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Hot corrosion behavior of magnesia-stabilized ceramic material in a lithium molten salt

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HIGHLIGHTS

- Corrosion mechanism of MSZin LiCl-Li_2O molten salt is proposed.
- Formation of $Li_2ZrO_3$is main corrosion mechanism.
- There were no cracks, pores and spallation after corrosion test.
- MSZ shows high corrosion resistance to LiCl-Li_2O molten salt.

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ABSTRACT

The isothermal and cyclic corrosion behaviors of magnesia-stabilized zirconia in a LiCl-Li_2O molten salt were investigated at 650 °C in an argon atmosphere. The weights of as-received and corroded specimens were measured and the microstructures, morphologies, and chemical compositions were analyzed by scanning electron microscopy, X-ray energy dispersive spectroscopy, and X-ray diffraction. For processes where Li is formed at the cathode during electrolysis, the corrosion rate was about five times higher than those of isothermal and thermal cycling processes. During isothermal tests, the corrosion product Li_2ZrO_3 was formed after 216 h. During thermal cycling, Li_2ZrO_3 was not detected until after the completion of 14 cycles. There was no evidence of cracks, pores, or spallation on the corroded surfaces, except when Li was formed. We demonstrate that magnesia-stabilized zirconia is beneficial for increasing the hot corrosion resistance of structural materials subjected to high temperature molten salts containing Li_2O.

1. Introduction

In recent years, pyroprocessing has been regarded as an alternative solution for recycling nuclear fuel due to its low environmental impact, proliferation resistance, and economic efficiency. Pyroprocessing is an electrolysis process using high temperature molten salts as a reaction medium, and is one of the key technologies for reducing the amount of spent nuclear fuel and eliminating toxic waste products, including long-life fission products [1–3]. Electrolytic reduction is one of the unit processes in pyroprocessing and involves electrolytically reducing spent oxide fuel to its metallic form [4–7]. Even though pyroprocessing has many advantages, molten salts can cause corrosion of container materials and various components of the electrolysis equipment. Long-term corrosion resistance is one of the important parameters determining the suitability of a given material for structural applications requiring continued exposure to molten salts at high temperature.

Corrosion of the equipment and structural materials that come in contact with high-temperature molten salts has been extensively studied and superalloys have been developed for such applications [8–19]. However, the corrosion resistance of these alloys primarily relies on the thermodynamic properties of a formed oxide layer

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that provides protection from further corrosion in the corrosive environment. Both the composition and physical properties of the oxide layer determine the corrosion resistance of the underlying metal. Hence, using ceramic structural materials is more effective than using metals for long-term chemical stability in elevated temperature molten salt environments [20–25]. However, there are very few reports in the literature that describe the effects of lithium chloride molten salts containing Li_2O on the corrosion resistance of ceramic structural materials. In the present study, we chose MgO-stabilized ZrO_2 (MSZ), a ceramic material known to be mechanically and chemically stable in elevated temperature corrosive environments [26,27], and we investigated its corrosion behavior under simulated electrolytic reduction conditions at high temperature.

2. Experimental

2.1. Specimen preparation

The MSZ used identically in this study had a nominal composition (wt.%) of MgO: 2.75, Al_2O_3: 0.60, TiO_2: 0.10, Fe_2O_3: 0.12, and ZrO_2: 96.21 (Nikkato Corporation, Japan). Specimens were prepared with dimensions of 70 mm (l) × 15 mm (w) × 3 mm (t). The specimens were ground with SiC paper, polished with diamond paste, and ultrasonically cleaned in acetone before being subjected to the elevated temperature corrosion test.

2.2. Hot corrosion tests

The experimental apparatus used for the corrosion testing is shown in Fig. 1. A mixture of as-received LiCl (Rare Metallic Co., Ltd., Japan; 99.9%) and Li_2O (Cerac, USA; −100 mesh, 99.5%) powders was introduced into a high-density MgO crucible and then heated to 300 °C for 3 h in an argon atmosphere to remove any moisture. After further heating to 650 °C, the MSZ specimens were immersed in the formed LiCl-Li_2O molten salt. Isothermal corrosion exposure times were 168 h, 216 h, and 360 h at 650 °C and the experiments were undertaken in an argon atmosphere inside a glove box. Cyclic corrosion tests consisted of 14 cycles, where each cycle involved exposing the MSZ specimens to 650 °C for 24 h in the LiCl-Li_2O molten salt and then to room temperature for 48 h in an argon atmosphere inside a glove box. The Li_2O concentration was 1 wt%, which is a commonly used concentration for electrolytic reduction processes. The Li concentration was 1 wt%, considering lithium formation at the cathode during the electrolytic reduction process. Following the elevated temperature corrosion tests, the specimens were withdrawn from the salt and kept in a cylindrical reactor under an argon atmosphere while the furnace cooled to room temperature.

