

# MECHANICAL ALLOYING OF NICKEL ALUMINIDES AND Ni AND PHASE TRANSFORMATION DURING HEATING OF MILLING PRODUCT

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**Abstract.** The nanocrystalline powders with stoichiometric  $\text{Ni}_3\text{Al}$  composition were prepared by ball milling of  $\text{AlNi}$  or  $\text{Al}_3\text{Ni}_2$  intermetallics with addition of Ni powder. The phase and structural changes occurring in the materials during mechanical alloying and during subsequent heating in a calorimeter were investigated with the use of X-ray diffraction. It was found that for both initial powder mixtures at the first stage of the mechanical alloying process, a supersaturated Ni(Al) solid solution was formed, and this phase remained as the only milling product. Upon heating of these powders in the calorimeter, the Ni(Al) solid solution transformed into the ordered  $\text{Ni}_3\text{Al}$  intermetallic compound. The microstructure of the  $\text{Ni}_3\text{Al}$  intermetallic compound was examined using transmission electron microscopy.

## 1. INTRODUCTION

The synthesis of alloys by mechanical alloying (MA) of elemental powder mixtures has been studied intensively over the last years [1-3]. The MA process leads to the alloys formation by the solid state reaction assisted by severe plastic deformation that occurs during ball milling. Therefore problems such as big difference in melting point of alloying components, segregation or evaporation that could occur during melting and casting can be overcome by using MA process. The advantage of this process originates also from the fact that it allows to obtain materials far from thermodynamic equilibrium. In particular the MA process can yield a nanocrystalline or amorphous structures [1-3]. Nanocrystalline

materials are potentially attractive for many applications since the reduction of the grain size to the nanometer scale can improve their physical and mechanical properties [4,5]. Due to the nanocrystalline structure, some properties such as high strength and hardness [6,7], ductilization of brittle materials [8,9] and enhanced diffusivity [10] superior to conventional materials may be obtained. One of the classes of materials that are widely produced by the MA process are supersaturated solid solutions. If they have proper chemical composition, their structure orders and they transform into intermetallic compounds upon thermal stimulus.

The Ni-Al based intermetallic compounds possess advantageous properties: high tensile strength

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and yield point, low density, high-temperature creep resistance and good corrosion and oxidation resistance at elevated temperatures [11,12]. Therefore the nickel aluminides are attractive for structural applications at elevated temperatures in hostile environments [11,12]. One of the intermetallics for high-temperatures application is  $\text{Ni}_3\text{Al}$  with the f.c.c. ordered  $\text{L1}_2$  structure.

The synthesis of alloy with composition Ni-25%Al (at.%) by MA of elemental powder mixtures was reported in a few works [13-15]. The final product of these processes was a supersaturated solid solution Ni(Al). Recently we obtained Ni-25%Al alloy with the same structure not by MA of elemental powders, but by milling of AlNi or  $\text{Al}_3\text{Ni}_2$  nickel aluminides with addition of Ni [16]. Further heating of produced powders in the calorimeter induced the transformation of Ni(Al) solid solution into the ordered  $\text{Ni}_3\text{Al}$  intermetallic compound. In the present work we extend the previous study.

