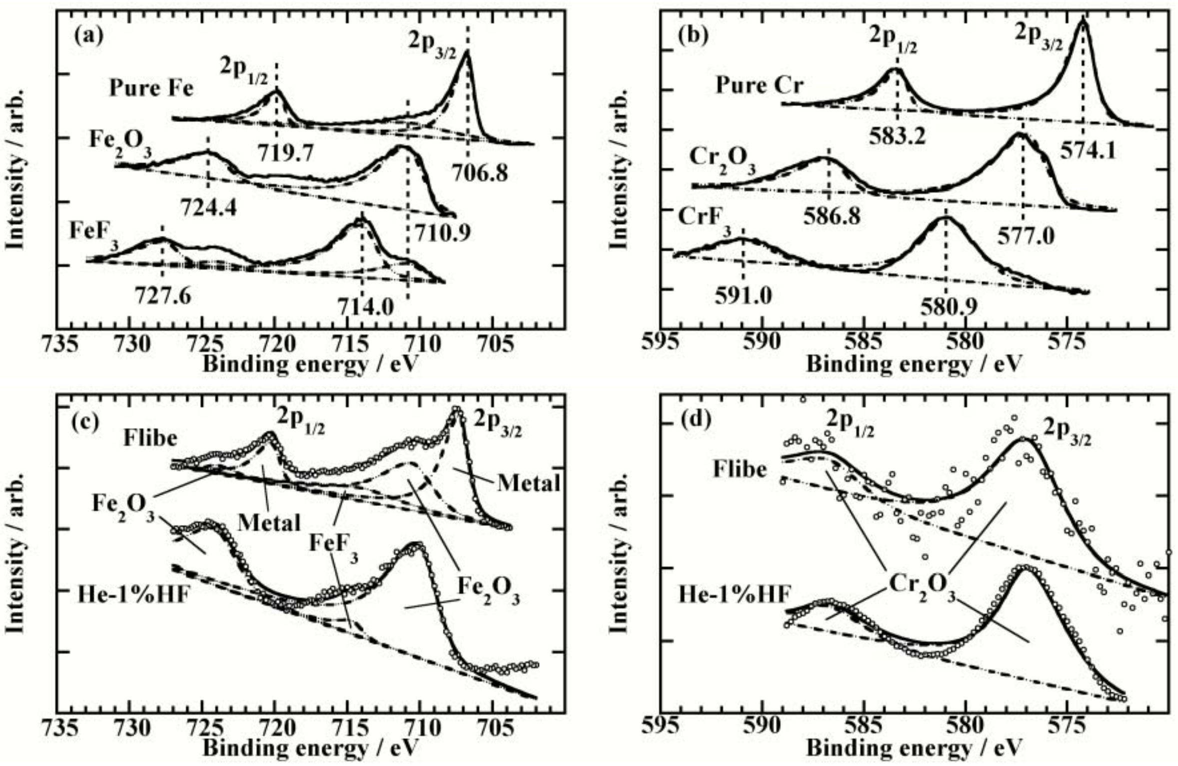
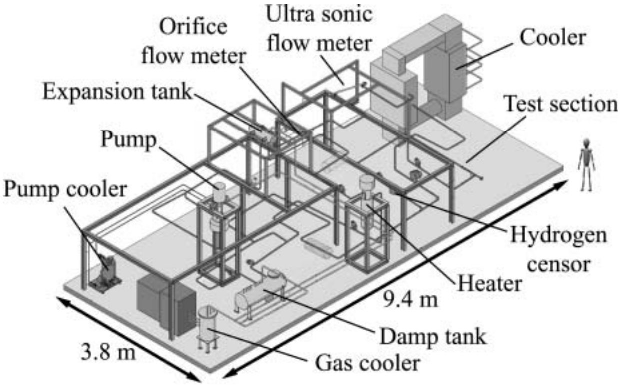


FIG. 4. Photoelectron Intensity for the Pure Materials, (a) Pure Fe, Fe_2O_3, FeF_3, (b) Pure Cr, Cr_2O_3, CrF_3, and for (c), (d) the Corrosion Products at the Position Indicated by Dashed Line in Fig. 3. Chemical state was analyzed for Fe and Cr in Figs. (c) and (d) by peak separation with the peak profiles obtained in Figs. (a) and (b).

TABLE V: RATIO OF CHEMICAL STATE IN THE CORROSION PRODUCTS. (unit: atomic %)

Element	Fe			Cr		
State	Matal	Fe_2O_3	FeF_3	Metal	Cr_2O_3	CrF_3
Flibe	44	39	17	-	100	-
He- 1% HF	-	94	6	-	100	-

estimation of corrosion rate for 316L SS and (3) large scale (> 200 kg) production of Flibe. For (1), a valve sample was fabricated, and fatigue test for open and close is undergoing. Ultra-sonic flow meters and orifice flow meters for liquid metal, such as Na and Pb-Bi, are thought to be utilized to Flibe conditions. For an ultra-sonic measurement, the acoustic property of Flibe-316L SS system is being investigated. A hydrogen impurity censor using proton conductor was developed and has already been demonstrated in liquid aluminum [10]. For (2), corrosion rate of 316L SS is applicable to the structural material. Natural convection loop has been



Pump head	0.6 MPa	Damp tank	330 L
Pump flow rate	40 L/min	Expansion tank	23 L
Heater	100 kW	Max. temp.	873 K
Cooler	100 kW		

FIG. 5. Material Research Loop and Its Specifications.

fabricated to investigate preliminary the enhancement of corrosion in flowing condition (~0.01 m/s). Over 200 kg Flibe is feasible with the scale-up of the above-established process.

5. Conclusion

High purity Flibe was successfully prepared for corrosion research on Flibe blanket. The blanket structural material, JLF-1, showed good corrosion resistance in static Flibe exposure tests, while flowing condition tests by a non-isothermal forced convection loop (Material Research Loop) is essential to predict corrosion behavior in the blanket condition. The loop structural material, 316L SS also showed acceptable corrosion rate. Feasibility of Material Research Loop was verified by these results and other related R&D.

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