NANOCRYSTALLINE Ni$_3$Al ALLOY OBTAINED BY MECHANICAL ALLOYING AND SUBSEQUENT HEATING

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Abstract. Nanocrystalline powders with stoichiometric Ni$_3$Al composition were prepared by ball milling of Al$_3$Ni intermetallic compound or Ni-4%Al solid solution with addition of Ni powder and Al powder respectively. The thermal stability of the milled powders was investigated using differential scanning calorimetry. The phase and structural transformations occurring in the samples during mechanical alloying and during subsequent heating in the calorimeter were investigated using X-ray diffraction. In the cases of both starting powders compositions, small zones of supersaturated Ni(Al) solid solution were formed during the first step of milling. Upon further milling, the Ni(Al) solid solution was formed in the whole content of the milled material. During heating of the milling products in the calorimeter, the Ni(Al) solid solution transformed into an ordered Ni$_3$Al intermetallic compound. The powders after milling as well as after subsequent heating were nanocrystalline.

1. INTRODUCTION

Mechanical alloying (MA) is a practical processing route for synthesis of alloys [1]. One of the classes of materials, that are widely produced by the MA process, are supersaturated solid solutions [1]. For the specified chemical composition their structure orders upon thermal stimulus and they transform into intermetallic compounds.

The Ni$_3$Al intermetallic compound possesses advantageous properties, in particular high specific strength (strength-to-density ratio), good high-temperature creep resistance and good corrosion and oxidation resistance at elevated temperatures [2]. These features make the Ni$_3$Al intermetallic compound a very attractive material for structural applications at elevated temperatures in hostile environments [2]. In the recent years a number of studies have been reported on obtaining Ni-25%Al (at.%) alloy by MA of elemental powder mixtures [3]. The disordered Ni(Al) solid solution was the product of the MA process in all mentioned cases.

Usually it is mixtures of elemental powders that are used as substrates of the MA process. However, a mixture of a powderised alloy and an elemental powder can also be used as a starting material. Recently we obtained Ni-25%Al alloy with the solid solution structure not by MA of elemental powders, but by milling of Al-Ni alloys – AlNi or Al$_3$Ni$_2$ nickel aluminides – with addition of Ni [4,5]. Further heating of produced powders in the calorimeter induced the transformation of Ni(Al) solid solution into the ordered Ni$_3$Al intermetallic compound [4,5]. Ordering of the Ni(Al) solid solution and its transformation into Ni$_3$Al intermetallic compound was also found during the compaction process of the powders after milling processes mentioned above [6], similarly as throughout heating in the calorimeter. Furthermore, very limited growth of grains took place in the material during the applied consolidation process and bulk nanocrystalline Ni$_3$Al intermetallic was obtained [6]. In the present work, we use as starting materials for mechanical alloying

