

Preparation and Characterization of Nickel and Iron Mixed Oxides for the Development of a Fuel CRUD Analysis Technique

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1. Introduction

Since the extended burn-up programs for a long-term fuel cycle were introduced in Pressurized Water Reactors (PWRs), safety and efficiency concerns have arisen due to a substantial increase of Chalk River Unidentified Deposits (CRUD) on the fuel surface. This fuel CRUD has been reported to create an axial offset anomaly (AOA) phenomena and an increase in the dose rate [1-2]. At present, many approaches have been developed to mitigate the formation of fuel CRUD. In particular, the chemical analysis of fuel CRUD is an important subject relative to the determination of optimal reactor coolant chemistry [3-5].

Recently, the development of a new analysis technique using laser spectroscopy commenced for the analysis of fuel CRUD. In developing this technique, it is essential to establish the emission spectrum database of CRUD samples with various chemical compositions.

In the present study, we prepared five simulated CRUD samples with different Ni/Fe ratios. These were synthesized by a hydrolysis of nickel nitrate and iron nitrate mixed solutions and were heat treated under a high temperature steam condition. Their structures and elemental ratios were determined using Energy Dispersive Spectrometer (EDS), X-ray Diffraction (XRD) patterns, and Fourier Transform Infra-Red Spectrometer (FT-IR) approaches, respectively. We confirmed the formation of nickel ferrite.

2. Methods and Results

For the preparation of simulated CRUD, nickel (II) nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and iron (III) nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ were used as the source of Ni^{2+} and Fe^{3+} ions, respectively. A lithium hydroxide $[\text{LiOH}]$ solution was used as the pH control agent. Molar ratios of $\text{Ni}^{2+}/\text{Fe}^{3+}$ were controlled to be Ni:Fe=1:0, 1:0.67, 1:1.36, 1:2.0, 0:1, respectively. The lithium hydroxide solution was added to the Ni and Fe containing solutions and stirred for 30 min. Afterwards, the Li was removed until it was below 100 ppm Li. The precipitates were dried at room temperature for 5 days and were treated at 500 °C for 8hr under steam conditions [6].

The structure analysis of the heat treated samples was carried out using X-ray diffraction (BRUKER-AXS, D5000) in the range 20 to 70° using Cu $K\alpha$ ($\lambda=1.5409\text{\AA}$) radiation.

The thermal decomposition behavior of the precipitates samples was examined by thermogravimetry (TG, TA SDT Q600) and differential scanning calorimetry (DSC) under argon gas condition with a heating rate of 5 °C/min.

2.1 Chemical analysis of the nickel-iron mixed oxides

Table 1 shows the chemical composition of heat-treated mixed oxides with various molar ratios of Ni and Fe. It was confirmed that the molar ratios of Ni and Fe mixed oxides were almost the same as the controlled ratios.

Table 1. Molar ratios of Ni and Fe mixed oxides heat treated at 500 °C for 8h. (Measured by EDS)

Sample (Mixing ratio)	Molar ratio	
	Ni	Fe
Ni:Fe=1:0	1	0
Ni:Fe=1:0.67	1	0.74
Ni:Fe=1:1.36	1	1.46
Ni:Fe=1:2.0	1	1.93
Ni:Fe=0:1	0	1

2.2 Crystal structure of the nickel-iron mixed oxide

Fig. 1 shows the X-ray diffraction pattern of mixed oxides with various molar ratios of Ni and Fe heat-treated at 500 °C for 8h. At the molar ratio of Ni:Fe=1:0 and 0:1, the XRD pattern showed a crystalline phase of NiO and Fe_2O_3 , respectively. When Ni and Fe were combined at a 1:2.0 ratio, it showed a crystalline phase of NiFe_2O_4 . At the molar ratio of Ni:Fe=1:0.67, it showed two different patterns of NiO and NiFe_2O_4 . As Fe content increasing, the NiFe_2O_4 portion increased.

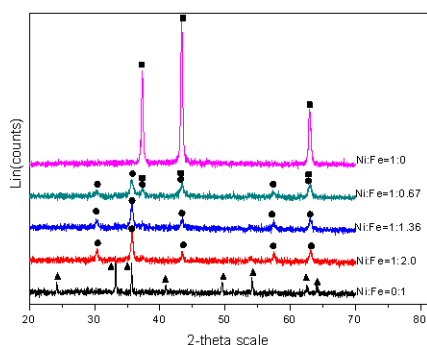


Fig. 1 X-ray diffraction patterns of the nickel-iron mixed oxides. Peaks corresponding to NiO(■), NiFe₂O₄(●), Fe₂O₃(▲)

2.3 Thermal property of nickel-iron mixed oxide

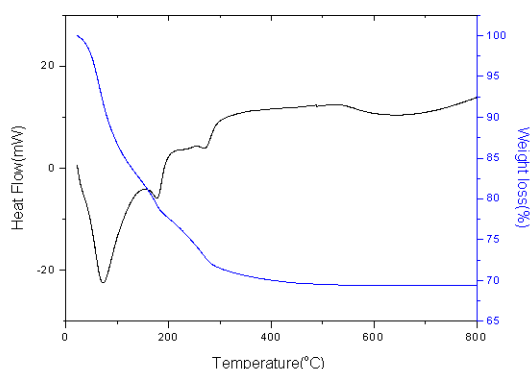


Fig.2 TG/DSC curve of the nickel-iron mixed oxide with Ni:Fe=1:2.0

Fig. 2 shows the TG/DSC curve of the nickel-iron mixed oxide with the molar ratio of Ni:Fe=1:2.0. The TG curve exhibited about 30% weight loss of the mixed oxide until 300 °C. The major cause of the weight loss is the drying of water and hydrate molecules in the mixed oxides. These water molecules are the source of steam during the heat treatment. The DSC curve shows three endothermic peaks. The endothermic peak at 80 °C clearly demonstrates the loss of residual water in the mixed oxide. The endothermic peak at 185 °C is regarded as the formation of NiFe₂O₄·xH₂O. The last endothermic peak observed at 275 °C is estimated to be the loss residual hydrates in the NiFe₂O₄·xH₂O.

3. Conclusions

We prepared five kinds of mixed oxides with different Ni/Fe ratios, and we examined their chemical composition and the structural properties. Chemical composition of the nickel-iron mixed oxides was confirmed by EDS. Further, the crystalline structures of mixed oxides were determined to be NiO, Fe₂O₃,

NiFe₂O₄ through analysis of their XRD patterns. As the Fe content increased, the NiFe₂O₄ portion increased. In the TG curve, the nickel-iron mixed oxide with Ni:Fe=1:2.0 was observed to reflect about 30% weight loss until 300 °C. During the heat treatment, the nickel-iron mixed oxide with Ni:Fe=1:2.0 showed three different endothermic peaks. The peak at 80 °C is the loss of residual water in the mixed oxide. The second peak at 185 °C is regarded to be the formation of NiFe₂O₄·xH₂O. The last peak observed at 275 °C is estimated to be the loss residual hydrates in the NiFe₂O₄·xH₂O.

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