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Structure Studies on Mechanically Alloyed $Ni_{50}Ti_{50-x}Mo_x$ (x = 10, 25, 40 at.%) Systems during Milling and after Annealing

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The subject of this study is the phase composition evolution of $Ni_{50}Ti_{50-x}Mo_x$ (x = 10, 25, 40 at.%) systems prepared by mechanical alloying in as-milled state and after subsequent heat treatment. During milling a mechanically induced solid state reaction between nickel, titanium and molybdenum was observed leading to the formation of nanocrystalline disordered solid solutions. As a result of heat treatment a creation of NiMo intermetallic phase was observed as well as structure relaxation of previously formed solid solutions.

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1. Introduction

Ni–Ti and Ni–Mo systems obtained by mechanical alloying have been widely studied as they are very important materials for biomedical applications, corrosion protection, and for catalysis [1–5]. Mechanical alloying is a promising method for synthesizing and processing of these alloys which results in nanocrystalline or amorphous materials exhibiting attractive physical, mechanical, and chemical properties [6]. Ni–Ti–Mo ternary alloys can be used as electrode materials for electocatalysis like $Ni_{50}Mo_{40}Ti_{10}$ alloy, which was applied as electroactive cathode for hydrogen evolution reaction [7].

The aim of this work was to investigate the changes of phase composition of mechanically alloyed $Ni_{50}Ti_{50-x}Mo_x$ (x = 10, 25, 40 at.%) systems during milling and after annealing.

2. Experimental

Elemental powders of Ni, Ti, and Mo with a particle size under 150 μm were used as reagents for mechanical alloying process of $Ni_{50}Ti_{50-x}Mo_x$ (x = 10, 25, 40 at.%) systems. The total mass of milled powder was 15 g. The reagents were mixed to give the desired composition and next they were milled in a planetary ball mill (Pulverisette 6, Fritsch GmbH) at a rotation velocity of 500 rpm, under the argon protective atmosphere. Hardened steel vial (80 cm^3) and balls (15 mm in diameter) were used. The ball-to-powder weight ratio was 10:1. To limit excessive welding between reagent particles, the milling process was stopped periodically, which provided cooling of the milling reactors.

After selected time intervals the milled mixtures were analyzed by X-ray diffraction (XRD) method. The mechanical alloying (MA) process was conducted to obtain reproducible XRD patterns. The milled materials were subject to heat treatment in order to reach an equilibrium structure. For this purpose the milled powders were put into quartz tubes sealed under vacuum (10^{-4} Pa) and next annealed at 1173 K for 60 min.

Phase composition changes during milling and after heat treatment were examined by XRD method. XRD patterns were obtained with the use of PANalytical Philips X'Pert PW 3040/60 diffractometer with graphite monochromator on the diffracted beam and the Cu K_α radiation. The phase analysis was performed by application of ICDD (PDF-4+, 2014) files. The crystallite sizes and lattice strains of identified phases were analyzed according to the Williamson–Hall method [8] using the High Score Plus PANalytical software basing on the whole XRD pattern analysis. The LaB_6 powder was applied as a line profile standard for the instrumental broadening determination.

3. Results and discussion

Mechanical alloying of $Ni_{50}Ti_{50-x}Mo_x$ (x = 10, 25, 40 at.%) powders was performed and subsequently followed by heat treatment. For comparison $Ni_{50}Ti_{50}$ and $Ni_{50}Mo_{50}$ systems were also investigated. The XRD patterns of all studied mixtures are shown in Figs. 1 and 2.

For the as-mixed powders, the X-ray diffractograms consist of a sum of the Ni (Fm-3m, ICDD 00-004-0850), Ti ($P6_3/mmc$, ICDD 00-005-0682) and Mo (Im-3m, ICDD 00-042-1120) patterns (Figs. 1, 2). From the first stages of milling, decrease in intensity and considerable broadening of the diffraction lines were observed, which indicates reduction in the crystallite size to nanoscale in milled materials (Figs. 1, 2, Table I). Moreover, Ni diffraction lines are slightly moved towards lower angles which reveals the formation of disordered Ni-based solid solutions: Ni(Ti), Ni(Mo) or Ni(Mo,Ti). For powders with greater content of Ti: $Ni_{50}Ti_{25}Mo_{25}$, $Ni_{50}Ti_{40}Mo_{10}$ and $Ni_{50}Ti_{50}$ the presence of Ti(Ni) solid solution (Fm-3m, ICDD 01-079-6208) was also observed (Figs. 1a, 2b,c).