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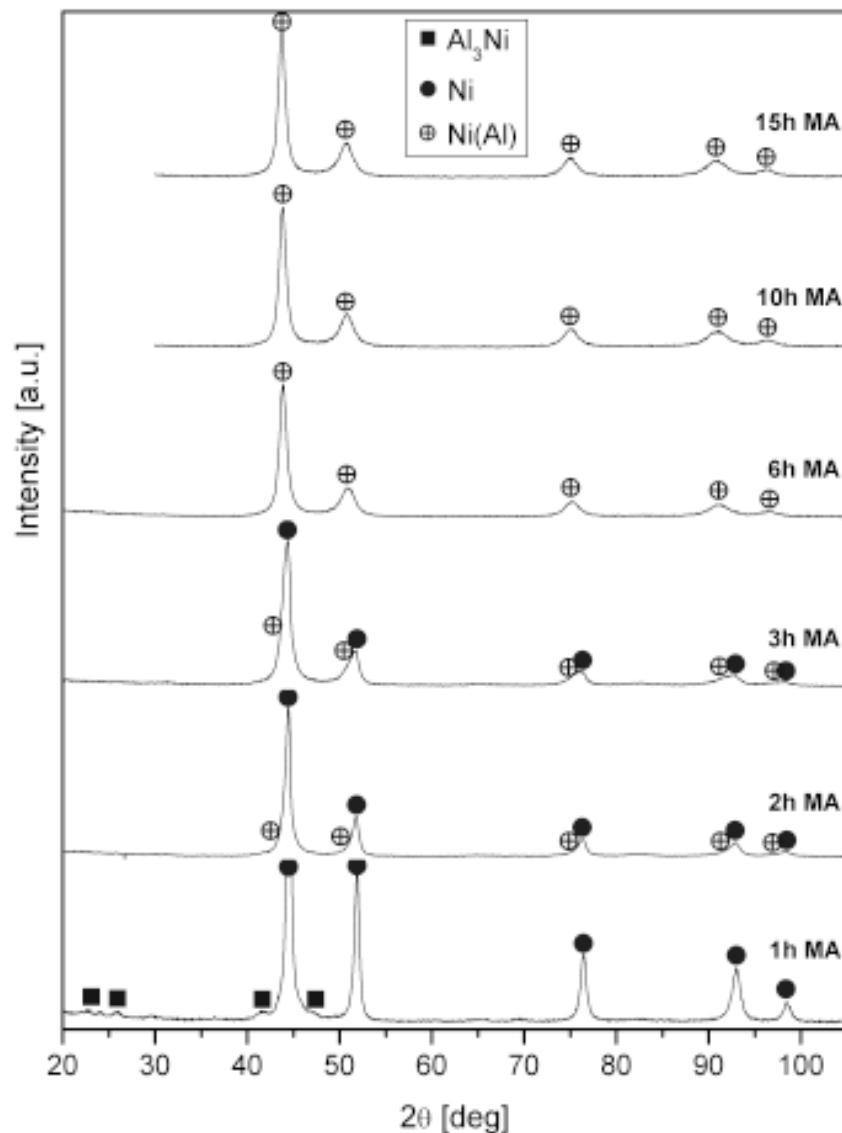
Fig. 1. XRD patterns of the Al₃Ni + Ni powder mixture after various milling times.

other alloys from the Al-Ni system – Al₃Ni aluminide or Ni-4%Al solid solution, which are milled with Ni and Al powder respectively.

2. EXPERIMENTAL

Powderised Al₃Ni aluminide and $Ni_{96}Al_4$ solid solution were blended with Ni and Al powder respectively, in proportions appropriate to obtain overall Ni-25%Al (at.%) composition in both cases. The Al₃Ni alloy was produced by vacuum casting while the $Ni_{96}Al_4$ one by arc melting. Then the alloys were crushed into powder. The prepared powder mix-

