

Effects of Pre-oxidation on Corrosion Behavior of High-Aluminum Alloys in molten NaCl-KCl

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***Keywords** : molten salt reactors, materials, corrosion, pre-oxidation

1. Introduction

Molten salt reactors (MSRs) are gaining attention as a promising nuclear energy technology, with various applications in hydrogen production and industrial heat supply. MSRs use molten salts as both fuel and coolant, achieving high temperatures (600-800 °C) that benefit efficient processes. However, these high temperatures pose significant corrosion challenges for structural materials. While Ni-based alloys have been extensively studied for fluoride salt environments [1-3], research on chloride salts, particularly for nuclear applications, is limited. Recent findings suggest that Fe-based alloys with high aluminum content could form protective oxide layers, potentially serving as cost-effective materials in corrosive chloride environments [4].

This study aims to examine the effect of pre-oxidation on the corrosion resistance of high aluminum-content steel alloys in molten NaCl-KCl at 750°C. Two new alloys were tested with and without pre-oxidation. Corrosion tests were conducted over 500 hours in an inert glovebox, and the performance of specimens was assessed through various analytical techniques.

2. Methods and Results

2.1 Experimental setup

Two different types of high-Al containing alloys, ACES (Advanced Creep-resistance Enhanced Stainless steel) and ADSS (Alumina-forming Duplex Stainless Steel), were synthesized by induction melting furnace process. The detailed elemental composition of each alloy is shown in Table 1. Both ACES and ADSS are primarily based on iron with varying amounts alloying elements. Specifically, ACES contains a high content of Ni to enhance creep resistance, while ADSS contains a

high content of Al to promote alumina formation. After synthesis and fabrication, half of the alloy samples were oxidized in a vacuum at 1100 °C to produce an aluminum oxide scale on the surface.

Table 1: Elemental composition of two alloys

	Fe	Ni	Cr	Al	Ti	Nb	Si	Zr	C	B
ACES	Bal.	35	16	4.5	3	1	0.2	0.3	0.08	0.015
ADSS	Bal.	19	16	6	-	0.2	0.3	-	0.125	-

Sodium chloride (NaCl, >99% purity) and potassium chloride (KCl, >99% purity) were purchased from Sigma Aldrich. These salts were mixed in the eutectic ratio of 44:56 (in weight %) and preheated to remove any remaining moisture before being used for the corrosion test. Solidified salts were ground into fine powders using a ceramic mortar and then loaded into an alumina crucible. The salt analyzed by ICP-OES showed no alloying elements, indicating that metal impurities were below the detection limit and thus had a negligible impact on the corrosion reaction during the test.

For the long-term static corrosion test, alumina crucibles with lids were employed. Each crucible contained two specimens. These two specimens, separated by an alumina spacer, were hung with a tungsten wire and fully immersed in the molten salt. Whole preparation and corrosion tests were conducted inside the glovebox filled with inert argon gas (O₂, H₂O < 1 ppm), and the furnace was maintained at 750 °C for 500 hours.

2.2 Weight loss

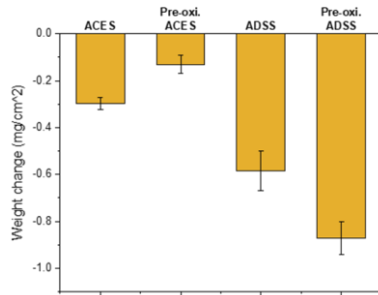


Fig. 1. Weight change of the specimens after the corrosion test. All values are the average of the weight loss of two specimens.

Figure 1 shows the weight change of four types of specimens after the corrosion test. The weight loss increased in the following order: pre-oxidized ACES, ACES, ADSS, and pre-oxidized ADSS. The fact that the pre-oxidized ADSS exhibited the worst corrosion resistance was contrary to the author's expectations, as ADSS contained a higher content of Al compared to ACES. This implies that the aluminum oxide scale formed on the ADSS prior to the test provided no protection and even resulted in greater weight loss, whereas the scale on the pre-oxidized ACES provided sufficient protection against corrosion attack.

2.3 Morphological changes

The surface morphology of the specimens after the test and the following elemental composition at specific spots are shown in Figure 2 and Table 2, respectively.

