

Corrosion characteristic of AlN, Y₂O₃, Er₂O₃ and Al₂O₃ in Flinak for molten salt blanket system

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For liquid breeder blanket system using molten salts, tritium barrier, anti-corrosion barrier, tritium recovery system and heat exchanger make important roles. Especially in the heat exchanger, the tritium permeation from primary coolant loop to secondary coolant loop must be inhibited by the tritium barrier for safety. To develop it, it is essential to optimize chemical stability of the barrier material against molten salts. In the present study, the corrosion on bulk specimens of AlN, Y₂O₃, Er₂O₃ and Al₂O₃ in Flinak was investigated. The static corrosion tests were performed for 230 and 1010 hours using these specimens with high purity Flinak at 600°C in Ar atmosphere. Weight measurement and surface analysis of the specimens were carried out before and after the corrosion test. Chemical analysis of the Flinak also did before and after the corrosion test. AlN showed corrosion resistance, even though the surface was slightly oxidized and corroded. Er₂O₃, Y₂O₃ and Al₂O₃ dissolved into Flinak. In Er₂O₃ corrosion, Zr in the matrix as an impurity might affect on the corrosion. The Y₂O₃ corrosion was small. The weight loss due to the corrosion was affected by the breaking of the specimens with porous structure. And the Al₂O₃ corrosion was large. The surface structure changed to rough surface. These corrosion behaviors agreed with prediction based on thermodynamic evaluation.

Keywords: corrosion, blanket, molten salt, hydrogen permeation, ceramics, coating.

1. Introduction

Force Free Helical type Reactor (FFHR) with self-cooled liquid blanket system has been designed [1]. Molten salt is known as a promising self cooling tritium breeder for the system for fusion reactor because of the attractive advantages on safety aspects: low tritium solubility, low reactivity with air and water, low pressure operation, and low MHD resistance. LiF-BeF₂ (Flibe) is planned to be employed as tritium breeder and coolant of the blanket due to inherent safety and high thermal efficiency operated above 500°C [2].

46.5LiF-11.5NaF-42KF (mol%) called as Flinak possesses similar characteristics to Flibe. It would mean potentiality to be used as a simulant for the heat and mass transfer investigation. Flinak would be also one of alternative candidates of the coolant and tritium breeder of the blankets [3]. For the blanket system, the corrosion of the structural materials and the development of tritium barrier, anti-corrosion barrier, tritium recovery system and heat exchanger are key issues. Especially in the heat exchanger, the permeation of tritium to secondary coolant loop must be inhibited by the tritium barrier [4]. And deterioration of heat transfer efficiency of the heat exchanger by the barrier must be prevented concurrently.

Corrosion of several candidate structural materials in Flinak has been studied for the blanket. It was found that the corrosion of reduced activation ferritic steel, JLF-1(Fe-8.92Cr-2W) is caused by the impurity as H₂O, O₂ and HF dissolved in the molten salts [5]. In the corrosion of austenitic steel, Ni rich corrosion resistant

layer was formed after certain time for the corrosion via Cr dissolution [6]. And the corrosion resistance of Ni based alloy was demonstrated [7]. The corrosion could be controlled by the impurity control.

Ceramic coating to prevent tritium permeability has also been studied because of the low hydrogen diffusivity and the low hydrogen surface recombination constants [8]. Ceramics such AlN, Y₂O₃, Er₂O₃ and Al₂O₃ are promising as candidate materials for tritium barrier. But the stability in molten salt is not made clear so far. To develop liquid blanket system using molten salts, we hence have to optimize the heat and mass transfer property between Flinak and the metal specimen coated with the barrier material. In the present study, the corrosion resistance of those ceramics in Flinak was studied by static corrosion test.

