Investigation of Site-Selectivity and Crystal Structure of Boron- Incorporated B2- Type AlNi Matrix

M. Elhadi¹,²,³,*, M. ElMassalami¹, B. Ouladdiaf⁴

¹Instituto de Física, Universidade Federal do Rio de Janeiro, Brazil
²Department of Physics, Faculty of Science and Technology; Al Neelain University, Sudan
³Department of Physics, Faculty of Science, Shaqra University, Saudi Arabia
⁴Institut Laue-Langevin, Diffraction Group (DIF), B.P.156, 38042 Grenoble Cedex 9, France

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Abstract We investigated in the B site-selectivity and induced modifications in the crystal structure, when B is introduced into the B2-type AlNi matrix (Pm-3m; Al at 1a, Ni at 1b). A rapid-quench from higher temperatures of all nominal AlNiBₓ and Al₂Ni₃Bₓ/₃ compositions (0≤ x ≤ 3) leads to the formation of a cubic solid solution. On the other hand, diffraction studies indicate that all (unquenched) AlNiBₓ (1≤ x ≤ 3) compositions are chemically unstable. By contrast, for 0≤ x ≤ 1 there is a strong preference of B to enter substitutionally into the 1b site: then composition balance is achieved by transferring a Ni atom into a 1a antisite.

Keywords Intermetallic, Composition, Ternary Phase Diagram, Rapid Quench

1. Introduction

The binary intermetallic AlNi compound crystallizes in the cubic B2 structure wherein Al and Ni occupation, respectively, 1a and 1b sites of space group Pm-3m (see inset of Fig. 1). This matrix is well known for the considerable interchange among its atomic constituents and, moreover, for its ability to accommodate a large number of point defects without being destabilized [1]. Additional attractive and technologically advantageous properties [2] include shape memory, higher melting points, higher mechanical strength and stiffness at elevated temperatures, low density, and good oxidation or corrosion resistance. But, as common among these AlNi-type alloys, their inadequate high-temperature creep-resistance and poor room-temperature ductility make them unsuitable for wider technological applications. One possible means of overcoming these drawbacks is to carry out alloying with boron [3-6]. For the purpose of understanding and optimizing this alloying process, various studies were carried out (see, e.g., Ref.[7] and references there in). However, there are no systematic investigations of the correlation between the B content and the phase stability, structural, thermal, and electronic properties of B-alloyed AlNi. It is interesting then to investigate how much B can be incorporated and where does it enter (whether substitutionally or interstitially) into the AlNi unit-cell. This work investigates these questions by carrying out extensive experimental studies as well as first-principles total-energy and electronic band structure calculations [8].

To meet these objectives, in particular those of phase stability and site-preference of boron incorporation, we proceed first by analyzing the Al and Ni atoms intermixing within the Al₁₋ₓNiₓBₓ alloy; afterwards, the whereabouts of B within the Al-deficient Al₁₋ₓBₓNi, Ni deficient Al₃₋ₓBₓNi, and AlNiBₓ compositions is considered. The role of the rapid-quench process in assisting the incorporation of B into these matrices is highlighted. Throughout these procedures, structural, magnetization, specific heat, and resistivity characterizations are applied so as to probe the induced variation in the lattice as well the electronic and thermodynamical properties.

Figure 1. The Al-Ni-B ternary phase diagram [9-12]. Stars: presently studied nominal Al₁₋ₓNiₓBₓ compositions; filled circles: Al₅Ni₅B₅ compositions [13]. Triangles: Al₅Ni₅B₅ compositions. The thin dotted lines are taken from the experimental isotherm section at 1000 °C given in Ref. 9. Inset: unit-cell of AlNi (Pm-3m) with some high-symmetry Wyckoff special positions: Al at 1a (0,0,0), Ni at 1b (½,½,½), and the two empty sites 3c (0.5,0.5,0) and 3d (0.5,0,0).
2. Material & Methods

Structures of various starting (pseudo) ternary compositions (see Fig. 1) were investigated. For ease of presentation, these compositions were grouped into three classes: (i) Al(Al$_{1-y}$Ni$_{y}$)$_{1-x}$Ni$_{x}$, (Al$_{1-y}$Ni$_{y}$)Ni$_{1-x}$Al(Al$_{1-y}$Ni$_{y}$)$_{1-x}$Ni$_{x}$ (y = 0.06 or 0.2), (ii) AlNiB$_{x}$ (0 ≤ x ≤ 3), and (iii) Al$_{2}$Ni$_{3}$B$_{w}$ (w = 0, 0.25, 0.5, 1). For each nominal composition, proper amount of pure Ni (99.9%), Al (99.9%), and B (99.8 %) were melted under argon atmosphere (99.9 %) in conventional arc-melt or induction furnaces.

