

Flow Accelerated Corrosion and Erosion-Corrosion of RAFM Steel in Liquid Breeders

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Abstract. Corrosion experiments for RAFM, JLF-1 steel (Fe-9Cr-2w-0.1C) in 3types of flowing liquid breeders (i.e. Li, Pb-17Li and Flinak) were performed at the same conditions, and the compatibility was compared with each other. The weight loss of the specimens in the fluids was evaluated by the corrosion model based on mass transfer. The model can be applied to different test systems with different quantity of liquid breeders and different surface area of the systems. The flow enhanced the dissolution of element of the steel in the fluids. The mechanism of an erosion-corrosion in the liquid breeders was the peeling off of the corroded steel surface by the flow.

1. Introduction

Compatibility of liquid breeders, i.e. lithium (Li), lithium-lead eutectic (Pb-17Li), 46.5LiF-11.5NaF-42KF (Flinak) and 66LiF-34BeF₂ (Flibe), with structural materials is one of the critical issues for the development of fusion blanket systems [1-3]. The corrosion rate must be higher at higher flow rate of these fluids, and the phenomenon was called a flow accelerated corrosion (FAC) [4]. An erosion of a corroded surface by the shear stress of the flow called an erosion-corrosion [5] is also an important phenomenon. However, these characteristics in liquid metals and molten salts are not made clear so far. In the present study, the compatibility of reduced activation ferritic/martensitic (RAFM) steel, JLF-1, in the liquid breeders in static and flowing condition was investigated by means of the corrosion tests. The tests were performed at the same conditions, and the compatibility with the fluids was compared with each other. The characteristics of the FAC and the erosion-corrosion in the fluids were discussed.

2. Experimental conditions

Table 1 shows experimental conditions. Test material tested was RAFM steel JLF-1 (JOYO-HEAT) [6] and the chemical components was 9Cr- 0.49Ni- 1.98W- 0.49Mn- 0.2V- 0.009C- 0.015N - Fe balanced. The specimens were heat-treated at 1050°C /3.6ks/air cooled (normalizing) and 780°C /3.6 ks/air cooled (tempering).

The initial impurity of the liquid breeders was summarized in Table 2. The impurity in Flinak was removed by an electro- refining method [7]. The corrosion test was performed using a static pot and a stirred pot (Fig.1) [8-10]. The size of specimen was mainly 10mm x 15mm x 2mm. The volume of Li filled in the crucible was 3cc, 65cc or 92cc. The crucible was made of Mo [9] or 12Cr steel. The ratio of liquid volume to total surface area including the crucible, which influences the corrosion, in each test is summarized in Table 1. Mo crucible is not included because Mo is corrosion resistant in liquid metals [9]. The specimens were fixed to the specimen holder. In the stirred pot, the averaged flow velocity and Reynolds number for mixing are estimated as follows;

$$v = \pi dn \quad (1)$$

$$Re_{\text{mixing}} = \frac{\rho n d^2}{\mu} \quad (2)$$

After the tests in Li, specimens were rinsed in water at room temperature. The specimen tested in Pb-17Li was rinsed in Li at 300 °C for 3 hours to remove Pb-17Li from the specimen due to the dissolution of Pb-17Li into Li [11-13]. The adhered Li on specimen was then removed by water. The specimen tested in Flinak was rinsed in LiCl-KCl at 500 °C, and the adhered LiCl-KCl was rinsed in water. All the specimens were finally rinsed in acetone to remove water. The weight change of the specimens by the exposure to the liquid breeders was measured using an electro reading balance with accuracy of 0.1mg. The surface of specimen was metallurgically analyzed using SEM/EDX.

3. Results and discussion

The weight change of the specimens by the corrosion was summarized in Figs.2 (a) to (c). The weight change in Test C was smaller than that in Test B. This was because the area corroded in Li in Test C was larger than that in Test B due to the surface area of the crucible made of 12Cr, though the quantity of the fluid was the same.

