Residual Salts Separation from Metal Reduced Electrolytically in a LiCl-Li₂O Molten Salt

Jin-Mok Hur, Seung-Chul Oh, Sun-Seok Hong, Chung-Seok Seo, Seong-Won Park
Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon, Korea, jmhur@kaeri.re.kr

1. Introduction

The PWR spent oxide fuel can be reduced electrolytically in a hot molten salt for the conditioning and the preparation of a metallic fuel. Then the metal product is smelted into an ingot to be treated in the post process. Incidentally, the residual salt which originated from the molten salt and spent fuel elements should be separated from the metal product during the smelting. In this work, we constructed a surrogate material system to simulate the salt separation from the reduced spent fuel and studied the vaporization behaviors of the salts.

2. Methods and Results

The components of the spent oxide fuel can be categorized into four groups according to their chemical behavior: (a) uranium and transuranics (TRU), (b) alkali(AM), alkaline earths(AEM), (c) rare earth elements (RE), and (d) noble metal elements (NM). After the electrolytic reduction in a LiCl-Li₂O molten salt at 650 °C, the metallized spent fuel consists of uranium, TRU, and NM in a powder form [1, 2]. The high heat load alkali and alkali earth oxides change chemically to corresponding chlorides during the electrolytic reaction and can be separated from the reduced spent fuel. Consequently, the heat load and radioactivity of the reduced spent fuel can be significantly decreased. Most rare earth elements accompany the reduced spent fuel in the oxide form due to their low solubility in a LiCl molten salt.

The vapor pressure variation of the chloride compounds with the temperature was calculated by using thermodynamic data. In the case of LiCl and CsCl, the main components of the residual salts, a drastic increase of the vapor pressure was observed above 900 °C. Considering the vaporization behaviors of the chloride compounds, the removal of the residual salts at 950 °C was set up for the 1st step of a smelting. The metal elements in the targets of the smelting have a relatively low vapor pressure when compared to the chloride compounds. Actually, the vaporization of U and Pu is negligible during the smelting process. However, Am is a very peculiar element which has a very stable gas phase ground state and accordingly shows a high vapor pressure. To prevent the vaporization of Am, the heating condition should be carefully controlled. Mn shows a similar vaporization behavior to Am. Therefore, Mn was used as a surrogate material for Am in this study.

Table 1. Surrogate material system

<table>
<thead>
<tr>
<th>Surrogate</th>
<th>TRU</th>
<th>AM, AEM</th>
<th>RE</th>
<th>Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>CsCl, SrCl₂</td>
<td>Y₂O₃</td>
<td>LiCl-Li₂O</td>
<td></td>
</tr>
</tbody>
</table>

Removal of volatile materials will be facilitated in a vacuum condition by an enhanced diffusion rate. Fig. 1 shows the vaporization behaviors of the surrogate materials during the inactive experiments. The final temperature was held for 5 hours in a vacuum condition of ~10⁻² torr.

In the case of the mono-component vaporization experiments, the chloride compounds except for SrCl₂ were completely removed from the metal products at
950 °C. Mn, the surrogate of Am, and SrCl₂ were partially vaporized at 1,200 °C in our experimental condition. The separation of Am from the metal product is not desirable. On the other hand, SrCl₂, a high heat load fission product, should be separated from the metal product. For the selective vaporization of SrCl₂, we studied the mixing effect of the salts. 8 wt% Li₂O and 8 wt% SrCl₂ are soluble in LiCl at 650 °C, respectively, and the DSC (differential thermal calorimetry) experiment using a closed pen showed the strong interaction of Li₂O and SrCl₂ with LiCl. The lowering of the vaporization temperature of Li₂O and SrCl₂ in a bi-component sample was explained accordingly. Mn and Y₂O₃ are actually not soluble in a LiCl molten salt in the tested temperature range and the DSC experiments did not show any interaction of them with LiCl. Consequently, the mixing effect was not observed in the case of Mn and Y₂O₃.

3. Conclusion

The separation of residual salts has been studied by using surrogate materials. The residual chloride salts were selectively separated from the metal product while suppressing the vaporization of Mn, the surrogate of Am. Y₂O₃, the representative surrogate of the rare earth elements, can be recovered as dross after a smelting. Considering the vaporization behaviors, salt vaporization at 950 °C was set up for the 1st step of the spent fuel smelting.

Acknowledgement

This work has been carried out under the Nuclear R&D Program by the Ministry of Science and Technology (MOST), Korea.

REFERENCES