2. Experimental

2.1 Specimen preparation

The bulk specimens were prepared as follows: after AlN powder including polyvinyl butyral as a binder was shaped to a tablet by compression at 500 tons, it was calcined at 1850 °C for 4 hours. After Er(NO₃)₃·5H₂O was calcined at 1000 °C for 5 hours, it was ground. The obtained powder was shaped to a tablet by compression at 60 kg/cm² and calcined at 1700 °C for 2 hours. Y₂O₃ powder was shaped to a tablet at 60 kg/cm² and calcined at 1650 °C for 5 hours. Al₂O₃ powder including polyvinyl alcohol as a binder was shaped to a tablet by hand press machine at 80 °C. It was calcined at 400 °C for 3 hours, 800 °C for 3 hours and finally 1600 °C for 5 hours step by

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step. These specimens were cut to adjust into the size of 10 mm × 15 mm × 5.0 mm. Initial composition of the specimens was analyzed by X-Ray Fluorescence Spectroscopy (XRF). Table 1 shows initial composition of the specimens.

2.2 Test condition

The Flinak used in the present corrosion tests was purified by electrolytic refining method, and had initial impurity as shown. The Flinak contained lower metal impurity and moisture than that in the previous study [5].

Figure 1 shows a capsule for corrosion test made from SS316L. The specimens were putted in SS316L crucibles filled with Flinak [7] and packed in dry Ar atmosphere. The capsule was heated at 600°C [4]. After 230 hour and 1010 hour immersion, the specimens were extracted from the capsules.

The specimens were rinsed in pure water for 4 days at room temperature to remove Flinak from the specimens. After drying the specimens, the weight was measured using micro-balance with 0.1mg in accuracy, and

compared to that before the corrosion test. X-ray diffraction (XRD) patterns were measured before and after the corrosion test. The surface was observed by scanning electron microscopy (SEM). Chemical analysis at the specimen surface was carried out by X-ray photoelectron spectroscopy (XPS). Chemical composition of Flinak was also analyzed by inductively coupled plasma mass spectrometry (ICPMS) and Karl Fischer titration.

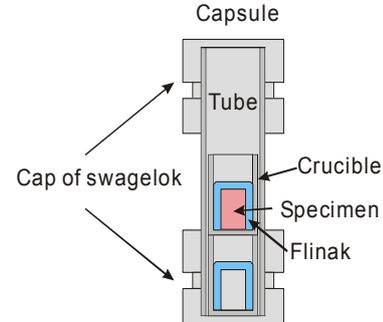


Fig.1 Capsule for corrosion test

Table 1 Composition of specimens (at%)

AlN	Al	Y	Si	Mg	S	Ca	O	N		
	49.63	0.47	0.16	0.08	0.01	0.01	0.00	49.63		
Er ₂ O ₃	Er	Zr	Pb	Y	Al	Si	P	O		
	37.91	1.24	0.15	0.09	0.17	0.11	0.07	60.25		
Y ₂ O ₃	Y	Fe	Si	Al	Mg	O				
	39.61	0.02	0.06	0.03	0.04	60.22				
Al ₂ O ₃	Al	Ce	Si	S	Mg	Cl	Sr	K	Ca	O
	39.68	0.09	0.07	0.03	0.04	0.03	0.02	0.01	0.02	60.01

3. Results

3.1 Surface observation

Figure 2 shows the photos of specimens before and after the corrosion test. The initial AlN specimen was gray. Although it got slightly light gray after the corrosion test, no shape change was significantly observed. In case of Er₂O₃, the specimen was pink before corrosion test and the color has been kept through the corrosion test. It, however, got fragile after corrosion test and chipped off especially at the corners. Y₂O₃ specimens were white before corrosion test. It broke and got blackish after the test. Al₂O₃ specimens were white before corrosion test. After the test, the specimens colored to gray.

Figure 3 shows SEM images for specimen surface before and after the corrosion tests and relationship between spattering time and atomic ratio obtained from XPS measurement. The spattering time is corresponding to the depth from surface. The spattering rate was about 3 nm/sec for SiO₂. The actual spattering rate for the tested ceramics could be close to this value. The AlN specimen had rough structure at the surface before the corrosion test. After the test, the surface became smooth. The initial Er₂O₃ surface consisted of round shape grains before the corrosion test. After the corrosion test, the grains lost roundness, got rough, and formed porous structure. The initial Y₂O₃ consisted of rough grains. The image also

shows the cross sections of large grains over several micrometers. After the corrosion test, the larger part of the surface area became more porous than that before the corrosion test. Initial Al₂O₃ consisted of grains like gathering pine cones. After corrosion test, the structure was lost and changed to be rough structure.