For neutron diffraction analysis, enriched $^{11}$B isotope was used. A variety of heat treatment routes (as-prepared, rapid-quenching, and annealing) were employed. The rapid-quenching was carried out by hitting a small piece of a re-melted sample with a mechanical copper-hammer which was implemented in an argon arc-furnace. Annealing of Ta-wrapped buttons of selected samples was carried out, usually for an overnight, in a quartz tube under argon atmosphere.

X-ray room-temperature powder diffractograms were collected at room temperature on a Cu K$_{\alpha}$ diffractometers.

3. Results & Discussion

3.1. Al$_{1-x}$Ni$_{1+x}$, Al$_{1-x}$B$_{x}$Ni, and AlNi$_{1-x}$B$_{x}$ ($\delta = \pm 0.3$, $\alpha = 0.2$)

Compositions and Lattice Parameters Calculations

Table I shows that the unit-cell parameters of both Ni-deficient Al(Ni$_{0.8}$B$_{0.2}$) and Al$_{0.53}$Ni$_{0.47}$ compositions are strongly reduced in comparison with that of the parent AlNi; on the other hand, the a-parameters of Al-deficient (Al$_{0.94}$Ni$_{0.06}$)Ni and Al$_{0.8}$NiB$_{0.2}$ compositions are very weakly reduced.

A closer look at the diffractograms of Al$_{1-x}$Ni$_{1+x}$ [Fig. 2(b)] shows that the intensity of the (200) peak at 64.8° is almost the same as that of the (110) peak: $I_{200}/I_{110} \sim 1$. By contrast, for Al$_{1-x}$Ni$_{1+x}$ [Fig. 2(a)], the $I_{200}/I_{110}$ ratio is ~ 0.1 which is similar to the theoretical value calculated for such compounds [17]. Various effects may give rise to such a discrepancy: e.g. (i) a contaminating contribution (however no additional contaminating peaks were observed), (ii) a preferred orientation (however no intensity rise is observed for any of the other (n00) peaks), or (iii) a formation of a body-centered unit cell occurring due to atomic intermixing on both 1a and 1b sites: this requires the presence of both AlNi and NiAl defects. Although such an intermixing was previously suggested for Al$_{1.05}$Ni$_{0.95}$ (Ref. [18]), nonetheless, as mentioned above, the excess Al would generate constitutional defects; this is driven by the high-energy cost for creating Al$_{N0}$ defects in this structure.

3.2. AlNiB$_{x}$

Both X-ray and neutron diffraction studies on a series of non-quenched AlNi$_1^{11}$B$_{x}$ (n=1, 2, 3) samples (not shown) indicate a multi-phase character; in fact for each sample, the lattice parameters of the AlNi-type phase is equal to that of the parent matrix. These results emphasize the instability of AlNiB$_{x}$ compositions (1 ≤ x ≤ 3); even for samples having either different heat treatment (except quenching) or varying nominal compositions. This conclusion is consistent with the features of the ternary phase diagrams [9].
Figure 3. Representative XRD diffractograms of AlNiB$_x$ (0 < $x$ < 1). Logarithmic scale is used for the intensities. The short vertical bars (at the bottom) represent the Bragg positions of the cubic AlNi-type phases (see text). In spite of the inherited XRD lack of good resolution for B, this indicates a single-phase character.

By contrast, the diffractograms of AlNiB$_x$ (x < 1) (see Fig. 3) indicate a well-formed AlNi-type major phase which has lattice parameter that evolve smoothly (but non-monotonically) with B content (see Fig. 4). The stability of these AlNiB$_x$ (x < 1) compositions can be discussed in terms of the qualitative arguments [8].

