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Effect of Cu additions over the lattice parameter and hardness of the NiAl intermetallic compound

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ABSTRACT

A set of NiAl intermetallic alloys was prepared with several Cu additions, exploring the Ni-rich and the Al-rich side of the NiAl intermetallic compound. An abrupt increment in hardness was obtained in the Al-rich alloys, while the opposite occurs in the Ni-rich alloys. This may be due to the presence of β-phase (Ni,Cu) Al and γ′-phase $(Ni,Cu)_3Al$, in addition to the variation of the β-phase lattice parameter.

1. Introduction

The intermetallic compounds are materials with a highly atomic order, they exhibit attractive properties such as elevated melting point, chemical stability, and oxidation resistant at high temperatures, besides a high strength [1–3]. Thus, making the intermetallic compounds as potential materials for structural applications at high temperatures and corrosive and oxidant media [4–6]. However, the fragile nature of these compounds at low and intermediate temperatures made them undesirable for applications at room temperature, showing excessive hardness, and unsubstantial ductility. Several attempts have been made to increase room temperature ductility in intermetallics. Among them, the addition of micro- and macro-alloying elements [7–9], the microstructural control through processing [10–12], and rapid solidification techniques [13,14] stand out. A grate variety of intermetallic compounds exist, the most important systems are as follows: AlFe, Ni_3Fe, AlNi, Ni_3Al, AlTi, Al_3Ti, CoAl, and NiTi. However, the intermetallic NiAl system is particularly attractive because it also shows low density. It has been reported that the addition of elements like Cu, Co, Ti and Fe can affect beneficially their mechanical properties [8,10,13]. In this work the stoichiometric NiAl composition system (Al–50 Ni-50 at.%) was studied exploring their ductility effect by macro-alloying with Cu, the Al-rich and Ni-rich sides.

2. Experimental procedure

Ten intermetallic alloys were melted using an induction furnace surrounded by Ar atmosphere: five alloys Al-rich (A-alloys) and five alloys Ni-rich (N-alloys). All the intermetallic alloys melted were pouring in an iron recipient producing blocky ingots of about 500 g in weight. The calculation of the alloy element proportions were performed according to the equilibrium phase diagram illustrated in Fig. 1. A Jeol JSM 6400 scanning electron microscope was used for microstructural characterization of the intermetallic ingots. In a Siemens 5000 X-ray diffractometer X-ray patterns were obtained employing Cu radiation and a Fe filter. Microhardness Vickers tests (0.025) were carried out in a Bhueler MHT2 Microhardness tester.

3. Results and discussion

3.1. Chemical analysis

Table 1 shows the results of the chemical analysis of the studied alloys. It can be observed that the deviation of the stoichiometry is not considerable and the compositions acquired in the ingots fall down within the limits of the proposed phases as shown in Fig. 1.

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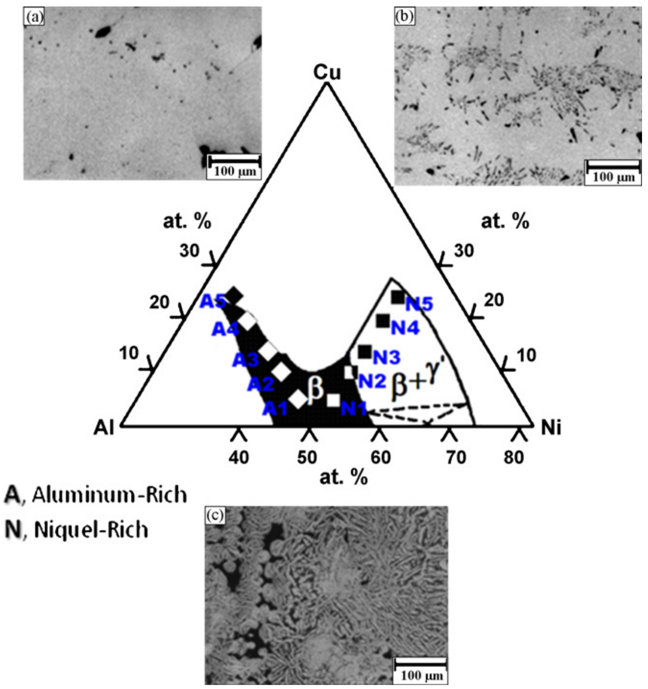

Fig. 1. NiAlCu equilibrium phase diagram [15] and representative microstructures observed on (a) Al-rich alloys A1 to A5. (b) Ni-rich alloys Ni, N1 and N3, (c) Ni-rich alloys, N4 and N5.

