Chemistry

27B/2004G064

Chlorination of polyvalent metal oxide in molten salts

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Introduction

In the pyrochemial reprocessing of spent nuclear fuels, chlorination of polyvalent oxides like UO_2 etc. is an important reaction. Recently, a chlorination reaction using $ZrCl_4$ with LiCl-KCl eutectic melt was proposed by Sakamura et al.[1]. For example, the chlorination of yttrium oxide is expressed as following chemical reaction,

$$Y_2O_3 + (3/2)ZrCl_4 \rightarrow 2YCl_3 + (3/2)ZrO_2$$

It is very significant to know nature of the chlorination reaction, for example, a temperature dependence etc. In the present work, the chlorination reaction of Y_2O_3 was observed by using in situ XAFS measurement.

Experimental

The Y K-edge (E_0=17.080keV)) XAFS measurements of Y_2O_3 and YCl_3 were performed in transmission method at the BL27B station in the KEK-PF. The Zr K-edge (E_0=17.998keV) XAFS data was also obtained by extending the Y K-edge XAFS measurement. The starting sample was a mixture of Y_2O_3-$ZrCl_4$(1:2) in LiCl-KCl eutectic. The samples were sealed off in a quartz cell under reduced pressure. Details of the XAFS measurement of molten salts are described in ref.[2]. The XAFS data was analyzed by using WinXAS code[3].

Results and discussions

Fig.1 shows raw XAFS spectra of the LiCl-KCl-Y_2O_3-$ZrCl_4$ mixture sample before and after heating. There are two XAFS data in each curve. They are Y K-edge and Zr K-edge(E_0=17.998keV) XAFS, respectively. The Y K-edge XAFS curve before heating is clearly different from that after heating. An edge jump of the Zr K-edge XAFS became very weak after the heating. It suggests that Y_2O_3 changed to YCl_3 and $ZrCl_4$ disappeared by the heating.

Fourier transform magnitude functions $|FT(k^3\chi(k)|$ of the mixture sample before and after heating are shown in Fig.2. Chemical state of Y can be evaluated from difference in the distance between Y-O and Y-Cl correlation. At 500°C, the Y-O correlation is predominant, although the sample is in molten state. On the other hand, the 1st peak shows the Y-Cl correlation at 550°C. It can be concluded that the reaction occurs between 500 and 550°C. The XAFS result after cooling to 500°C was almost the same as that of LiCl-KCl-YCl_3 mixture melt[4].

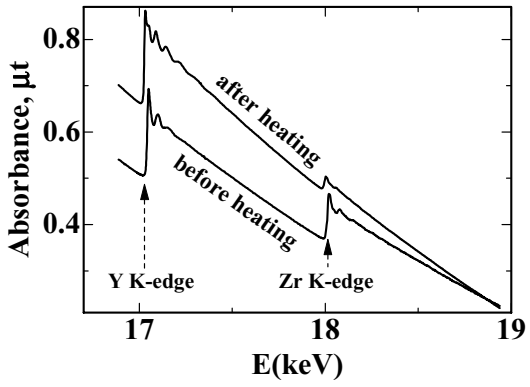

Fig.1 Raw XAFS spectra of the LiCl-KCl-Y_2O_3-$ZrCl_4$ sample before and after heating.

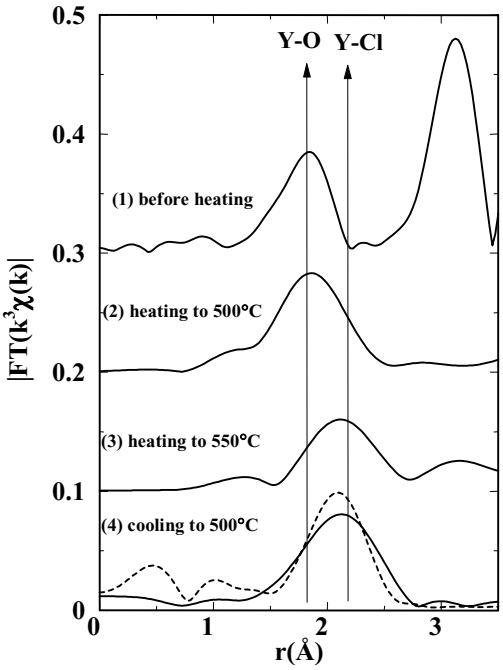

Fig.2 Fourier transform magnitude $|FT(k^3\chi(k)|$ of the LiCl-KCl-Y_2O_3-$ZrCl_4$ sample before and after heating. Dashed line shows XAFS result of molten 15%YCl_3 in LiCl-KCl eutectic[4].

References

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