

ORIGINAL RESEARCH PAPER

Synthesis and Characterization of Nanocrystalline $\text{Ni}_{50}\text{Al}_{50-x}\text{Mo}_x$ ($X=0-5$) Intermetallic Compound During Mechanical Alloying Process

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Abstract

In the present study, nanocrystalline $\text{Ni}_{50}\text{Al}_{50-x}\text{Mo}_x$ ($X = 0, 0.5, 1, 2.5, 5$) intermetallic compound was produced through mechanical alloying of nickel, aluminum, and molybdenum powders. AlNi compounds with good and attractive properties such as high melting point, high strength to weight ratio and high corrosion resistance especially at high temperatures have attracted the attention of many researchers. Powders produced from milling were analyzed using scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The results showed that intermetallic compound of NiAl formed at different stage of milling operation. It was concluded that at first disordered solid solution of (Ni,Al) was formed then it converted into ordered intermetallic compound of NiAl. With increasing the atomic percent of molybdenum, average grain size decreased from 3 to 0.5 μm . Parameter lattice and lattice strain increased with increasing the atomic percent of molybdenum, while the crystal structure became finer up to 10 nm. Also, maximum microhardness was obtained for NiAl49Mo1 alloy.

1. INTRODUCTION

There is an increasing interest in producing nanocrystals because of their excellent physical and mechanical properties in comparison to coarse-grain materials [1]. NiAl intermetallic compound can be used as a high-temperature material owing to its high melting point, low density, excellent thermal conduct, good temperature stability and good oxidation resistance [2-5]. Unfortunately, this

compound has a big disadvantage: low toughness at low temperature and low creep strength at high temperatures, which limits the application of this intermetallic compound [6]. Considerable efforts have been made in terms of increasing the mechanical properties of NiAl via reducing the size of materials microstructure to nanometer dimension, micro and macro-alloying, and using alloying elements [7-9]. Although extensive

research has been done on this alloy, recent investigations on revealing interesting properties of NiAl system are still continuing so that promising results have been obtained in terms of improving fragility through modifying grain size [10-14].

Several methods like powder metallurgy, self-combustion synthesis and mechanical alloying have been used for synthesizing intermetallic compounds. Mechanical alloying is one of the solid state methods, which is suitable for producing compounds with high steam pressure and elements with different melting points that are not produced using the conventional methods [15, 16]. Also, this method can be used to directly produce nanocrystalline structures [17].

Formation of NiAl intermetallic compound during mechanical alloying is a self-expanding reaction in separate particles, which is accompanied by a sudden release of energy and thermodynamic factors play an effective role in the formation of final phase. One of the elements which promotes the deficiencies of intermetallic compounds is molybdenum and its most useful effect is in terms of increasing room temperature ductility of this compound [18]. Main effect of negligible element such as Fe, Ga, and Mo on microstructure of NiAl alloy is the formation of a solid solution with NiAl intermetallic compound. Adding Mo leads to a different behavior from adding Fe and Ga. Also, adding Mo has slight tendency to modify grain size of NiAl alloy. average grain size in the presence of Mo is less than 20 nm, while it is 20-50 nm in NiAl alloy Mo-free [19].

Therefore, to promote mechanical properties of NiAl intermetallic compound, this article sought to examine the effect of Mo microalloy on the production process of nanocrystalline Ni-Al intermetallic compound. All the alloys were obtained from pure elements with a combination

close to the stoichiometric NiAl compound using mechanical alloying.

2. Experimental procedure

2.1. Materials

In this study, aluminum powders with the purity of more than 99% and particle size of less than 200 μm , nickel powders with the purity of more than 99.9% and particle size of less than 10 μm and molybdenum powders with the purity of more than 99.99% and particle size of less than 150 μm were used. The powder mixtures were milled in a planetary ball mill. The mill atmosphere was protected by argon gas to prevent the oxidation of powder particles. In all the experiments, 4 large and 12 small balls with the respective diameters of 2 and 1 cm were used. By selecting different sizes, the balls chose a random motion [20] and more energy was transferred to the powder [21].

2.2. Characterization

Vial and balls were made of hardened chrome steel. Total weight of the used powder was 12 g. Rotation speed of milling vial was constant in all experiments and equal to 250 rpm. Ball to powder weight ratio was 15:1. By changing the amount of molybdenum, 5 samples were prepared with the composition of $\text{Ni}_{50}\text{Al}_{50-x}\text{Mo}_x$ ($X = 0, 0.5, 1, 2.5, 5$) which were milled for 128 h.

