PHASE TRANSFORMATIONS DURING MECHANICAL ALLOYING OF NICKEL ALUMINIDES AND SUBSEQUENT HEATING OF MILLING PRODUCT

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Abstract. In this work, nanocrystalline powders with stoichiometric Ni_3Al composition were prepared by ball milling of AlNi or Al_3Ni_2 intermetallic compounds with addition of Ni powder. The powders at different stages of the milling process were investigated by X-ray diffraction and differential scanning calorimetry to study phase transformations that occurred during mechanical alloying and during subsequent heating in calorimeter. It was found that in both cases at first stage of the milling process, a metastable 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 became ordered and transformed into the Ni_3Al intermetallic compound. The results obtained show that during heating in the calorimeter, a limited growth of grains occurred and nanocrystalline structure of powders was preserved.

1. INTRODUCTION

The synthesis of alloys, among others supersaturated solid solutions, by mechanical alloying (MA) from mixture of pure elements has been an intensively studied in the recent years [1-7]. During MA process alloys are formed by solid-state reaction. 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. This process yields an amorphous, crystalline or nanocrystalline structures [1,7]. Reduction of grain size to nanometer scale is attractive way to improve the mechanical properties of nanocrystalline alloys [8].

The Ni-Al based intermetallic compounds have good physical and mechanical properties: high tensile strength and yield point, low density, high-temperature creep resistance and good corrosion and oxidation resistance at elevated temperatures [9,10]. Therefore the nickel aluminides are attractive for structural applications at elevated temperatures in hostile environments [9,10]. One of the intermetalics for high-temperatures application is Ni_3Al. This phase has the fcc ordered $L1_2$ structure. Although there was a wide research activity in intermetallics in the last years, commercial utilization of nickel aluminides was hampered because of processing problems (big difference in melting point of Al and Ni, the exothermic nature of formation of nickel aluminides) and the low ductility of aluminides [9,10]. The MA process which, as was mentioned above, can overcome some processing problems, could be an alternative for traditional manufacturing processes like melting and casting. Furthermore nanocry-

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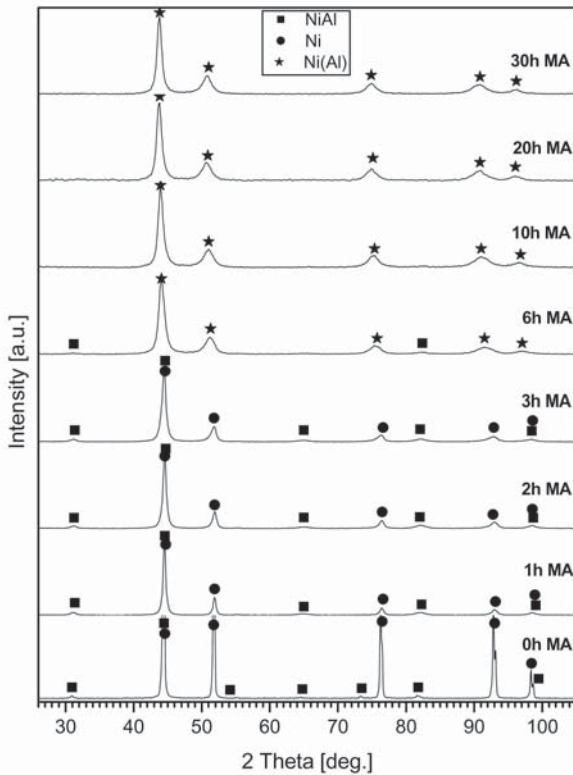
Fig. 1. XRD patterns of powder mixture AlNi+Ni after various times of milling.
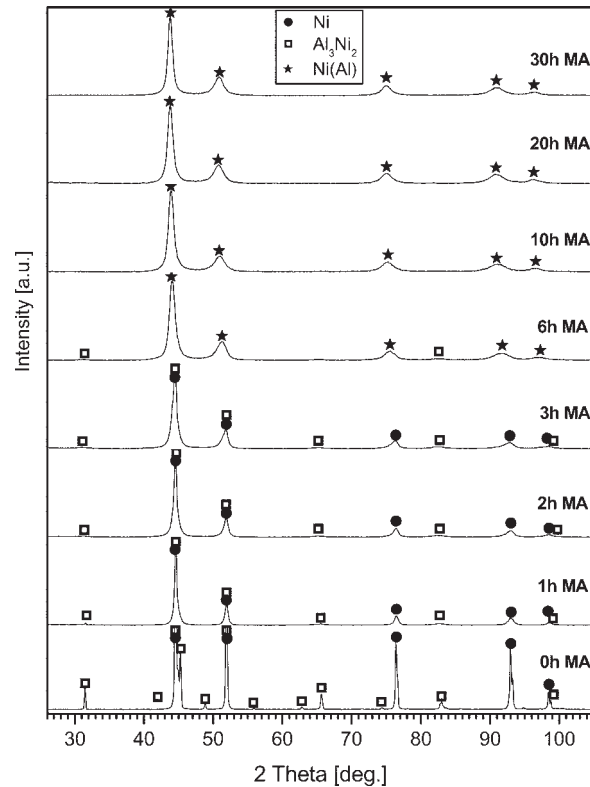

