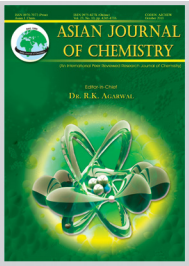
Asian Journal of Chemistry; Vol. 24, No. 9 (2012), 4188-4190

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Crystal Structure and Chemical Bonding Properties of B Containing Ni-Fe Oxides Synthesized Under High Temperature Steam Conditions†

SANG-HYUK JUNG[1,2], JEI-WON YEON[1,*], YONG KANG[2,*] and KYUSEOK SONG[1]

[1]Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daeduk dadero 989-111, Yuseong-gu, Daejeon 305-353, South Korea
[2]School of Chemical Engineering, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, South Korea

*Corresponding author: E-mail: yeonysy@kaeri.re.kr; kangyong@cnu.ac.kr

AJC-11351

Boron containing nickel iron mixed oxides were synthesized under a high temperature steam conditions. The mixed oxides were controlled with an Ni/Fe ratio at 1.5 and the boron content of 2 wt %. The crystal structure and the chemical bonding of the B containing Ni-Fe mixed oxides were measured as a function of temperature by an XRD and FT-IR spectrometer. The presence of B in the mixed oxides promoted the formation of a crystal structure and chemical bonding of $NiFe_2O_4$. Through the chemical bonding analysis, we confirmed that the chemical bonding of bonaccordite Ni_2FeBO_5 started forming at a temperature range of between 400 and 500 ºC.

Key Words: Boron, High temperature, Chemical bonding, $NiFe_2O_4$, Bonaccordite.

INTRODUCTION

Boric acid has been widely used as a soluble neutron absorber in the primary coolant of pressurized water reactors (PWRs)[1]. With boric acid, there are many kinds of Ni and Fe ionic and oxide species in the coolant due to the corrosion and erosion of structural materials such as stainless steels and Ni-based alloys. As Ni and Fe are the major component elements of the structural materials exposed in the reactor coolant, nickel ferrites are reported[2] as common deposits observed on fuel surface.

Boron present in boric acid has been known to be included in the deposits formed on high temperature fuel surfaces with other metal oxides such as Ni and Fe oxides[3]. As the boron containing deposits absorb the neutrons due to the high neutron cross section of boron, it causes an asymmetric profile of neutron flux which decreases the operation efficiency of the reactor. Therefore, many researchers[3,4] have been studying the characteristics of B containing Ni-Fe mixed oxides to reduce formation on fuels. Moreover, even when radiation conditions are excluded, it is difficult to realize the fuel surface environment, that is, high temperature and high pressure condition. In the previous study[5,6], a simple technique was developed to simulate the reaction condition by removing the pressure term by using a thermodynamic relationship. The equation, Gibb's free energy change of a reaction does not depend on the reaction pressure, as long as there is no volume change after the reaction.

In the present study, we employed B containing Ni-Fe oxides at different reaction temperatures by using the simulation technique. Furthermore, the crystal structures and chemical bonding were analyzed by using XRD patterns and FT-IR spectra, respectively. The results indicated that the presence of boron enhanced the formation of nickel ferrite and the chemical bonding of bonaccordite Ni_2FeBO_5 began to form in a temperature range between 400 and 500 ºC.

EXPERIMENTAL

All the chemicals used in this study were an analytical grade and were used without any further purification. The Ni and Fe hydroxide mixture with a weight ratio of Ni/Fe = 1.5 was obtained by neutralizing $Ni(NO_3)_2$ and $Fe(NO_3)_3$ mixed solution with LiOH solution. For the preparation of the B containing Ni-Fe mixed oxide, H_3BO_3 solution was added to the Ni and Fe hydroxide mixture. The mixtures were dried at 25 ºC and then heated at various temperatures for 8 h under steam environments[5,6]. Finally, we obtained Ni-Fe mixed oxides containing 2 wt % B. The characteristics of the mixed oxide were examined by using X-ray diffraction (XRD) patterns and FT-IR spectra, respectively.

