STRUCTURAL CHEMISTRY OF SOME PHASES IN THE YC-Ni-B SYSTEM

B. C. CHAKOUMAKOS

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6393

ABSTRACT

NiB, monoclinic Ni_4B_3 , Ni_2B and Ni_3B were prepared by arc-melting and their room-temperature crystal structures were refined by Rietveld analysis of neutron powder diffraction data. The NiB refinement is altogether new data. Although the B atoms in NiB form characteristic zigzag chains, the primary coordination of each atom by atoms of the other kind is similar and distinctively sevenfold, with one short (2.117 Å), two intermediate (2.152 Å), and four long (2.163 Å) bonds. Other samples with stoichiometries $(\text{YC})_n\text{Ni}_2\text{B}_2$, $n = 3, 4$, did not yield single-phase material, but both x-ray and neutron powder diffraction suggest that the $n = 4$ structure is present in both of these samples. Phase-pure samples of these homologues may require non-stoichiometry and a more controlled thermal history than is attainable by arc melting.

INTRODUCTION

The YC-Ni-B ternary section of the Y-C-Ni-B quaternary includes the new homologous series¹, $(\text{LnC})_n(\text{Ni}_2\text{B}_2)$ $n = 1, 2$, and a number of well-known to poorly-characterized nickel borides, yttrium carbides, and yttrium borocarbides (Fig. 1). To search for other homologues and new structural families in this chemical system, we have begun to synthesize known and potential phases that occur therein, and test and refine their expected structural models. The atomic arrangement of $(\text{YC})\text{Ni}_2\text{B}_2$ is simply viewed as a "stuffed" derivative of the common layered ThCr_2Si_2 -type structure, by inserting C atoms in the lanthanide (actinide) layer. Given that the parent structure-type tolerates a rich chemical diversity²⁻⁵, the derivative structure should as well. In addition, these compounds are built up from distinct atomic layers, consequently, many other related structures can be envisioned (and are being isolated⁶) that are composed of different stacking sequences of the fundamental layer modules. That it is not possible to account for the chemical formulas of the borocarbides in terms of the normal valences of the metals, and that B and C have a propensity to concatenate, only provides further latitude for theoretical structures. Neutron powder diffraction is an useful tool to characterize the light atom positions in these materials.

EXPERIMENTAL

Samples weighing 5 to 8 g of the nickel borides, NiB, Ni_4B_3 , Ni_2B , Ni_3B , and the quaternary compositions $(\text{YC})_n\text{Ni}_2\text{B}_2$ ($n = 1, 3, 4, \infty$) and $(\text{YC})(\text{Ni}_2\text{B}_2)_2$ were prepared by standard arc melting methods using a water-cooled copper hearth in a high-purity argon atmosphere, using Y (99.9%, Johnson Matthey), Ni (99.999%, Johnson Matthey), ¹¹B (99.5%, Eagle-Picher Industries) and graphite C (99.9995%, Johnson Matthey). The samples were remelted 3 to 4 times and turned over between each melting. For all of the samples, NiB was used as the starting material, a large homogeneous mass of which was initially prepared by induction melting twice in an argon atmosphere. The sample yields were greater than 98.5% of the starting material weights. X-ray powder diffraction and metallography were used to assess the phase purity. To screen samples for superconductivity, ac susceptibility measurements were made using the mutual inductance method with ac signal of 200 Hz.

