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# Structural and physical properties of bulk Ni-B alloys processed through powder metallurgy

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Bulk Ni-B alloys with different boron contents of 3, 6, 9 and 12 wt.% were fabricated by a combination of mechanical alloying and hot-pressing of Ni and B powders as starting materials. The various structural phase evolutions depending on the boron contents and processing time were monitored from X-ray diffraction profiles. The core-level and valence-band spectra of the Ni-B alloys based on X-ray photoelectron spectroscopy showed that they were remaining metallic phases within the studied compositions. Furthermore, these materials showed the relatively low electrical resistivities, 1 to 10 ( $10^{-3} \Omega/m$ ) at a wide range of temperature (25-500 °C). On the other hand, the thermal diffusivities of these materials were ranged from 2.5 to 7 ( $10^{-6} m^2/$ s), which are markedly lower than that of the conventional metallic materials and similar to those for engineering ceramics. The relatively low thermal conductivities are likely the result of a phonon scattering induced by their fine microstructures.

Key words: Powder metallurgy, X-ray Photo-emission Spectroscopy, Electrical conductivity, Thermal conductivity.

## Introduction

Due to their excellences in oxidation, wear resistance, chemical stability, high-temperature resistivity and unique thermal and electronic properties, transition metal boride compounds (also called metal-rich borides) are attractive and considered as potential candidates for various applications such as armor materials, aluminum evaporation boats, cathode materials for hall-heroult cell, cutting tools, electro discharge machining (EDM) electrodes, wear parts, high temperature materials, and electrical devices in aerospace, foundry and refractory industries [1-6]. Among them, nickel borides belong to a series of compounds which have appropriate properties for the potential structural, thermal and electrical applications [7-12]. For example, electroless Ni-B plating offers excellent wear and abrasion resistance [7-9]. High electrocatalytic activity of nickel borides on hydrogen oxidation as well as high catalytic activity of nickel ions on the acid hydrolysis of borohydride makes them also good heterogeneous electrodes for the hydrogen evolution reaction processes [10-12].

Previously, there are considerable works regarding the usage of Ni-B alloys for the engineering coating and electrocatalytic applications [7-14]. In these applications, the Ni-B alloys have been prepared by the chemical reduction of nickel salts with borohydride solution. However, this method has advantage to produce only the small amounts of Ni-B alloys and their boron contents are limited to about 10 wt.%. In addition, the structure of the chemically synthesized Ni-B alloys was mixture of microcrystalline nickel and amorphous Ni-B phases in the as-synthesized condition. Therefore additional heat treatment is necessary to obtain homogeneous microstructure with crystalline nickel boride phases [9, 13].

Recently, it has been showed that the Ni-B alloys are good electrical conductors with very low electrical resistivities (of order of  $10^{-4} \Omega/m$ ) [14], which may enable them to be formed into complex shapes using EDM. Moreover, the Ni-B alloys exhibit good corrosion resistance and high hardness [9], which makes them promising candidates for refractory materials and electrically conductive crucible such as evaporation boats. However, despite their potential usages in various applications, the detailed physical properties of bulk Ni-B alloys have not been studied so far. This might be related to the difficulties in the preparation of bulk nickel boride using the conventional casting route, since the Ni and B have wide miscibility gap in the liquid state at high temperature. Owing to the big differences of Ni and B in specific gravity and in melting temperature, Ni-B system has strong segregation tendency upon solidification [15]. On the other hand, mechanical alloying (MA) that has been used for more than two decades to produce many unique materials, is a well established tool to prepare fine and uniform nonequilibrium microstructures including amorphous alloys, extended solid solutions, metastable crystalline phases, quasicrystals and nanocrystalline

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materials [16, 17]. In the MA process, starting materials and milling balls are placed together in a milling vial, which are exposed to a strong vibrational or rotational acceleration causing impacts of milling balls leading to the repeated fractioning and cold welding of the powder particles. This technique allows one to overcome problems such as large difference in melting points of the alloying components as well as unwanted segregation or evaporation that could occur during melting and casting.

