

# Preparation and Crystallographic Characterization of Ni-Zn-Fe Mixed Oxide for the Development of CRUD Analysis System Using a Laser Induced Breakdown Spectroscopy

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## 1. Introduction

In terms of an economic evaluation and reduction of the spent fuel, an extended burn-up program for a long-term fuel cycle of 18-24 months has been introduced to many pressurized water reactor (PWR) plant. However, a long term fuel cycle brings about an increased the amount of the corrosion products deposited to the surface of both the fuel cladding and the steam generator. The corrosion products called as Chalk River Unidentified Deposits (CRUD) have been reported to create an axial offset anomaly (AOA) phenomenon an increase in the dose rate [1,2,3]. In order to reduce the dose rate of the coolant system, Zn ions have been added into the coolant to form zinc ferrite instead of nickel ferrite. Therefore, under this circumstance, ZnO and  $ZnFe_2O_4$  may be included as the CRUD components [4,5].

In the present study, we prepared five different Ni-Zn-Fe mixed oxides with the various molar ratios of Ni, Zn, and Fe, as a part of development of a CRUD analysis system by using a laser induced breakdown spectroscopy. These oxides were prepared by grinding of the  $Ni(OH)_2$ ,  $Zn(OH)_2$  and  $Fe(OH)_3$  and were heat treated under a high temperature condition [6,7]. Their structures and elemental ratios were determined by using inductively coupled plasma - atomic emission spectroscopy (ICP-AES) and X-ray diffraction (XRD) patterns.

## 2. Methods and Results

All the reagents were of analytical grade and were not purified further before use. The  $Ni(OH)_2$ ,  $Zn(OH)_2$  and  $Fe(OH)_3$  powders obtained by neutralizing nickel nitrate [ $Ni(NO_3)_2 \cdot 6H_2O$ ], zinc nitrate [ $Zn(NO_3)_2 \cdot 6H_2O$ ] and ferric nitrate [ $Fe(NO_3)_3 \cdot 9H_2O$ ], with lithium hydroxide [ $LiOH \cdot H_2O$ ], respectively. After the neutralization process, the products were centrifuged and washed with the deionised water until the concentration of lithium was removed below 200 ppm.

For the preparation of the Ni-Zn-Fe mixed metal oxides, the metal oxides controlled with molar ratios of Ni: Zn: Fe = 1: 0: 2, 0.75: 0.25: 2, 0.5: 0.5: 2, 0.25: 0.75: 2, 0: 1: 2 and were grinded in a mortar with water. Afterwards, the mixtures were dried at 50°C for 24 h and mixed powders with moisture of about 0.1g were compressed at an air pressure of 5-6 metric tones for 2 min. Each pellet was put into a quartz tube and sealed under a vacuum. The samples in the quartz tubes were heated at 500°C for 8 h [6].

The elemental composition analysis of Ni-Zn-Fe mixed oxides is carried out by using inductively coupled plasma - atomic emission spectroscopy (HORIBA, ULTIMA 2C). The structure analysis of the heat treated samples was carried out by using X-ray diffraction (BRUKER-AXS, D5000) in the range between 20° and 70° using Cu  $K\alpha$  ( $\lambda=1.5409\text{\AA}$ ) radiation. The thermal decomposition behavior of the Ni-Zn-Fe mixture powder was examined by thermogravimetry (TG, Setsys 16/18) and differential scanning calorimetry (DSC) under argon gas condition with a heating rate of 10°C/min.

### 2.1 Chemical analysis of the Ni-Zn-Fe mixed oxides

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

Table I: Molar ratios of Ni-Zn-Fe mixed oxides

| Molar ratios                  | Measured molar ratios<br>(by ICP-AES) |      |    |
|-------------------------------|---------------------------------------|------|----|
|                               | Ni                                    | Zn   | Fe |
| Ni: Zn: Fe =<br>1: 0: 2       | 1.12                                  | 0    | 2  |
| Ni: Zn: Fe=<br>0.75: 0.25: 2  | 0.80                                  | 0.27 | 2  |
| Ni: Zn: Fe =<br>0.5: 0.5: 2   | 0.49                                  | 0.53 | 2  |
| Ni: Zn: Fe =<br>0.25: 0.75: 2 | 0.27                                  | 0.86 | 2  |
| Ni: Zn: Fe =<br>0: 1: 2       | 0                                     | 1    | 2  |

