INFLUENȚA CONȚINUTULUI ÎN Al ASUPRA COMPUŞILOR PSEUDO-TERNARI *RENi$_{4-x}$AlB$_x$* (*RE = Gd, Y*)
INFLUENCE OF Al CONTENT ON THE PSEUDO-TERNARY COMPOUNDS *RE*Ni$_{4-x}$AlB$_x$ *(RE = Gd, Y)*

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We have studied the influence of the substitution of Al for Ni in the ternary systems RENi$_{5-x}$B$_x$ (RE=Gd, Y). The compounds synthesized in the pseudo-ternary systems RENi$_{4-x}$AlB$_x$ (RE=Gd, Y) were studied in terms of their crystal structure, chemical composition and hydrogen sorption properties. Most of the compounds obtained in these systems crystallize with the CeCo$_4$B-type structure RENi$_3$AlB, with Al atoms replacing Ni. The partial replacement of Ni by Al observed leads to a decrease of lattice parameters compared to ternary RENi$_4$B compounds. The new pseudo-binary phase GdB$_3$ was also observed in this study for the first time. Finally, it is reported that the compounds do not show any affinity towards hydrogen, with no absorption observed.

A fost studiată influența substituției parțiale a Ni de către Al în sistemele ternare RENi$_{5-x}$B$_x$ (RE=Gd, Y). Compușii sintetizați în sistemele ternare RENi$_{4-x}$AlB$_x$ (RE=Gd, Y) au fost studiați din punct de vedere al structurii cristalografice, compoziției chimice şi proprietăților de sorbție a hidrogenului. Majoritatea compuşilor obținuți în aceste sisteme cristalizează cu o structură de tip CeCo$_4$B, RENi$_3$AlB, atomii de Al înlocuind Ni. Înlocuirea parțială a Ni de către Al observată duce la descreşterea parametrilor de rețea, în raport cu compuşii ternari RENi$_4$B. De asemenea, o nouă fază pseudo-binară de tip GdB$_3$ a fost identificată pentru prima dată în cadrul acestui studiu. În fine, compuşii obținuți nu prezintă afinitate față de hidrogen, absorbția de hidrogen nefiind observată.

Keywords: *intermetallics, borides, ternary compounds*

1. Introduction

Among the binary intermetallics, Haucke phases of stoichiometry AB_5, such as $LaNi_5$, present a great interest for hydrogen storage. Indeed, this compound reversibly absorbs 1.5 wt% hydrogen at room temperature [1,2]. Many ternary compounds can be derived from $LaNi_5$: the $RENi_{5-x}M_x$ compounds are obtained by substitution of metal atoms for nickel on *3g* sites (M = Al, Fe, Co, Mn ...) or 2c sites (M = Cu) and for lanthanum on sites 1a (*RE* = Y, Gd, Pr …) [3,4].

In this study, we have observed the influence of the substitution of aluminum for nickel, along with the substitution of boron. Aluminum is often used as a substitute for nickel in order to vary the lattice parameter and adjust the equilibrium pressure for hydrogenation [5]. The compounds we have synthesized in the pseudo-ternary systems *RE*Ni$_{4-x}$AlB$_x$ (*RE* = Gd, Y) are of the *RE*Ni$_4$B type.

2. Experimental details

The intermetallic compounds were synthesized from pure elements by melting in two steps: first fusion in an induction furnace, followed by a second one in an electric arc furnace. The fusion in an induction furnace does not melt the boron, due to its low electrical conductivity and its low thermal diffusion coefficient. The use of the electric arc furnace is necessary in order to ensure the fusion and diffusion of boron in the alloy.

This step was followed by heat treatment using variable durations and temperatures. Annealing allows in some cases to obtain improved crystallinity and purity of the samples. We have observed that the annealing conditions used in our study do not affect the composition and proportion of phases present.

Small blocks of materials thus obtained were pulverized using an agate mortar and pestle, and then characterized by X-ray powder diffraction; the data obtained was then used to perform a Rietveld refinement [6]. The background noise at low θ, visible on most diffraction patterns, is due to the sample holder in PMMA and the adhesive used to fix the powder on the sample holder.

X-ray diffraction analysis was performed using a Philips PANalytical X'Pert diffractometer, type PW1820 (ICMCB) or PW1050 (UPB) with Bragg-Brentano θ-θ geometry and Cu Kα radiation

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($\lambda_{K\alpha1}$=1.5405 Å and $\lambda_{K\alpha2}$=1.5443 Å). Data acquisition (8°<2θ<80°) was performed with a 0.02° step and 30s constant counting time.