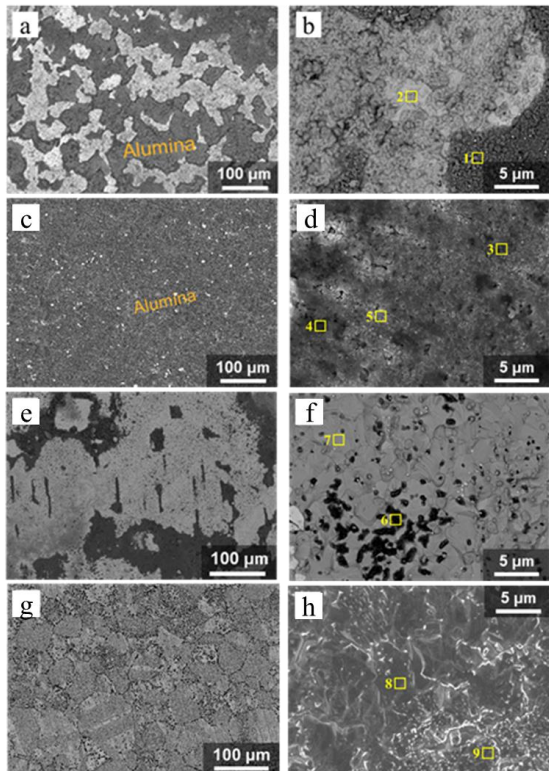


Fig. 2. Surface morphology of the specimens after the corrosion test: (a, b) ACES (c, d) pre-oxidized ACES (e, f) ADSS (g, h) pre-oxidized ADSS

Table 2: EDS spot analysis results

EDS spot	Element (wt%)											
	C	O	Al	Si	Ti	Cr	Mn	Fe	Ni	Zr	Nb	Na
1	-	48.8	23.6	-	12.2	8.1	0.8	5.5	-	1.0	-	-
2	5.2	26.7	0.4	0.2	4.4	9.0	0.2	20.2	25.0	-	8.7	-
3	0.3	47.9	34.5	-	9.8	0.7	0.5	1.1	-	-	5.2	-
4	-	21.0	13.0	0.4	32.3	0.4	0.1	1.2	0.2	0.0	31.5	-
5	1.6	54.0	25.1	0.4	8.9	0.4	-	0.3	0.3	0.8	8.3	-
6	0.1	4.1	12.1	0.1	2.1	14.7	2.8	62.3	-	-	-	1.7
7	3.8	3.2	1.1	0.3	0.3	12.3	0.8	57.0	21.1	-	-	-
8	2.9	3.1	0.9	0.2	0.1	13.1	0.3	63.0	16.4	-	-	-
9	4.9	2.9	1.2	0.4	0.3	11.4	0.6	54.9	23.2	-	0.2	-

The surface of the ACES specimen was partially covered with a dark-colored layer, as seen in Fig. 2(a), which was found to be mainly composed of aluminum oxide. It is likely that the oxygen ions (O^{2-}) dissolved in the molten salt reacted with metal ions, primarily aluminum ions (Al^{3+}) in this case, to form Al_2O_3 . However, since the oxygen content in the salt is limited and immediately consumed by the reaction mentioned above, the surface was not fully covered with the oxide layer.

On the contrary, the surface of the pre-oxidized ACES specimen was fully covered with the aluminum oxide scale as can be seen in Figure 2(c), suggesting that the preformed oxide scale was successfully suppressing the active dissolution of the alloy, leading to the smallest weight loss.

While the ADSS specimen exhibited a similar morphology to the ACES specimen, with the surface partially covered by the dark-colored layer, the EDS results indicated that the layer was not aluminum oxide but a mixture of iron and chromium. XRD pattern of ADSS also evidences the absence of oxide scale on the surface.

Lastly, no preformed aluminum oxide scale was detected on the surface of the pre-oxidized ADSS specimen, indicating that the oxide scale was not protective in the molten chloride salt. The specific reason why the oxide scale of the pre-oxidized ADSS did not provide sufficient resistance, while that of the pre-oxidized ACES did, will be investigated through further analysis.

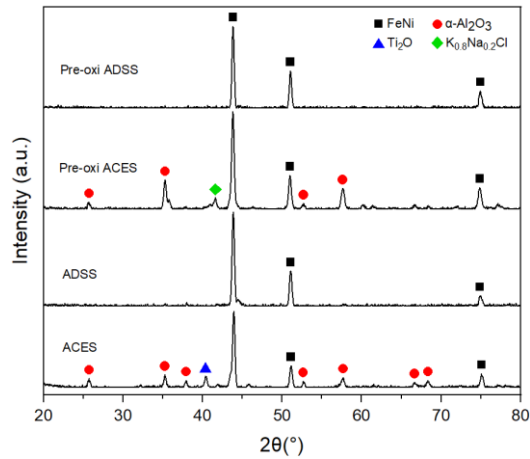


Fig. 3. XRD patterns of four alloys after the corrosion test

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3. Conclusions

This study evaluated the corrosion resistance of ACES and ADSS alloys in molten chloride salt at high temperatures. Pre-oxidized ACES showed the least weight loss, indicating effective protection by the aluminum oxide scale. In contrast, pre-oxidized ADSS exhibited the highest weight loss, suggesting that its oxide scale failed to provide any protection. These results highlight that the corrosion resistance of these alloys depends not only on aluminum content but also on the stability and adherence of the oxide scale. Further research is needed to understand the factors affecting the protective behavior of these oxide scales.

ACKNOWLEDGEMENTS

This research was supported by the Nano & Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT (RS-2023-00229215). This work was also supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 2022400000120).

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