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The effect of transition metals on the structure of h-BN intercalation compounds

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Abstract

In this study, hexagonal boron nitride (h-BN) were synthesized by the modified O'Connor method in the presence of various metal nitrates [$M(NO_3)_x$, M = Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ag]. The composites were analyzed by FTIR, XRF, XRD, and SEM techniques. XRD results indicated a change in the interlayer spacing due to the intercalation of Cr, Mn, Fe and Ag. SEM analyses illustrated the grain growth upon metal intercalation even at a temperature of 1320 K.

Keywords: Hexagonal boron nitride; Intercalation compound; Interlaying spacing; Grain growth

1. Introduction

In recent years, much attention has been devoted to hexagonal boron nitride and its composites with transition metals due to their excellent physical and chemical properties. A variety of intercalation compounds of hexagonal boron nitride (h-BN), which contains non-metallic guest molecules, was reported extensively [1]. On the other hand, there are several papers about the intercalation compounds of h-BN with copper [2,3] and silver [4].

Two methods [3] were used to obtain Cu-h-BN composites. The first one includes mechanical mixing and heating of h-BN with copper powder, while the second consists of the chemical treatment of the mixtures of boric oxides, urea and copper nitrate. Both methods are considered to yield the same product, which contains copper atoms between h-BN layers. In the report mentioned above, it was also stated that a donor–acceptor interaction exists between copper electronic orbitals and π-electrons of adjacent BN facets similar to ferrocenes; therefore, the positive role of the copper was observed on the growth of the grain size of h-BN.

Intercalation with other transition metals might be expected to have similar effects on the structure and grain size of h-BN as reported with copper. In the present study, the effect of Cr, Mn, Fe, Co, Ni, Cu, Zn and Ag has been comparatively discussed.

2. Experimental

Boron nitride was prepared by the modified O'Connor method [5]. One part by weight of boron oxide was mixed with 2 parts of urea and 1/100 parts of $M(NO_3)_x$ (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag). The mixture was preheated at 493 K for 2 h and the precursor thus was pulverized in a grinder and annealed in a stream of NH_3 gas (flow rate = 1.5 mL/s) at 1320 K for 2 h in a tube furnace.

The product was boiled in 0.1 M HCl solution, leached in ethanol and dried in an oven at 378 K. The obtained powder was pressed by 10 tons at room temperature.

BN stretching was determined by Jasco 430 FTIR spectrophotometer. Qualitative determination of metals was performed by an ARL 8060 X-ray fluorometer. XRD patterns were obtained by the Philips 1352/20 diffractometer using Co$K\alpha$ radiation. Micrographs were taken by scanning electron microscope to determine the grain size.

3. Results and discussion

There are several reports in the literature characterizing the formation and structure of h-BN by IR

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spectroscopy [6,7]. A typical IR spectrum of h-BN contains three main absorption peaks at ~3550, ~1430 and, ~800 $\mathrm{cm^{-1}}$. The peaks at 1430 and 800 $\mathrm{cm^{-1}}$ refer to the in-plane and out-of-plane vibrations of h-BN while the 3550 $\mathrm{cm^{-1}}$ peak is assigned to the O–H stretching vibration of the terminal OH groups that always appears when the O'Connor synthetic procedure is applied [8]. Table 1 summarizes the IR data of h-BN and its intercalation products. The metal intercalated samples gave the same special pattern (Fig. 1) as h-BN with slight but insignificant changes in the peak positions.

In the next step, existence of the metal in the intercalated compounds was qualitatively investigated by XRF. The XRF data showed emission lines characteristic for each metal supplied from its nitrate salt used for intercalation experiments. In addition to this qualitative determination of the metals in the h-BN, more detailed structural information was obtained from XRD investigations. Fig. 2 shows the XRD patterns of the metal-h-BN composites. Besides the well-known d_{002}, d_{100}, and, d_{004} peaks of h-BN [3], every diffractogram includes small peaks due to the diffraction lines of intercalated metals.