From the results of XPS measurement before and after the corrosion test, fluorine was detected at the surface of all the specimens as a common tendency. Potassium was detected in AlN and Er₂O₃ specimens after corrosion test. It is noted that substitution from nitrogen to oxygen near surface was clarified about the AlN specimen after the corrosion test. In the Al₂O₃ specimens after corrosion test, fluorine, lithium, sodium and potassium were detected. Those were due to the deposition of the corrosion products and Flinak remaining in the pore structure.

XRD measurement was carried out to investigate the affected depth due to corrosion reaction. The patterns from the specimens were compared with those from JCPDS. Comparison shows that the specimen's patterns are crystallographically equivalent ones from JCPDS. When the patterns before and after the corrosion test were imposed, significant difference between the patterns was not recognized. This means that substance near surface dissolved into Flinak and that the corrosion reaction does not reach over tens of micrometer depth.

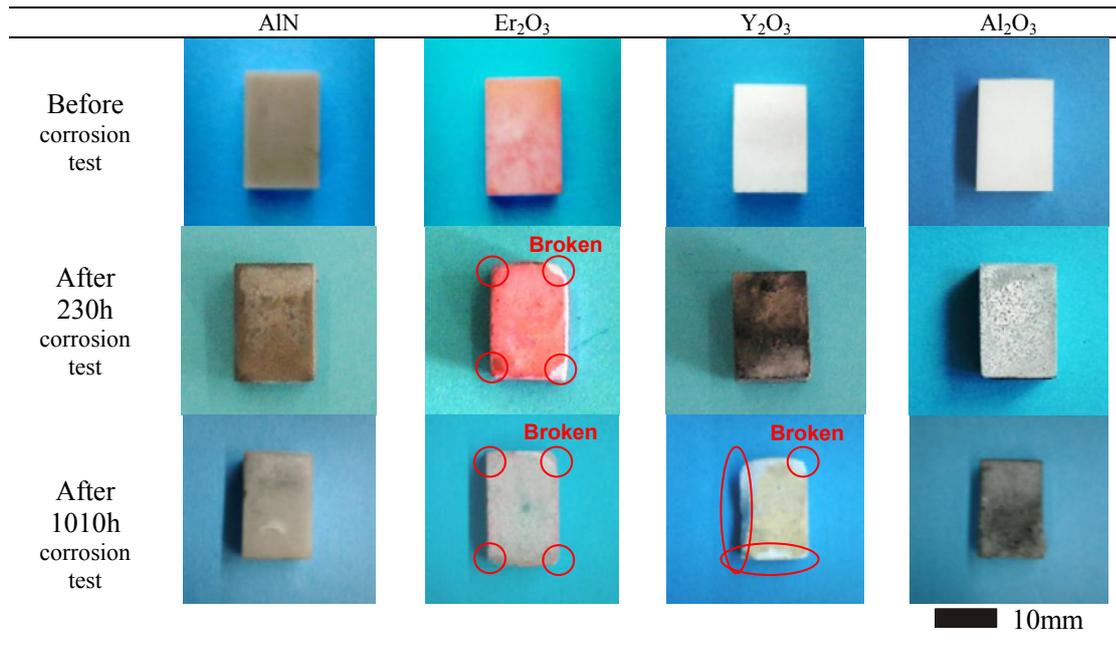


Fig.2 Photos of specimens before and after corrosion test

Table 2 Weight Change for corrosion test (unit: g/m²)

Time	230 hours	1010 hours
AlN	-0.233	-0.0928
Al ₂ O ₃	+981	+74.0
Y ₂ O ₃	+195	-58.9 (broken)
Er ₂ O ₃	-446 (broken)	-8.21 (slightly broken)

3.2 Weight change of specimens

Table 2 shows weight change per unit area before and after the corrosion test. The weight loss in AlN specimen was small. The losses in the Er₂O₃ specimens and the Y₂O₃ specimen after 1010 hour corrosion test were large and their specimens were broken. The weight loss includes loss of fragments due to breaking during the corrosion test and water rinse. On the other hand, the Y₂O₃ specimen after 230 hour corrosion test and the Al₂O₃ specimens gained in weight. These specimens possess porous structure. The gain of the weight is possibly due to the Flinak and water permeated into the pores of those specimens.

