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Feasibility tests of nickel as a containment material of molten Li_2O-LiCl salt containing Li metal at 650 °C during electrolytic reduction

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HIGHLIGHTS

- The behavior of Ni in four different LiCl salts was analyzed using immersion tests.
- Leaching of Ni was observed when exposed to Li_2O-LiCl salts containing Li metal.
- Excessive Li metal and oxygen in the salt must be maintained at low levels.

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ABSTRACT

In this study, we investigated the feasibility of nickel (Ni) as a material to contain molten Li_2O-LiCl salt containing lithium (Li) metal at 650 °C as an electrolyte during the electrolytic reduction process of pyroprocessing (also known as oxide reduction, OR). First, the behaviors of Ni in four different LiCl salts (0.1 wt% Li-LiCl, 1 and 8 wt% Li_2O-LiCl, and 8 wt% Li_2O-0.1 wt% Li-LiCl) in an argon atmosphere were examined through immersion tests. Then, Ni was used as a vessel material for five consecutive OR runs of simulated oxide fuel using 1.0 wt% Li_2O-LiCl salt. The tested Ni was analyzed by microbalance, X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Concentrations of Ni in the salt were measured using inductively coupled plasma atomic emission spectroscopy. No corrosion product of Ni, except Cr_2Ni_3, was observed on the Ni used for both the salt-immersion tests and the OR runs because the Ni was not exposed to oxygen gas. However, leaching of Ni in the OR salt containing excessive Li metal was observed. Therefore, Ni can be used as the salt containment material in the OR process when excessive Li metal and oxygen gas in the salt are maintained at low levels.

1. Introduction

Pyroprocessing technology is used to recycle spent oxide fuel from nuclear power plants into metal fuel for nuclear fast reactors. Pyroprocessing involves electrochemical processes using high-temperature molten salt as an electrolyte to fabricate the metal fuel. One of the key electrochemical processes is electrolytic reduction (known as oxide reduction, OR) to reduce the spent oxide fuel to a metallic form. The heat, volume, and radioactivity of the spent fuel decrease during the OR because its heat-loaded fission products are dissolved in a molten salt [1–5].

The OR cell consists of an electrolyte, a cathode, and an anode. A molten LiCl salt at 650 °C is generally used as the OR electrolyte. Li_2O (solubility 8.7 wt% in LiCl) is added to LiCl to speed up the OR reaction and reduce the electrolysis time. The common range of Li_2O concentration in LiCl is 0.5–1.5 wt% because plutonium (Pu) and americium (Am) oxides are not reduced at high concentration (>3.4 wt%), and the anode can be dissolved at low concentration (<0.5 wt%) [6–8]. Oxide fuels are used as a cathode by loading them in a permeable basket such as a stainless steel (STS) basket. The cathode reactions are as follows:

$$MO_2 + 4e^- \rightarrow M + 2O^{2-}\ (salt) \tag{1}$$

$$Li^+\ (salt) + e- \rightarrow Li\ (salt) \tag{2}$$

$$MO_2 + 4Li\ (salt) \rightarrow M + 4Li^+\ (salt) + 2O^{2-}\ (salt) \tag{3}$$

Here, M denotes actinides such as uranium (U) and Pu. Lithium (Li) metal (solubility 0.29 wt% in LiCl at 650 °C [9]) produced by the reaction (2) is present in the Li_2O-LiCl salt. A platinum (Pt) is

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typically employed as an anode. The O^{2-} ions are transported through the salt and are discharged at the anode as follows [10–13]:

$$2O^{2-} \rightarrow O_2\,(g) + 4e^- \quad (4)$$

The OR process is operated in a corrosive environment and hot O_2 gas is discharged at the anode. Moreover, the Li_2O added to the LiCl salt and the Li metal produced by the cathode reaction (reaction (2)) lead to damage of the material for salt containment. Hence, corrosion-resistant materials have been regarded as important for enhancing OR efficiency and the lifetime of its apparatus [14]. Metal alloys with various elemental contents (nickel (Ni), chrome (Cr), iron (Fe), and silicon (Si) etc.) have been typically used as the salt containment material [15–19]. Since Ni is an important element for corrosion-resistance, the Ni content in the metal alloys varies depending on its application. For example, the STS and Ni-based alloys contain 8–12% and ~70% of Ni, respectively [20–24]. Metal alloys with high Ni content have received previous attention as a material for OR application [20].

