Preparation and Characterization of Simulated Crud: Effect of Boron Compounds

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1. Introduction

Corrosion products in the primary-side system of nuclear power plants can be deposited on fuel surfaces. Accumulation of these corrosion products, which are mainly composed of nickel ferrite, nickel oxide, and iron oxides, and nickel-iron-boron oxides, can lead to an axially un-symmetric heat flux depression (AOA), which in turn decreases the heat efficiency of the fuel. To investigate this problem, the formation mechanism of nickel-iron-boron mixed oxides, and possible mechanisms for the deposition of corrosion products, should be elucidated. The present work deals with the synthesis of nickel-iron-boron oxide powders and evaluates the characteristics of the as-prepared powders.

2. Methods and Results

2.1 Materials and Test Procedures

Reagent-grade $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $LiOH \cdot H_2O$, H_3BO_3, and $LiBO_2$ were used as received. Solutions with molar ratios of Ni:Fe=1:2 and 1:1 were prepared by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in water. After 1 h of stirring with nitrogen gas purging, the mixed solution was co-precipitated with LiOH solution (2 M) until the solution reached pH = 10 and was then subjected to constant magnetic stirring for 3 h at room temperature. The resultant precipitates were separated from the above solution using a filtration assembly and then washed three times with 500 ml of de-ionized water to remove any soluble impurities. Four sets of samples were prepared under different conditions for this study. Samples with a molar ratio of Ni:Fe = 1:2 are denoted as S1-P, and those with Ni:Fe = 1:1 are denoted as S2-P, S3-P, S4-P, respectively. The S1-P, S2-P, and S4-P samples were washed with de-ionized water three times, whereas S3-P was not in order to investigate the effects of high pH. To examine the effects of soluble H_3BO_3, S4-P was re-dispersed in an 1800 ppm (as B) H_3BO_3 solution and then filtered again. The samples, respectively denoted S1, S2, S3, and S4 after the above treatments, were used as starting materials for the investigation. The obtained products were dried in a vacuum oven at 70℃ for 24 h and then ground to a powder for use as starting materials. In order to investigate the effects of H_3BO_3 and $LiBO_2$ powders,

each as-prepared precursor (S1, S2, S3, or S4) was well mixed with H_3BO_3 or $LiBO_2$ powder a weight ratio of 1:1 and ground for a few minutes. 0.2 g of the sample was then pressed into a pellet of 10 mm diameter and 2-3 mm thickness using a laboratory press (FRED S. CARVER INC. USA) at 200 atm. The produced samples are denoted as S1-B, S2-B, S3-B, S4-B, S1-LB, S2-LB, S3-LB, and S4-LB, respectively. Thermal treatment of the above samples was performed in an electric furnace between 280℃ and 700℃ for 10 h in air. The crystalline process and phase structure were identified from X-ray diffraction (XRD) results taken on a Siemens D5000 diffractometer using Cu-Kα radiation.

2.2 Effect of Boron Compounds

The effects of H_3BO_3 and $LiBO_2$ powders on the formation of $Ni_2Fe(BO_3)O_2$ were also investigated. The samples, S1, S2, S3, and S4, were homogeneously mixed with the H_3BO_3 and $LiBO_2$ powders and then pressed into pellets. After annealing at 700℃ for 10 h, the pellets were ground and then used for XRD measurements. Ferrihydrite ($Fe_5O_7(OH)4H_2O$, $FeO(OH)$) phases appeared for all samples mixed with H_3BO_3 powders, whereas no nickel-iron borates were formed. As the melting point of the H_3BO_3 powder is about 160℃, most of the H_3BO_3 powders melts before reacting with nickel-iron oxides at 700℃. Fig. 1 presents the XRD patterns of samples mixed with $LiBO_2$ powders. The $NiFe_2O_4$ phase was formed for all samples and the $Ni_2Fe(BO_3)O_2$ phase appeared for S2-LB, S3-LB, and S4-LB samples. This suggests that the $Ni_2Fe(BO_3)O_2$ phase can be formed at higher temperature than the temperature at which the $NiFe_2O_4$ phase is formed. Lithium tetra borate ($Li_2B_4O_7$) phases formed for the S4-LB sample and un-reacted $LiBO_2$ appeared in all XRD results. These results indicate that the $Ni_2Fe(BO_3)O_2$ phase formed when the sample has a Ni-to-Fe molar ratio of 1:1 and contains $LiBO_2$ powder. Furthermore, the pH value of the sample affects the peak intensity of the $Ni_2Fe(BO_3)O_2$.