In this article, Ni-B alloys with boron contents of 3, 6, 9 and 12 wt.% were synthesized by mechanical alloying process, and their bulk samples were prepared using hot press sintering. In order to explore the potential applicability of these materials for refractory and electrically conductive crucibles, the thermal and electrical properties along with their structural properties of sintered Ni-B alloys were investigated.2.

## **Experimental Procedure**

Nickel powder (99.9%, 2-3 µm, supplied by High Purity Chemicals Inc., Japan) and boron powder (99%, 325 mesh, supplied by High Purity Chemicals Inc., Japan) were mixed in four different mass ratios of 97:3, 94:6, 91:9 and 88:12 (i.e. boron contents of 3, 6, 9 and 12 wt.%). The elemental powder mixtures were then put into steel vial with bearing steel balls. The MA of the powder mixtures were carried out in a highenergy vibration mill under argon atmosphere for 200 hours. The vibration frequency of ball mill was kept to 25 Hz during the MA process. A total of 60 g of powder and ball-to-powder mass ratio of 50 : 1 were used. The MA processed powders were hot pressed in a uniaxial press with carbon plunger and die in vacuum atmosphere under  $10^{-5}$  Torr. A pressure of 30 MPa was applied at 600 °C and kept during heating the powder with a heating rate of 10 °C/min to the desired pressing temperature of 1,000 °C. Then, the pressure was increased to 50 MPa and the powders were consolidated for 4 hours.

Both the MAed powders and the sintered samples were characterized via X-ray diffraction (XRD, Rigaku, RINT2100, Cu Ka) and X-ray photoelectron spectroscopy (XPS, VG Scientific, ESCALAB 250). Electrical and thermal properties were measured in a direction parallel to the pressing axis. The temperature dependent electrical resistivity (p) was determined using an ULVAC ZEM-1 apparatus in He atmosphere. The thermal diffusivity (k<sub>d</sub>) was also measured by Laser flash method (ULVAC, TC-7000 Thermal Constant Analyzer). Density (d) and heat capacity  $(C_p)$  of the bulk samples were investigated by the standard Archimedes method and a differential scanning calorimeter (DSC, Netsch, DSC404), respectively. Then, thermal conductivity (k) could be calculated from the density, the heat capacity and the thermal diffusivity by the following formula:

$$k = d \cdot C_p \cdot k_d \tag{1}$$

# **Results and Discussions**

The milling time dependent XRD patterns of the Ni-12%B powder are shown in Fig. 1. It can be clearly seen that the XRD peaks got broader during MA process, due to the presence of microstrain and the smaller grain size. For the 25 hr milled powder, the crystalline Ni phase appeared. With increasing the milling time, the peaks of Ni gradually broadened and their intensities also decreased. After 50 hr of milling, crystalline orthorhombic Ni<sub>3</sub>B structure began to appear. For 100 hr milled sample, the dramatic reductions in the intensities of the nickel peaks were observed, whereas both the orthorhombic Ni<sub>3</sub>B and the tetragonal Ni<sub>2</sub>B reflections occurred. Finally, the sintered Ni-12%B sample shown in Fig. 1, NiB phase was identified in addition to the Ni<sub>2</sub>B phase.

Fig. 2 shows the evolution of valence-band spectra of the Ni-12%B powder during MA process. The peaks near the Fermi energy ( $E_f$ ), which involved primary emission from the Ni 3d electrons [18], were very similar to that of the pure Ni. With increasing the milling time, the intensity of the peak was slightly decreased. However, the peak position of the Fermi energy did not change during MA process up to 100 hr, suggesting that the formation of nickel boride phases did not alter the neighboring electronic structure of Ni. Both of the presence of Ni 3d peaks in the powders and their continuous conduction bands reveal that the Ni-12%B powder remains metallic and electrically conductive during MA process.

Typical scanning electron micrographs of fracture surfaces of the sintered Ni-B alloys are shown in Fig. 3. Almost fully dense, segregation-free and fine microstructures were observed in all samples. Fig. 4 presents the XRD patterns of the sintered samples. It was found that the phase assemblage of sintered Ni-3%B



Fig. 1. X-ray diffraction patterns at selected milling times and after sintering for Ni-12%B.