## 2. EXPERIMENTAL

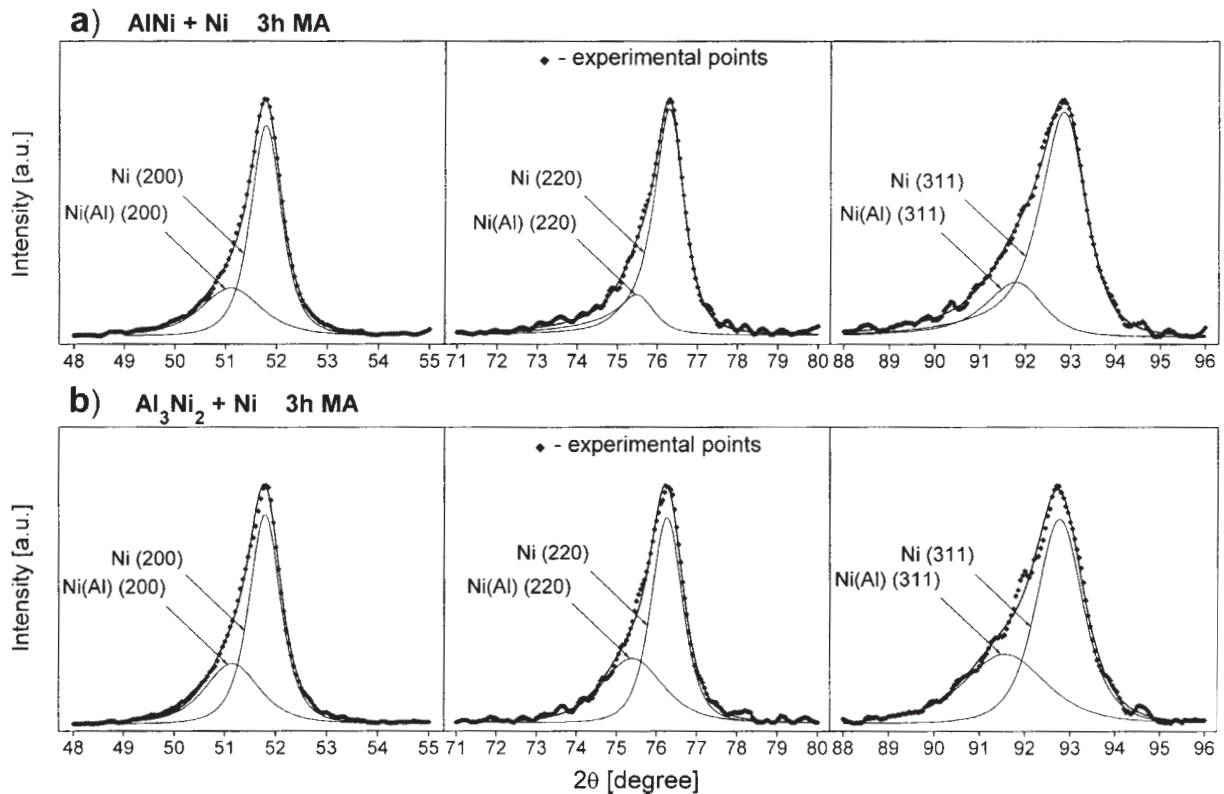
Powderised AlNi or  $\text{Al}_3\text{Ni}_2$  intermetallic compounds were blended with Ni powder in appropriate proportions to obtain overall Ni-25%Al (at.%) composition in both cases. The AlNi and  $\text{Al}_3\text{Ni}_2$  phases were produced by arc melting and then crushed into powder. The prepared powder mixtures were subjected to mechanical alloying. The milling process was performed using a SPEX 8000 D high-energy ball mill, with a steel vials and balls, under argon atmosphere, to prevent sample oxidation. The ball-to-powder weight ratio was 10:1. The sampling was carried out after 1, 2, 3, 6, 10, 20, and 30 hours of milling process, using glove bag, under argon atmosphere.

The phase evolution that occurred in the powders during milling was investigated by X-ray diffraction (XRD) in a Philips PW 1830 diffractometer using  $\text{CuK}_{\alpha}$  radiation. The lattice parameters were calculated from the XRD data taking into account  $\text{Cu K}_{\alpha 1}$  radiation, after  $\text{K}_{\alpha 2}$  stripping. The thermal behavior of the milling products were examined by differential scanning calorimetry (DSC) in a Perkin Elmer DSC7 calorimeter in a temperature range 50 -720 °C with a heat-up rate of 20 °/min. Specimens after heating in the calorimeter were investigated by XRD and transmission electron microscopy (TEM). Structural observations of the milling product by were carried out with a Philips EM300 microscope. The specimens for the TEM investigations were prepared by embedding the annealed powder in an epoxy

resin followed by thinning by mechanical grinding, dimpling and finally Ar ion beam milling.