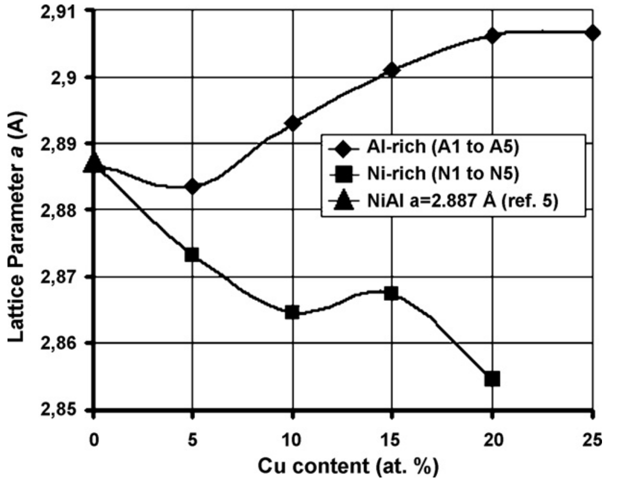

Fig. 2. Lattice parameter *a* variation related to Cu content in the different alloys.

3.2. Microstructure and X-rays analysis

From the equilibrium phase diagram shown in Fig. 1, the Al-rich alloys (A1 to A4) fall into the monophasic field, the β-Al (Ni,Cu) phase, leaving alloy A5 out of this field. Fig. 1a shows a representative micrograph of the microstructure observed in the Al-rich alloys, the phase observed, corresponds to β-Al (Ni,Cu). On the other hand, Ni-rich alloys (N3 to N5), are located in the biphasic field, formed by β-(Ni,Cu)Al and γ'-(Ni,Cu)$_3$Al phases. Alloy N1 is located in the β-(Ni,Cu)Al phase field and, N2 alloy is in the limit between monophasic and biphasic fields. Fig. 1b shows the microstructure corresponding to N1 and N3 alloys. Formed by β-(Ni,Cu)Al columnar dendrites with presence of a $\beta + \gamma'$ eutectic type phase in the inter-dendritic regions. Fig. 1c corresponds to N4 and N5 alloys, showing an interesting microstructure formed by β-(Ni,Cu)Al matrix phase and few martensite needles identified as γ'-(Ni,Cu)$_3$Al. X-rays analysis was performed in all samples and its results are shown in Table 1. The phases identified correspond to most of the phases shown in the equilibrium phase diagram.

Fig. 2 shows the variation of the calculated lattice parameter "*a*" as a function of Cu content. It can be seen that in the Al-rich alloys the lattice parameter is reduced and for the Ni-rich alloys this parameter increases. For comparison among the present alloys in Fig. 2 NiAl stoichiometric intermetallic compound is marked [5].

Noebe et al. [5], Liu and Stiegler [16] and Sauthoff [17] reported that the binary NiAl intermetallic compound, has principally two types of constitutional defects, that strongly depend on elemental composition and/or alloy stoichiometry. According to Refs. [5,16,17] by moving to the Ni-rich region an excess of Ni atoms substitute Al atoms occupying their sites, forming the (Ni$_{Al}$) antistructure atoms. On the other hand, towards the Al-rich portion within the crystalline compound, lattice vacancy Ni (V_{Ni}) sites are formed. This is an indication that Al atoms do not move, staying in their respective locations in the unit cell. Hence, from previous

Table 1
Chemical composition (at.%) and phases identified by X-ray diffraction and lattice parameters calculated for β-Al(Ni,Cu) and β-(Ni,Cu)Al phases.

Intermetallic alloys: A and N, Chemical composition in at.%

Al-rich				Ni-rich			
Alloy	Cu	Ni	Al	Alloy	Cu	Al	Ni
A1	5 ± 0.8	45 ± 1.2	Bal.	N1	5 ± 0.9	45 ± 0.36	Bal.
A2	10 ± 0.5	40 ± 0.8	Bal.	N2	10 ± 1.1	40 ± 0.5	Bal.
A3	15 ± 1.01	35 ± 0.9	Bal.	N3	15 ± 1.3	35 ± 1.02	Bal.
A4	20 ± 0.5	30 ± 0.6	Bal.	N4	20 ± 0.8	30 ± 1.1	Bal.
A5	25 ± 0.6	25 ± 1.2	Bal.	N5	25 ± 0.9	25 ± 1.5	Bal.

