

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

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### 1. Introduction

Since an extended fuel cycle of 18-24 months has been introduced to PWR system, efficiency concerns have arisen due to a substantial increase of CRUD (Chalk River Unidentified Deposits) on the fuel surface. This CRUD may cause the increased level of irradiation in the coolant system, and accelerate the generation of the radioactive waste products. And subsequently, CRUD is one of the conditions causing an axial offset anomaly (AOA) phenomenon. In addition, it was reported that the radioactive CRUD in the coolant system increased the irradiation dose rate [1,2].

Until recently, the cause of an AOA phenomenon has been attributed to the hideout of boron in CRUD deposits. As PWR system is operated at a high burn-up for a long term fuel cycle, the plants typically undergo local sub-cooled boiling in the highest-power channels. The corrosion products are apt to deposit at boiling domain and these deposits offer the hideout of boron. The boron in the CRUD causes a neutron flux depression at the top of a PWR core [3,4]. If we can obtain the boron content in the CRUD, it will be helpful to optimize the coolant chemistry. However, the current analysis methods of CRUD have many difficulties due to the high radiation level of CRUD.

The analysis method using the laser induced breakdown spectrometer (LIBS) is one of the promising techniques to analyze the CRUD without any treatments. We have to establish a database of breakdown spectrum for various CRUD samples.

In this study, we prepared three different Ni-Fe-B mixed oxides with the various molar ratios of Ni, Fe, and B, as a part of development of a CRUD analysis system by using a laser induced breakdown spectroscopy. These oxides were prepared by mixing of the Ni(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> and B(OH)<sub>3</sub>, and then they were heat treated under a high temperature condition [5,6]. Their elemental ratios and structures were determined by using inductive coupled plasma - atomic emission spectrometer (ICP-AES) and X-ray diffractometer (XRD).

### 2. Methods and Results

All the reagents were of analytical grade and were not purified further before use. The Ni(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> powders obtained by neutralizing nickel nitrate

[Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], ferric nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], with lithium hydroxide [LiOH·H<sub>2</sub>O], 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-Fe-B mixed metal oxides, the Ni(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> powders controlled with molar ratios of Ni/Fe= 1, 2, 3 and added 1 mole of boric acid [B(OH)<sub>3</sub>, Aldrich, 99.5%]. These mixed powders were grinded in a mortar with water and dried at 50 °C for 6h.

The mixtures of about 0.1g were compressed at a pellet maker 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 heat treated at various temperatures for 8 h under steam conditions.

The elemental composition analysis of Ni-Fe-B mixed oxides is carried out using inductive coupled plasma - atomic emission spectroscopy (HORIBA, ULTIMA 2C).

The structure analysis of the heat treated samples was carried out using X-ray diffraction (BRUKER-AXS, D8 ADVANCE) in the range between 20° to 70° using Cu K $\alpha$  ( $\lambda=1.5409\text{\AA}$ ) radiation. The thermal decomposition behavior of the Ni-Fe-B mixture was examined by thermogravimetric analyzer (TGA, Setsys 16/18) and differential scanning calorimeter (DSC) under argon gas condition with a heating rate of 10°C/min.

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

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

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

Sample (mixing molar ratios)	Molar ratios (measured by ICP-AES)		
	Ni	Fe	B
Ni:Fe:B = 1:1:1	1.05	1	0.85
Ni:Fe:B = 2:1:1	2.02	1	0.89
Ni:Fe:B = 3:1:1	3.2	1	1

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

Fig. 1 shows the X-ray diffraction pattern of the mixed oxide with the molar ratio of Ni: Fe: B = 2: 1: 1 heat-treated at various temperature for 8h. The Ni-Fe-B mixed oxide showed a crystalline phase of  $\text{Fe}_2\text{O}_3$  at  $350^\circ\text{C}$ . The mixed oxide heat treated at  $500^\circ\text{C}$  showed the crystalline phases of  $\text{Ni}_3(\text{BO}_3)_2$  and  $\text{Fe}_2\text{O}_3$  and the mixed oxide heat-treated at  $750^\circ\text{C}$  showed crystalline phase of  $\text{Ni}_2\text{Fe}(\text{BO}_3)_2$ .