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

RESULTS AND DISCUSSION

Effects of temperature on crystal structure of the B containing Ni-Fe mixed oxide: X-Ray diffraction patterns for Ni-Fe mixed oxides were obtained as a function of the formation temperature as shown in Fig. 1. In Fig. 1a, after heat treatment of Ni-Fe mixed hydroxides at 250 ºC, it was thought that $NiFe_2O_4$ and NiO phases were observed. However, it is difficult to differentiate the pattern at 250 ºC from pattern at 200 ºC. Therefore, it is obscure to find exactly the formation temperature of $NiFe_2O_4$ and NiO by the analysis of XRD patterns. On the other hand, for the B containing Ni-Fe mixed oxides, the crystalline phases of $NiFe_2O_4$, NiO and Fe_2O_3 were observed at temperatures between 200 and 300 ºC. At 400 ºC, however, $NiFe_2O_4$ and NiO are stable species as shown in Fig. 1b. From the result, it is thought that $NiFe_2O_4$ is more stable than the coexistence of NiO and Fe_2O_3 at 400 ºC. The diffraction patterns of Ni_2FeBO_5 at 600 ºC were observed. This indicates the crystal structure of Ni_2FeBO_5 is formed at temperatures between 500 and 600 ºC.

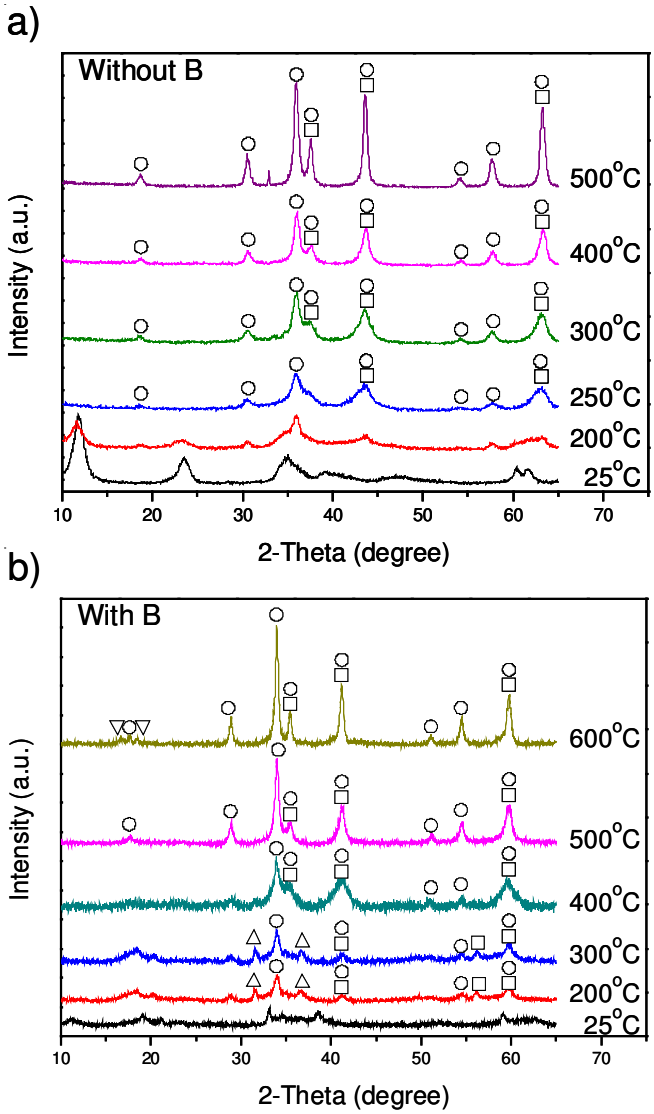


Fig. 1. XRD patterns of Ni-Fe oxides formed at different temperatures up to 600 ºC for 8 h: (a) absence of boron, (b) adding boron 2 wt % B. Peaks corresponding to $NiFe_2O_4$(○), NiO(□), Fe_2O_3(△), Ni_2FeBO_5 (▽)

Effects of temperature of chemical bonding of the B containing Ni-Fe mixed oxides: Fig. 2 shows the FT-IR spectra of Ni-Fe mixed oxides as a function of the formation temperature. As shown in Fig. 2a, $NiFe_2O_4$ absorption band 595 cm^{-1} was clearly observed in the temperature above 300 ºC. On the other hand, in presence of boron, $NiFe_2O_4$ absorption bands were observed from temperatures of 200 ºC. This indicates that B in Ni-Fe hydroxides promotes the formation of $NiFe_2O_4$. In addition, in Fig. 2b, we assumed the absorption band of B-O in Ni_2FeBO_5 to be 702 cm^{-1}. The absorption of Ni_2FeBO_5 was observed at a temperature of 500 ºC. The result suggested that the chemical bonding of Ni_2FeBO_5 would start to form at temperatures between 400 and 500 ºC, while its crystal structure was initially formed at temperatures between 500 and 600 ºC.