Phases identified by X-ray diffraction and lattice parameters calculated for β-Al(Ni,Cu) and β-(Ni,Cu)Al phases

Alloys	Cu (%at.)	Identified phases	β-Phase lattice parameter (Å)
A1	5	β-Al(Ni,Cu)	2.8835
A2	10	β-Al(Ni,Cu)	2.8913
A3	15	β-Al(Ni,Cu)	2.9009
A4	20	β-Al(Ni,Cu)	2.9062
A5	25	β-Al(Ni,Cu)	2.9065
N1	5	β-Al(Ni,Cu) + γ'-(Ni,Cu)$_3$Al	2.8732
N2	10	β-Al(Ni,Cu) + γ'-(Ni,Cu)$_3$Al	2.8646
N3	15	β-Al(Ni,Cu) + γ'-(Ni,Cu)$_3$Al	2.8675
N4	20	β-Al(Ni,Cu) + γ'-(Ni,Cu)$_3$Al	2.8546
N5	25	γ'-(Ni,Cu)$_3$Al	–

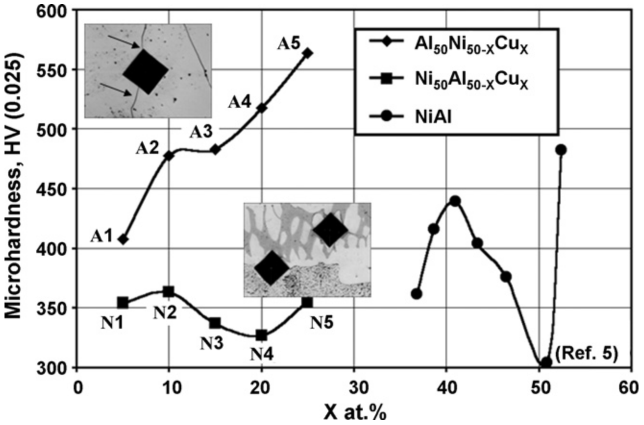

Fig. 3. Vickers microhardness (HVN 0.025) related to at.% of the alloys under study.

assumptions Ni vacancies (V_{Ni}) prevails in all A-type alloys and Ni anti-structure atoms (Ni_{Al}) on the N-type alloys.

Regarding Cu additions to the NiAl intermetallic system, a substitution of Al for Cu atoms takes place in their crystalline lattice. This behaviour produces a lattice distortion, due to the different atoms size. Consequently, the "*a*" parameter and proportions of the V_{Ni} value decreases increasing Cu concentration. According to this, a lower value of the A1 alloy lattice parameter is observed (Fig. 2). Subsequently, the lattice parameters tend to increase gradually until it reaches a maximum value at around 2.90 Å for alloys A4 and A5 with a slight difference among them (see the bottom part of Table 1). This critical point reached, is due to the number of Cu atomic planes that tend to be the same to the Ni atomic planes. Therefore, the portion of such increment over the interplanar distance *d*, decreases gradually until became almost inhibited. Fig. 2 illustrates this phenomenon on alloys A4 and A5.

On the other hand, N-alloys rich in Ni show that the lattice parameters tend to decrease increasing the Cu content. From N1 alloy to N2 alloy the lattice becomes smaller, and for N3 alloy shows a slight increment up to 2.8677 Å. Finally, once more a reduction of the N4 alloy lattice parameter takes place with 20 at.% of Cu, being this value the lowest registered in this system.

This reduction of the lattice constant "*a*" in Ni-rich alloys is due to a replacement of the Al atoms by Cu and Ni atoms. Furthermore, Cu and Ni atoms have lowest dimensions compared with the Al atom, vanishing Al content, and by increasing either Ni or Cu until 50 at.% of the Al atoms these are substituted by atoms or atomic planes of one of two Ni or Cu elements. Hence, observing the decrease of interplanar distance as well as for the lattice constant. The preceding results are in good agreement with the theoretical data obtained by Bozzolo et al. [18] by means of the BFS method, confirming the validity of his model.