Fig. 2. XRD patterns of powder mixture Al_3Ni_2+Ni after various times of milling.

stalline structure obtain by milling can improve ductility of intermetallics [11].

The synthesis of alloy with composition Ni-25%Al (at.%) by MA of elemental powder mixtures was reported in a number of works [12-14]. The final product of these processes was supersaturated solid solution Ni(Al). In the present work we produced the same product not by MA of elemental powders, but by milling of nickel aluminides with addition of Ni.

The aim of this work was to study phase transformations during mechanical alloying of AlNi or Al_3Ni_2 with addition of Ni powder and during subsequent heating of milling product.

2. EXPERIMENTAL

Nanocrystalline powders with stoichiometric Ni_3Al composition were prepared by ball milling of powderised AlNi or Al_3Ni_2 intermetallic compounds with addition of Ni powder in appropriate amount. The AlNi and Al_3Ni_2 phases were produced by arc melting and then crushed into powder. The MA 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 in the powder during milling was investigated by X-ray diffraction (XRD) using a Philips PW 1830 diffractometer with CuK_α radiation. The lattice parameters were calculated from the XRD data. Based on the XRD patterns, the mean crystallite size was estimated by Williamson-Hall method.

The thermal effects occurred during heating of powders after different milling times were examined by differential scanning calorimetry (DSC) in a Perkin Elmer DSC7 calorimeter in a temperature range 50 – 720 °C with a heatup rate 20 °C/min. Specimens after heating were investigated by XRD.

3. RESULTS AND DISCUSSION

The XRD patterns of the powder mixtures AlNi+Ni and Al_3Ni_2+Ni in the initial stage and after different times of milling process are shown in Figs. 1 and 2. The sequence of milling results runs from the bot-
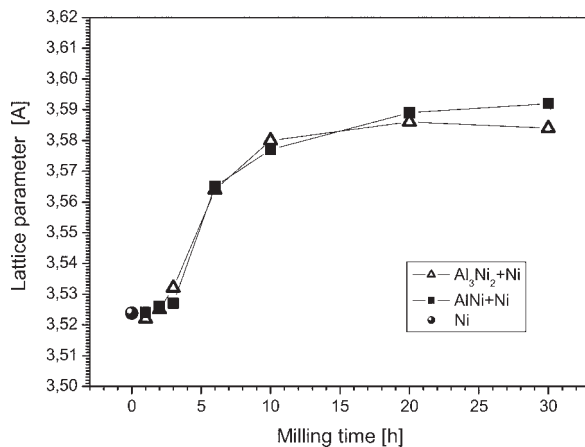
Fig. 3. Lattice parameter of Ni(Al) for AlNi+Ni and Al₃Ni₂+Ni powder mixtures after various times of milling.
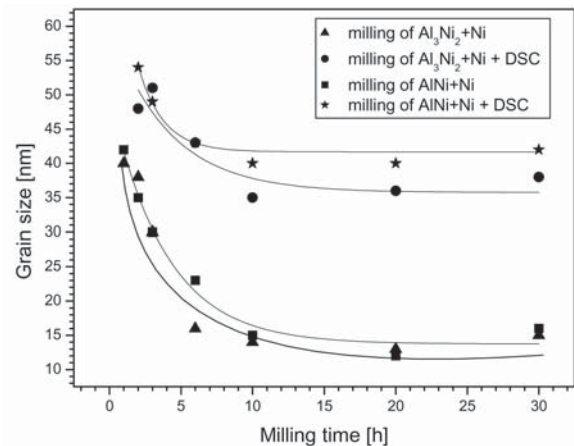