All samples synthesized in this study were also analyzed by electron microprobe, in order to determine their chemical composition. The samples were investigated by electron microprobe analysis using a CAMECA SX-100 instrument using pure metal samples as reference.

The hydrogen absorption and desorption tests were performed using an automated Sieverts-type gas titration apparatus C2-3000 (HERA® Hydrogen Systems) [7].

3. Results and discussion

3.1 $GdNi_3AlB$

The phases observed by microprobe analysis are also visible in the X-ray diffraction pattern; approximated lattice parameters for $GdNi_3AlB$ are : *a*=5.056 Å; *c*=6.816 Å. The *a* parameter has an increase of 0.94%, while the *c* parameter decreases by 2% (Fig.1,2). This corresponds to a 0.36% increase in cell volume. This slight increase in volume is lower than generally observed in the case of compounds substituted with aluminum. For example, in the case of pseudo Laves phases $GdNi_{4-x}Al_xMg$, the replacement of one nickel atom by an aluminum atom resulted in an increase of the cell volume of 2.75% [8]. The Rietveld refinement did not resolve this structural problem satisfactorily. The values obtained for the figures of merit were very high and the presence of two parasite phases further complicated refinement. However, the evolution of the lattice parameters suggests that the substitution of aluminum for nickel takes place preferentially at certain sites and is therefore not perfectly random.

$GdNi_3AlB$ crystallizes with the same structure type as $GdNi_4B$. The other two observed phases are $GdNi_4Al$ (a derivate of $GdNi_5$) and the binary Gd_3Ni. We shall however note that several peaks, *e.g.* the first peak at low theta (2*θ*=13°) could not be indexed.

The multiphase alloy obtained is highly inhomogeneous. The two heat treatments, long term at average temperature (2 months at 600°C) and short term at high temperature (10 days at 900°C) did not result in better homogeneity.

Some of the phases present ($GdNi_4Al$ and Gd_3Ni) do not contain boron. It is therefore accurate to say that all B is concentrated in a single phase, of composition close to the nominal composition ($GdNi_3AlB$). This compound would be a derivative of $GdNi_4B$ by the substitution of an aluminum atom for nickel.

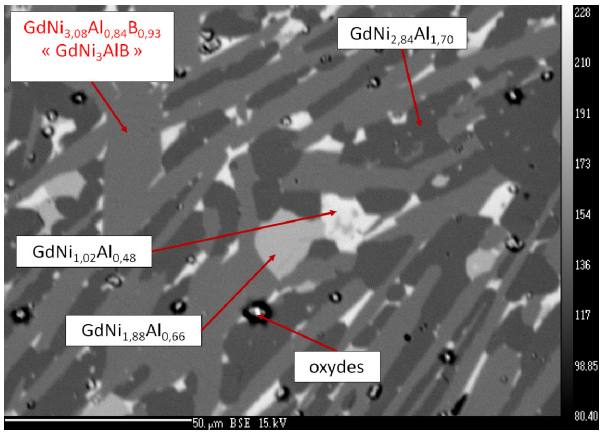

Fig. 2 - Electron microprobe analysis of $GdNi_3AlB$ / *Analiza prin microsonda Castaing a $GdNi_3AlB$.*