3.3. Microhardness

The Vickers microhardness results for A-type alloys and N-type alloys are shown in Fig. 3 as a function of the elemental composition. By comparison with the NiAl compound reported [16], for the Al-rich alloys, it could be observed for all the composition range, the microhardness substantially exceeds the NiAl microhardness values. Although, the A1 alloy with the lowest Cu content, which is close to the stoichiometric composition of NiAl the rest of the Al-rich alloys behaves distinctly.

Regarding the Ni-rich alloys their microhardness values are lower from the NiAl reported within the composition range of $37 < Al < 50$ in at.%; however, is slightly higher compared to the stoichiometry NiAl composition value.

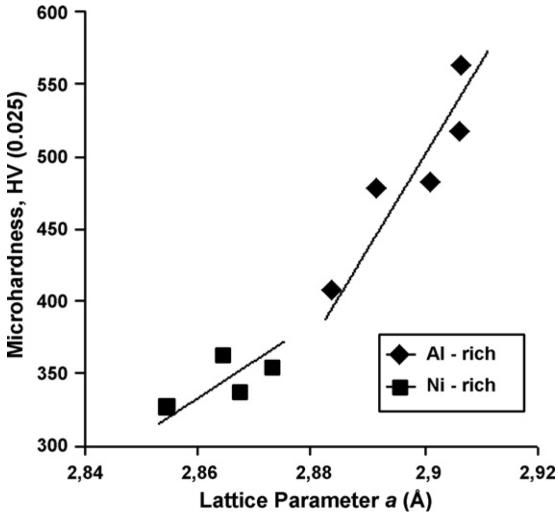

Fig. 4. Vickers microhardness (HVN 0.025) variation as a function of the lattice parameter of the alloys under study.

Furthermore, in Fig. 3 there are two insets showing the indent impression. For Al-rich alloys show a brittle behaviour (see arrows), being related to the introduction of alloying elements that could augment the β-phase lattice parameter and does not induce a second phase formation that will be able to generate alloys with elevated hardness and excessive brittleness. For Ni-rich alloys, the alloying addition induce a slight increment of the β-lattice parameter and at the same time promote the generation of a second phase like $\beta + \gamma'$, are willing to develop less hardness alloys with a fewer susceptibility to brittle fracture, as shown in Fig. 3.

Therefore, the results indicate that the microhardness in the two alloy groups studied is different depending on the path followed starting at the binary NiAl stoichiometric composition, also suggesting a strong dependence of the elemental composition.

Lattice defects provoke the intermetallic reinforcement as reported elsewhere [16]. However, lattice defects can increase or decrease intermetallic hardness among other mechanical properties. The strengthening of the binary NiAl intermetallic compound is drastically amplified moving forward the Al-rich side as in the case of A-alloys. This condition can be explained in the basis of a major lattice distortion due to substructure defects, leading higher microhardness values as already observed for Al-rich alloys.

In Fig. 4 the microhardness values as a function of the lattice parameter of the studied alloys were plotted. Strong lattice parameter dependence over the microhardness is depicted. Consequently, the introduction of alloying elements that could enhance the β-phase lattice parameter and does not induce a second phase formation will be able to generate alloys with elevated hardness and excessive brittleness.

4. Conclusions

Cu additions to the NiAl rich in Al, produce a Cu atom substitution in Ni sites (Cu_{Ni}) leading to an increment in the lattice parameter "*a*" of the β-phase. Such increment on the lattice parameter is due to Cu atom slightly bigger than Ni atom. This atom substitution induces a strong distortion of the lattice and higher Vickers microhardness values can be observed as a consequence. Elevated embrittlement and almost null fracture resistance is generally present too. In Ni-rich alloys, Cu additions produce Cu atoms substitution in Al sites reducing the β-phase lattice parameter values "*a*" and also microhardness values. Furthermore these values are lower than that reported in the literature for the NiAl binary system. So, these results suggest that for the NiAl intermetallic system, the addition of alloy elements that increment the lattice parameter value, lead to the formation of alloys with elevated brittleness and hardness. On the other hand, such elements that do not increment the lattice parameter and can be capable to form a second phase, led to obtain alloys with lower hardness values and better mechanical properties. Bozzolo model [18] was experimental corroborated with respect to the Cu atoms with the ability to substitute Ni atoms in Al-rich alloys and that Cu substitutes Al sites in Ni-rich alloys.

There is a correlation between the Cu content with the microhardness values and the "*a*" parameter; in the present case the Al-rich tend to increase and Ni-rich shows a random behaviour.

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