Table 1 Experimental condition

Test ID	Static or Stirred	Temp. (°C)	Exposure time (hours) [Ref.]	Material of crucible	V/ S _{total} (m)	Re number for mixing	
Li	A		100	Mo	0.11	-	
	B	Static	600	250[8], 750[8]	Mo	3.3x10 ⁻²	-
	C			250[9], 750	12Cr steel	1.0 x10 ⁻²	-
D	Flowing	600	250[10]	12Cr steel	9.8x10 ⁻³	2859	
Pb-17Li	E	Static	600	750, 3000	JLF-1	2.6x10 ⁻³	-
	F	Flowing	600	250	12Cr steel	9.8x10 ⁻³	18512
Flinak	G	Static	600	200[7],1000[7], 2200	JLF-1 steel	2.6x10 ⁻³	-
	H	Flowing	600	250[7], 2200	SUS316L*	9.8x10 ⁻³	949

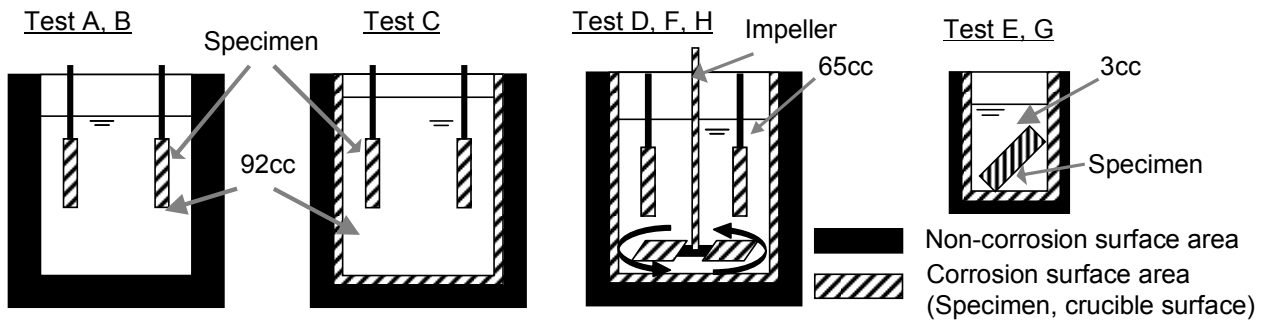


Fig. 1 Corrosion test apparatus

Table 2 Initial impurity of liquid breeders (wppm)

	Fe	Cr	W	Non metal	Ref.
Li	0.85	0.12	0.31	Nitrogen:65	[8,9,10]
Pb- 17Li	2.2	0.17	0.52	-	-
Flinak	52	2.6	-	H ₂ O: 42.6	[7]

The weight loss for 750- hour tests in static Li showed the suppression of the corrosion due to the saturation. The weight loss in Test D, which was performed in a flowing condition, was twice larger than that tested in a static condition for 250 and 750 hours (Test C).

In the static Pb-Li, the weight loss of the specimen seems to be larger than that in Li. However, these data cannot be compared directly since the ratio of liquid volume to surface area (V/S_{total}) was slightly different as presented in Table 1. This ratio controlled the total mass loss by the corrosion since the total corrosion loss was possibly determined by the quantity and the solubility of an element in the fluids. The weight loss of the specimen in Flinak in a flowing condition was almost the same as those at static condition. The weight loss became smaller for longer exposure in static condition. This is possibly because a fluoridation or an oxidation of the surface.

An overall mass transfer ratio in the corrosion was evaluated according to following equations [10];

$$\rho \frac{V}{S_s + S_c} \frac{dC}{dt} = J = h\rho(C_s - C) \quad (3).$$

In this equation, V/S_{total} was considered as the parameter. Therefore, this equation can be applied to all the tests. The concentration of the metal impurity in the fluids is drawn from eq. (3) as

$$C = C_s \left(1 - \exp\left(-\frac{h(S_s + S_c)t}{V}\right)\right) \quad (4).$$

Then, the weight loss of the specimens were given by eq. (4) as

$$\Delta m = \rho V C_s \left(1 - \exp\left(-\frac{h S t}{V}\right)\right) \quad (5).$$

The solubility of metals in liquid breeders is summarized in Table 2. The solubility of metal element in Li is larger when nitrogen concentration in Li is higher [14]. This is because the dissolution of the element is controlled by chemical reaction of metal element with Li and dissolved nitrogen. The thermodynamic stability can determine this process. Then, it is known that Cr in the steels selectively reacts with nitrogen in Li [16, 17]. In this work, the solubility of Cr in Li with nitrogen (65wppm) is determined as 94.3wppm from the weight loss data after the saturation in Fig.2 (a). The Pb-Li has higher solubility of Fe than Cr [19, 20]. However, it was reported that the dissolution ratio of Cr is 5 times higher than that of Fe in Pb-17Li at 500 °C [21]. The solubility in Pb-17Li is almost the same as that in pure Pb [22]. The metal solubility in Flinak is quite limited, though it was already made clear that the dissolution of metal elements in the Flinak is larger with the higher concentration of dissolved H₂O in the Flinak [7]. The solubility was determined from the corrosion data by the authors [7].