Here, the feasibility of Ni was investigated as a salt containment material for the OR process. We focused on the behavior of Ni in Li_2O-LiCl salt containing Li metal at 650 °C because Li metal is usually present in the salt due to the cathode reaction (reaction (2)) during OR, which can affect the stability of the salt containment material. Initially, immersion tests of Ni coupons in four different LiCl salts (0.1 wt% Li-LiCl, 1 and 8 wt% Li_2O-LiCl, and 8 wt% Li_2O-0.1 wt% Li-LiCl) were conducted in an inert argon (Ar) atmosphere. Unlike previous studies on the corrosion of Ni and Ni or STS-based alloys [18–20], we also examined Ni by using it as a vessel material containing 1.0 wt% Li_2O-LiCl for five consecutive OR runs of simulated oxide fuel (simfuel). The tested Ni was analyzed by means of microbalance, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX). Concentrations of Ni in the salt were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2. Materials and methods

LiCl (99% purity) and Li_2O (99.5% purity) were purchased from Alfa Aesar. The Ni and Li metals (>99% purity) were purchased from Sigma-Aldrich. All experiments using the molten salts were performed in a high-purity Ar atmosphere glove box. Thermal dehydration of LiCl was conducted before use by heating to a temperature of 650 °C at a linear rate of 0.5° C/min under reduced pressure (<1 Torr) before cooling. As shown in Fig. 1a, the immersion tests of Ni coupons were independently conducted for 24 h in four different LiCl salts (40 g for each), listed in Table 1. Two LiCl salts only contained Li_2O, with concentrations of 1 and 8 wt%, respectively. Two LiCl salts contained Li metal of 0.1 wt% (0.1 wt% Li-LiCl and 8 wt% Li_2O-0.1 wt% Li-LiCl). An STS vessel was used to load each salt for the immersion tests. Ni coupons cut from its original material were used. The Ni coupons obtained after the immersion tests were characterized by microbalance (Mettler Toledo), XRD (Bruker, D8 Advance), EDX (Horiba, EX-250 X-max), and SEM (Hitachi, SU-8010) after removing the residual salt on their surfaces using distilled water.

Fig. 1b shows the schematic set-up for the OR using Ni as a vessel material. First, after 300 g of LiCl was loaded in a Ni vessel (ϕ 80 mm × 55 mm (H)) at room temperature, it was heated to 650 °C for 4 h and maintained at that temperature. Then, 3.0 g of Li_2O was fed into the vessel to reach the desired concentration. The electrodes (anode, cathode, and reference electrodes) were immersed into the Li_2O-LiCl salt. A 10-mm-wide Pt plate was used as the anode. The anode shroud (made of MgO-stabilized ZrO_2) was used to provide a path for the O_2 gas. A cylindrical STS wire mesh cathode basket was used to contain the simfuel of 10 g. Porous simfuel pellets (3.59 g/cm^3) with a cylindrical shape (ϕ6.4 mm × 6.2 mmH) were used as the simfuel. The fabrication method of the simfuel has been reported by a previous study [25]. The main component of simfuel is UO_2 (97.0 wt%) and the remaining simfuel components are 1.82 wt% rare earth oxides (Nd_2O_3, CeO_2, La_2O_3, Pr_6O_{11}, Sm_2O_3, Y_2O_3, and Gd_2O_3), 0.72 wt% ZrO_2, and 0.46 wt% salt-soluble fission products (BaO, SrO, and Eu_2O_3). A liquid Li-Pb alloy (32 mol% Li) was used as a reference electrode.

Prior to the start of the OR processes, the Ni coupons were immersed in the salts by loading a STS wire mesh basket (Fig. 1b). When each OR run finished, one Ni coupon was removed from the

Table 1
Mass changes before and after immersion tests of Ni coupons in various salts.

Tested salts	Mass of Ni [g]		Change [%]
	Before test	After test	
1 wt% Li_2O-LiCl	1.201	1.203	+0.1655
8 wt% Li_2O-LiCl	0.711	0.721	+1.407
8 wt% Li_2O-0.1 wt% Li-LiCl	0.545	0.539	−1.101
0.1 wt% Li-LiCl	1.309	1.299	−0.7639

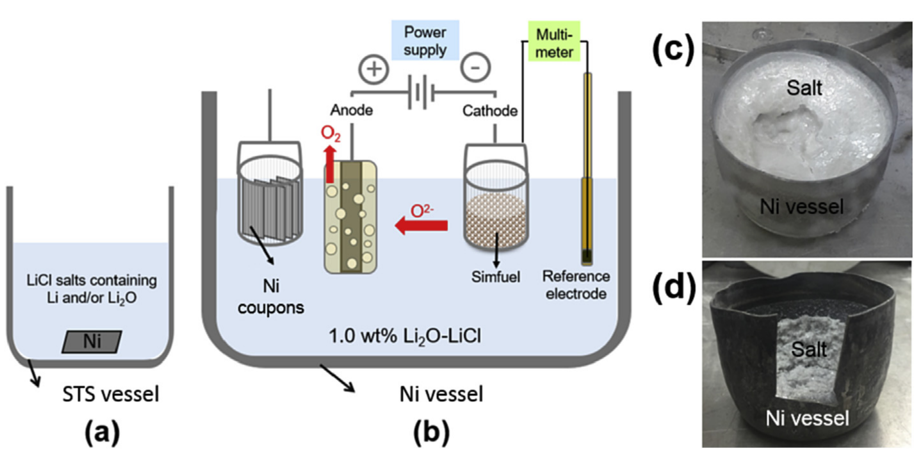

Fig. 1. Schematic drawings of: (a) immersion test of Ni coupon in salt contained in a STS vessel and (b) OR cell in a Ni vessel; (c) image of the Ni vessel used for the five OR runs; and (d) image of the Ni vessel partically cut for characterization.