In order to examine the effect of reaction temperatures on the formation of the $Ni_2Fe(BO_3)O_2$ phase, the S4 samples mixed with $LiBO_2$ were used. The XRD patterns for various heat treatments are given in Fig. 2. The $NiFe_2O_4$ phase and $Ni_2Fe(BO_3)O_2$ phase were formed at 600℃ and 650℃, respectively. From

the XRD evolution patterns, the $NiFe_2O_4$ phase and $Ni_2Fe(BO_3)O_2$ phase should form in a temperature range of 500℃-600℃ and 600℃-650℃, respectively. It can be seen that the $NiFe_2O_4$ and $Ni_2Fe(BO_3)O_2$ peaks gradually increased in sharpness with increasing temperature from 600℃ to 700℃, indicating that the degree of crystallinity increases. The above results suggest that higher reaction temperature is needed for the formation of the $NiFe_2O_4$ and the $Ni_2Fe(BO_3)O_2$ phases if the samples contain $LiBO_2$ powder.
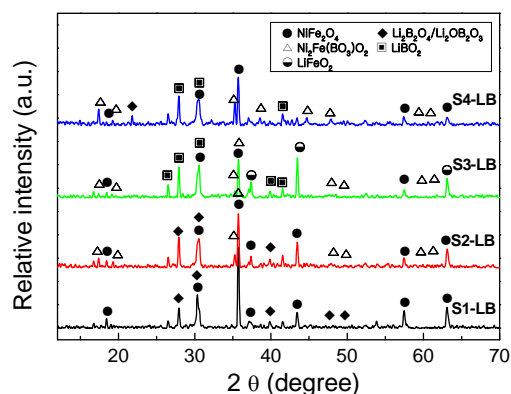

Fig. 1. The XRD patterns of the samples mixed with $LiBO_2$.

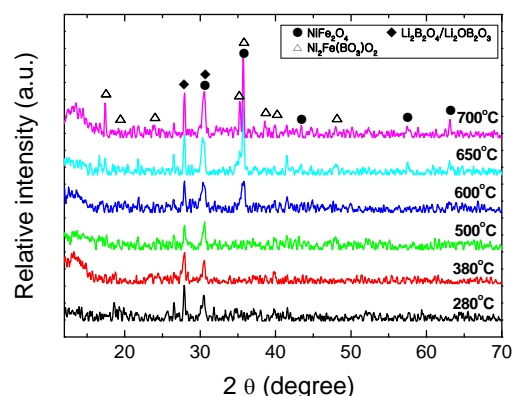Fig. 2. The XRD patterns of the samples mixed with $LiBO_2$ with varying temperatures from 280℃ to 700℃.

3. Conclusions

Nickel-iron and nickel-iron-boron oxides were synthesized and characterized. Bonaccordite, which is suspected to be a root cause of AOA, was examined using XRD. The $Ni_2Fe(BO_3)O_2$ phase formed when the samples had a Ni-to-Fe molar ratio of 1:1 and contained $LiBO_2$ powder. Furthermore, the pH value of the sample affected the peak intensity of the $Ni_2Fe(BO_3)O_2$. In addition, higher reaction temperature was needed for the formation of the $NiFe_2O_4$ and $Ni_2Fe(BO_3)O_2$ phases if the samples contained $LiBO_2$ powder.

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