Structural changes of the samples during mechanical alloying were studied using a Philips X'Pert diffractometer with Cu-K α ($\lambda = 0.15405$ nm) radiation over 20–100 2θ . Morphology and microstructure of powder particles were characterized by SEM in a Philips XL30. The mean powder particle size was estimated from SEM images of powder particles by image tool software. The average size of about 50 particles was calculated and reported as mean powder particle size. Crystallite size and lattice strain were

also calculated using Williamson-Hall method [22]. In this method, peak width caused by lattice strain and grain size is considered [23, 24]. This relationship is expressed as follows:

$$\beta \cos\theta = 0.9\lambda / D + 2\varepsilon \sin\theta \quad (1)$$

Where β is the peak breadth in mid height, λ represents the X-ray wave length of the incident copper X-ray radiation, D is the average crystallite size, ε is the mean value of internal strain, θ is the Bragg diffraction angle and K is a constant with a value of 0.89. Accordingly, if $\beta\cos\theta$ is plotted in terms of $\sin\theta$, a line with the slope of 2ε and intercept of $0.9\lambda/D$ will be obtained. By extracting these data from the drawn lines, size of crystals and lattice strain can be determined and their effect can be also separately specified. In order to determine width of peaks at half height, Sigma Plot 12.0 software, which is advanced software in drawing and processing curves, was used. Powders produced by milling were converted into tablet-like pieces with the diameter of 25 mm and thickness of 3 mm during mechanical cold pressing process under the pressure of 849 MPa in 20 sec. Samples were studied using Vickers microhardness method with the applied force of 254.2 mN for 10 sec using Struers Duramin hardness tester. The reported hardness value was the average of 6 times of hardness test for each sample.

3. Results and discussion

3.1. Morphology and XRD analysis

Figs. 1 and 2 show SEM images and average size of powder particles in terms of change in the amount of molybdenum after 128 h of milling, respectively. As shown in Fig. 2, with increasing the atomic percent of molybdenum, average particle size of the powder followed a decreasing trend. Minimum average particle size of the powders containing 5 at.% Mo was obtained as approximately 0.5 μm . Higher magnification of

powder particles showed that large particles in this step were in fact the result of the accumulation of a large number of small particles [25]. Further, Fig. 3 demonstrates X-ray diffraction pattern of the mixture of initial powder and mechanical alloying samples with different molybdenum percentages after 128 h of milling. As seen in the XRD patterns of the samples before milling, only the peaks of Ni, Al, and Mo were observed. With increasing Mo percentage, NiAl peaks intensity and width were reduced and increased, respectively.

After 128 h of milling, there was no trace of nickel and aluminum peaks in the XRD pattern (Fig. 3). Reactions finished in the vial before milling completion and the final product was 100% nickel aluminide. Since the atomic diffusion is time dependent, therefore, sufficient milling time is required to obtain the final products [26]. After the formation of (Ni, Al) solid solution and continuing the process of milling and topical heating, powder particles were gradually converted into NiAl. The main factors that affect the mechanisms occurring in MA process are fracture and cold welding repetition of particles followed by an increase in their [27]. Reactivity In long time periods, the powders became so homogeneous that rapidly got regulated. Powders became finer and particles size distribution went uniform with spherical and same sized shapes. This issue showed the equality of cold welding rate and failure of powders due to cold working. With increasing the amount of molybdenum, more molybdenum was dissolved in NiAl intermetallic given the changes in lattice parameters. As a result of Mo dissolution in NiAl intermetallic compound, stacking faults energy was reduced and effect of hard working became higher than that of the molybdenum-free sample, more dislocations and sub boundarie were formed and consequently grain sizes became finer.

Furthermore, by the dissolution of Mo atoms in the Ni matrix, hardworking effects were increased; as a result, more powder particles were brittle and more failure occurred in them which led to finer particles. In general, dissolution of alloying elements in metal crystals and generation of distortion in them increase hard working in the cold working process [28, 29]. In fact, Mo saturation in Ni reduces such an effect. This results are in agreement with previous results given by azimi et al. [30].

