

Purification of Zr from Zr-Hf Resources Using Crystallization in HF-HCl Solvent Mixture

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Abstract : Zirconium (Zr) has been used as a fuel cladding tube for nuclear reactors, because of the excellent corrosion resistance and the low adsorptive material for neutron. Generally speaking, the natural resource of Zr is often containing Hf that has similar properties. The content of Hf in the Zr resources is about 2~4 wt%. In the industrial use, the content of Hf in Zr resources should be lower than the 100 ppm. However, the separation of Zr and Hf is not so easy, because of similar chemical and physical properties such as melting point, boiling point and things. Solvent extraction method has been applied for the separation of Zr and Hf from Zr natural resources. This method can separate Hf with high efficiency (Hf < 100ppm), however, it needs much amount of organic solvents for solvent extraction and the cost of its disposal treatment is high. Therefore, we attached attention for the fractional crystallization. This separation method depends on the solubility difference of Zr and Hf in the solvent. In this work, hexafluorozirconate (hafnate) ($K_2Zr(Hf)F_6$) was used as model compound. Solubility of K_2ZrF_6 in water showed lower than that of K_2HfF_6 . By repeating of this treatment, it is possible to purify Zr, practically. In this case, 16-18 times of recrystallization stages were needed for its high purification. The improvement of the crystallization process was carried out in this work. Water, hydrofluoric acid (HF) and hydrofluoric acid (HF) +hydrochloric acid (HCl) mixture were chosen as solvent for dissolution of Zr and Hf. In the experiment, 10g of K_2ZrF_6 was added to each solvent of 100mL. Each solution was heated for 1 hour at 353K. After 1h of this operation, they were cooled down till 293K, and were held for 5 hours at 273K. Concentration of Zr or Hf was measured using ICP analysis. It was found that Hf was separated from Zr-Hf mixed compound with high efficiency, when HF-HCl solution was used for solvent of crystallization. From the comparison of the particle size of each crystal by SEM, it was confirmed that the particle diameter of the crystal showed smaller size with decreasing of Hf content. This paper concerned with purification of Zr from Zr-Hf mixture using crystallization method.

Keywords : crystallization, zirconium, hafnium, separation

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