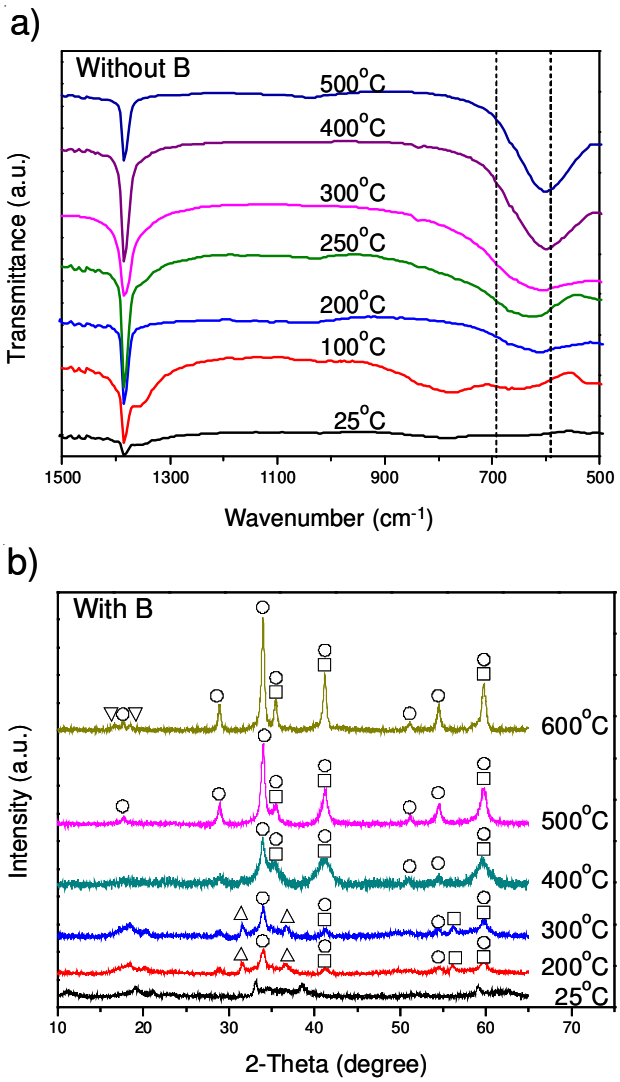


Fig. 2. FT-IR spectra of Ni-Fe mixed oxides formed at different temperatures up to 600 ºC for 8 h: (a) absence of boron, (b) adding boron 2 wt % B. $NiFe_2O_4$ characteristic band: 595 cm^{-1}, Ni_2FeBO_5 characteristic band: 702 cm^{-1}

Conclusion

The effect of B was investigated on the formation of Ni-Fe mixed oxides under high temperature steam conditions by using XRD patterns and FT-IR spectra, respectively. It was

observed that the presence of B in Ni-Fe hydroxides promotes the formation of $NiFe_2O_4$ by lowering the formation temperature. As the temperature increases, $NiFe_2O_4$ becomes more stable rather than coexistence of NiO and Fe_2O_3 under high temperature steam conditions. In the presence of boron, Ni_2FeBO_5 starts to be formed chemically at temperatures of 400-500 ºC, while its crystal structure was formed at temperatures of 500-600 ºC.

ACKNOWLEDGEMENTS

This work was supported by the Nuclear R&D Program of the Ministry of Education, Science and Technology. In addition, this work was partially supported by R&D Program of the Ministry of Knowledge Economy, Republic of Korea.

REFERENCES

1. G.R. Choppin, J.-O. Liljenzin and J. Rydberg, Radiochemistry and Nuclear Chemistry, Oxford; Boston: Butterworth-Heinemann, edn. 3, p. 544 (2002).
2. J.-W. Yeon, I.-K. Choi, K.-K. Park, H.-M. Kwon and K. Song, *J. Nucl. Mater*., **404**, 160 (2010).
3. S. Uchida, Y. Asakura and H. Suzuki, *Nucl. Eng. Des*., **241**, 2398 (2011).
4. J.A. Sawicki, *J. Nucl. Mater*., **374**, 248 (2009).
5. J.-W. Yeon *et al*., *Solid State Phenom*., **124-126**, 1565 (2007).
6. K.-S. Choi, J.-W. Yeon, Y.-S. Park, Y.-K. Ha, S.-H. Han and K. Song, *J. Alloy. Compd*., **486**, 824 (2009).