Interlayer distances calculated from XRD are shown in Table 2. There is a decrease in the interlayer spacing of h-BN from chromium to cobalt while the values remain constant and equal to non-intercalated h-BN with Co, Ni, Cu and, Zn. A significant increase was observed with Ag. A correlation between the interlayer spacing and the sizes of the metal atoms and their electronic properties can be established. The sizes of the transition metals are almost the same throughout the period due to the increasing effective nuclear charge. Although the sizes of the first row transition metals used are the same, electronic factors play additional roles in changing the interlayer spacing. Metals having filled or nearly filled valance shells like Co, Ni, Cu, and Zn, cause no expansion of the interlayer distance. On the other hand, the interlayer distance decreases steadily from Cr to Fe with increasing number of valance electrons. These observations support the previous suggestions that the electronic interactions between the metal outermost orbitals and the adjacent BN layers determine the interlayer spacing [3]. Rather than the electronic effects, as a second row transition metal, Ag has a larger size than all the other metals studied in this work and hence resulting in a greater interlayer distance.

Table 1
Infrared data for h-BN and intercalation compounds of h-BN

Compound	OH stretching ($\mathrm{cm^{-1}}$)	BN in-plane mode ($\mathrm{cm^{-1}}$)	BN out-of-plane mode ($\mathrm{cm^{-1}}$)
h-BN	3422	1433	781
Cr-h-BN	3414	1377	778
Mn-h-BN	3397	1383	776
Fe-h-BN	3403	1378	772
Co-h-BN	3409	1375	772
Ni-h-BN	3393	1388	782
Cu-h-BN	3397	1388	790
Zn-h-BN	3403	1389	792
Ag-h-BN	3396	1384	786

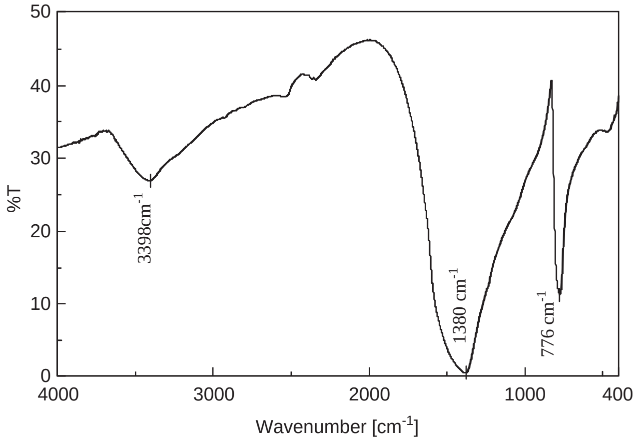

Fig. 1. Typical FTIR spectra of metal-h-BN composites.

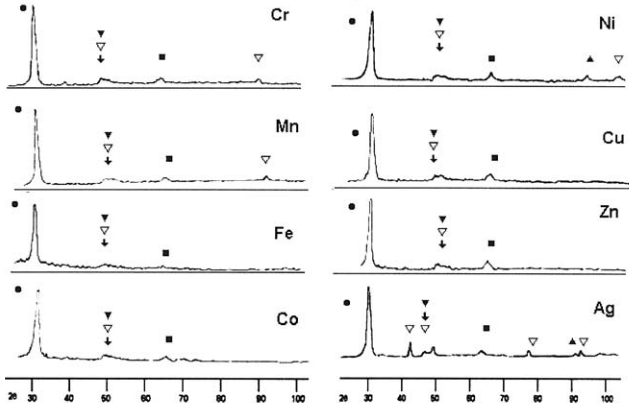

Fig. 2. XRD patterns of metal-h-BN composites. ●, d_{002} of h-BN; ▼, d_{100} of h-BN; ▽, the used metal; ↓, d_{101} of h-BN; ■, d_{004} of h-BN; ▲, d_{006} of h-BN.