Fig. 2. Valence-band spectra obtained from X-ray photoelectron spectroscopy of Ni-12%B powder at selected milling times.



**Fig. 3.** Typical scanning electron micrographs of fracture surfaces of the sintered Ni-B alloys (x3,000). (a) Ni-3%B, (b) Ni-6%B, (c) Ni-12%B and (d) Ni-12%B.



Fig. 4. X-ray diffraction patterns of the sintered Ni-B alloys.

sample consisted of Ni and Ni<sub>3</sub>B phases. In Ni-6%B sample, Ni<sub>2</sub>B phase was identified in addition to the Ni<sub>3</sub>B phase. Sintered Ni-9%B and Ni-12%B samples consisted of monolithic Ni<sub>2</sub>B and binary mixture of Ni<sub>2</sub>B/NiB phases, respectively. The B 1s core-level binding energy obtained from XPS of the sintered nickel boride samples is shown in Fig. 5. The reference binding energies for Ni-B (188 eV) [19] and B-B (189.4 eV) [20] bond are also



Binding Energy (eV)

**Fig. 5.** X-ray photoelectron spectra of B *1s* of sintered nickel borides. Dotted red and blue lines represent the reference values for Ni-B bonds (188 eV) [19] and B-B bonds (189.4 eV)[20], respectively. The solid curves represent the smoothing curve of the measured data for better visualization.



Fig. 6. Temperature dependence of electrical resistivities for the sintered Ni-B alloys.



Fig. 7. Temperature dependence of thermal diffusivities for the sintered Ni-B alloys.

depicted for comparison. The small peaks around 192.7-193 eV in the spectra of Ni-9%B and Ni-12%B are assigned to oxidized boron due to the additional surface oxidation of the sample before introducing to

the XPS chamber [19]. In all XPS spectra of sintered samples, the strong peak centered at around 188 eV is clearly seen and no extra peak around 189.4 eV is observed. The results in Figs. 4 and 5 indicated that most of the B atoms were linked to Ni atoms with formations of nickel boride phases, and very few or no B atoms remained unreacted in the sintered samples during fabrication.

Fig. 6 shows the temperature dependent electrical resistivities for the sintered samples. With both increasing boron contents and temperature, the electric conductivities of the sintered Ni-B alloys were decreased. The electrical resistivities of the samples were varied approximately from 1 to 10 ( $10^{-3} \Omega/m$ ), which is generally acceptable for use in electrical applications and also for EDM machining. The thermal diffusivities of the sintered samples are shown in Fig. 7. With increasing boron contents, the thermal conductivities of the sintered samples were varied from 2.5 to 7 ( $10^{-6} \text{ m}^2/\text{s}$ ), which are markedly lower than that of the conventional metallic materials and similar to those for sintered engineering ceramics [21, 22].

The reason for the low thermal diffusivities of these materials can be inferred from Fig. 8, where the temperature dependences of thermal conductivities that obtained from Eq. 1 are shown. Here, the thermal conductivities were expressed as the sum of electrical contribution  $k_e$  and phonon contribution  $k_{ph}$  (= k-k<sub>e</sub>) using Widemann-Franz's law [23] with the Lorenz factor of  $2.44*10^{-8}$  (WQ/°C<sup>2</sup>). The values of  $k_e$  for the sintered samples were around  $2-5*10^{-2}$  (W/m°C<sup>2</sup>), which were nearly two order of magnitude lower than their values of k<sub>ph</sub>. In this case, the heat transfer is dominated by the phonon transport. Since the rate of heat conduction due to the phonons is very sensitive to the grain size due to the effect of the grain boundary scattering, it is likely that the low thermal diffusivities of the samples are caused primary by their fine microstructures. As shown in Figs. 6-8, the sintered Ni-B alloys appeared to have a unique combination of electrical and thermal properties, making them candidate materials for various applications especially where low thermal conductivity, good electrical conductivity and excellent machinability are desired.

