



Metallurgical study on corrosion of austenitic steels in molten salt LiF–BeF₂ (Flibe)

Masatoshi Kondo^{a,b,*}, Takuya Nagasaka^{a,b}, Akio Sagara^{a,b}, Nobuaki Noda^a, Takeo Muroga^{a,b}, Qi Xu^b, Masaru Nagura^c, Akihiro Suzuki^c, Takayuki Terai^c

^a National Institute for Fusion Science, Toki, Gifu 509-5292, Japan

^b The Graduate University for Advanced Studies, Toki, Gifu 509-5292, Japan

^c The University of Tokyo, 2-22 Shirakata-Shirane, Tokai, Naka, Ibaraki 319-1188, Japan

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ABSTRACT

Static corrosion tests for SS304 and SS316L austenitic steels in high purity LiF–BeF₂ (Flibe) were carried out at 500 and 600 °C for 1000 h. After the exposure, the steel surfaces were corroded due to the fluoridation by HF dissolved in Flibe. The grain boundary of the steel surfaces was preferentially attacked. The mechanism of corrosion including selective intergranular attack was discussed. The corrosion rate of SS304 and SS316L in Flibe at 600 °C was estimated as 10.6 and 5.4 μm/year, respectively.

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1. Introduction

Molten salt LiF–BeF₂ (Flibe) is one of the candidates for coolant and tritium breeding material in liquid blanket system of fusion reactors. For the development of fusion reactor with Flibe blanket system, compatibility of structural materials with Flibe is one of the critical issues.

Low activation ferritic steel, JLF-1 (Fe–9Cr–2W) is the candidate structural material of Force Free Helical Reactor (FFHR) in which Flibe self-cooled blanket is the primary option [1–2]. In the Flibe blanket system, tritium fluoride (TF) is going to be formed by neutron irradiation. The corrosion tests for JLF-1 in static Flibe have been performed [3], and the fluoridation characteristics of JLF-1 in Flibe with dissolved hydrogen fluoride (HF) were investigated. However, the corrosion test at flowing conditions must be performed. This is because the Flibe flow may promote the corrosion/erosion occurrence [4] due to the shear stress applied to the surface. For the purpose of verifying the feasibility of the flowing test in the Flibe blanket conditions, the design study on the forced convection loop was performed [5], in which the corrosion of the loop tubes was considered to be one of the critical issues. The austenitic steels of SS304 and SS316L are the candidates of structural material of the forced convection loop. In addition, these materials can be used as structural materials of the blanket compo-

nent placed on the downstream of the system. Thus, it is necessary to examine the performance of these steels in Flibe environments.

In the present study, metallurgical investigation on corrosion of austenitic steels of SS304 and SS316L in static Flibe was carried out. The purpose is to investigate the corrosion characteristics of these steels in Flibe.

2. Experimental procedure

The corrosion tests were carried out using the test capsule shown in Fig. 1. The chemical components of SS304 and SS316L are 0.05C–18.16Cr–8.79Ni–0.84Mn–0.51Si–0.025P–0.03S and 0.009C–17.16Cr–12.66Ni–2.05Mo–1.64Mn–0.56Si–0.018P–0.01S, respectively. One coupon specimen was placed in a crucible. The size of specimen was 10 × 15 × 0.5 mm. Flibe of 2.5cc was filled in the crucible. In the process of the purification of Flibe, HF was used to reduce the Be and other metal oxides [3]. Part of HF introduced for the purification remained in Flibe. The metallic impurities in initial Flibe are presented in Table 1. The crucible was made of the same material with the specimen to remove the occurrence of electrochemical corrosion. The exposures were carried out at 500 and 600 °C for 1000 h. These temperature conditions corresponded to the highest and the lowest temperatures of the expected loop operation. After the tests, the specimens were extracted from the crucibles. Flibe adhered on the specimen surface was removed in the LiCl–KCl pool at 500 °C and acetone at room temperature. The weight changes of the specimens before and after the exposure were measured by electro reading balance with accuracy of 0.00001 g. The specimen surfaces were observed by using scanning electron microscope with

* Corresponding author. Tel.: +81 572 58 2139; fax: +81 572 58 2676.

