

Corrosion behaviors of high-Al containing austenitic stainless steels in Cl-based molten salt environment

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1. Introduction

Molten salt reactors (MSRs), recognized as one of the Generation IV (Gen IV) nuclear systems, offer significantly enhanced safety and economic benefits compared to traditional reactors [1]. MSRs operate at atmospheric pressure, effectively mitigating the risk of severe accidents such as hydrogen explosions and large-scale radioactive material releases. However, identifying structural materials that meet the requirements of operating environment of MSRs like molten salt corrosion resistance, mechanical properties and irradiation resistance in high temperature remains a challenge. To minimize corrosion of materials, alumina has been researched as one of corrosion mitigating options by its capability of enhancing the corrosion resistance of structural materials [2,3].

In this study, the corrosion behaviors of high-aluminum (high-Al) containing austenitic stainless steels (ASSs), developed by our research group, was investigated with a commercial alloy Hastelloy N. The alloys were exposed to Cl-based molten salt at 750 °C for an initial 100-hour periods, followed by an additional 400-hour exposure.

After the corrosion test, weight change measurement, surface and cross-sectional analyses by electron microscope were conducted to evaluate the corrosion behavior of test materials.

2. Methods and Results

2.1 Alloy Design

The design of the newly developing alloy, ACRS, aimed to improve the corrosion, creep and radiation resistance as a structural material of MSRs. The Al content was selected to be near 5.5 wt.% for forming B2 phase which plays as an aluminum reservoir for forming alumina oxide layer providing corrosion resistance to molten salt environment [3] and provides desired mechanical properties to alloys at operating temperature of MSRs [4]. The Cr content was for air oxidation resistant property. In addition, the Ni content is for maintaining the fully austenitic matrix of alloy balancing with the Al and Cr contents. Meanwhile, the Ti content was selected to form gamma prime (γ')

within the matrix to provide creep resistance [5]. The Nb and C contents were also selected to form Nb-rich carbide as a strengthening method of the alloy [6].

2.2 Material

A commercial alloy, Hastelloy N, and high-Al containing austenitic stainless steels developed by our research group were used for molten salt corrosion test. For ACRS, a casting ingot of 1.2 kg was made by vacuum pressure casting (VPC). In this study, as-cast ACRS and pre-oxidized ACRS were subjected to the molten salt corrosion test. The ACRS ingot was pre-oxidized at 900 °C for 40 hours under a vacuum environment (10^{-6} torr) to form an alumina layer on its surface. **Figure 1** presents a cross-sectional microstructural image of pre-oxidized ACRS (pre-oxi ACRS). ACRS formed alumina layer with an approximate thickness of 150 nm, along with an Ti(Ta)N layer located in between.

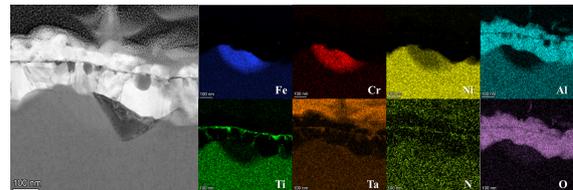


Fig. 1. TEM EDS images of pre-oxi ACRS

2.3 Molten Salt Corrosion Test

For the molten salt corrosion test, all materials were fabricated into coupon-type specimens with a diameter of 12 mm and a thickness of 1 mm by electrical discharge machining (EDM). A 1.8 mm of hole was drilled near the edge to hang the specimen on a alumina hanger during testing. Prior to the corrosion test, the specimens were mechanically polished on both side using 1200 grit SiC paper and ultrasonically cleaned in ethanol.

The anhydrous KCl (> 99 %) and NaCl (> 99 %) were supplied by Sigma Aldrich. The eutectic KCl-NaCl (50 mol.%-50 mol.%) was prepared within an Ar-filled glove box, with controlled ambient of oxygen

and moisture content under 3 ppm each. To purify and stabilize the molten salt mixture, it was sustained at a temperature of 700 °C for 24 hours before the test. Two coupon specimens from each alloy were hung on a alumina hanger within an alumina crucible, which was charged with the eutectic salt mixture to immerse the specimens. The static molten salt test was performed at 750 °C for an initial 100 hours. After the initial immersion test, all specimens were carefully cleaned with distilled water to remove any residual salt and dried. Then, 400 hours of additional immersion test was carried out in the same manner.

