Effect of the Lithium Oxide Concentration on a Reduction of Lanthanide Oxides

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1. Introduction

The pyrochemical reduction process of spent oxide fuel is one of the options to handle spent PWR fuels in Korea.[1-3] After spent oxide fuel is converted to a metallic form, fission products will be removed from the resultant uranium and higher actinide metals by an electrorefining process.[4,5]

The chemical behaviors of lanthanide oxides during the pyrochemical process has been extensively studied.[6] It was also reported that about 30 to 50% of several lanthanide oxides were reduced to corresponding metals by an electrolytic reduction process having 1 wt% of a lithium oxide concentration.[7] Korea Atomic Energy Research Institute (KAERI), however, has been used 3 wt% of lithium oxide to increase the applied current of the electrolytic reduction process.

Though it was reported that U_3O_8 was reduced to uranium metal having a high reduction yield at 3 wt% of the Li_2O concentration,[8] the effect of the lithium oxide concentration on the reduction of lanthanide oxides has not been clarified.

2. Experimental and Results

It has been known that most lanthanide oxides react with lithium oxide to produce mixed oxides ($LiLnO_2$, where Ln represents lanthanide elements) at a high lithium oxide concentration.

Each lanthanide oxide has a critical lithium oxide concentration to form a mixed oxide. The bigger the ionic radius of a lanthanide ion is, the higher the lithium oxide concentration needed to form a mixed oxide is. Fig. 1 shows the correlation between lithium oxide concentration and ionic radius of lanthanide ions.

When 3 wt% of lithium oxide is used for the electrolytic reduction process, Fig. 1 shows that only Gd, Yb, Lu, and Sc oxides produce a mixed oxide. Since an electrolytic reduction process produces lithium metal at the cathode where lanthanide oxides are located, reactions between lanthanide oxides and lithium metal were investigated by changing the lithium oxide concentration.

Initial concentrations of lithium oxide were 0, 1, and 3wt% and a mixture of about 250mg of each lanthanide oxide was reacted with a slightly excess amount of lithium metal.

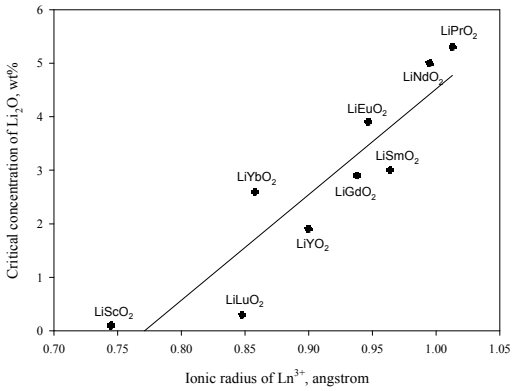

Fig. 1. Li_2O concentration to form $LiLnO_2$ versus ionic radii of Ln^{3+}.

Table 1 shows the reduction yield of each lanthanide oxide at different initial lithium oxide concentrations. By increasing the lithium oxide concentration from 0 to 3 wt% in LiCl, the reduction yields were dramatically decreased.

Table 1. Reduction yield (%) of lanthanide oxides at different Li_2O concentrations.

Oxides	Initial Li_2O concentration		
	0 wt%	1 wt%	3 wt%
Nd_2O_3	32.1	1.9	0.07
Sm_2O_3	17.6	4.6	0.07
Y_2O_3	42.2	10.6	0.12
Eu_2O_3	62.5	3.6	0.13
Gd_2O_3	3.7	1.7	0.08
Lu_2O_3	48.8	14.7	0.13
Pr_2O_3	20.7	2.1	0.08
Sc_2O_3	26.5	5.3	0.12

When Li_2O was initially absent, reduction yields of the lanthanide oxides to their metallic forms were about 20 to 40% except for Gd_2O_3 which had only 3.7%. At 1 wt% of an initial Li_2O concentration, the reduction yields of them decreased rapidly and at 3 wt% of a Li_2O concentration

which is KAERI's electrolytic reduction condition, the reduction yields became trivial.

The result indicates that the lithium oxide concentration should be minimized to reduce the lanthanide oxides to a metallic form.

Reduction of lanthanide oxides to corresponding metals at the same Li_2O concentration seems not to be related to the trend of the mixed oxides formation. Though Sc and Lu formed mixed oxides at a very low Li_2O concentration, the reduction yields of them were relatively high. When Lu_2O_3 was added into LiCl molten salt containing a sufficient amount of Li metal and 0.4 wt% of Li_2O, the Li_2O concentration decreased to 0.28 wt% after 3 hours. It indicates that Lu_2O_3 consumed some amount of Li_2O to form a mixed oxide. X-ray diffraction pattern of the final product was that of $LiLuO_2$.

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