E-mail addresses: kondo.masatoshi@nifs.ac.jp (M. Kondo), nagasaka@nifs.ac.jp (T. Nagasaka), sagara.akio@LHD.nifs.ac.jp (A. Sagara), noda.nobuaki@nifs.ac.jp (N. Noda), muroga@nifs.ac.jp (T. Muroga), xu.qi@nifs.ac.jp (Q. Xu), nagura@nuclear.jp (M. Nagura), suzuki@nuclear.jp (A. Suzuki), tera@n.t.utokyo.ac.jp (T. Terai).

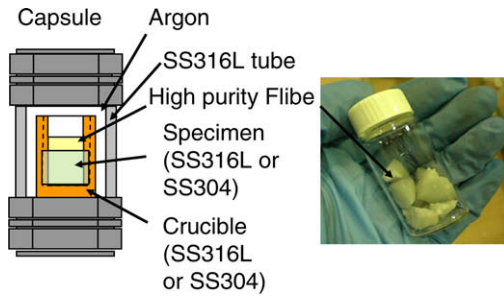


Fig. 1. Corrosion test capsule and high purity Flibe before exposure.

served and analyzed. Chemical composition of Flibe was analyzed by Inductive Coupled Plasma–Mass Spectroscopy (ICP–MS) to investigate the transition of metal impurity before and after the exposure.

3. Results and discussion

3.1. Surface observation

The photos of specimens and Flibe after the exposure are shown in Fig. 2. The color of the specimen was changed from initial metallic luster into dark grey. Occurrence of significant corrosion was not observed on the specimens by visual inspection. The color of Flibe also changed into black from the initial transparent condition (Figs. 1 and 2).

The results of SEM/EDX analysis for the specimen surfaces are shown in Fig. 3. On the surface of SS304 specimen tested at 500 °C, the corrosion products of 2–3 μm diameter were adhered on the surface (Fig. 3(a)). In this portion, Cr content was low and Ni content was high. In the case of SS304 tested at 600 °C, the grain boundary of the specimen surface was corroded. In the grain boundaries, the content of Fe and Cr was lower and Ni concentration was larger than the other part. The corrosion products were observed at the boundaries (Fig. 3(b)).

The grain boundary was corroded in SS316L at 500 and 600 °C (Fig. 3(c) and (d)).The number of corrosion products on SS316L specimen was less than that on SS304 at 500 °C. The size of the cor-

energy-dispersive X-ray spectroscopy (SEM/EDX). These specimens were cut at span wise center, and the cross section was ob-

Table 1

Transition of impurity in Flibe before and after the exposure (Unit: wppm).

Test	Fe	Cr	Ni	Mo	Mn	W	Ta	Cu	V
<i>Flibe before exposure</i>									
	70	5	16	<1	–	<1	<2	<1	1
<i>Flibe after exposure</i>									
SS304(500 °C)	42	210	20	<1	88	<1	–	–	–
SS304(600 °C)	110	810	28	3	110	<1	–	–	–
SS316L(500 °C)	170	54	34	1	53	<1	–	–	–
SS316L(600 °C)	160	530	12	<1	94	<1	–	–	–

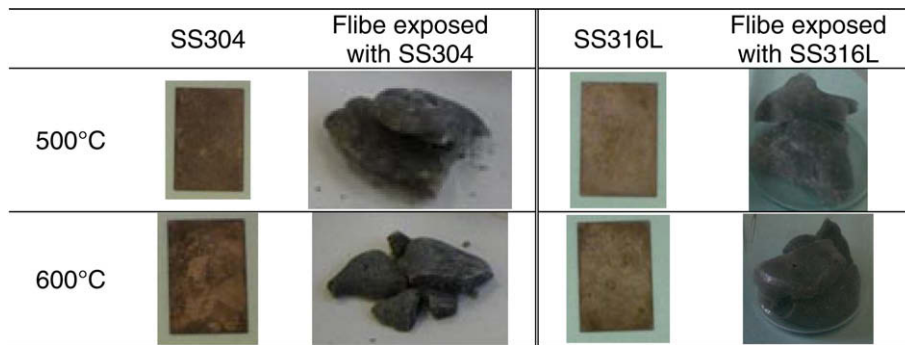


Fig. 2. Specimens and Flibe after exposure.