## 3. RESULTS AND DISCUSSION

The phase changes occurring in the powder during milling and the results of structural investigations carried out using XRD and DSC have already been described [16]. It was concluded that during the MA processes of the AlNi+Ni and  $\text{Al}_3\text{Ni}_2$ +Ni powder mixtures, in both cases, Ni(Al) supersaturated solid solutions is formed. After about 15 h of milling, for both processes, the steady-state stage is reached and after 30 h of MA the product – Ni(Al) – is nanocrystalline with a crystallite size, estimated by the Williamson-Hall method, of about a dozen nm [16]. Now we analyze the early stage of performed processes in more detail. The XRD results demonstrate that in both cases at the early stage of the MA process (less than 6 h of milling in this experiment) the intensity of the aluminides diffraction peaks decreases progressively with respect to that of the f.c.c. Ni peaks [16]. Simultaneously the Ni diffraction peaks profiles become asymmetric - broader on the low-angle shoulder. This can be due to the appearance of broad and low intensive peaks on the left side of the Ni peaks. These additional peaks can be attributed to a new phase which possesses the same structure type as the f.c.c. Ni, but a little larger unit cell parameter. Taking into account vanishing of aluminides peaks and that milled phases consist of Ni and Al atoms, we expect that the new phase is the f.c.c. Ni(Al) solid solution. The asymmetric peaks in the diffraction pattern can be fitted using the pseudo-Voigt function with pairs of overlapping symmetric peaks – more intense one related to Ni and the other one, less intense, attributed to Ni(Al). This fitting allows to the deconvolution of asymmetric diffraction profiles and to analyse peaks of each phase. Since the (111) peaks of Ni and Ni(Al) are superimposed by the NiAl (110) peak or by the  $\text{Al}_3\text{Ni}_2$  (110) and (102) peaks deconvolution of diffraction profile situated at 45.5° is incredible, so we ignored the Ni (111) peak in analysis. In the case of milling of the  $\text{Al}_3\text{Ni}_2$ +Ni powder mixture the (200) peaks of Ni and Ni(Al) are superimposed by the  $\text{Al}_3\text{Ni}_2$  (200) peak. However, in the XRD pattern of the specimen after 2 h of the MA process the free of overlapping  $\text{Al}_3\text{Ni}_2$  (101) peak (which has a relative intensity of 30% [17]) is not present, therefore we can assume that the contribution of the  $\text{Al}_3\text{Ni}_2$  (200) peak (which has a relative intensity of 4% [17]) in the intensity of asymmetric diffraction profile situated at 51.9° is negligible. This allows us to fit and



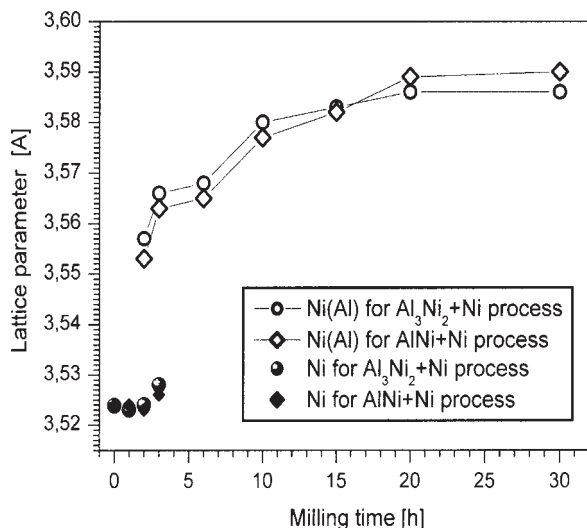
**Fig. 1.** Based on fitting decomposition of asymmetric XRD profiles into Ni and Ni(Al) peaks for a) AlNi+Ni and b) Al<sub>3</sub>Ni<sub>2</sub>+ Ni powder mixtures after 3 h of MA process.