Fig. 4. Grain size of Ni(Al) for AlNi+Ni and Al₃Ni₂+Ni powder mixtures after various times of milling and after milling and subsequent heating.

tom to the top of the figure. From this results, it can be noticed that the AlNi and Al₃Ni₂ peaks disappear gradually and they are absent in the pattern after 10 h of milling. In the case of both milled powder mixtures, the Ni peaks become slightly shifted towards lower angles with the increase of the process time, which indicates increasing of the lattice parameter of Ni. These changes indicate that in the both cases a fcc Ni(Al) solid solution forms during the process. After 10 h of milling only this phase is present in the powders. It is interesting to note that the lattice parameter of the Ni(Al) (Fig. 3) after 1, 2, and 3 h of MA is at the same level, with the value similar to that of pure Ni (3.524 Å). After 6 h the value of lattice parameter raises and after 10 h of milling stabilizes reaching 3.575 Å for the AlNi+Ni milled mixture and 3.580 Å for the Al₃Ni₂+Ni milled mixture. Since, according to the equilibrium diagram [15] 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). Another feature, which can be seen in this patterns, is that all the diffraction peaks broaden with increasing milling time. This broadening is due to the reduction of the grain size and the increase of the rms atomic-level strain that take place during milling. On the base of Williamson-Hall estimation we can say that with increase of the process time, the crystallite size of appearing Ni(Al) decreases and after 10 h reaches about a dozen nm for both milled mixtures (Fig. 4).
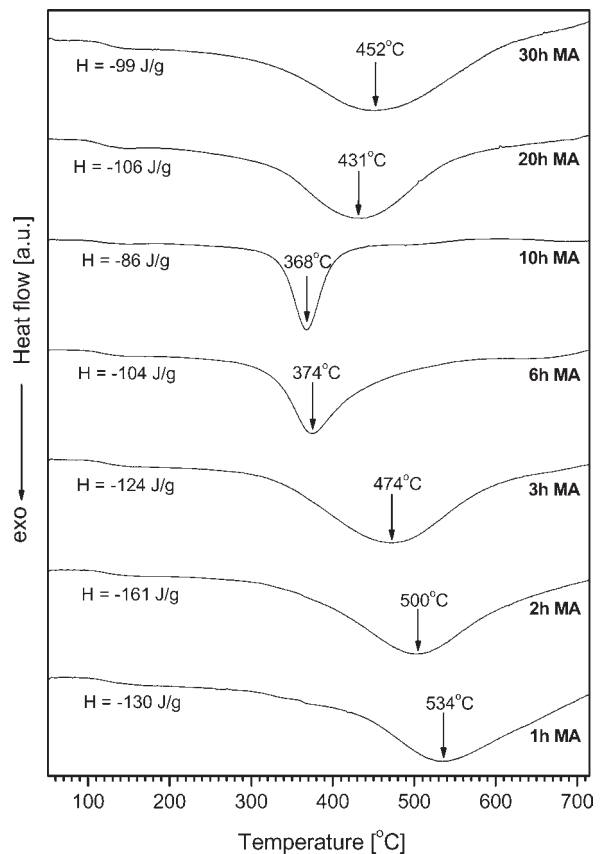

Fig. 5. DSC curves for AlNi+Ni powder mixture after various times of milling.