tures were subjected to mechanical alloying. The milling process was performed under argon atmosphere, using a SPEX 8000 D high-energy shaker ball mill. The ball-to-powder weight ratio was 10:1. The sampling of the powder after various milling times was carried out under argon atmosphere. The phase evolution that occurred in the powders during milling was investigated by X-ray diffraction (XRD) method in a Philips PW 1830 diffractometer using CuK_α radiation. The lattice parameters, the mean crystallite size and the mean lattice strain (the latter two estimated by the Williamson-Hall
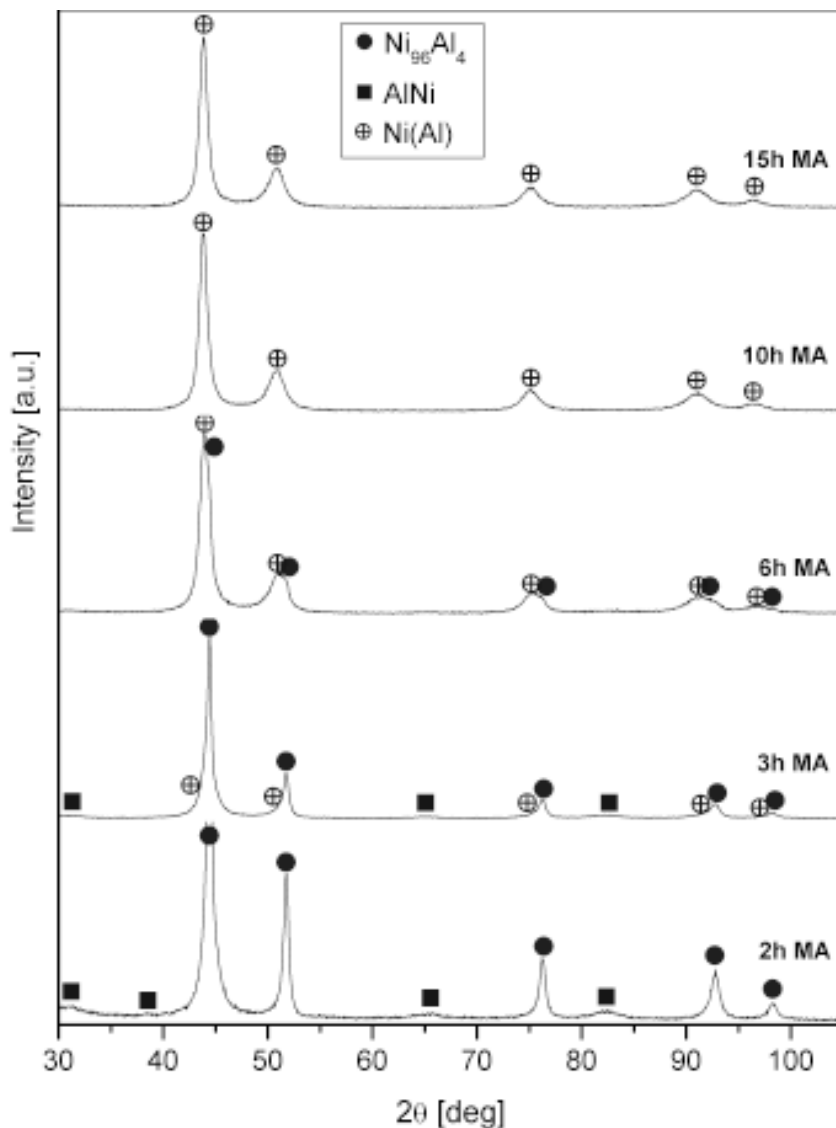
**Fig. 2.** XRD patterns of the $Ni_{96}Al_4$ + Al powder mixture after various milling times.

method) were calculated from the XRD data taking into account $CuK_{\alpha 1}$ radiation, after $K_{\alpha 2}$ stripping. The instrumental broadening was determined using a Si standard and subtracted from the experimental breadth to obtain the physical broadening of each diffraction line, which was then used for the Williamson-Hall calculations. The thermal behaviour of the milling products was examined by differential scanning calorimetry (DSC) in a Perkin Elmer DSC7 calorimeter in the temperature range from 50 to 720 °C at a constant heating rate of 20 °C/min.

3. RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the XRD patterns of the powder mixtures Al_3Ni + Ni and $Ni_{96}Al_4$ + Al respectively after various times of the milling process. It can be seen that in the case of Al_3Ni + Ni (Fig. 1), in the initial stage of milling process, the diffraction peaks attributed to Al_3Ni fade after 2 h, whereas the profiles of the Ni diffraction peaks become asymmetric – their low-angle shoulders are broadened. The reason for this is the appearance of broad and low intensive peaks on the left side of the Ni peaks. These additional peaks can be at-
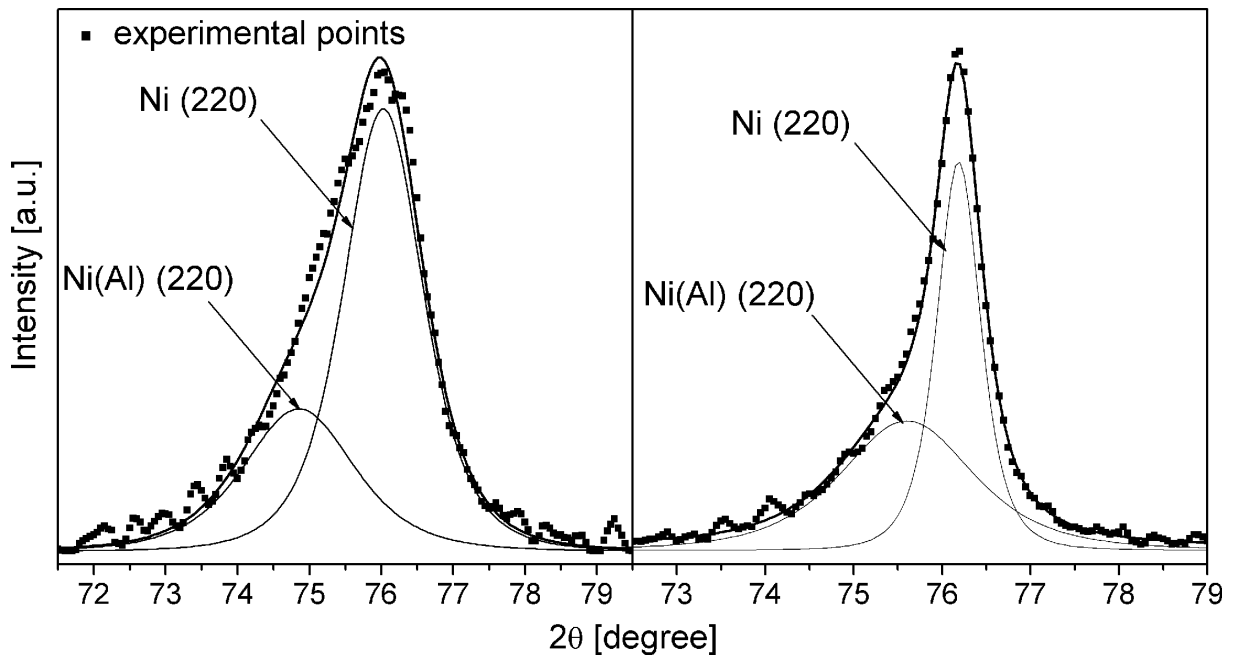
Fig. 3. Deconvolution of the observed (220) peak profiles after 3 h of milling: a) for Al$_3$Ni + Ni and b) for Ni$_{96}$Al$_4$ + Al powder mixtures.
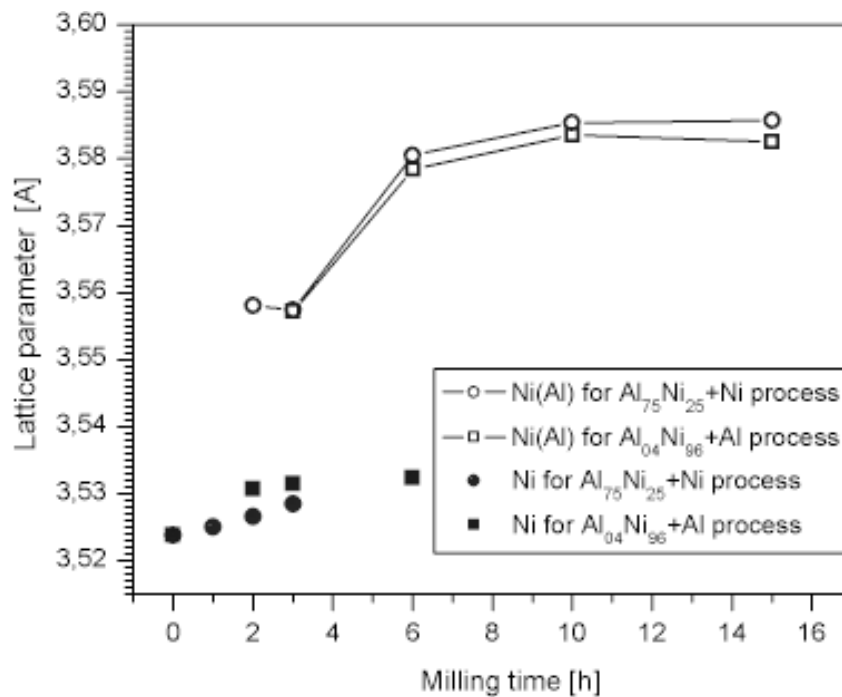
Fig. 4. Lattice parameter of Ni(Al) for Al$_3$Ni + Ni and Ni-4% + Al powder mixtures after various times of milling.