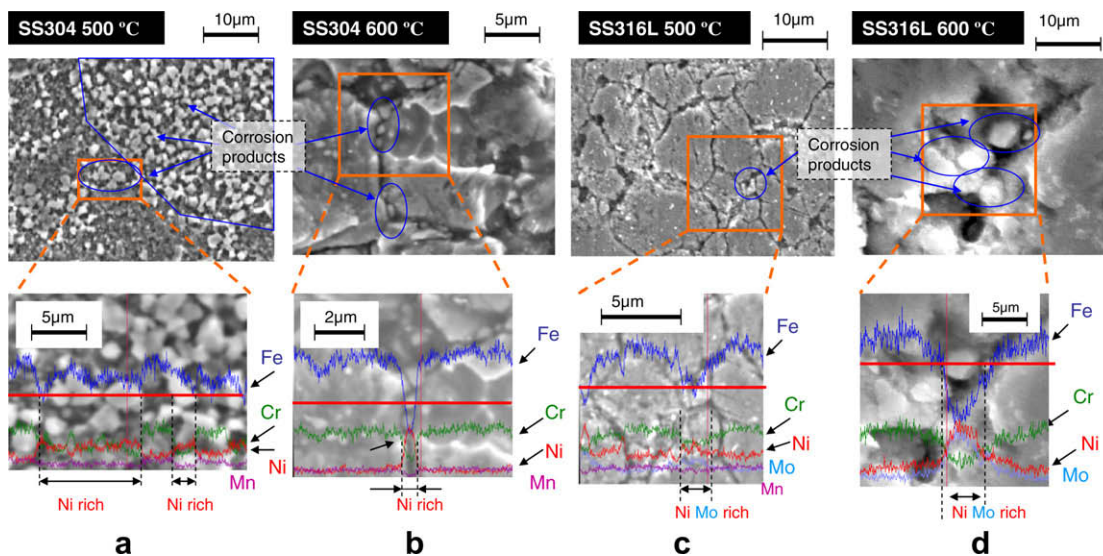


Fig. 3. Results of SEM/EDX analysis for specimen surfaces: (a) SS304 tested at 500 °C, (b) SS304 tested at 600 °C, (c) SS316L tested at 500 °C, (d) SS316L tested at 600 °C.

rosion products was bigger than those observed on SS304 specimens. In the corrosion products, Ni and Mo were enriched.

The results of SEM/EDX analysis for the specimen cross sections are shown in Fig. 4. In the SS304 specimens tested at 500 °C, slight decrease of Cr concentration on the surface was found. Ni was enriched on the surfaces (Fig. 4(a)). In the test at 600 °C, decrease of the Fe and Cr concentration and slight enrichment of Ni were observed (Fig. 4(b)). In SS316L specimens tested at 500 °C, the surface was smooth and the change of concentration profile on the surface was small as shown in Fig. 4(c). In the test at 600 °C, dissolution of Fe and Cr were observed, and Ni and Mo were enriched on the surface (Fig. 4(d)).

3.2. Transition of metal impurities in Flibe

The transition of metal impurities in Flibe before and after the tests was analyzed with ICP-MS (Table 1). The increase of impurity concentration in Flibe was larger at higher temperature. The anal-

ysis results for each test agreed with those of SEM/EDX analysis. For example, the impurity of Cr in Flibe increased significantly in the tests for SS304 at 500 °C and 600 °C and for SUS316L at 600 °C in agreement with dissolution of Cr element near the specimen surface shown in Figs. 3(a), (b) and (d), and 4(a), (b) and (d). In SS316L tested at 500 °C, the increase of Cr concentration in Flibe is small, and this agreed with the very slight decrease of Cr concentration on specimen surface (Figs. 4(c) and 5(c)). In the test at 600 °C, the increase of Cr concentration was larger than that of Fe for the both steels.