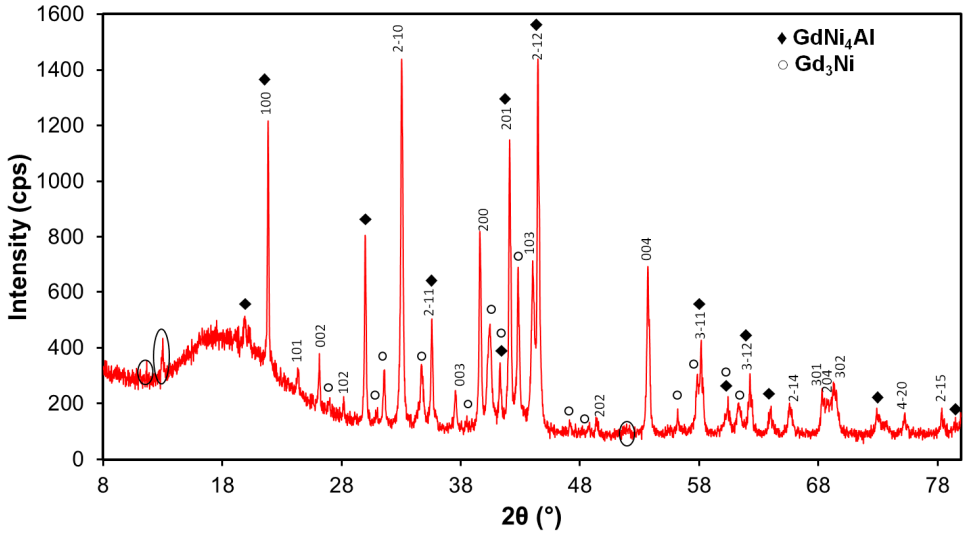

Fig. 1- X –ray diffraction pattern for $GdNi_3AlB$, with indexed peaks for $GdNi_3AlB$ ($CeCo_4B$-type structure) / *Difractograma de raze X pentru $GdNi_3AlB$, cu indexarea picurilor corespunzătoare $GdNi_3AlB$ (structură tip $CeCo_4B$).*

3.2. $GdNi_{3,5}AlB_{0,5}$

According to the X-ray diffraction pattern, the approximated lattice parameters for the quaternary compound Gd-Ni-Al-B are *a*=4.811 Å and *c*=6.859 Å (Fig. 3). Compared to the $GdNi_4B$ compound, the *a* parameter decreases by 3.9% and the *c* parameter decreases by 1.3%(Fig. 4). This corresponds to a 9% decrease in cell volume. This strong decrease in volume is surprising, as it is contrary to the results observed in the case of aluminum-substituted compounds: the substitution of aluminum for nickel increases the cell volume by steric effect, due to the superior atomic radius of aluminum.

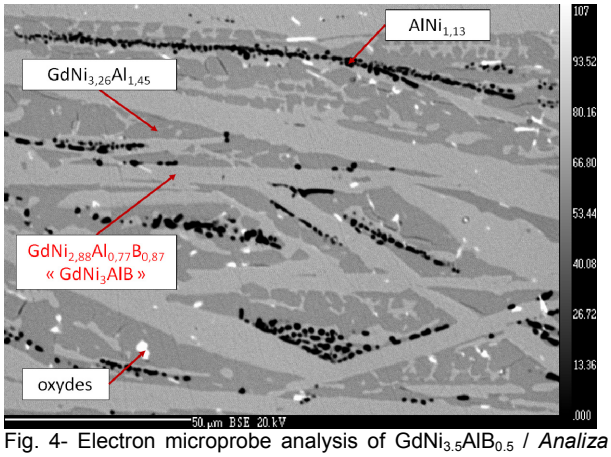

Fig. 4- Electron microprobe analysis of $GdNi_{3.5}AlB_{0.5}$ / *Analiza prin microsonda Castaing a* $GdNi_{3.5}AlB_{0.5}$.

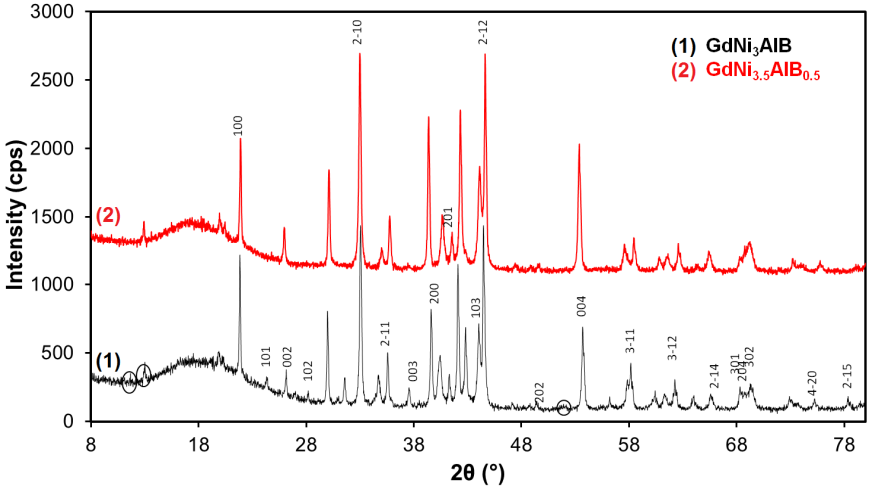

Fig. 3- X –ray diffraction pattern for $GdNi_{3.5}AlB_{0.5}$ as compared to $GdNi_3AlB$ ($CeCo_4B$-type structure) / *Difractograma de raze X pentru* $GdNi_{3.5}AlB_{0.5}$ *în comparație cu* $GdNi_3AlB$ *(structură tip* $CeCo_4B$*).*

As previously observed, only one phase observed by microprobe analysis contains boron; its composition and lattice parameters are close to those of $GdNi_3AlB$. However, the decrease of the lattice parameters as observed and reported earlier remains unexplained. Note the presence of a binary AlNi phase and of a ternary phase "$GdNi_{3.26}Al_{1.45}$" we can assume to be derived from $GdNi_5$, with the same structure.