tributed to a new phase which possesses the same structure type as the fcc Ni but is characterised by a slightly larger lattice parameter. This fact, coupled with vanishing of the peaks of Al$_3$Ni phase, which is Al rich, suggests that the new phase is the fcc Ni(Al) solid solution. The asymmetric peaks in the diffraction pattern can be fitted, using the pseudo-Voight function, with pairs of overlapping symmet-
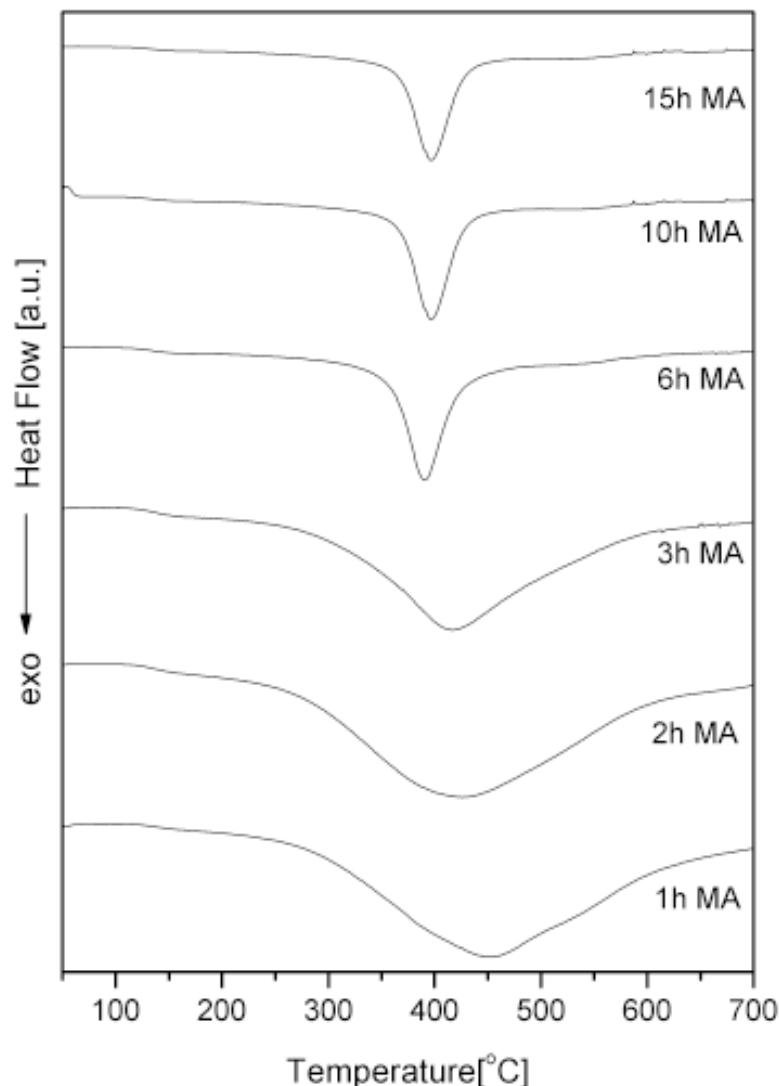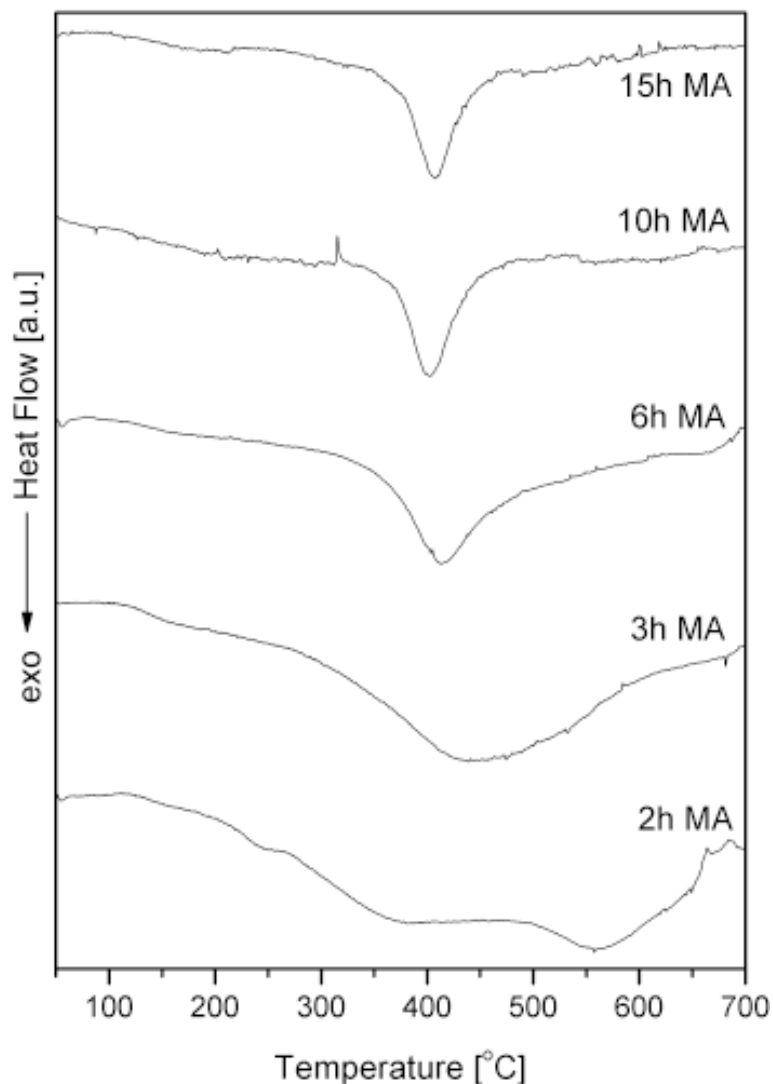
Fig. 5. DSC curves for the Al$_3$Ni + Ni powder mixture after various milling times.