3.3 Chemical analysis

The chemical composition of Flinak after the corrosion test was compared with the initial that of Flinak in Table 3. While the Flinak used for AlN 230 hour corrosion test contains Al at 61 wppm, those used for Er₂O₃, Y₂O₃ and Al₂O₃ corrosion tests contain Er at 1.47×10^4 wppm, Y at 3.30×10^3 wppm and Al at 930 wppm, respectively. In 1010-hour corrosion test, similar tendency was also observed. These results mean that Er₂O₃, Y₂O₃ and Al₂O₃ dissolved into Flinak and that the corrosion is not negligible on Er₂O₃, Y₂O₃ and Al₂O₃. Figure 4 shows relationship between impurity concentration in Flinak and testing time on corrosion test. It shows no increase of the impurity concentration with

testing time after 230 hours although these results contain the breaking of specimens placed in the Flinak.

4. Discussion

4.1 Thermodynamic stability

Table 4 shows standard Gibbs energy for reaction about these ceramics with LiF and KF, respectively. LiF occupies the largest part in Flinak used in this study. It is more stable than NaF and KF. KF was most unstable due to largest free energy for formation in the Flinak. The energy values provide us the equilibrium tendency about the reactions in the condition in this study and allow us prediction of thermodynamical stability in Flinak. According to the reaction energy estimation, AlN could be stable in Flinak if it mainly reacted with LiF, which had the largest part in the Flinak. On the other hand, Er₂O₃, Y₂O₃ and Al₂O₃ would be unstable.

4.2 Solubility of oxide and nitride in Flinak

The corrosion tests for the ceramics were carried out at 600°C for 230 hours and 1010 hours. The results of weight loss measurement in these tests did not clearly show time dependence on the corrosion, because the weight loss was significantly affected by breaking of the specimens, particularly in the specimens of Er₂O₃ and Y₂O₃. The specimen surface structure after the 230 hour test was similar to that for 1010 hour test. Although the repeatability of the corrosion characteristics were

confirmed by the tests, significant time dependence on the corrosion was not obtained.

One possible reason is saturation of the dissolved elements within 230 hours. The corrosion might be suppressed after reaching it. The Flinak contained 950 wppm of Al after the immersion of Al₂O₃ for 1010 hours, which is comparable with Al amount in Flinak after 230 hour immersion. If the corrosion products were dissolved to Flinak via the fluoridation shown in Table 4, Al

amount in Flinak after the 1010 hour corrosion test would correspond to solubility of Al in Flinak. Considering Al dissolving into Flinak via fluoridation, it would mean the solubility of fluoride, AlF₃. It is 2.95×10^3 wppm obtained from molecular weight ratio of Al and AlF₃.

In case of Er and Y, the concentration would similarly give us the solubilities of ErF₃ and YF₃, which are 321 wppm and 180 wppm, respectively.