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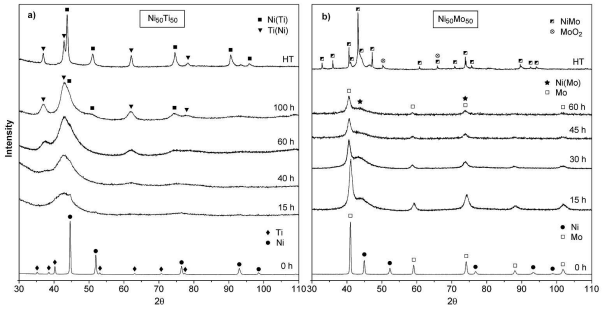

Fig. 1. X-ray diffraction patterns of $Ni_{50}Ti_{50}$ (a) and $Ni_{50}Mo_{50}$ (b) powders after mechanical alloying for various milling times and after subsequent heat treatment (HT).

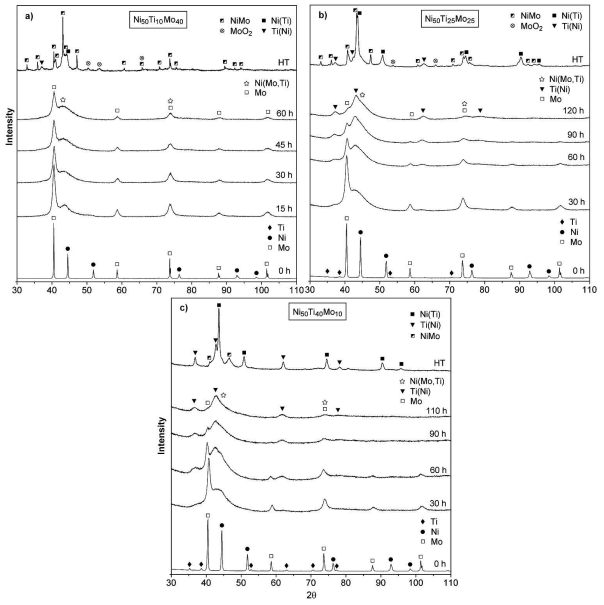

Fig. 2. XRD patterns of $Ni_{50}Ti_{50-x}Mo_x$ powders after mechanical alloying for various milling times and after subsequent heat treatment (HT): (a) $Ni_{50}Ti_{10}Mo_{40}$, (b) $Ni_{50}Ti_{25}Mo_{25}$, and (c) $Ni_{50}Ti_{40}Mo_{10}$.

TABLE I

Structural characteristic of $Ni_{50}Ti_{50-x}Mo_x$, $Ni_{50}Ti_{50}$, and $Ni_{50}Mo_{50}$ systems after completion of MA (ΔD, $\Delta\varepsilon \approx 15\%$).

Chemical composition	Phase constitution	Space group	a_0 [Å]	Crystallite size D [Å]	Lattice strains ε [%]
$Ni_{50}Ti_{50}$	Ni(Ti)	Fm-3m	3.5972(3)	30	0.04
	Ti(Ni)	Fm-3m	4.2124(1)	74	0.86
$Ni_{50}Ti_{40}Mo_{10}$	Ni(Ti,Mo)	Fm-3m	3.6151(1)	30	1.17
	Ti(Ni)	Fm-3m	4.1314(3)	30	0.04
$Ni_{50}Ti_{25}Mo_{25}$	Ni(Mo,Ti)	Fm-3m	3.6141(3)	30	0.17
	Ti(Ni)	Fm-3m	4.1260(2)	30	0.37
	Mo	Im-3m	3.1502(4)	80	0.40
$Ni_{50}Ti_{10}Mo_{40}$	Ni(Mo,Ti)	Fm-3m	3.6124(6)	30	0.37
	Mo	Im-3m	3.1439(2)	80	0.40
$Ni_{50}Mo_{50}$	Ni(Mo)	Fm-3m	3.6224(4)	30	1.17
	Mo	Im-3m	3.1458(4)	80	0.40

For $Ni_{50}Ti_{50}$ system, in the intermediate stages of milling (15 h, 40 h) the creation of an amorphous phase was stated, which — by further milling — turns into a mixture of fcc Ti(Ni) and Ni(Ti) solid solutions. As a result of subsequent heat treatment one can observe the structure relaxation of solid solutions (Fig. 1a). More detailed description of the mechanical alloying of $Ni_{50}Ti_{50}$ system is presented elsewhere [9].