### 2.2 Crystal structure of the Ni-Zn-Fe mixed oxides

Fig. 1 shows the X-ray diffraction pattern of Ni-Zn-Fe mixed oxides with various molar ratios of Ni, Zn and Fe heat-treated at 500°C for 8h. At the molar ratio of Ni: Zn: Fe = 1: 0: 2, the XRD pattern showed a crystalline phase of NiO,  $Fe_2O_3$  and  $NiFe_2O_4$ . At the molar ratio of Ni: Zn: Fe = 0: 1: 2, the XRD pattern showed a crystalline phase of ZnO,  $Fe_2O_3$  and  $ZnFe_2O_4$ . The XRD pattern of Ni-Zn-Fe mixed oxides, as Zn content decreasing, the  $NiFe_2O_4$  and NiO portion increased.

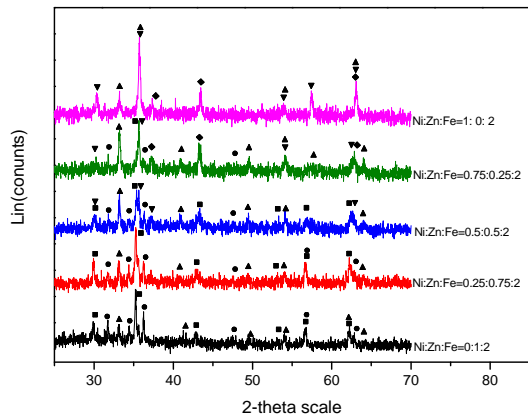


Fig. 1. X-ray diffraction patterns of the Ni-Zn-Fe mixed oxides. Peaks corresponding to NiO (◆), Fe<sub>2</sub>O<sub>3</sub> (▲) NiFe<sub>2</sub>O<sub>4</sub> (▼), ZnO (●), ZnFe<sub>2</sub>O<sub>4</sub> (■).

### 2.3 Thermal property of the Ni-Zn-Fe mixed oxides

Fig. 2 shows the TG/DSC curve of the Ni-Zn-Fe mixed oxides with the molar ratio of Ni: Zn: Fe = 0.5: 0.5: 2. The TG curve exhibited about 15 % 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 Ni-Zn-Fe 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 100°C and 140°C regarded as the loss of residual water in the mixed oxide. The endothermic peak at 272°C is regarded as the formation of metal oxides.

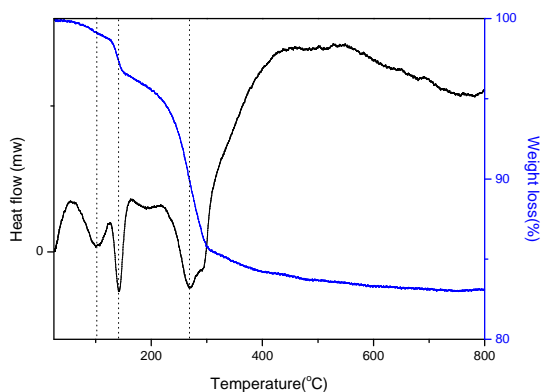


Fig. 2. TG/DSC curve of Ni-Zn-Fe mixed oxides with the molar ratio of Ni: Zn: Fe = 0.5: 0.5: 2.

### 3. Conclusions

We prepared Ni-Zn-Fe mixed oxides with the molar ratios of various Ni, Zn, and Fe and examined their chemical composition and the structural properties.

Chemical composition of the Ni-Zn-Fe mixed oxides was confirmed by ICP-AES. Further, the crystalline structures of mixed oxides were determined to be NiO, ZnO, Fe<sub>2</sub>O<sub>3</sub>, NiFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> through analysis of their XRD patterns. In the TG curve, the mixed oxide with Ni: Zn: Fe = 0.5: 0.5: 2 was observed to reflect about 15% weight loss until 300°C. During the heat treatment, the mixed oxide showed three different endothermic peaks. The peak at 100°C and 140°C is the loss of residual water in the mixed oxide. The peak at 272°C is regarded to be the formation of metal oxides.

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