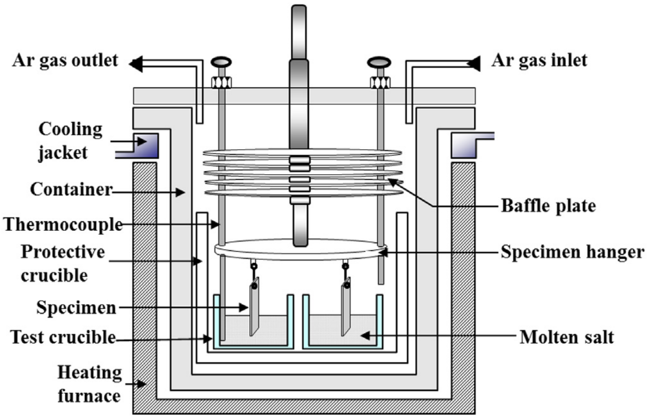

Fig. 1. Schematic diagram of the apparatus used for corrosion testing.

2.3. Characterization

The reactor was opened and the specimens were removed and visually examined. Next, they were ultrasonically cleaned in acetone and dried for more than 24 h in a drying oven at 80 °C. The final weights of the specimens exposed to the molten salt were measured and compared to the initial weights to assess the degree of corrosion. The corroded specimens were cut using a diamond saw and ultrasonically cleaned in acetone for the characterization experiments. The microstructures, morphologies, and chemical compositions of the corroded surfaces were characterized using scanning electron microscopy (SEM; JEOL, JSM-6300) equipped with an energy dispersive X-ray spectroscopy system (EDS). X-ray diffraction (XRD; Rigaku, DMAX/1200) was employed to analyze the structural phase evolution of the corroded specimen surface.

3. Results and discussion

3.1. Corrosion rate

The criterion for calculating the corrosion rate is usually dependent on the dry corrosion or wet corrosion environment. If lithium is generated during the electrolytic reduction process, ZrO_2 is reduced, and then the concentration of Li_2O can be increased. Specifically, the high-temperature molten salts, including Li_2O, create a chemically aggressive environment that is excessively corrosive; Li_2ZrO_3 is formed by the reaction between ZrO_2 and Li_2O and continuous elimination of the corrosion product occurs. In this study, MSZ is chemically attacked by both Li_2O and Li and the main corrosion product is Li_2ZrO_3. The density difference between MSZ (~5.7 g/cm^3) and Li_2ZrO_3 (~4.16 g/cm^3) causes spallation due to the volume change on the MSZ surface and disintegration of the stabilized crystal structure of MSZ. Some weight gain due to the formation of Li_2ZrO_3 could occur; however, we believe it to be negligible compared to the weight loss as the corroded surface layer was removed during cleaning of the specimens after the corrosion experiments. The weight changes of MSZ specimens after isothermal and cyclic corrosion tests at 650 °C in a LiCl-Li_2O molten salt for 168 h–360 h, 7 and 14 thermal cycles, or a LiCl-Li_2O-Li molten salt for 168 h, are shown in Fig. 2. The corrosion rates of the specimens exposed to the isothermal tests were lower than those of the specimens subjected to thermal cycling. However, for the process where Li was formed at the cathode, the corrosion rate was about five times higher than that of the isothermal or thermal cycling processes. Both the morphology and composition of the corroded surface are discussed in Section 3.3. The corrosion mechanism of the ceramic material under these electrolytic conditions was mainly determined by the reaction between the specimen and Li_2O in molten LiCl and by crack formation due to phase transformation and/or thermal shock, as described in Section 3.3. The weight loss of the MSZ was about 1% of that of a nickel-based alloy (N108; 12.64 mg/cm^2) at 650 °C in a LiCl-Li_2O molten salt after 168 h [28], and the corrosion rates for the commercial alloys, Inconel 713LC; 14.3 mg/cm^2, Inconel MA754; 18.5 mg/cm^2, Haynes 214; 26.5 mg/cm^2, and Haynes HR160; 31.5 mg/cm^2 at 650 °C in a LiCl-3%Li_2O molten salt after 168 h [29].

3.2. Phase structure

Fig. 3 shows the XRD patterns of the as-received MSZ specimen and the MSZ surface corroded in LiCl-Li_2O at 650 °C for 168 h and