During milling of $Ni_{50}Mo_{50}$ system a creation of nanocrystalline disordered fcc Ni(Mo) solid solution was observed, however some amount of elemental (Im-3m) Mo phase remains undissolved, which can be inferred from a strong diffraction line at about $2\theta = 40.5°$ (Fig. 1b). The presence of unreacted Mo in milled powder might be a result of a low solubility of Mo in Ni (about 17 at.%) at room temperature [5]. The addition of 10 at.% of Ti instead of Mo does not cause major changes in phase composition of milled powder, as shown in diffraction pattern of $Ni_{50}Ti_{10}Mo_{40}$ (Fig. 2a). Thus it can be stated that Ti and some amount of Mo dissolved in Ni create Ni(Mo,Ti) solid solution. Phase composition of heated $Ni_{50}Ti_{10}Mo_{40}$ powder is also similar to those observed for $Ni_{50}Mo_{50}$ system (Figs. 1b, 2a). For both materials, a formation of ($P2_12_12_1$) NiMo (ICDD 00-048-1745) intermetallic phase was revealed as well as some amounts of MoO_2 (ICDD 00-005-0452).

In milled $Ni_{50}Ti_{25}Mo_{25}$ and $Ni_{50}Ti_{40}Mo_{10}$ powders the growing contribution of Ti(Ni) solid solution and a decrease in the content of undissolved Mo phase can be seen (Fig. 2b,c). Intensity of Mo diffraction lines on $Ni_{50}Ti_{25}Mo_{25}$ pattern clearly diminishes though they are still present, whereas on $Ni_{50}Ti_{40}Mo_{10}$ Mo lines almost disappear. As a consequence, in heated $Ni_{50}Ti_{25}Mo_{25}$ and $Ni_{50}Ti_{40}Mo_{10}$ samples the content of NiMo intermetallic phase diminishes whereas the contribution of Ti(Ni) solid solution increases.

The crystallites size of Ni-based solid solutions is about 30 Å, whereas for Ti-based solid solution is different: 74 Å for the $Ni_{50}Ti_{50}$ system and 30 Å for the $Ni_{50}Ti_{50-x}Mo_x$ ($x = 10$, 25 at.%) systems.

4. Conclusions

Mechanical alloying of $Ni_{50}Ti_{50-x}Mo_x$ ($x = 10$, 25, 40 at.%) systems was performed and subsequently followed by heat treatment. Based on the obtained results, the following conclusions can be drawn:

1. Prolonged mechanical alloying of $Ni_{50}Ti_{50}$ mixture produces nanocrystalline disordered Ni(Ti) and Ti(Ni) solid solutions with amorphization process in the intermediate milling stage. The created solid solutions are characterized by fcc (Fm-3m) structure and the crystallite size of about 30 Å. Heat treatment of milled $Ni_{50}Ti_{50}$ powder results in the structure relaxation of Ni(Ti) and Ti(Ni) solid solutions.

2. Mechanical alloying of $Ni_{50}Mo_{50}$ system leads to creation of nanocrystalline disordered fcc Ni(Mo)

solid solution phase, however some amount of elemental bcc (Im-$3m$) Mo phase remains undissolved in Ni. Heating of the milled $Ni_{50}Mo_{50}$ powder causes formation of ($P2_12_12_1$) NiMo intermetallic phase. Some amounts of MoO_2 were also detected.

3. During milling of $Ni_{50}Ti_{50-x}Mo_x$ systems a formation of disordered fcc solid solutions based on Ni and Ti is observed. With the increase in Mo content in the milled powder the amount of Ti(Ni) phase diminishes whereas the contribution of Ni-based solid solution and undissolved bcc Mo phase is higher. Heat treatment of milled $Ni_{50}Ti_{50-x}Mo_x$ powders results in the structure relaxation of previously formed solid solutions and the creation of ($P2_12_12_1$) NiMo intermetallic phase. The contribution of this phase in annealed powders increases with the increase in Mo content in milled materials. Some amounts of MoO_2 were also detected.

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