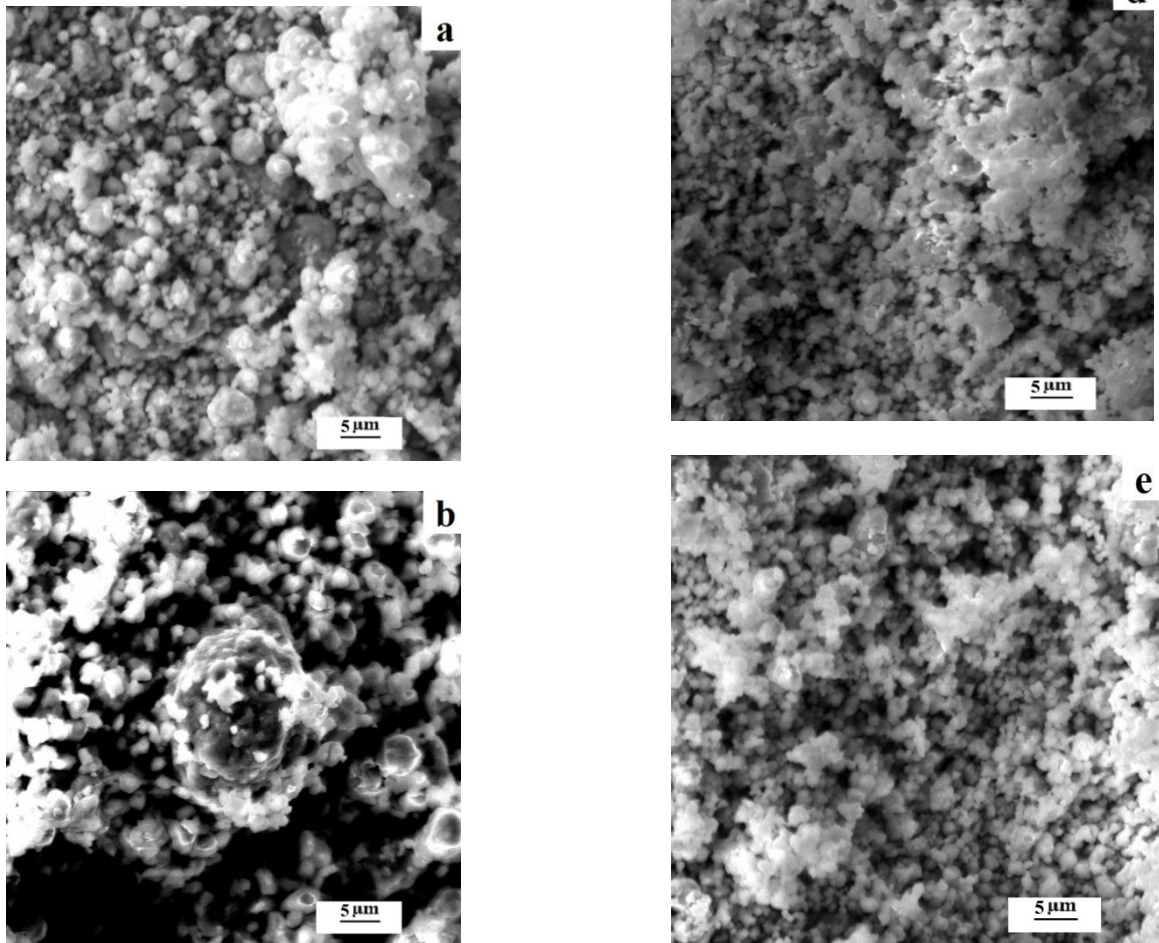


Fig. 1. SEM images of powders milled for 128 h in a) 0, b) 0.5, c) 1, d) 2.5, e) 5 at.% Mo.

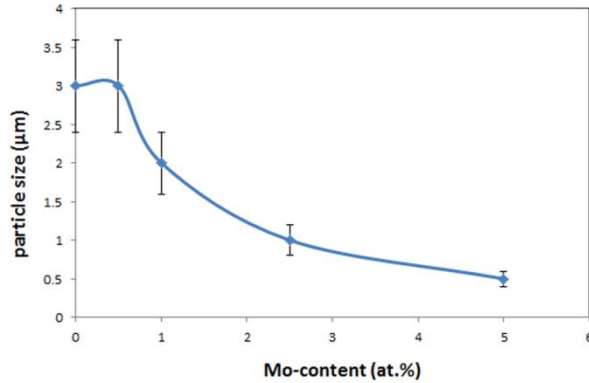


Fig. 2. Average particle size of the powder for different amounts of molybdenum after 128 h of milling.