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Fig. 1. The YC-B-Ni ternary section (molar quantities) of the quaternary Y-C-B-Ni showing the known phases as solid circles and hypothetical phases as open circles. Two homologous chemical series are identified by the general formulas, $(YC)_nNi_2B_2$ and $(YC)(Ni_2mB_{m+1})$

Neutron-diffraction data were collected on selected samples using the HB4 high-resolution powder diffractometer at the High-Flux Isotope Reactor at ORNL. This instrument has a Ge (115) monochromator which, when $2\theta = 80^\circ$, selects an incident neutron beam of $\lambda \approx 1.4 \text{ \AA}$. The neutron wavelength was determined more precisely to be $1.417 \text{ \AA}$ on the basis of unit cell refinements for the NIST Standard Reference Material Si 640a. Soller slit collimators of $12'$ and $20'$ are positioned before and after the monochromator crystal, respectively. An array of 32 equally spaced (2.7°) ^3He detectors, each with a $6'$ mylar foil collimator, can be step-scanned over a range of up to 40° for scattering angles between 11° and 135° . The samples were placed in vanadium cans for data collection at 296 K over the 2θ range of 11° to 135° in steps of 0.05° . For these data collections, the detector array was scanned in two segments to overlap 8 detectors per step for the middle of the pattern. Overlapping detectors for a given step serves to average the counting efficiency and the 2θ zero-point shift for each detector.

Structure refinements were made by the Rietveld method⁷ using the GSAS software⁸. The pseudo-Voigt peak-profile function truncated at 0.3% of the peak height as described by Thompson *et al.* was used, including 8 terms⁹⁻¹⁰. Peak asymmetry and sample displacement parameters were also refined. The background was defined by a cosine Fourier series with 3 terms. The coherent scattering lengths used were: Y (7.75 fm), Ni (10.3 fm), ^{11}B (6.66 fm) and C (6.646 fm)¹¹. To avoid extreme absorption, boron enriched in mass number 11 is necessary.

Intensities were corrected for the Lorentz effect. The function minimized in the least-squares procedure was $\sum w_i(Y_{io} - Y_{ic})^2$, where Y_{io} and Y_{ic} are the observed and calculated intensities at each step i in the pattern. The weight w_i assigned to each step intensity is the reciprocal of the variance σ_i^2 at the i^{th} step and was evaluated by $w_i = 1/\sigma_i^2 \approx n/Y_{io}$ where n is the number of detectors contributing to the average step intensity. The following agreement factors were calculated:

$$R_p = \sum |Y_{io} - Y_{ic}| / \sum Y_{io}$$

$$R_{wp} = [\sum w_i(Y_{io} - Y_{ic})^2 / \sum w_i Y_{io}^2]^{1/2}$$

$$\text{Goodness-of-fit} = \sum w_i(Y_{io} - Y_{ic})^2 / (N - P),$$

where N and P are the number of observations and adjustable parameters, respectively.

Starting values for the structural parameters were obtained from known data for the nickel borides or their isostructural analogs in the case of NiB^{12} , and models based on $(\text{LnC})_n(\text{Ni}_2\text{B}_2)_m^1$. The least-squares refinements were continued until the sum of the squared errors, i.e., (parameter shifts/estimated standard deviations)², was less than 1%.

RESULTS & DISCUSSION

Good quality structural refinements were determined only for the nickel borides NiB , monoclinic Ni_4B_3 , Ni_2B , and Ni_3B , and YCNi_2B_2 . Except for the latter, which has already been previously described¹³, structural data are given in Tables I, II, III, and IV. An example neutron powder pattern displays the least-squares fit for NiB (Fig. 2) and illustrates the typical low and flat background achieved with the HB4 neutron powder diffractometer. The Ni_4B_3 sample contained a minor unidentified impurity, which was not consistent with the known phase relations in the Ni-B system¹⁴, and these peaks were excluded. The Ni_2B sample contained about 2.5 volume % of Ni_3B , which was included in the refinement.

The refined structures of these nickel borides are not significantly different from previous refinements made 25 years ago for Ni_4B_3 , Ni_2B , and Ni_3B using single-crystal x-ray data.¹² Neutron powder data apparently is comparable in these cases. The NiB refinement is altogether new structural data. Although the B atoms in NiB form characteristic zigzag chains, the primary coordination of each atom by atoms of the other kind is similar and distinctively sevenfold, with one short (2.117 Å), two intermediate (2.152 Å), and four long (2.163 Å) bonds.