#### Conclusions

In this work, the bulk Ni-B alloys with boron contents of 3, 6, 9 and 12 wt.% were fabricated by mechanical alloying and subsequent hot-press sintering, and their electrical and thermal properties were investigated. The results can be summarized as follows:

(1) It was feasible to synthesize bulk Ni-B alloys by the mechanical alloying and hot-press sintering techniques. These techniques were appropriate to produce bulk Ni-B alloys which have near fully dense, segregation-free and fine microstructures.

(2) High energy ball milling process strongly accelerated the formations of nickel boride compounds from the elemental blends of Ni and B powders. After 200 hr milling and hot-press sintering, most of B atoms in the Ni-B alloys were linked to Ni atoms with formations of nickel boride phases.

(3) The formation of nickel boride phases did not alter much the electronic structure of Ni. As a consequence, bulk Ni-B alloys exhibited relatively low electrical resistivities which ranged from 1 to 10 ( $10^{-3} \Omega/m$ ). However, their thermal diffusivities were ranged from 2.5 to 7 ( $10^{-6} \text{ m}^2/\text{s}$ ), which are similar to those for sintered engineering ceramics.

(4) This unique combination of electrical and thermal properties of the bulk Ni-B alloys is likely to be the result of phonon scattering induced by their fine microstructures. It was noted that the bulk Ni-B alloys offered good electrical conductivity with low thermal diffusivity, and therefore would be beneficial for in the various engineering field usages.

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### References

- V. Tennery, C. Finch and C. Yustand, in "Science of Hard Materials", (Plenum, 1983) p. 891-909.
- 2. V.I. Matkovich, in "Boron and refractory borides", (Springer Berlin Heidelberg, 1977).
- C. Mrozl, AM.CERAM.SOC.BULL. 74 [6] (1995) 158-159.
- R. Cutlerl, in "Engineered Materials Handbook Volume 4: Ceramics and Glasses", (ASM International, 1991) p.787-803.
- 5. K. Sakail, J.CERAM.SOC.JPN. 24 (1989) 526-532.
- G.V. Samsonov, in "Boron, its compounds and alloys", (U.S. Atomic Energy Commission, Division of Technical Information, 1962).
- 7. D. Baudrand and J. Bengstonl, MET.FINISH. 93 [9] (1995) 55-57.
- F. Delaunois and P. Lienardl, Surf.Coat.Technol. 160 [2] (2002) 239-248.
- 9. C. Dervos, J. Novakovic and P. Vassilioul, Mater.Lett. 58 [5] (2004) 619-623.
- B. Mahdavi, D. Miousse and J. Fournier, Can.J.Chem. 74
  [3] (1996) 380-388.
- 11. D. Hua, Y. Hanxi and A. Xinping, Int.J.Hydrogen.Energy. 28 [10] (2003) 1095-1100.
- 12. A.V. Paustovskii, B.M. Rud and V.E. Shelud'ko, POWDER.METALL.MET.C+. 43 [1-2] (2004) 94-98.
- P.S. Kumar and P. Nairl, NANOSTRUCT.MATER. 4 [2] (1994) 183-198.
- 14. A.I.H. Committee, in "ASM Handbook Volume 5: Surface Engineering", (ASM International, 1994).
- L. Battezzati, C. Antonione and M. Bariccol, J.ALLOY.COMPD. 247 [1] (1997)164-171.
- 16. C. Koch and R. Cahn, in "Processing of metals and alloys",

(1991) p. 193-245.

- 17. C. Kochl, MAT.SCI.ENGA-STRUCT. 244[1](1998)39-48.
- 18. S. Hüfner, G. Wertheim and J. Wernickl, PHYS.REV.B. 8 [10] (1973) 4511-4524.
- 19. S.-P. Lee and Y.-W. Chenl, J.Mol.Catal.A.Chem. 152 [1] (2000) 213-223.
- 20. E. Il'Inchikl, J.Appl.Spectrosc., 75 [6] (2008) 883-891.
- 21. S. Howlett, R. Taylor and R. Morrelll, J.Mater.Sci.Lett. 4 [2] (1985) 227-229.
- 22. G. Ziegler and D. Hasselmanl, J.MATER.SCI. 16 [2] (1981)495-503.
- 23. F.J. Blatt, in "Physics of electronic conduction in solids", (McGraw-Hill, 1968).