ric peaks – more intense ones related to Ni and the other ones, less intense, attributed to Ni(Al). This fitting procedure allows the deconvolution of asymmetric diffraction profiles and the analysis of the peaks of each phase. The result of the fitting procedure is shown in Fig. 3a for the fcc (220) peak of 3 h milled Al$_3$Ni + Ni sample, as an example. One can see that the Ni(Al) (220) peak is very broad, which suggests very small crystallite size in the solid solution. The lattice parameter values of the Ni(Al) solid solution and Ni, estimated using angular peaks' positions determined on the basis of fitting results, are illustrated in Fig. 4 as a function of milling time. As one can see, during the first

3 h of the milling process the lattice parameter of Ni is nearly constant, whereas after 2 h the lattice parameter of the newly-created Ni(Al) becomes noticeably larger than that of Ni, which indicates significant concentration of Al in the Ni based solid solution. After 6 h of MA the Ni peaks disappear, so that diffraction lines are no longer asymmetric and can be related to one fcc phase – Ni(Al). With the increase of milling time, the lattice parameter of Ni(Al) increases and after 10 hours reaches a steady value of about 3.586 Å. The mean crystallite size of produced Ni(Al) solid solution is of about 16 nm and the mean lattice strain of 0.73%.

Fig. 6. DSC curves for the $Ni_{96}Al_4$ + Al powder mixture after various milling times.