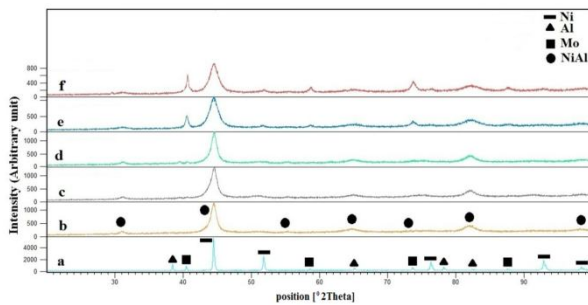


Fig. 3. X-ray diffraction pattern of a) non-milled powder mixture and 128 h milling of b) $\text{Ni}_{50}\text{Al}_{50}$, c) $\text{NiAl}_{49.5}\text{Mo}_{0.5}$, d) $\text{NiAl}_{49}\text{Mo}_1$, e) $\text{NiAl}_{47.5}\text{Mo}_{2.5}$, f) $\text{NiAl}_{45}\text{Mo}_5$

3.2. Internal strain

Fig. 4 shows internal strain changes of NiAl lattice for different percentages of molybdenum after 128 h of milling. As is determined, with increasing the amount of molybdenum, first, a strong increase occurred in the rate of received internal strain. Then, at 2.5 at.% Mo, the amount of internal strain stored in powder particles increased with less intensity. In addition to the internal strain transferred to the powder particles from the milling device, with increasing molybdenum and dissolution of its atoms in Ni matrix, more defects, specifically dislocations, were formed in the materials. As a result, strain of the material increased compared to molybdenum-free NiAl

compound. Nevertheless, with increasing molybdenum content to more than 2.5 at.%, increased accumulation of cold working effect led to matrix saturation of cold working and reduced strain increase rate at high amounts of molybdenum. Alizadeh et al. [31] reported increased internal strain in NiAl system with the increased Cr atomic percent and showed that high levels of chromium had a more impact than molybdenum on the internal strain of NiAl.

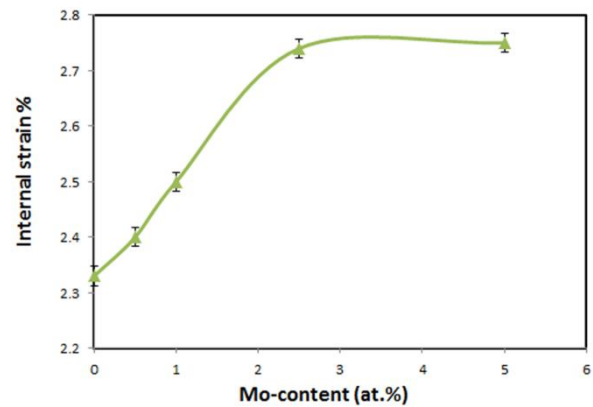


Fig. 4. Strain changes of NiAl lattice after 128 h of milling for the 5 samples with 0, 0.5, 1, 2.5, and 5 at.% Mo.

3.3. Crystal size

Fig. 5 shows effect of the amount of molybdenum on changes in the size of NiAl crystals after 128 h of milling. Crystal size in NiAl molybdenum-free samples after 128 h of milling was 26 nm and with increasing molybdenum up to 5 at.%. This value was decreased to 10 nm. With increasing molybdenum, crystallite size suddenly decreased for the powders containing 0.5 at.% Mo; but, this trend reached saturation with more increase of molybdenum, which can be due to the solubility saturation of Mo atoms in nickel lattice. As a result, hardworking effect was reduced and consequently dislocations and sub boundaries were formed to some extent and then the intensity of

crystallite size reduction was decreased. Intense grain size reduction is one of the methods for improving ductility so that nanometric dimensions of grains led to further improvement in ductility and creeping resistance compared to micron grains [32, 33]. Above DBTT temperature, there was strong dependence between tensile ductility and grain size [34]. Room temperature yield strength of Ni-50AL is independent from grain size; in contrast, even in alloys with small deviation from stoichiometry, it strongly depends on grain size and increased with the reduction in grain size [3].

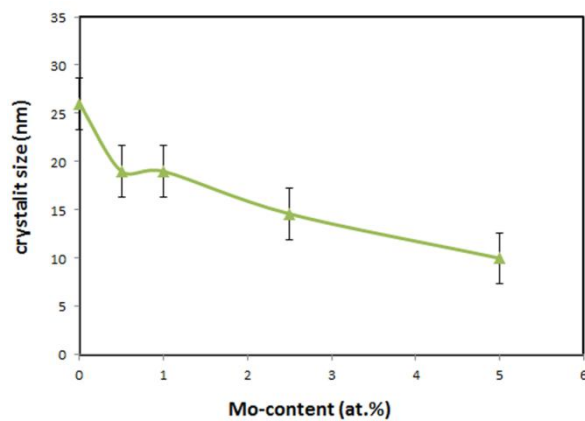


Fig. 5. Size changes of NiAl crystal after 128 h of milling for samples with 0, 0.5, 1, 2.5, and 5 at.% Mo.