analyse this asymmetric peak as well as (220) and (311) peaks of Ni and Ni(Al), which are free of overlapping by peaks of aluminides. This procedure was performed for the powders mechanically alloyed for 2 and 3 h. The results of the fitting of the XRD pattern of 3 h milled AlNi+Ni sample and Al<sub>3</sub>Ni<sub>2</sub>+Ni sample, are shown in Fig. 1a and Fig. 1b, respectively (for 2 h of milling the results of fitting are very similar). One can see that the Ni(Al) peaks are very broad, suggesting very small crystallite size in the solid solution. After 6 hours of the MA process the diffraction lines of AlNi or Al<sub>3</sub>Ni<sub>2</sub> aluminides disappear whereas remaining lines are no more asymmetric and can be related to one f.c.c. phase - Ni(Al) [16]. The lattice parameter values, estimated using angular peaks positions determined on the basis of fitting results, are illustrated in Fig. 2 as a function of milling time. The calculations based on peaks positions were performed using both the Ni and Ni(Al) lines for 2 and 3 h, and the Ni(Al) lines for longer milling times. As one can see during the first 3 hours of the milling process the lattice parameter of Ni is

nearly constant, whereas after 2 hours the lattice parameter of the newly-created Ni(Al) is noticeably larger than that of Ni. During the first 15 hours of milling the lattice parameter of Ni(Al) increases and reaches steady value of about 3.588 Å. Since, according to the equilibrium diagram [18] the maximum concentration of Al that can be dissolved in Ni lattice at room temperature is about 5 at.%, the product of both performed MA processes is metastable supersaturated solid solution Ni(Al).

From the XRD results we can conclude that for both milled compositions – AlNi+Ni and Al<sub>3</sub>Ni<sub>2</sub>+Ni powder mixtures – in the first step of milling small zones of supersaturated f.c.c. Ni(Al) solid solution form. After 2 and 3 h of both MA process three phases: Ni, Ni(Al) and nickel aluminide coexist in the milled material. On the basis of our up to date results we can not conclude definitely about the mechanism of formation of Ni(Al) supersaturated solid solution at this stage of the MA processes. However, two paths can be considered as possible: (i) under severe plastic deformation, which takes