In the case of mechanical alloying of $Ni_{96}Al_4$ + Al powder mixture (Figs. 2 and 3b) the similar situation i. e. appearance of $Ni_{96}Al_4$ asymmetric diffraction peaks profiles is found. However, this occurrence is observed for a longer milling time than previously – till 6 h of the process. This fact indicates that during milling of $Ni_{96}Al_4$ + Al powder mixture the phase evolution proceeds slower than during milling of Al_3Ni + Ni powder mixture. Another feature which can be seen in Fig. 2 is that at the early stage of the milling process (up to 3 h) the diffraction lines of the NiAl phase appear. This phase can be easily formed by MA given its low enthalpy of formation [7]. The NiAl peaks disappear after 6 h of milling, while after 10 h of the process the remaining diffraction lines are no more asymmetric and the steady-state processing stage is reached. Fig. 4 shows the dependence of lattice parameter of Ni(Al) and Ni on milling time. After 15 h of milling process the lattice parameter of the milling product – Ni(Al) – is equal to 3.583 Å, its mean crystallite size is of about 19 nm and the mean lattice strain of about 0.93%. Since, according to the equilibrium diagram [8], 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 a metastable supersaturated solid solution Ni(Al).
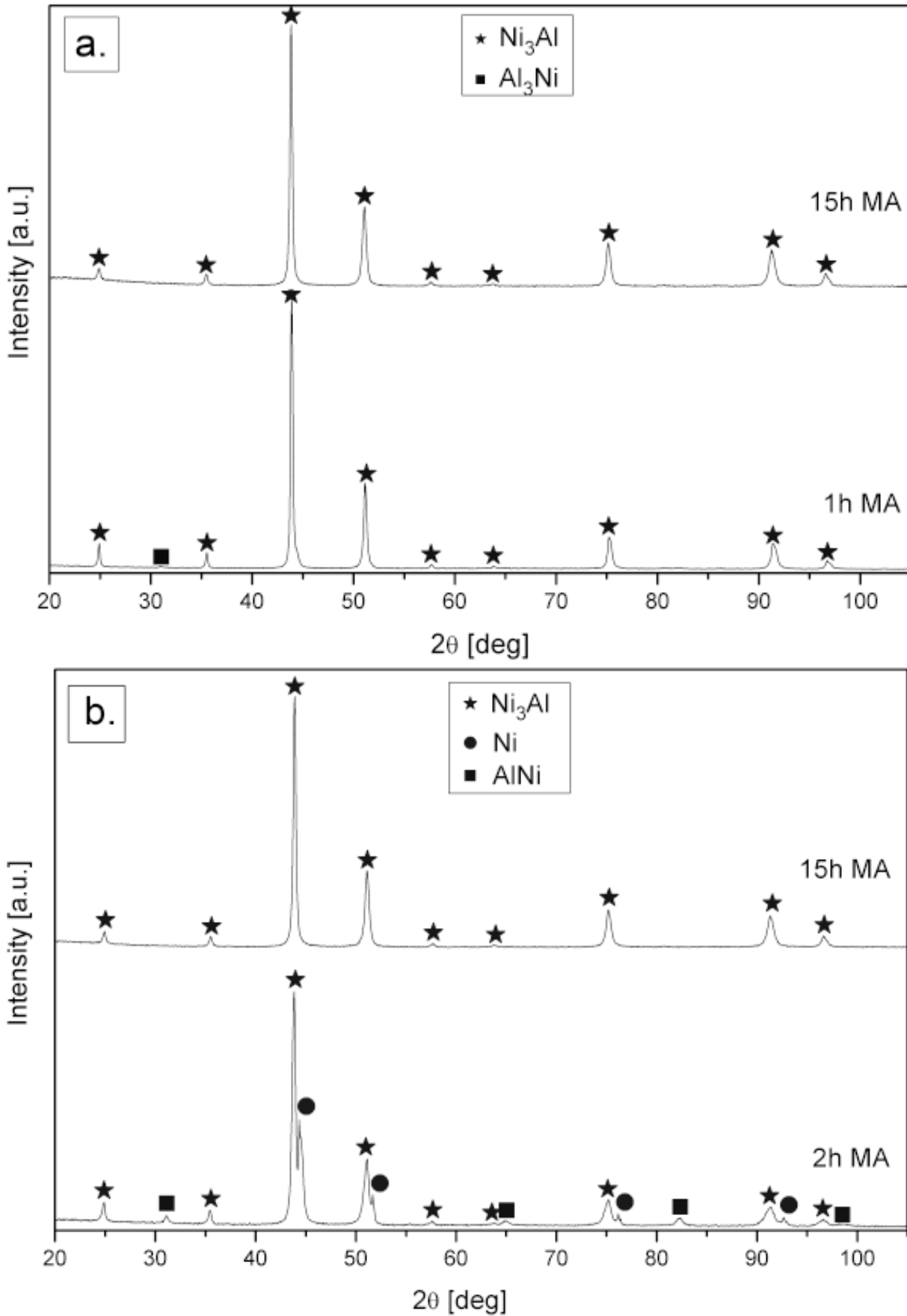
Fig. 7. XRD patterns after heating in the calorimeter of the milling products of: a) Al_3Ni + Ni, b) $Ni_{96}Al_4$ + Al powder mixtures.