An experimental overall mass transfer coefficient at static and flowing condition, h_s and $h_{m,e}$, was estimated from eqs. (3-5) and the weight loss data (Figs.2 (a)-(c)). Then, the

underlined solubility in Table 2 was applied to the estimation of the coefficient. The coefficient for the static Li was estimated according to the data of test A. The theoretical weight loss (eq.5) agreed with the experimental data in Tests A, B and C. In the same way, the overall mass transfer coefficient of liquid breeders in static and flowing condition was estimated (Table 3).

Table 3 Solubility and diffusion coefficient of metal elements in liquid breeders

		Li (65wppm nitrogen)	Pb-17Li	Pb	Flinak (42.5wppm H ₂ O)
Cs wppm <appm >	Fe - *	52.4[14](800 °C)	<u>47 (600°C)</u> ~[18]<145>	<u>34 (600°C) [18]</u> <126>	50 (600°C)
	Cr	<7>~ <u>94.3 (600°C)</u> <12.6>***	10 (500°C) [20] <40>	<u>1 (600°C) <3.7 ></u>	50 (600°C)
D (m ² /s)	Fe	<u>4 x10⁻⁸ [15](600°C)</u>	<u>4 ±2 x10⁻¹⁴ (500°C)</u> [20]	<u>1.2x 10⁻⁹(600°C)</u> [14]	5.4x10 ⁻⁸
	Cr	<u>2.1x10⁻⁸ [15] (570 °C)</u>	<u>8 ±2.5 x10⁻¹¹ (500°C)</u> [20]	-	<u>2x10⁻⁹***</u>
hs (m/s)		2.8x10 ⁻⁸	1.2x10 ⁻⁹	-	=
hm,e (m/s)		(erosion-corrosion) 1.3x10 ⁻⁴ (eqs. (6, 8))	4.2x10 ⁻⁹	-	<u>1.2x10⁻⁸</u> 3.5x10 ⁻⁴ (eqs. (6, 8))
hm,t (m/s)		9.9x10 ⁻⁵ (eqs. (6, 9))	1.4x10 ⁻⁷ (eqs. (6, 8)) 2.1x10 ⁻⁸ (eqs. (6, 9))	-	2.2x10 ⁻⁵ (eqs. (6, 9))

* In the present work, it is assumed that Fe in steel was not dissolved and Cr was selectively dissolved in Li

** Underlined solubility value was applied in current work *** Diffusion coefficient of Li in Flinak [22]

Total corrosion loss in Pb-17Li must be larger than that in Li because of larger solubility as shown in Table 2. However, the experimental data indicated that the overall mass transfer ratio in Li was larger than that in Pb-17Li possibly because the corrosion in Li involved strong chemical reaction by nitrogen.

The dissolved element must be transferred by the flow, and the theoretical ratio is expressed according to the coefficient given as mass transfer ratio as follows;

