

§7. Corrosion Characteristic of AlN, Y₂O₃, Er₂O₃ and Al₂O₃ in Flnak for Molten Salt Blanket System

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Regarding the heat exchanger for liquid breeder blanket system using molten salts, tritium barrier and anti-corrosion barrier play important roles. To develop the heat exchanger, it is essential to optimize chemical stability of the barrier material against molten salts. In the present study, the corrosion of AlN, Y₂O₃, Er₂O₃ and Al₂O₃ in Flnak was examined to consider possibility as barrier materials.

The static corrosion tests on these ceramic specimens were performed in high purity Flnak (46.5LiF-11.5NaF-42KF mol%) for 230 and 1010 hours. The specimens and Flnak were heated in SS316L crucibles at 600°C in Ar atmosphere. Weight change by the corrosion test was measured. Surface analysis of the specimens was carried out by SEM and XPS. Elution of elements from the specimens was determined based on chemical analysis of the Flnak after the corrosion test using ICP. With the corrosion test, the compatibility of the ceramics in molten Flnak was also considered based on the standard Gibbs energy for formation. According to the estimation as shown table 1, AlN is expected to be stable in Flnak. On the other hand, Er₂O₃, Y₂O₃ and Al₂O₃ are expected to be unstable.

Figure 1 shows SEM images and weigh change before and after the corrosion test. While AlN rarely changed in structure and weight, the structure of Er₂O₃, Y₂O₃ and Al₂O₃ drastically changed in weigh and structure through the corrosion test.

The rough structure at the surface of the AlN specimen before the corrosion test had changed to slightly smooth after the corrosion test. According to surface analysis by XPS measurement, substitution from nitrogen to oxygen near surface was clarified after the corrosion test. This means that Al₂O₃ was formed at the surface. In Flnak after the corrosion tests, Fe and Cr from the SS316L crucibles were detected. When Al was dissolved into molten Flnak in the corrosion process, Fe and Cr would be oxidized as a redox reaction.

The weight loss in the Er₂O₃ specimens after corrosion test was large with breaking. It includes loss of fragments due to breaking during the corrosion test and Flnak removing process by water rinse. The initial Er₂O₃ surface consisted of round shape grains. After the corrosion test, the grains became rough and formed porous and interstitial structure. According to XPS measurement, fluorine was detected on the specimen surface after the corrosion test. Er dissolution was also detected in the Flnak. These suggest that the surface of Er₂O₃ specimens was corroded via the fluoridation process.

The initial Y₂O₃ specimens consisted of large grains appeared over several micrometers. After the corrosion test, the surface became more porous and interstitial structure than that before the corrosion test. Although the Y₂O₃

specimen gained in weight after 230 hour corrosion test, this weight gain would be due to residual Flnak and water remained in the pores of the specimens. The fluorine was also detected on the surface. These suggest that the surface could be corroded via fluoridation process.

Although initial Al₂O₃ consisted of grains like gathering pine cones, after corrosion test, the structure was drastically changed to be rough structure. In the Al₂O₃ specimens after corrosion test, fluorine, lithium, sodium and potassium were detected. The weight increased after the corrosion test. The weight gain of the Al₂O₃ specimens would also be due to retaining Flnak and/or water in the porous structure.

These results mean that Er₂O₃, Y₂O₃ and Al₂O₃ dissolved into Flnak and that the corrosion is not negligible and that the AlN specimens seem to possess corrosion resistance against Flnak. For details, the slight weight loss was detected. Reaction of AlN with moisture forms Al(OH)₃ and ammonia.¹⁾ And the hydroxide could change to Al₂O₃ and/or its hydrate. After the corrosion test, the substitution of nitrogen to oxygen was detected at the surface. The oxygen rich layer such Al(OH)₃ or Al₂O₃ at the specimen surface would promote the corrosion behavior.

In conclusion, it was found that these corrosion behaviors agreed with the prediction based on thermodynamic evaluation. AlN indicates compatibility in molten Flnak. This suggests that AlN is suitable for surface coating of the structural materials for blanket system using molten salt like a Flnak.²⁾

Table 1 Gibbs energy for reaction of ceramics material in Flnak at 600°C

	Possible Reaction	Δ Gr [J/K.mol]	Thermodynamic Stability
AlN	AlN + 3LiF = AlF ₃ + Li ₃ N	+2.015	Stable
	AlN + 3KF = AlF ₃ + 3K + 1/2N ₂	-148.607	Unstable
	AlN + 3H ₂ O =	-318.676	Unstable
	NH ₃ + 1/2Al ₂ O ₃ ·3(H ₂ O)	(-325.219 at 27°C)	Unstable
Al ₂ O ₃	AlN + 3/4O ₂ = 1/2Al ₂ O ₃ + 1/2N ₂	-51.351	Unstable
	Al ₂ O ₃ + 6LiF = 2AlF ₃ + 3Li ₂ O	-23.293	Unstable
	Al ₂ O ₃ + 6KF = 2AlF ₃ + 3K ₂ O	-18.280	Unstable
Y ₂ O ₃	Y ₂ O ₃ + 6LiF = 2YF ₃ + 3Li ₂ O	-2.227	Unstable
	Y ₂ O ₃ + 6KF = 2YF ₃ + 3K ₂ O	+2.786 at 597°C negative under 527°C	Stable over 527°C Unstable under 527°C
Er ₂ O ₃	Er ₂ O ₃ + 6LiF = 2ErF ₃ + 3Li ₂ O	-24.365	Unstable
	Er ₂ O ₃ + 6KF = 2ErF ₃ + 3K ₂ O	-19.355	Unstable
ZrO ₂	ZrO ₂ + 4LiF = ZrF ₄ + 2Li ₂ O	-16.484	Unstable
	ZrO ₂ + 4KF = ZrF ₄ + 2K ₂ O	-13.139	Unstable

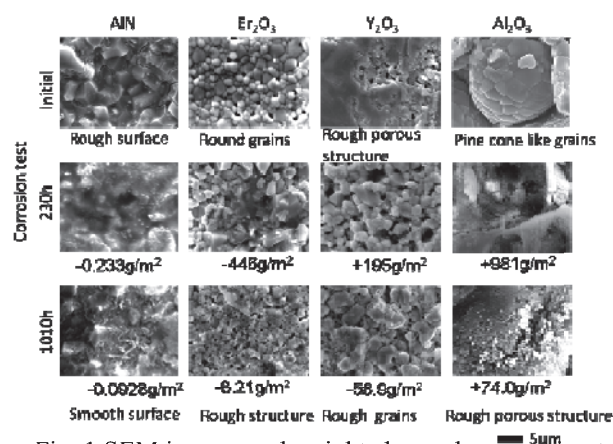


Fig. 1 SEM images and weight change by corrosion test.

- 1) Krnel, K. et al.: J. Euro. Ceram. Soc., **21** (2001) 2075
- 2) Watanabe, T. et al.: J. Plasma Physics and Research, in press