3.3 $GdNi_{2.5}AlB_{1.5}$

On the X-ray diffraction pattern, the peaks corresponding to a $GdNi_3AlB$-type phase can be indexed, with lattice parameters *a*=4.752 Å and *c*=6.829 Å (Fig. 5). As before, there is a decrease of the lattice parameters (*a* decrease by 5.1% and *c* decreases by 1.8%), which corresponds to an 11.6% decrease in cell volume (Fig. 6).

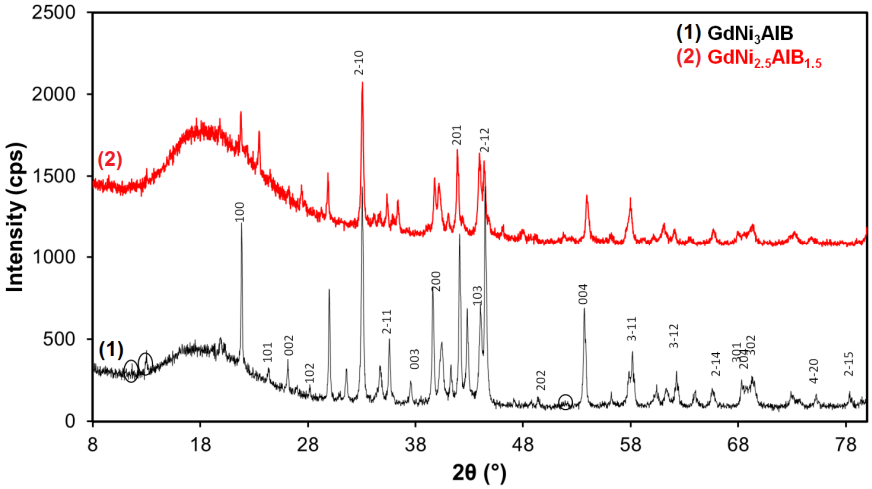

Fig. 5- X –ray diffraction pattern for $GdNi_{2.5}AlB_{1.5}$ as compared to $GdNi_3AlB$ ($CeCo_4B$-type structure) / *Difractograma de raze X pentru* $GdNi_{2.5}AlB_{1.5}$ *în comparație cu* $GdNi_3AlB$ *(structură tip* $CeCo_4B$*).*

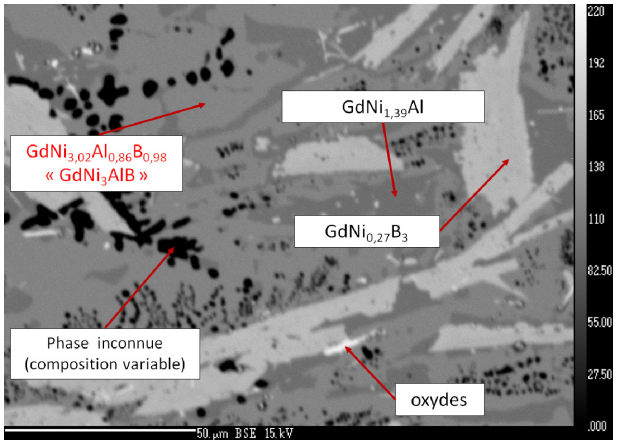

Fig. 6- Electron microprobe analysis of $GdNi_{2.5}AlB_{1.5}$ / *Analiza prin microsonda Castaing a* $GdNi_{2.5}AlB_{1.5}$.

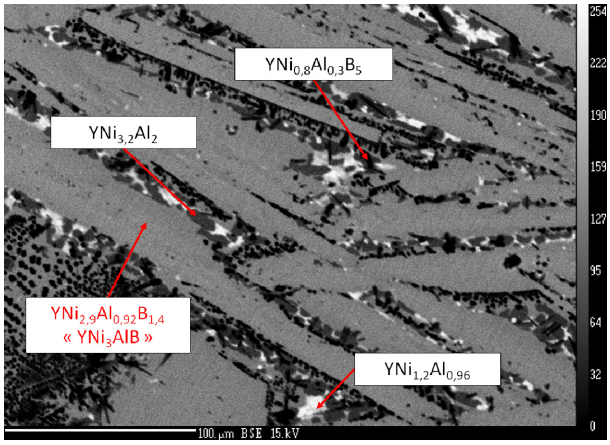

Fig. 7- Electron microprobe analysis of YNi_3AlB / *Analiza prin microsonda Castaing a* YNi_3AlB.

