

Thermal behavior of PrCl₃ in an oxidizing condition

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1. Introduction

Pyrochemical processing of a spent nuclear fuel is now considered as one of the more promising options for an innovative nuclear fuel cycle[1]. Electrorefining in molten salts is the main step in this process, where the actinides are separated from the lanthanides[2]. During the electrorefining, certain amounts of waste salts containing lanthanide chlorides are generated. It is reported that the oxygen sparging method for a recovery of reusable salts from the waste salts is very effective for an economical as well as an environmental aspect[3,4].

In this study, a thermo-gravimetric analysis of PrCl₃ as one of the lanthanide chlorides was carried out by an injection of O₂ gas in an oxidizing condition to investigate the thermal behavior of PrCl₃. Based on the results, an oxidation of PrCl₃ in LiCl-KCl molten salts was performed by sparging O₂ gas with changing temperatures.

2. Methods and Results

2.1 Thermo-gravimetric analysis (TGA) of PrCl₃

Anhydrous PrCl₃ with a purity of 99.99% was prepared. Before carrying out a TGA of PrCl₃, PrCl₃ was dried at 107 °C in a dry vacuum oven. The TGA of PrCl₃ was performed from room temperature to 1400 °C at a fixed heating rate (5 °C/min) under an oxidizing condition. O₂ gas injected into TGA furnace has a purity of 99.999% without moisture. Fig. 1 shows a thermal reduction of PrCl₃ according to temperature. REOCl is easily formed by heating hydrated RECl₃ in air condition at around 300 °C[5]. A weight reduction occurs when RECl₃ is converted to REOCl. Therefore, TGA curve indicates a thermal behavior of PrCl₃. According to Fig. 1, three reduction patterns existed as a thermal behavior of PrCl₃. It is thought that a dissociation of chlorine in PrCl₃ quickly occurred and minor PrCl₃ was converted to PrOCl in step I, and a dissociation of chlorine in PrCl₃ was slowly progressed and a formation of PrOCl caused actively. It was found that in case of non-hydrated RECl₃ PrOCl is not easily formed, compared to hydrated RECl₃. It was conjectured that PrOCl was converted to PrO₂ (or Pr₆O₁₁) in step III. Above the results could be confirmed by SEM-EDS and XRD results of samples terminated at 400, 600 and 1400 °C.

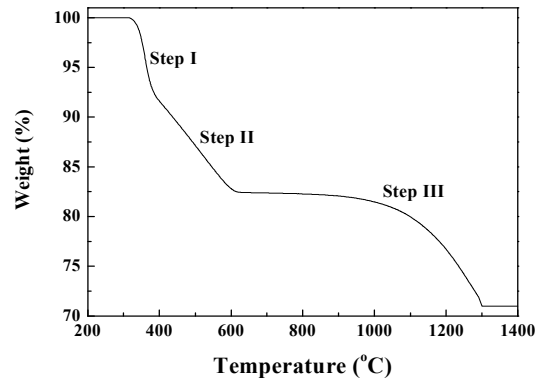


Figure 1 Thermal reduction of PrCl₃ at a fixed heating rate (5 °C/min) under oxidizing condition (O₂ 100%).

Table 1 Conversion of PrCl₃ to insoluble Pr compounds by sparging O₂ gas according to temperature

T (°C)	450	550	650	750
Conversion (%)	55.1	87.8	99.9	99.9

2.2 Oxidation of PrCl₃ in LiCl-KCl molten salts by sparging O₂ gas

Based on the TGA data of PrCl₃, an oxidation of PrCl₃ in LiCl-KCl molten salts was done by sparging O₂ gas. Anhydrous PrCl₃ was premixed with LiCl-KCl molten salts (LiCl : 44.2 wt%) in an alumina crucible. When the temperature reached given temperature (450 – 750 °C), sparging O₂ gas was started for about 6 hr. PrCl₃ was converted to PrOCl in the LiCl-KCl molten salts of temperature range of 450 to 650 °C and some PrO₂ was also formed at 750 °C. Oxidative products of PrCl₃ were insoluble in the LiCl-KCl molten salts and were precipitated into bottom of the alumina crucible. Thus a conversion of PrCl₃ to insoluble Pr compounds could be calculated by analyzing a concentration of soluble Pr in the salts. The results were listed in Table 1. As shown in Table 1, PrCl₃ was almost converted to insoluble compounds at a higher temperature than 650 °C. This result is well agreed with TGA data of PrCl₃.

3. Conclusion

Thermal behavior of PrCl₃ was investigated in an oxidizing condition. According to the TGA data of PrCl₃, a dissociation of PrCl₃ occurred rapidly by about 400 °C and a conversion of PrCl₃ to PrOCl was

completed at about 600 °C. It was confirmed that these results conformed to the conversions of PrCl_3 to insoluble Pr compounds in LiCl-KCl molten salts by sparging O_2 gas.

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