3.3. Corrosion mechanism of SS304 and SS316L in Flibe

The corrosion might be caused via fluoridation process. The fluoridation was caused by the dissolved HF in Flibe. Alloying elements of Fe and Cr in the steels could form the fluorides (e.g. FeF₂ and CrF₂) because these fluorides are more stable than HF according to Gibbs free energy of formation [3]. As the results of

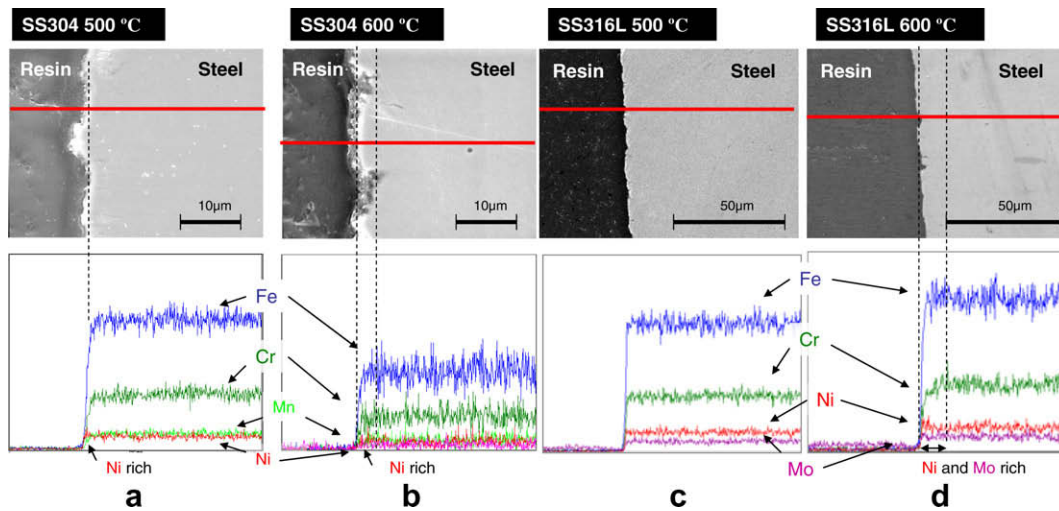


Fig. 4. Results of SEM/EDX analysis for surface cross section: (a) SS304 tested at 500 °C, (b) SS304 tested at 600 °C, (c) SS316L tested at 500 °C, (d) SS316L tested at 600 °C.

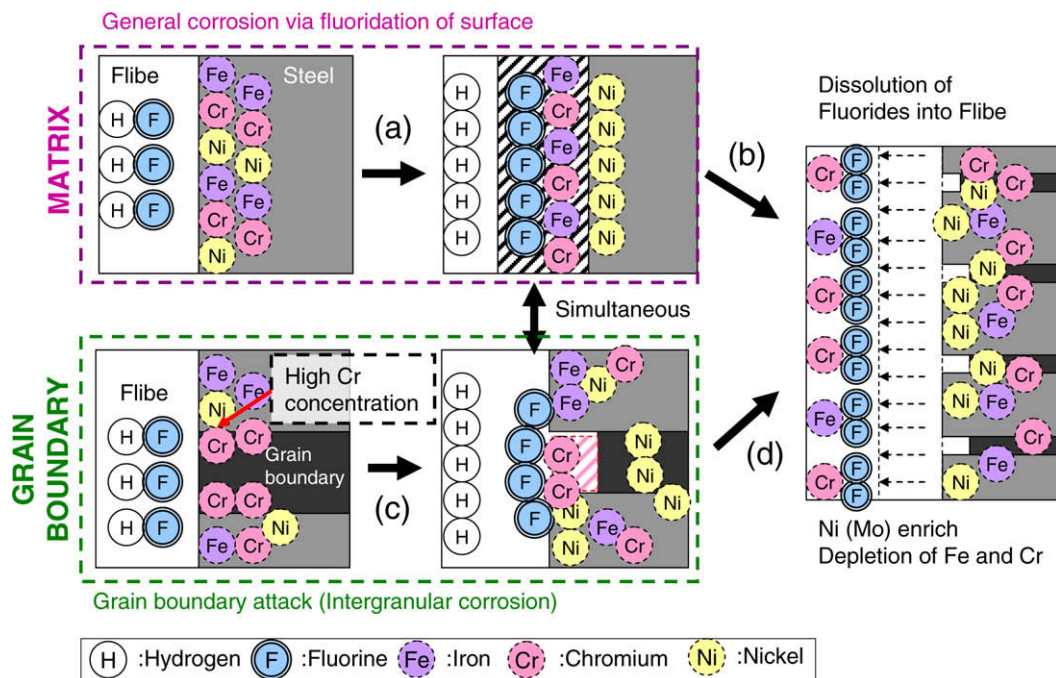


Fig. 5. Corrosion behavior of SS304 and SS316L steels in Flibe.