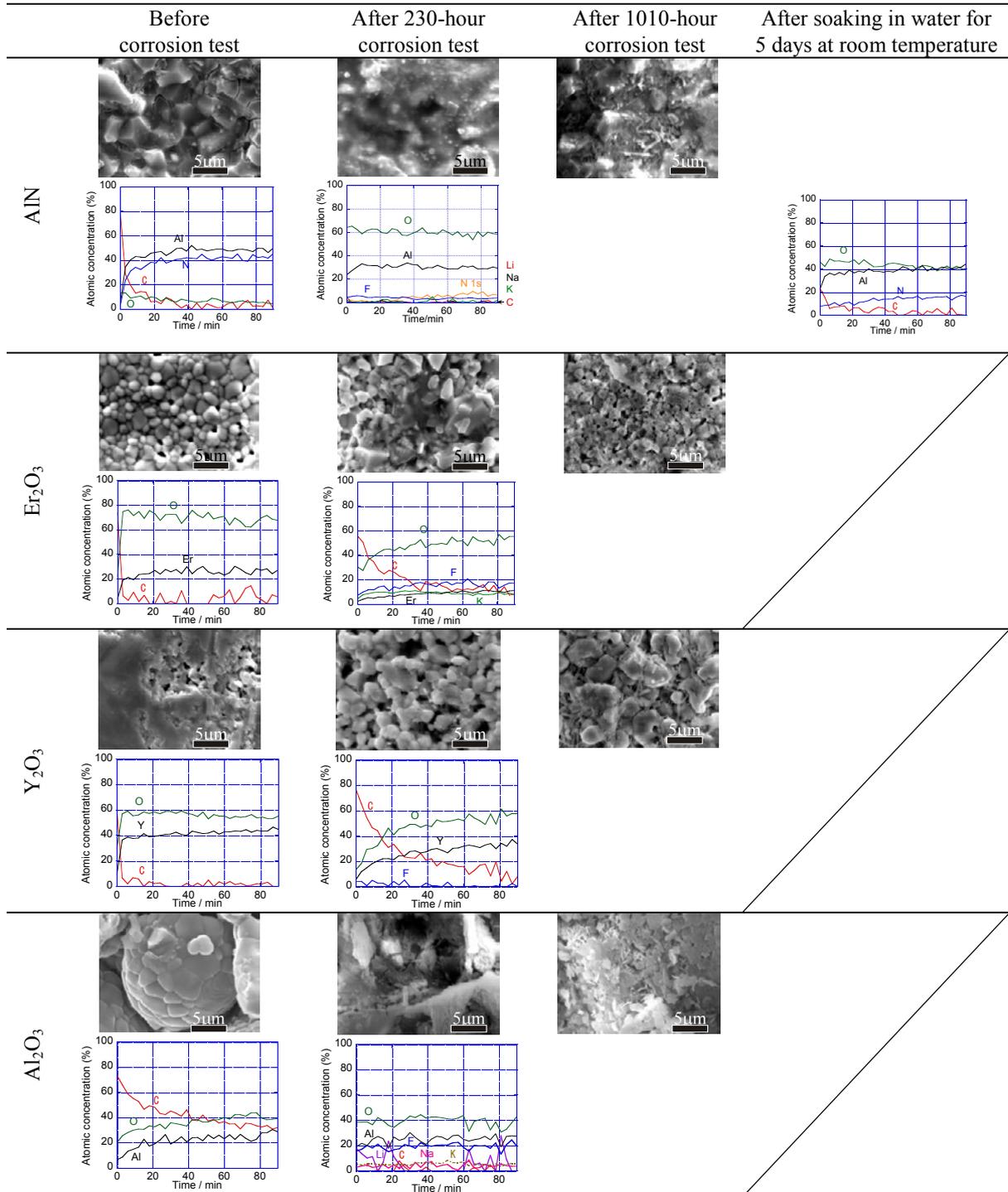


Fig.3 Surface images of specimen by SEM and surface element analysis by XPS before and after corrosion test in Flinak at 600°C for 230 and 1010 hours.

Table 3 Impurity composition in Flinak before and after corrosion test

Element	Initial Flinak [wppm]	Flinak after AlN corrosion test [wppm]		Flinak after Er ₂ O ₃ corrosion test [wppm]		Flinak after Y ₂ O ₃ corrosion test [wppm]		Flinak after Al ₂ O ₃ corrosion test [wppm]	
		230h	1010h	230h	1010h	230h	1010h	230h	1010h
Fe	52	16	19	11	13	4.1	14	120	120
Cr	2.6	39	58	34	33	13	42	150	150
Ni	39	8.3	-	3.5	-	1.3	-	<1	-
Mn	0.07	27	-	28	-	21	-	-	-
Er	<0.01	-	-	1.47 × 10 ⁴	240	-	-	-	-
Y	<0.01	-	-	-	-	0.33 × 10 ⁴	110	-	-
Al	7.4	61	27	-	-	-	-	930	950
Na	5.8 × 10 ⁴	5.98 × 10 ⁴	-	6.11 × 10 ⁴	-	6.11 × 10 ⁴	-	5.89 × 10 ⁴	-
K	35.6 × 10 ⁴	36.2 × 10 ⁴	-	37.3 × 10 ⁴	-	37.5 × 10 ⁴	-	36.1 × 10 ⁴	-
Li	6.90 × 10 ⁴	7.17 × 10 ⁴	-	7.30 × 10 ⁴	-	7.63 × 10 ⁴	-	7.81 × 10 ⁴	-
HF	42.6	<10	-	<10	-	<10	-	<10	-
H ₂ O	10	15.8	58.4	63.8	48.1	13.4	63.4	77.5	51.7