These nickel borides illustrate the general trend of structural arrangements of the metal borides and borocarbides, with increasing B content the degree of concatenation (B-B bonding) increases.¹⁵ The arrangements of B atoms in the nickel borides are described as follows:

Ni_3B	-->	Ni_2B	-->	orthorhombic $\text{Ni}_4\text{B}_{3-\delta}$	-->	monoclinic Ni_4B_3	-->	NiB
isolated		isolated		1/3 isolated & 2/3 zigzag chains		zigzag chains B-B=1.83, 1.91 Å B-B-B=114°		zigzag chains B-B=1.78 Å B-B-B=112°

The structure-type of Ni_2B is that of CuAl_2 - θ , which has a distorted fluorite atomic arrangement with alternate Ni layers rotated by 45° relative to one another. The B atoms are situated in the square antiprisms formed by two square Ni groups in adjacent layers. The Ni_2B structure is a likely model for the multiple $(\text{Ni}_2\text{mB}_{m+1})$ layer modules in the hypothetical homologous series $(\text{YC})(\text{Ni}_2\text{mB}_{m+1})$. Ni_2B also can be used as a flux to grow large crystals of $(\text{LnC})\text{Ni}_2\text{B}_2$.¹⁶

Table I. Structural parameters of NiB at room temperature.

Atom	Position	x	y	z	B (Å ²)	occupancy
Ni	4c <i>m2m</i>	0	0.4332(2)	1/4	0.08(3)	1
B	4c <i>m2m</i>	0	0.1467(1)	1/4	0.33(4)	1

Cmcm (No. 63), $a = 2.9255(1)$ Å, $b = 7.3941(3)$ Å, $c = 2.9616(1)$ Å, $V = 64.066(8)$ Å³
 $R_p = 6.52\%$, $R_{wp} = 7.83\%$, $\chi^2 = 1.14$.

Table II. Structural parameters of Ni₄B₃ at room temperature.

Atom	Position	x	y	z	B (Å ²)	occupancy
Ni(1)	8f 1	0.0441(4)	0.2481(6)	0.4836(2)	0.41(4)	1
Ni(2)	8f 1	0.2026(4)	0.5705(4)	0.2862(2)	0.36(4)	1
B(1)	4e 2	0	0.931(1)	1/4	0.7(1)	1
B(2)	8f 1	0.2311(6)	0.9215(7)	0.4385(5)	0.56(6)	1

C2/c (No. 15)

$a = 6.4279(3)$ Å, $b = 4.8809(2)$ Å, $c = 7.8169(3)$ Å, $\beta = 103.30(1)^\circ$, $V = 238.67(3)$ Å³
 $R_p = 7.50\%$, $R_{wp} = 9.42\%$, $\chi^2 = 1.68$.

Table III. Structural parameters of Ni₂B at room temperature.

Atom	Position	x	y	z	B (Å ²)	occupancy
Ni	8h <i>m.2m</i>	0.1681(1)	0.6681(1)	1/4	0.47(2)	1
B	4a 422	0	0	1/4	0.58(4)	1

I4/mcm (No. 140), $a = 4.9903(1)$ Å, $c = 4.2472(1)$ Å, $V = 105.774(8)$ Å³
 $R_p = 8.16\%$, $R_{wp} = 10.05\%$, $\chi^2 = 2.16$.

Table IV. Structural parameters of Ni₃B at room temperature.

Atom	Position	x	y	z	B (Å ²)	occupancy
Ni	4c <i>m</i>	0.0282(2)	1/4	0.8699(5)	0.28(3)	1
Ni	8d 1	0.1804(2)	0.0610(1)	0.3451(3)	0.20(3)	1
B	4c <i>m</i>	0.8832(5)	1/4	0.4399(5)	0.16(5)	1

Pnma (No. 62), $a = 5.2182(1)$ Å, $b = 6.6171(1)$ Å, $c = 4.3911(1)$ Å, $V = 151.625(9)$ Å³
 $R_p = 5.41\%$, $R_{wp} = 6.42\%$, $\chi^2 = 1.14$.