Table 2
Weight changes of specimens in Flibe.

	Test temperature (°C)	Weight loss (g)	Weight loss per unit area (g/m ²)	Lost depth (μm)	Corrosion rate (μm/year)
SS304	500	2.92×10^{-3}	9.28	1.17	10.25
	600	3.00×10^{-3}	9.60	1.21	10.60
SS316L	500	9.37×10^{-4}	2.97	0.37	3.26
	600	1.54×10^{-3}	4.94	0.62	5.42

Density of SS304: 7930 kg/m³, SS316L: 7980 kg/m³.

preferential dissolution of Fe and Cr via fluoridation process, Ni and Mo remained and were enriched on the surfaces.

The results indicated that general corrosion including intergranular attack occurred on the surface. The corrosion mechanism is summarized in Fig. 5. General corrosion was caused due to the fluoridation of alloying elements of Fe and Cr on surfaces (Fig. 5(a)). Then, FeF₂ and CrF₂ were dissolved into Flibe as shown in Fig. 5(b). At the same time, selective corrosion was caused in the grain boundary, where the Cr concentration might be higher than the other part because of the formation Cr carbide of Cr₂₃C₆ (Fig. 5(c)). The fluoridation would be stronger for Cr more than that for Fe, because CrF₂ was thermodynamically more stable than FeF₂. Therefore, Cr-enriched grain boundary might be corroded more strongly than the normal surface subject to the general corrosion. In consequence, CrF₂ was dissolved into Flibe (Fig. 5(d)). The alloying elements of Ni and Mo remained and were enriched on the surface because these fluorides were less stable than HF. The Ni enriched layer on the surface may be corrosion resistant for fluoridation.

3.4. Estimation of corrosion rate

The results of weight loss measurement were presented in Table 2. In both cases of SS304 and SS316L, the weight losses were increased with temperature. SS316L had smaller weight losses than SS304. This is possibly because the high concentration of Ni in SS316L suppressed the corrosion. The formation of Ni rich layer on the surface might suppress the fluoridation of Cr. This is in agreement with the results of ICP–MS analysis for Flibe.

The allowable corrosion rate of structural material in liquid sodium in 'Joyo' fast experimental reactor was reported as 10 μm/year [6], and this value could be considered as a reference standard for the allowable corrosion rate for the present components. The

estimated corrosion rate of SS304 in the present work was around 10 μm/year, which is comparable with the reported corrosion limit of steel for Na. The corrosion rate of SS316L in the Flibe is well below 10 μm/year, and this indicating that the corrosion rate of the SS316L in Flibe is sufficiently low. However, the effect of flow, temperature difference in the corrosion system and electrochemical conditions on the corrosion need be investigated for improving the accuracy of the estimate of corrosion rate.

4. Conclusions

Static corrosion tests for SS304 and SS316L steels in Flibe were carried out at 500 and 600 °C for 1000 h. Major conclusions are as follows:

- (1) The general corrosion and intergranular corrosion were caused by the fluoridation. The alloying elements of Fe and Cr dissolved into Flibe via fluoridation process. Ni and Mo were enriched on the steel surfaces.
- (2) The corrosion rate of SS304 and SS316L in Flibe at 600 °C was estimated as 10.6 and 5.4 μm/year, respectively. It was indicated that the corrosion rate of SS316 steel in Flibe was sufficiently low and acceptable as the loop structural material.

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References

- [1] A. Sagara, Fusion Engineering and Design 81 (2006) 2703.
- [2] T. Muroga, T. Tanaka, A. Sagara, Fusion Engineering and Design 81 (2006) 1203.
- [3] H. Nishimura, T. Terai, M. Yamawaki, S. Tanaka, A. Sagara, O. Motojima, J. Nucl. Mater. 307 (2002) 1355.
- [4] M. Kondo, M. Takahashi, T. Suzuki, K. Ishikawa, K. Hata, S. Qiu, H. Sekimoto, J. Nucl. Mater. 343 (2005) 349.
- [5] M. Kondo, T. Nagasaka, A. Sagara, N. Noda, T. Muroga, Annual Report of National Institute for Fusion Science, P.445 (2006).
- [6] A. Maruyama et al., Nihon Genshiryoku Gakkaishi 26 (4) (1984).