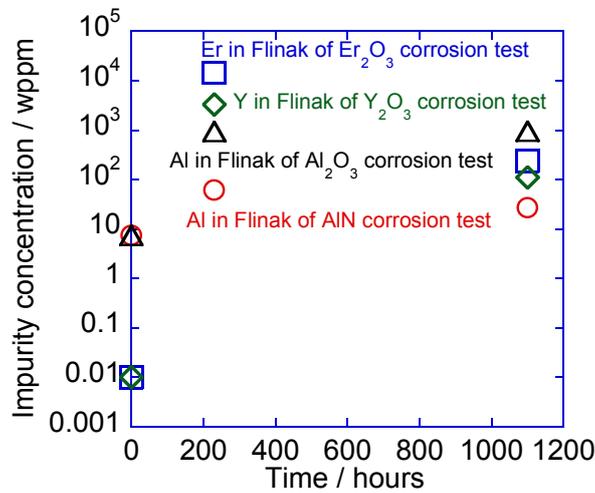


Fig.4 Impurity concentrations in Flinak before and after corrosion test.

Table 4 Gibbs energy for reaction of ceramics material in Flinak at 600°C

	Possible Reaction	Δ Gr [J/K.mol]	Thermodynamic Stability
AlN	Fluoridation	AlN + 3LiF = AlF ₃ + Li ₃ N	+2.015
		AlN + 3KF = AlF ₃ + 3K + 1/2N ₂	-148.607
	Oxidation	AlN + 3H ₂ O =	-318.676
		NH ₃ + 1/2Al ₂ O ₃ .3(H ₂ O)	(-325.219 at 300K)
	AlN + 3/4O ₂ = 1/2Al ₂ O ₃ + 1/2N ₂	-51.351	
Al ₂ O ₃		Al ₂ O ₃ + 6LiF = 2AlF ₃ + 3Li ₂ O	-23.293
		Al ₂ O ₃ + 6KF = 2AlF ₃ + 3K ₂ O	-18.280
		Y ₂ O ₃ + 6LiF = 2YF ₃ + 3Li ₂ O	-2.227
Y ₂ O ₃	Fluoridation	Y ₂ O ₃ + 6KF = 2YF ₃ + 3K ₂ O	+2.786 at 870K (negative under 800K)
Er ₂ O ₃		Er ₂ O ₃ + 6LiF = 2ErF ₃ + 3Li ₂ O	-24.365
		Er ₂ O ₃ + 6KF = 2ErF ₃ + 3K ₂ O	-19.355
ZrO ₄		ZrO ₄ + 4LiF = ZrF ₄ + 2Li ₂ O	-16.484
		ZrO ₄ + 4KF = ZrF ₄ + 2K ₂ O	-13.139

4.3 Corrosion resistance of AlN in Flinak

The AlN specimens seem to possess corrosion resistance against Flinak compared with Er₂O₃ and Y₂O₃.