Table 2
Interlayer distances of the intercalated h-BN samples

Compound	Interlayer distance (nm)
h-BN	0.3328
Cr-h-BN	0.3379
Mn-h-BN	0.3368
Fe-h-BN	0.3348
Co-h-BN	0.3328
Ni-h-BN	0.3328
Cu-h-BN	0.3328
Zn-h-BN	0.3328
Ag-h-BN	0.3386

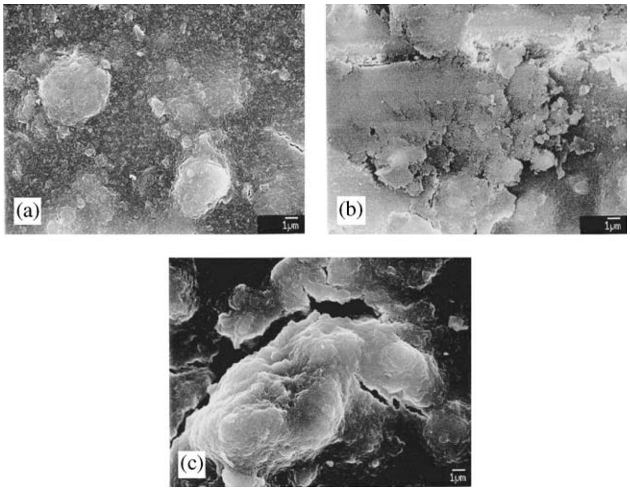

Fig. 3. SEM images of (a) Mn-h-BN, (b) Ni-h-BN, (c) Ag-h-BN.

A previous study emphasizes that high-crystalline h-BN can only be formed at temperatures above 1670 K [9]. However, other reports mention about the positive role of metals in obtaining the crystalline h-BN at lower temperatures [3,10,11]. We prepared our h-BN samples at 1320 K in the presence of transition metals and the effects of the metals on crystallinity can be followed from Fig. 2.

Boron nitride was not considered crystalline for practical purposes when the interlayer spacing is greater than the 0.335 nm and the crystallites smaller than 50 nm [9]. In Fig. 3, SEM micrographs of the intercalated h-BN with Mn, Ni, and Ag are shown and the grain size values are respectively 54.3, 131, and 167 nm. Though the Mn and Ag intercalated h-BN have larger interlayer spacing than 0.335 nm. These samples are crystalline as can be clearly seen from their XRD patterns.

Finally, metals play an important role not only in the crystallization of h-BN by aiding the construction of hexagonal phases through electronic interactions but also catalyzing the reductive nitration of boron oxide to yield boron nitride. The metal containing h-BN composites are expected to possess interesting physical and chemical properties that are considered for future studies.

4. Conclusion

The crystallization degree and grain growth of hexagonal boron nitride can be improved by intercalation with various transition metals at a relatively lower temperature (1320 K). The reduction reaction between the metal and h-BN overcomes the internal stress and, the electronic interaction between h-BN and valence orbital of metal affects the interlaying spacing.

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References

[1] C. Shen, S.G. Mayora, R. Biagioni, C. Piskoti, M. Ishigami, A. Zettl, N. Bartlett, J. Solid State Chem. 147 (1999) 74–81.
[2] M. Hubacek, M. Ueki, J. Am. Ceram. Soc. 79 (1) (1996) 283–285.
[3] M. Hubacek, T. Sato, M. Ueki, J. Mater. Res. 12 (1) (1997) 113–118.
[4] T. Oku, T. Kusunose, K. Niihara, K. Suganuma, J. Mater. Chem. 10 (2000) 255–257.
[5] T.E. O'Connor, J. Am. Chem. Soc. 84 (1962) 1753–1754.
[6] M. Hubacek, T. Sato, T. Ishii, J. Solid State Chem. 109 (1994) 384–390.
[7] J.Q. Hu, Q.Y. Lu, K.B. Tang, S.H. Yu, Y.T. Qian, G.E. Zhou, X.M. Liu, J.X. Wu, J. Solid State Chem. 148 (1999) 325–328.
[8] M. Hubacek, M. Ueki, J. Solid State Chem. 123 (1996) 215–222.
[9] V. Brozek, M. Hubacek, J. Solid State Chem. 100 (1992) 120–129.
[10] S. Kurooka, T. Ikeda, K. Kohama, T. Tanaka, A. Tanaka, Surf. Coat. Technol. 166 (2003) 111–116.
[11] G. Aslan, F. Kara, S. Turan, J. Eur. Ceram. Soc. 23 (2003) 1243–1255.