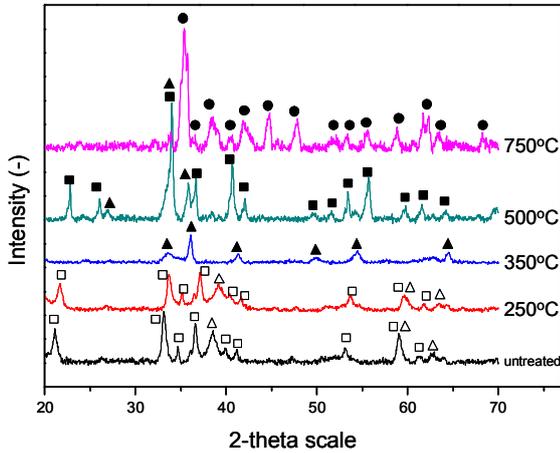


Fig. 1. X-ray diffraction patterns of the mixed oxide with Ni: Fe: B = 2: 1: 1 (molar ratio). Peaks corresponding to  $\text{Fe}_2\text{O}_3$  ( $\blacktriangle$ ),  $\text{Ni}_3(\text{BO}_3)_2$  ( $\blacksquare$ ),  $\text{Ni}_2\text{Fe}(\text{BO}_3)_2$  ( $\bullet$ ),  $\text{Ni}(\text{OH})_2$  ( $\square$ ),  $\text{FeO}(\text{OH})$  ( $\triangle$ ).

### 2.3 Thermal property of the Ni-Fe-B mixed oxide

Fig. 2 shows TG/DSC curve of the mixture with the molar ratio of Ni: Fe: B = 2: 1: 1. The TG curve exhibited about 20 % weight loss of the mixture until  $400^\circ\text{C}$ . The major cause of the weight loss is the drying of water and hydrate molecules in the mixture. The DSC curve shows two endothermic peaks and one exothermic peak. The endothermic peak at  $100^\circ\text{C}$  regarded as the loss of residual water in the mixture. The endothermic peak at  $310^\circ\text{C}$  is regarded as the formation of  $\text{Fe}_2\text{O}_3$  and  $\text{Ni}_3(\text{BO}_3)_2$ . The exothermic peak at  $780^\circ\text{C}$  is regarded as the transformation from  $\text{Fe}_2\text{O}_3$  and  $\text{Ni}_3(\text{BO}_3)_2$  into  $\text{Ni}_2\text{Fe}(\text{BO}_3)_2$ .

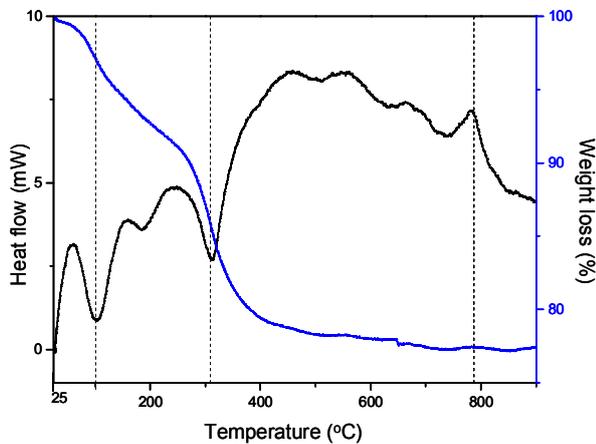


Fig. 2. TG/DSC curve of the mixture with Ni: Fe: B = 2: 1: 1 (molar ratio).

### 3. Conclusions

We prepared Ni-Fe-B mixed oxides with different ratios, and examined their chemical composition and structural properties.

Chemical composition of the Ni-Fe-B mixed oxides was confirmed by ICP-AES. The mixed oxide showed a crystalline phase of metal oxide at over  $350^\circ\text{C}$ . Depending on the heat treatment temperature, the mixed oxide showed the crystalline phase of  $\text{Fe}_2\text{O}_3$ ,  $\text{Ni}_3(\text{BO}_3)_2$  and  $\text{Ni}_2\text{Fe}(\text{BO}_3)_2$ . In the TG curve, the Ni-Fe-B mixture was observed to lose about 20% weight until  $400^\circ\text{C}$ . During the heat treatment, the mixture showed two endothermic peaks and one exothermic peak. The endothermic peak at  $100^\circ\text{C}$  is the loss of residual water in the mixture and the endothermic at  $310^\circ\text{C}$  is regarded to be the formation of  $\text{Fe}_2\text{O}_3$  and  $\text{Ni}_3(\text{BO}_3)_2$ . The exothermic peak at  $780^\circ\text{C}$  is regarded as the transformation from  $\text{Fe}_2\text{O}_3$  and  $\text{Ni}_3(\text{BO}_3)_2$  into  $\text{Ni}_2\text{Fe}(\text{BO}_3)_2$ .

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