$$J = hp(C_s - C) = \frac{D}{e} \rho (C_s - C) \quad (6),$$

$$Sh = \frac{hd}{D} = \Omega (Re_{\text{mixing}})^{2/3} (Sc)^{1/3} \quad (7),$$

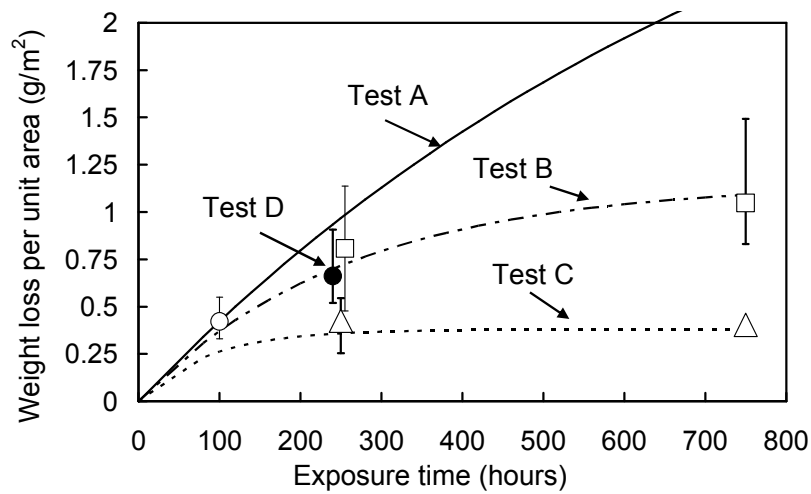
$$Sc = \frac{\nu}{D} \quad (8),$$

$$e = 5.67d^{-0.4} \nu^{0.344} D^{0.644} f^{0.7} \quad (9) [21].$$

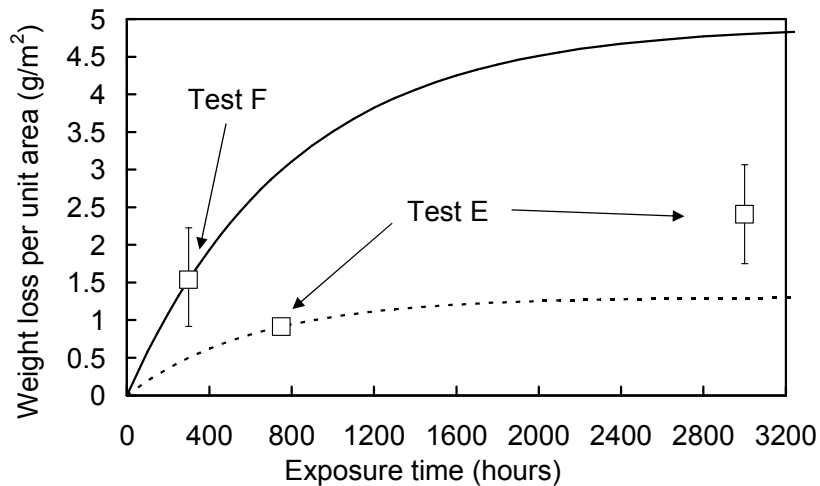
Thermo physical properties provided by ref. [23, 24] were applied in these equations, and the theoretical coefficients, $h_{m,t}$, were summarized in Table 3. These values were larger than

that obtained from the experiments (Table 3). This different indicates that there is the release ratio for the element from the steels in the corrosion process.

The weight loss obtained in Test D was larger than that was expected from the solubility. The surface morphology of the specimen was different from that in a static condition. The small cell was detected on the JLF-1 surface after the test in the flowing condition [10]. On the contrary, large ferrite grain was detected due to the transformation of phase from martensite to ferrite [8]. Li dissolves the carbide, and attacked the packet, block, lath and/or subgrain boundaries where had the carbide precipitated. From these facts, the mechanism of erosion-corrosion of JLF-1 steel in flowing Li was summarized in Fig.3. In the test F, the similar morphology was obtained and this indicated the occurrence of the erosion-corrosion. In the Flinak, the erosion-corrosion was not detected possibly because the sensitivity of the boundaries for the Flinak was not strong due to the chemical stability.



(a) Li



(b) Pb-17Li

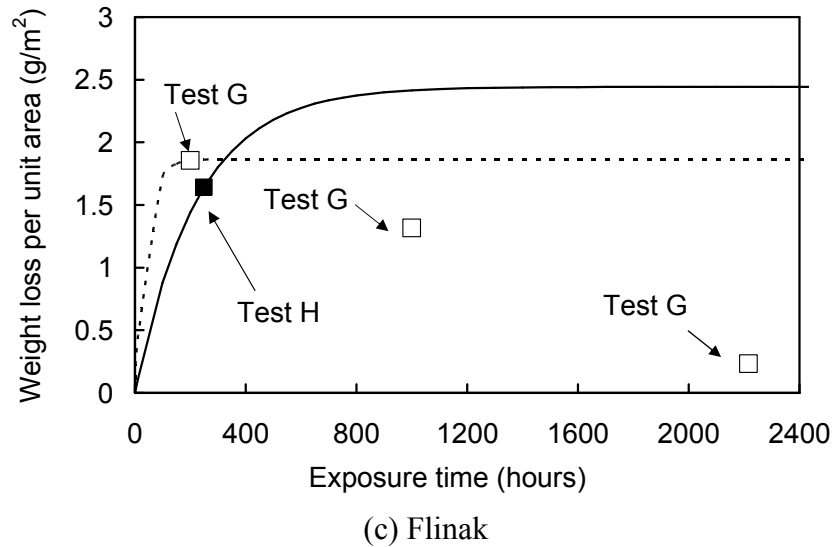


Fig. 2 Experimental and theoretical data of weight loss in liquid breeders (a) Li, (b) Pb-17Li and (c) Flinak (Solid and dotted line is obtained by model (eq.(5))