However, the AlN might be corroded, since the weight loss of the specimen was slightly detected. According to ref. [8], reaction of AlN with moisture forms Al(OH)₃ and ammonia. Moreover, the hydroxide might change to Al₂O₃

and/or its hydrate. After the corrosion test, the oxygen was detected on the surface by XPS as shown in Fig. 3. The surface of AlN specimen could be thinly covered with Al(OH)₃ and/or Al₂O₃. The oxygen rich layer could be formed in Flinak if there was reaction with moisture and/or oxygen in the Flinak. As another possibility, the oxygen rich layer might be formed when the specimens were rinsed in water after corrosion test. Then, to confirm substitution from N to O at the AlN surface in water, another AlN specimen (7.0 mm× 6.0 mm × 3.0 mm) cut from the identical lot was soaked in water for 5 days. Before and after the water soaking, XPS spectra were measured. The insets in Fig.3 show the depth profile of atomic composition ratio measured with XPS and show the replacement from N to O.

The AlN might be corroded if the surface was preliminary oxidized or oxidized in the Flinak due to the reaction with dissolved oxygen in Flinak as shown in Fig. 5.

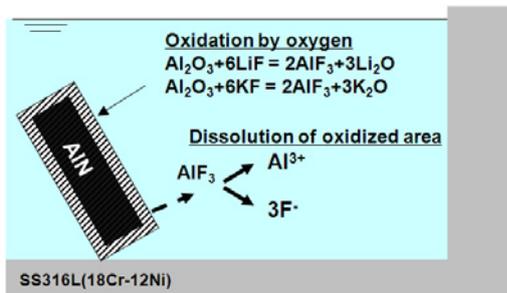
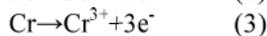
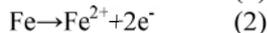


Fig. 5 Corrosion in AlN-Flinak-316L steel system.

4. 4 Corrosion of Al₂O₃, Er₂O₃ and Y₂O₃ in Flinak

In Al₂O₃ corrosion test, Fe and Cr were detected in Flinak after the corrosion tests as shown in Table 3. These would be derived from SS316L crucibles. When Al was ionized and dissolved into molten Flinak in the corrosion process, Fe and Cr would be oxidized as formulas (1)-(3).



Then, metal Al would be precipitated on the crucible surface. These reactions are redox reaction and would make an electrochemical circuit described as a schematism in Fig.6.

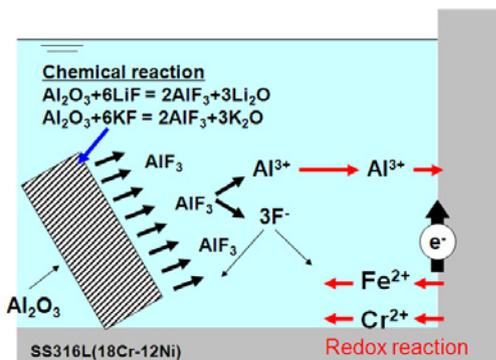


Fig. 6 Corrosion in Al₂O₃-Flinak-316L steel system.

In Er₂O₃ corrosion test, Er dissolution was detected. It was found that the molar ratio of Er was low at the surface.

At the same time, fluorine was also detected on the surface as shown in Fig.3. The surface was corroded via the fluoridation process. Er₂O₃ specimens contained Zr as an impurity as shown in Table 1. Since zirconia seems to be thermodynamically unstable as shown in Table 4, zirconia would promote the corrosion and brittleness.

Although the corrosion of Y₂O₃ specimen was small, the fluorine was slightly detected on the surface. This suggests that the surface could be corroded via fluoridation process.

5. Conclusion

Major results are as follows;

- (1) AlN showed corrosion resistance in Flinak. The surface could be oxidized by the oxygen or moisture.
- (2) The corrosion of Al₂O₃ was large. The corrosion of the 316L type austenitic steel was promoted by the redox reaction caused by the dissolved Al from Al₂O₃ in Flinak.
- (3) The corrosion of Er₂O₃ was caused via the fluoridation process. Zr oxide dissolved in the sample of Er₂O₃ might be promoted the corrosion.
- (4) The corrosion of Y₂O₃ was small, although weight loss due to the corrosion was affected by breaking of the specimens with porous structure.
- (5) The corrosion intensity of the ceramic materials in Flinak agreed with the tendency of chemical reaction indicated by the calculation of the Gibbs reaction energy.

In conclusion, AlN might be suitable for surface coating of the structural materials for blanket system using molten salt like a Flinak.

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