On the basis of the XRD results we can conclude that for both milled compositions – Al$_3$Ni + Ni and Ni$_{96}$Al$_4$ + Al powder mixtures – in the first step of milling small zones of supersaturated fcc Ni(Al) solid solution form. At this stage of the process this newly-created Ni(Al) coexists with Ni or Ni$_{96}$Al$_4$, in the case of the first and the second starting mixture respectively. We observed similar situation during mechanical alloying of AlNi+Ni and Al$_3$Ni$_2$+Ni powder mixtures [5]. We considered two possible paths of newly-created Ni(Al) formation [5]: (i) under severe plastic deformation, which takes place during ball collisions, defects concentration increases in some regions of nickel aluminides, they lose ordering and can 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, 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. Both suggested Ni(Al) formation mechanisms can also occur simultaneously. In the present work, the ways of Ni(Al) formation described above can be considered only in the case of the milling of Al$_3$Ni + Ni starting mixture. In the second case we infer that in the first step of milling, when the Ni$_{96}$Al$_4$ and Al powder particles are cold welded during ball collisions, very small regions appear in which Al atoms are dissolved in the lattice of Ni based alloy, creating "primary" fcc Ni(Al) solid solution zones with the lattice parameter considerably changed with respect to that of Ni$_{96}$Al$_4$ alloy. This indicates that the concentration of Al in these zones has a composition close to ultimate at the very beginning of the MA process. This kind of new phase development has been described for mechanical alloying of Al-Fe powders [9].

Figs. 5 and 6 show DSC traces for the Al$_3$Ni + Ni and Ni$_{96}$Al$_4$ + Al powder mixtures respectively, after different stages of milling process. In all cases for both compositions one can see a broad exothermic peak which becomes narrower and shifts to lower temperatures with the increase of milling time. This peak is most probably associated with ordering of Ni(Al) solid solution and transformation into Ni$_3$Al phase. To verify this suggestion, the samples subjected to DSC were next investigated by XRD. The results for the final milling products are plotted in Fig. 7. For both starting mixtures, in the XRD patterns of powders after 15 h of MA and heating in the calorimeter only diffraction lines of a phase identified as Ni$_3$Al intermetallic are present. The lattice parameter of Ni$_3$Al phase is equal to 3.575 Å and 3.573 Å for the heated products of milling of the Al$_3$Ni + Ni and Ni$_{96}$Al$_4$ + Al powder mixtures respectively. Hence, the XRD results confirm the origin of the exothermic effects, mentioned above. Comparing XRD patterns after DSC experiments with the ones obtained before heating, one can see that all the peaks become a little sharper than those in the pattern of the as-milled powder. This reduction of the peaks width is certainly due to the increase of the mean crystallite size and the decrease of the mean lattice strain. After heating the Al$_3$Ni + Ni powder mixture milling product in the calorimeter, the mean crystallite size and the mean lattice strain of Ni$_3$Al are 31 nm and 0.05% respectively. These values after heating of the second starting composition milling product are 32 nm and 0.08% respectively.

4. CONCLUSIONS

Supersaturated Ni(Al) solid solution was the final product of mechanical alloying of Al$_3$Ni + Ni or Ni$_{96}$Al$_4$ + Al powder mixtures blended in proportions appropriate to obtain an overall Ni-25%Al (at.%) composition in both cases. It was found that at the first stage of milling small zones of supersaturated Ni(Al) solid solution were formed. Upon further milling, the Ni(Al) solid solution was formed in the whole content of the milled material. The milling products were nanocrystalline with mean crystallite size of 16 and 19 nm. During heating of the milling products in the calorimeter up to 720 °C, the Ni(Al) solid solution transformed into an ordered Ni$_3$Al intermetallic compound. A limited growth of grains occurred during heating in the calorimeter, however the material remained nanocrystalline.

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