In other words, the sharp discrepancy between theory and experiment within the range 0.01 < $x$ < 1 indicates that lattice parameters are not only governed by the appearance of substitutional defects, but there must be additional processes such that their opposing and competing tendencies lead to a non-monotonic evolution of the unit-cell volume.

We also carried out a more thorough theoretical analysis of the stability of AlNiB$_x$ within the two limit regimes: the high-B-concentration limit (x = 1, 2, 3) and the low-B-concentration (point-defect) limit (x << 1). For the high concentration regime, consideration of ionic size and available volume within the unit cell suggests that B may occupy, partially or completely, the three equivalent 3c sites leading to either AlNiB, AlNiB$_2$, or AlNiB$_3$.

3.3. Rapid-quench and the Stability of Al$_2$Ni$_3$B$_x$ Compositions

Based on the features of the ternary phase diagrams [9-12], a nominal Al$_2$Ni$_3$B composition should segregate into a mixture of AlNi and $\tau$ phases. In contrast, Fig. 5 shows that the structure of a rapid-quenched Al$_2$Ni$_3$B is an almost single-phase cubic solid solution.

The single-phase character of quenched AlNiB$_3x$ and Al$_2$Ni$_3$B$_x$ (x < 1) can be attributed to a freezing out of a high-temperature randomly-distributed, cubic structure wherein Al fills the 1a sites, most of Ni goes to 1b site, the excess Ni compensates for the 1a site deficiency, and B either goes into the VNi sites or else being expelled out. Fig. 6 shows, for (Al$_{1-x}$Ni$_x$)$_3$NiB$_x$ (x = 0, 0.1, 0.2, 0.4) and (Al$_{1-x}$Ni$_x$)$_3$NiB$_{30}$ ($\beta = \frac{1}{9} \frac{10}{10} \frac{4}{10}$), an increase in B leads to a monotonic increase in the unit-cell parameter. This behavior [in apparent contrast to the non-monotonic evolution of the a-parameter of AlNiB$_x$ (x < 1) shown in Fig.4 is most probably caused by a combination of B incorporation and atomic intermixing.
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Figure 6. The lattice a-parameter of (\(\text{Al}_8\text{Ni}_{10}\)) \(x\) \(\text{NiB}_x\) (\(x = 0, 0.1, 0.2, 0.4\)), (\(\text{Al}_9\text{Ni}_{19}\)) \(\text{NiB}_2\), (\(\text{Al}_{10}\text{Ni}_{30}\)) \(\text{NiB}_6\), and (\(\text{Al}_{10}\text{Ni}_{40}\)) \(\text{NiB}_8\). The horizontal axis is given as the percentage of B in each unit formula. The dashed line is a guide to the eye. It is noted that the variation in the lattice parameter of the low B-content is different from that observed in Fig. 4 (see text). A comparison of the lattice parameters with the ones shown in Fig. 4 and Table I indicates that the modification in the lattice parameters caused by the variation in the ratio of Al and Ni is much stronger than the one caused by B alloying.

4. Conclusions

Using X-ray diffractometer, we investigated the site selectivity of B when it is being introduced into the AlNi matrix. We also investigated the influence of the B addition on the structural and thermodynamic properties [8]. Rapid-quench from high temperatures of all AlNiB \(x\) (\(0 < x \leq 3\)) or \(\text{Al}_2\text{Ni}_3\) \(y\) compositions leads to a formation of a cubic AlNi-type solid solution.

The experiments indicate that all non-quenched AlNiB \(y\) (\(1 \leq x \leq 3\)) compositions are chemically unstable since the energy cost of placing B at the \(3c\) site is prohibitively high; nonetheless, for \(x < 1\), there is a strong preference of B to enter substitutionally into the \(1b\) site; as a result, some Ni atoms are either moved to a \(1a\) site or else some vacancies are created at the \(1a\) site.

In addition, we observed that for all compositions, a reduction in the lattice constant occurs whenever the \(1b\) site is vacant or occupied by B. From the above result there is good agreement between measured and calculated lattice constants; in contrast, there is hardly any reduction in the lattice constant whenever the \(1a\) site is vacant or being occupied by Ni.

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