Before and after the corrosion test, the weight of each specimen was measured using a microbalance (XP6, Mettler Toledo) with a resolution of 0.001 mg. For analyzing microstructural feature, scanning electron microscope (SEM) were carried out with Hitachi SU-8230 equipped with energy dispersion spectroscopy (EDS).

2.4 Experimental Results

Figure 2 shows the weight changes of the test materials after exposure to molten KCl-NaCl at 750 °C for an initial 100 hours and an additional 400 hours. For Hastelloy N, a linear weight decrease was observed over time, indicating a consistent corrosion behavior, which aligns with previous studies [4,5]. For ACRS, the weight gain after 100 hours suggests a potential correlation with the increased oxide layer thickness. In contrast, pre-oxi ACRS exhibited a decreased in average weight after an additional 400 hours. However, the large standard deviation indicates that external factors, such as oxide layer spallation rather than corrosion behavior alone, may have influenced the results.

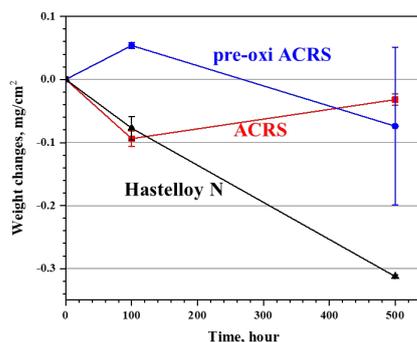


Fig. 2 Weight changes of tested alloys after exposure to molten KCl-NaCl salts at 750 °C for an initial 100 hours and an additional 400 hours

For surface and cross-sectional microstructural analysis, Hastelloy showed grain boundary attack after a total 500 hours of exposure, consistent with Cr-depletion depth measurements. ACRS and pre-oxi

ACRS formed an alumina layer on the surface with no measure Cr-depletion and no observed spallation, with B2-denuded depths of 1.5 μm and 2.5 μm, respectively. However, in pre-oxi ACRS, the alumina and Ti(Ta)N layers were less stable and exhibited weaker adhesion to the substrate compared to those in ACRS, as shown in Fig. 3. Since alumina exists in various phases depending on temperature [6], further analysis is being conducted using high resolution transmission electron microscopy (HRTEM) to identify the type of alumina formed during the pre-oxidation process and molten salt exposure,

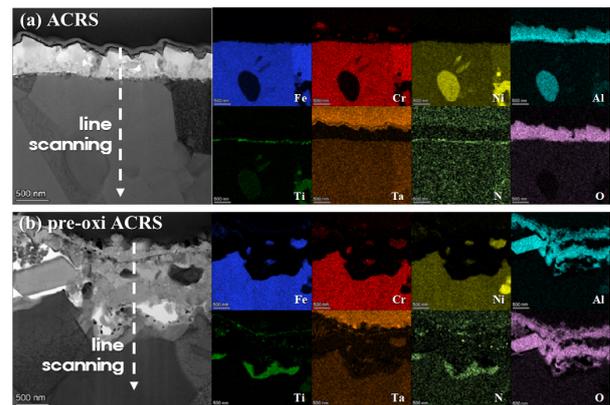


Fig. 3. Cross-sectional TEM/EDS mapping images of (a) ACRS and (b) pre-oxi ACRS after exposure to molten KCl-NaCl salts at 750 °C for an initial 100 hours and an additional 400 hours

3. Conclusions

Molten salt corrosion behavior of commercial alloy (Hastelloy N) and high-Al containing austenitic stainless steels (ACRS and pre-oxi ACRS) were investigated after exposure to KCl-NaCl at 750 °C for an initial 100 hours and an additional 400 hours. An alumina layer was formed in all high-Al containing alloys, in pre-oxi ACRS, the layer appeared unstable due to the presence of coarsened TiN particles in between alumina layers. To investigate different corrosion mechanisms of ACRS and pre-oxi ACRS, further microstructure analyses for ACRS are being conducted.

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