Fig. 2. Observed, calculated, and difference neutron powder-diffraction (wavelength = 1.417 Å) profiles for NiB. The observed data are indicated by crosses, and the calculated profile is the continuous solid line in the same field. The short vertical lines below the profiles mark the positions of all possible Bragg reflections, and the bottom curve is the difference between the observed and calculated intensity (plotted using the same vertical scale as the observed and calculated profiles).

The YC samples react rapidly with moist air, and produce acetylene. X-ray powder diffraction is not possible without a controlled atmosphere chamber. The neutron powder diffraction pattern of YC sealed under He is complicated by the presence of several polymorphs produced during the non equilibrium arc melting process. This YC reference pattern can be recognized as a major phase in the sample of $(YC)_nNi_2B_2$ with $n = 4$ and to a lesser extent in the sample with $n = 3$. The distinctive odor of acetylene also can be used to confirm the presence of YC in quaternary samples. Textured sample mounts of $(YC)_nNi_2B_2$ with $n = 3$ and 4 exhibit characteristic low-angle d -spacings expected for these hypothetical structures, i.e., 10.5 Å ($n = 3$) and 13.3 Å ($n = 4$), modeled by the insertion of multiple NaCl-type YC layers. The susceptibility screening for these samples measured to 7 K indicted no superconductivity.

The $(YC)(Ni_2B_2)_2$ sample also produced complicated diffraction patterns for which all the phases present could not be identified, however, a sharp superconducting transition occurred at 17 K, possibly due to the present of some $(YC)Ni_2B_2$.

ACKNOWLEDGMENTS

We thank B. C. Sales for technical assistance with the induction melting and M. Paranthaman for encouragement. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

1. T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski and W. F. Peck Jr., *Nature* **367**, 54 (1994).
2. W. B. Pearson, *J. Solid State Chem.* **56** (1985) 278.
3. Chong Zheng and R. Hoffmann, *J. Am. Chem. Soc.* **108** (1986) 3078.
4. H. F. Braun, N. Engel, and E. Parthe, *Phys. Rev. B* **28**, 1389 (1983).
5. R. Hoffmann and Chong Zheng, *J. Phys. Chem.* **89**, 4175 (1985).
6. Q. Huang, B. C. Chakoumakos, A. Santoro, R. J. cava, J. J. Krajewski, and W. F. Peck, Jr., *Physica C*, in press.
7. H. M. Rietveld, *J. Appl. Cryst.* **2**, 65 (1969).
8. A. C. Larson and R. B. Von Dreele, GSAS—General Structure Analysis System. Report LA-UR-86-748, Los Alamos National Laboratory, Los Alamos, NM 87545, 1990.
9. P. Thompson, D. E. Cox, and J. B. Hastings, *J. Appl. Cryst.* **20**, 79 (1987).
10. R. B. Von Dreele in Modern Powder Diffraction, edited by D. L. Bish and J. E. Post (Mineralogical Society of America, Washington, 1989) pp. 333-369.
11. V. F. Sears, *Neutron News* **3**, 26 (1992).
12. P. Villars and L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Vols. 1-4 (ASM International, Materials Park, Ohio, 1991).
13. B. C. Chakoumakos and M. Paranthaman, *Physica C* **227**, 143 (1994).
14. K. E. Spear, Applications of Phase Diagrams in Metallurgy and Ceramics, Vol. 2 (NBS Special Publication 496, 1978) pp. 744-762.
15. A. F. Wells, Structural Inorganic Chemistry, 5th ed. (Oxford University Press, New York, 1984) pp. 1052-1057.
16. M. Xu, P. C. Canfield, J. E. Ostenson, D. K. Finnemore, B. K. Cho, Z. R. Wang, and D. C. Johnston, *Physica C* **227**, 321 (1994).

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