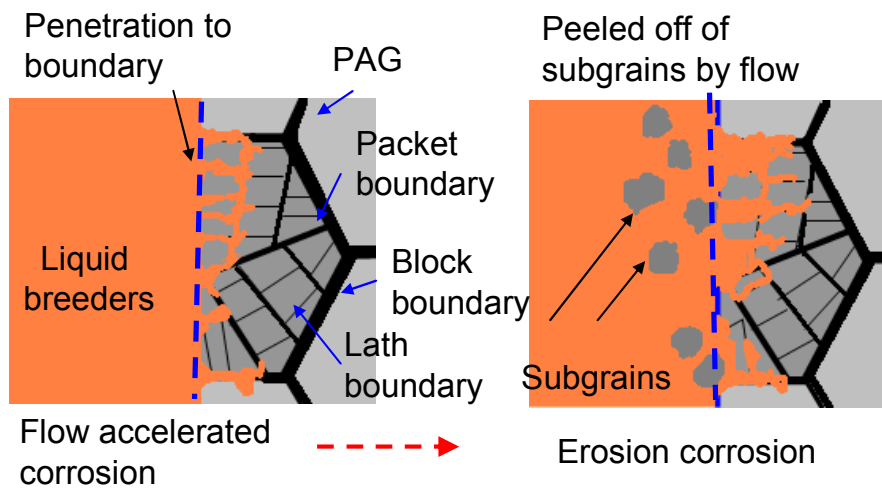


Fig.3 Erosion-corrosion of JLF-1 in Li and Pb-Li

4. Conclusions

Corrosion experiments for RAFM, JLF-1 steel (Fe-9Cr-2w-0.1C) in 3types of flowing liquid breeders (i.e. Li, Pb-17Li and Flinak) were performed at the same conditions. The compatibility of the fluids for the steel was compared with each other. Major conclusions are as follows;

- (1) The weight loss of specimens in liquid breeders was evaluated by a corrosion model based on mass transfer. It was found that the model can be applied for the different test system with different quantity of liquid breeders and different surface area of the systems.
- (2) The overall mass transfer ratio in Li at static condition was larger than that of Pb-Li, though the solubility of the metal element of the steel in Pb-17Li was higher than that of Li. The flow enhanced the dissolution of element of the steel in liquid metals. In the Flinak, the effect of the flow was negligible.

(3) An erosion- corrosion of JLF-1 in Li and Pb-Li was caused by the peeling off of the subgrain on the corroded surface by the flow.

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Nomenclature

C: concentration of metal element in fluids [wppm]
 Cs: Solubility of element in fluids [wppm]
 D: diffusion coefficient [m^2/s]
 d: Width of impeller [m]
 e: Thickness of boundary layer for concentration [m]
 J: Overall mass transfer ratio [$\text{g}/\text{m}^2\text{s}$]
 h: Overall mass transfer coefficient [m/s]
 $h_{m,e}$: Overall mass transfer coefficient at flowing condition in experiment
 $h_{m,t}$: Overall mass transfer coefficient at flowing condition in theory [m/s]
 n: Rotatig speed [s^{-1}]
 S_s : Surface area of specimens [m^2]
 S_c : Surface area of crucible [m^2]
 t: Test time [s]
 ρ : Density of liquid breeders [g/m^3]
 μ : Viscosity of liquid breeders [$\text{mPa}\cdot\text{s}$]
 ν : Kinetic viscosity of liquid breeders [m^2/s]
 V: Volume of liquid breeders [m^3]
 v : Averaged velocity of liquid breeder [m/s]
 Δm : Wight loss of specimen in total [g/m^2]
 Ω : Constant for mass transfer in mixing flow [25]

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