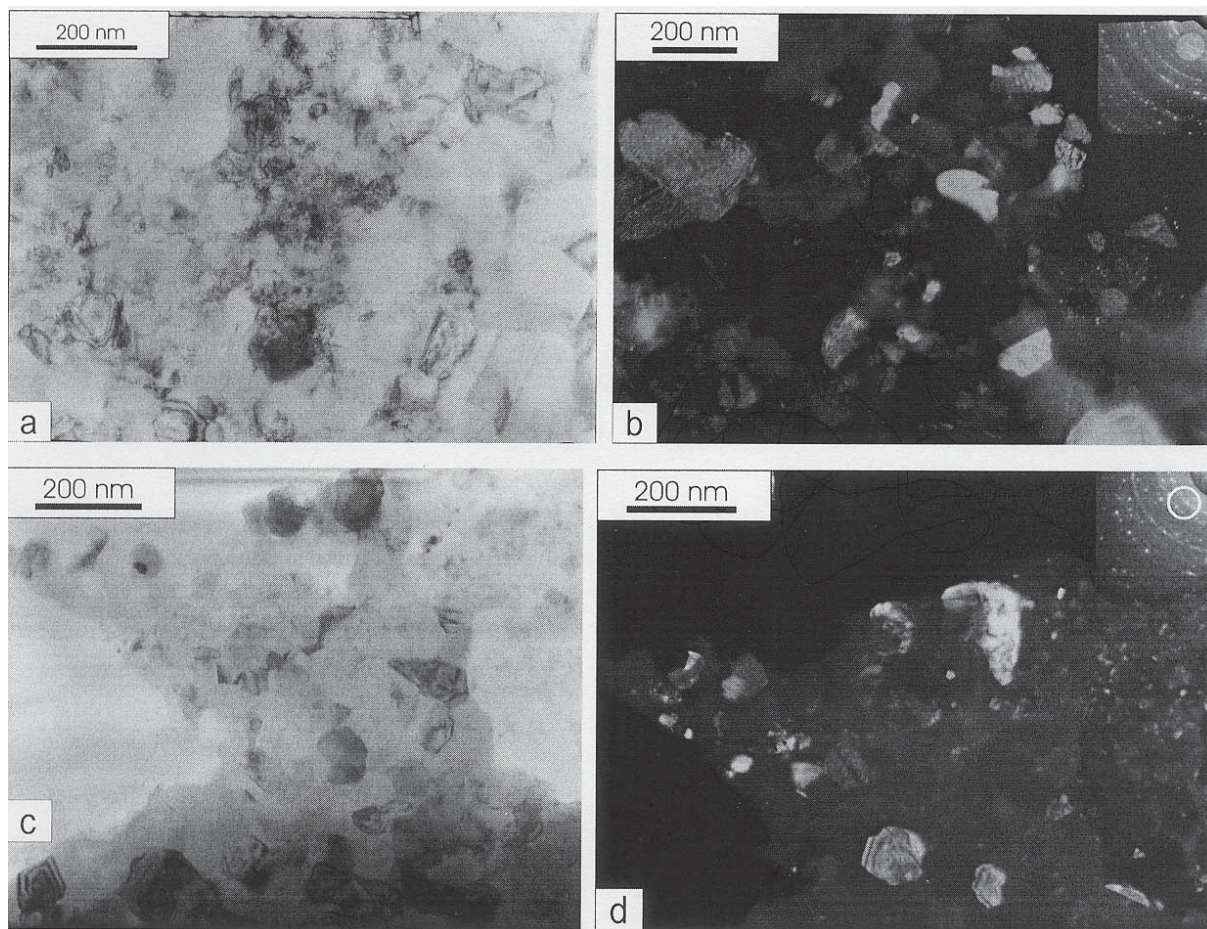




**Fig. 2.** The lattice parameter of Ni(Al) and Ni as a function of milling time.

place during ball collisions, defects concentration increases in some regions of nickel aluminides, they lost ordering and could transform into disordered Ni(Al) solid solution and (ii) when Ni and nickel aluminides powder particles are cold welded during ball collisions, in the vicinities of Ni/aluminides interfaces, very small interdiffusion regions with Ni(Al) solid solution structure appear. Enhanced diffusivity of Ni [15], presumably caused by the high concentration of defects, created by plastic deformation and by the local microscopic temperature rise, surely play an important role in both described cases. Also both suggested Ni(Al) formation mechanisms can occur simultaneously.

During heating of the MA process products in the calorimeter, for both milled compositions, the Ni(Al) solid solution transforms into the ordered Ni<sub>3</sub>Al intermetallic compound [16]. Structural observations of the milling products after heating in the calorimeter were carried out by TEM. The results of this investigations are illustrated in Fig. 3. Bright field



**Fig. 3.** TEM micrographs of the milling products after heating in the calorimeter: a) bright field image, b) dark field image and selected area diffraction pattern (SADP) (top-right corner) for AlNi+Ni initial mixture, c) bright field image, d) dark field image and SADP for Al<sub>3</sub>Ni<sub>2</sub>+Ni initial mixture. The selected fragments of the rings used to obtain dark field images are indicated in SADP.

and dark field images show that, for both milled compositions, the crystallite size of Ni<sub>3</sub>Al is between 30 and 150 nm. The mean crystallite size of this compound, estimated from XRD results by the Williamson-Hall method, was of about 40 nm [16]. This average value estimated using XRD data is not at variance with TEM results, which are qualitative, not quantitative.

#### 4. CONCLUSIONS

During the MA processes of the AlNi+Ni and Al<sub>3</sub>Ni<sub>2</sub>+Ni powder mixtures, in both cases, in the first step of milling small zones of supersaturated f.c.c. Ni(Al) solid solution form. In this stage of the MA process three phases: Ni, Ni(Al) and nickel aluminide coexist in the milled material. After 6 hours of the MA process the diffraction lines of AlNi or Al<sub>3</sub>Ni<sub>2</sub> aluminides disappear whereas remaining lines can be related to single f.c.c. phase – Ni(Al). TEM observations of the milling products after heating in the calorimeter reveal that, for both milled compositions, the crystallite size of Ni<sub>3</sub>Al intermetallic compound (into which Ni(Al) transformed during heating) is between 30 and 150 nm.

#### ACKNOWLEDGEMENTS

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