As in the two previous cases, the microprobe analysis confirms the existence of the $GdNi_3AlB$ phase observed by X-ray diffraction.

The existence of a binary compound "GdB_3", identified by microprobe analysis, remains to be verified (a hexagonal GdB_2 phase exists). GdB_3 synthesis essays are interesting and are the subject of further study, since we have not yet found any references to this compound in the literature.

3.4. YNi_3AlB

The X-ray diffraction pattern of the compound YNi_3AlB can be indexed with the same structure as $GdNi_3AlB$ and with lattice parameters *a*=4,729 Å et *c*=6,801 Å (Fig. 7). The decrease of the lattice parameters is 5.6% for the *a* parameter and 2.2% for the *c* parameter. The "YNi_3AlB" phase is also identified by microprobe analysis (Fig. 8). We can assume the existence of a family of compounds of type *RE*Ni_3AlB (*RE*=rare earth).

Although we were primarily interested in the hydrogen absorption properties and possible applications of the aluminum-substituted intermetallics, for all the compounds synthesized in this study, no hydrogen absorption could be measured. We have varied the activation conditions (up to 300°C under primary dynamic vacuum) and absorption conditions (up to 60 bar hydrogen pressure and 300°C) with no success.

4. Conclusions

In all of the aluminum-substituted compounds, it is surprising to see a decrease of the lattice parameters, while simple steric considerations lead us to expect an increase in cell volume. It is therefore likely that energy and/or electronic considerations would explain this decrease in lattice parameters. The strong chemical affinity of aluminum and boron, as well as the higher electronegativity of aluminum, lead to the formation of stronger - and therefore, shorter - bonds.

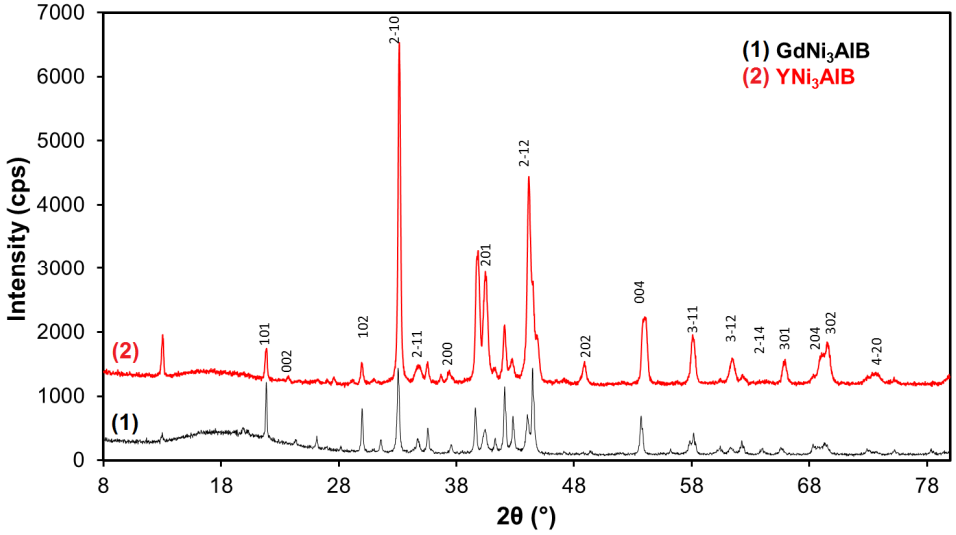

Fig. 7- X –ray diffraction pattern for YNi_3AlB ($CeCo_4B$-type structure): indexation and comparison to $GdNi_3AlB$ / *Difractograma de raze X pentru* YNi_3AlB *(structură tip* $CeCo_4B$*) şi comparaţie cu* $GdNi_3AlB$.

Ab initio calculations are necessary in order to confirm this hypothesis. Additionally, no hydrogen absorption (under conditions of up to 500°C and 60bar H_2) is observed for these aluminum-substituted compounds. The lack of hydrogen absorption is consistent with the results of our previous study on *RE*-*TM*-B compounds (*RE*=La, Gd, Y; *TM*=Ni, Co, Fe) [9].

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