Figs. 5 and 6 show DSC curves for the AlNi+Ni and Al₃Ni₂+Ni powder mixtures respectively after different stages of milling process. In the case of both mixtures, for all times of MA process one exothermic peak is visible. For the Al₃Ni₂+Ni milled powder mixture this peak shifted to lower temperatures with
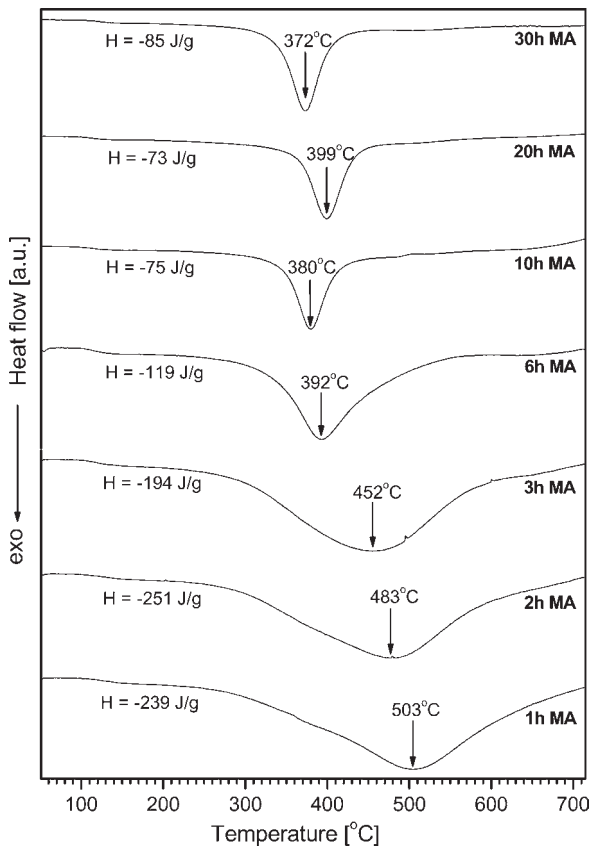
Fig. 6. DSC curves for Al_3Ni_2+Ni powder mixture after various times of milling.

Fig. 7. XRD patterns of powder mixture AlNi+Ni after various times of milling and subsequent heating.

Fig. 8. XRD patterns of powder mixture Al_3Ni_2+Ni after various times of milling and subsequent heating.

increase of MA time. In the case of the AlNi+Ni milled powder mixture the same shift of the peak is observed up to 10 h of MA and for longer milling times temperature of the peak increases. For explanation of these peak temperature changes further work is in progress. The observed exothermic peak is due most probably to the ordering of Ni(Al) solid solution and transformation into Ni_3Al phase. In order to verify this supposition the samples subjected to DSC were next examined by XRD.

The XRD patterns of the powders after heating in the calorimeter are plotted in Figs. 7 and 8. Comparing with XRD patterns before DSC experiments it can be notice that after 1 h of milling and heating in the powders appear new phase identified as Ni_3Al and small amount AlNi or Al_3Ni_2 phases is still present. After 30 h of milling and heating in the powder there is only one phase - Ni_3Al. The dependence of grain size of the formed during heating in the calorimeter Ni_3Al phase on MA time is showed in the Fig. 4. For all times the grain size after DSC heating is larger than after milling and is in the range
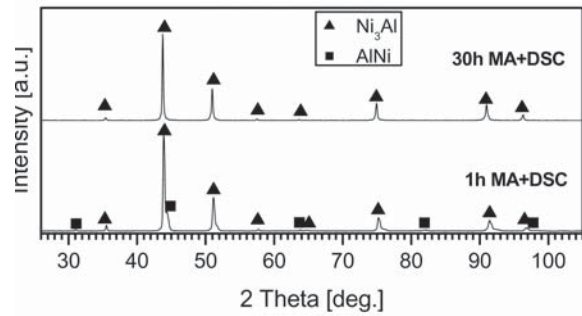
between 55 nm for shorter MA time and 40 nm for 30 h of MA.

4. CONCLUSIONS

During the MA processes of the AlNi+Ni and Al_3Ni_2+Ni powder mixtures, in both cases, Ni(Al) supersaturated solid solutions is formed. After 10 h of milling, for both processes, the steady-state stage is reached. After 30 h of MA the product - Ni(Al) - is nanocrystaline with a crystallite size of about a dozen nm.

During heating of milling products in the calorimeter the Ni(Al) solid solution transforms into the ordered Ni_3Al intermetallic compound with a crystallite size of about 40 nm. With the transformation that occurs during heating in the calorimeter an exothermic effect is associated.

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