

Reduction of Metal Oxides Compounds by Lithium Metal as a Reductant in Molten LiCl Salt

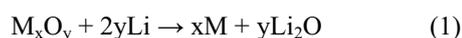
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1. Introduction

The lithium (Li) reduction process is a technique for chemically reducing actinide oxides to their metals using Li metal as a reductant in molten LiCl. The reaction of the actinide oxides with the Li metal as follows:



This technique has been developed to apply pyroprocessing for oxide fuels; the metallic products obtained through the Li reduction process are transferred to an integrated process, electrorefining and uranium and transuranic elements are recovered from the product [1-4].

The reduction of the actinide oxides through the Li reduction process was experimentally proven in the early 2000s. Nonetheless, electrolytic reduction process using Li₂O-LiCl salt as an electrolyte [5] has been actively researched to replace the Li reduction process due to some technical problems; the tricky handling of the Li metal, the continuous accumulation of Li₂O in LiCl salt by the reaction 1, the requirement of micro-size fuel, and the breakage of porous magnesia basket used as a material to contain the micro-size fuel etc. In this presentation, we introduce that the Li reduction process can be still usefully used to reduce the metal oxides to their metals under certain conditions where the electrolytic reduction is difficult.

2. Reduction of Zirconium Oxide Compounds

Pyroprocessing can be adopted for treatment of damaged fuel debris (mainly composed of (U,Zr) O₂) generated by nuclear accidents such as Fukushima. Originally, the Zr in the Zr alloy-based cladding was present in the metal state but oxidized during the accident process and existed in the form of ZrO₂ in the damaged fuel. The reduction of the damaged oxide to metallic form can enable the recovery of uranium, cladding, and fission products through electrorefining, which can allow its long-term storage or final disposal [1,6]. However, the complete reduction of ZrO₂ to Zr metal using the electrolytic reduction is difficult due to the reaction of Li₂O with ZrO₂.

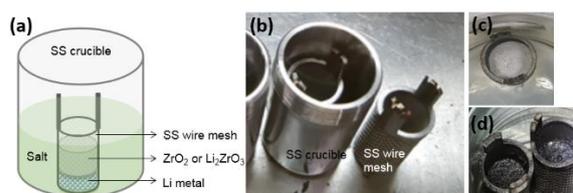
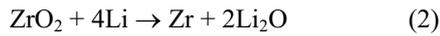
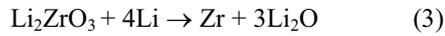


Fig. 1. Schematics and photos of the tests conducted in this study: (a) schematics of the reduction tests, (b) SS crucible and SS wire mesh basket, (c) Zr compound loaded in the basket, and (d) product in the basket after the reduction tests were completed.

It was experimentally demonstrated that ZrO₂ was reduced to Zr metal by Li metal in LiCl salt at 650°C without formation of Li₂ZrO₃ according to the following reaction:



Also, the reduction of Li_2ZrO_3 to Zr metal by reaction of Li was observed as follows:



The detailed experimental conditions and procedures were described elsewhere [7].

3. Reduction of Rare Earth Oxides

Unlike the actinide and noble metal oxides, rare earth oxides are reduced only partially and remain in their oxide form in the cathode after the electrolytic reduction. The standard Gibbs free energies of formation of rare earth oxides are more negative than that of Li_2O . We demonstrated that the low level of the rare earth oxides in the reduction product can be significantly increased by the extra Li reduction. Also, the long-term behavior of the Li metal in salt was monitored. The detailed experimental conditions and results were reported elsewhere [8].

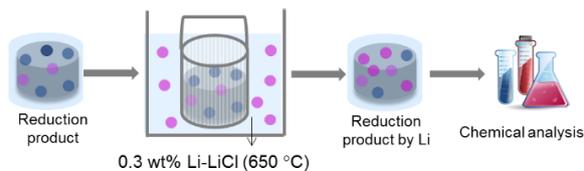


Fig. 2. Schematics: the Li reduction to increase the metal extents of rare earth oxides.



Fig. 3. The changes in Li-LiCl salt as a function of time.

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