3.4. Lattice parameter

Fig. 6 demonstrates changes in the lattice parameter of NiAl compound after 128 h of milling for different atomic percentages of molybdenum. According to this figure, lattice parameter had one increase for the powders containing 1 at.% Mo; but, this trend reached a stable state with more Mo increase, which could be due to solubility

saturation of Mo atoms in Ni lattice; consequently, intensity of increasing lattice parameter was reduced. Albiter et al. [19] added molybdenum to Ni56Al44 compound and reported similar results. They also reported that adding Fe to the same compound had a more effect on lattice parameter than Mo. The reason for more increase of lattice parameter with increasing molybdenum could be attributed to increased crystal defects and then dislocations as a result of severe plastic deformation of particles. Thus, sub grains were formed; sub grains and dislocations made vaster pathways for the movement of molybdenum atoms and were displaced by more plastic deformation of particles; however, molybdenum atoms were not displaced. By repetition, there would be an increased possibility for the penetration of Mo atoms.

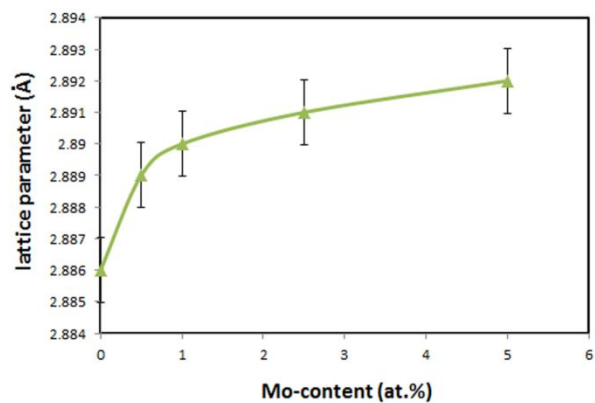


Fig. 6. Changes of NiAl lattice parameter after 128 h of milling for the 5 samples with 0, 0.5, 1, 2.5, and 5 at.% Mo.

3.5. Microhardness measurements

Fig. 7 shows microhardness changes in NiAl lattice after 128 h of milling for different percentages of molybdenum after cold pressing operations. As can be seen, with increasing molybdenum, microhardness changes first increased and then decreased. Microhardness changes in NiAl sample without molybdenum showed the number of 660 Hv after 128 h of milling. With increasing the amount of Mo to 1%, a sharp increase up to 690 Hv was observed in microhardness rate. Then, at 2.5 at.% Mo, this value was reduced to 603 Hv and, afterward, it remained almost constant.

This complexity can be considered as the interaction of two processes: one is cold working process that occurs before and after the formation of NiAl compound and the other is the formation of NiAl intermetallic compound that leads to heat release. With increasing atomic percent of molybdenum, more cold working effects were stored in (Ni, Al) solid solution and thus more energy was stored there. As a result, during the random conversion of (Ni, Al) solid solution into a regular intermetallic compound, more heat was released. More heat release would completely eliminate the remaining cold working effects generated in the (Ni, Al) solid solution. This factor could cause more hardness drop at high molybdenum amounts. Therefore, several factors are effective in this regard and it needs to be further investigated since: this subject and cold working elements during mechanical alloying and before and after the formation of NiAl intermetallic compound are complex; after the formation of intermetallic compound, heat is released and both material and phase change and at the same time, in addition to phase change, the structure itself can change under the influence of the two above-mentioned elements.

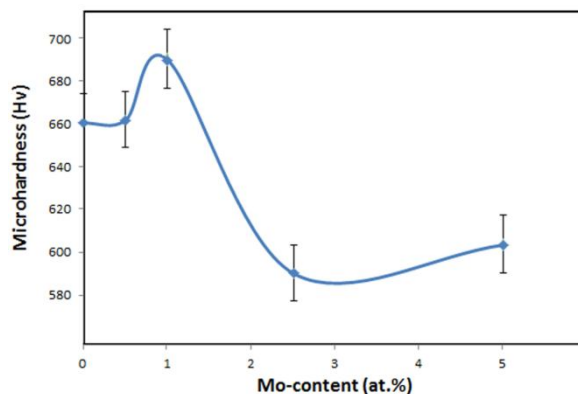


Fig. 7. Microhardness changes after 128 h of milling for the 5 samples with 0, 0.5, 1, 2.5, and 5 at.% Mo.

4. Conclusion

nanocrystalline $\text{Ni}_{50}\text{Al}_{50-x}\text{Mo}_x$ ($X = 0, 0.5, 1, 2.5, 5$) intermetallic compound was successfully produced by mechanical alloying of different amounts of molybdenum. Molybdenum increase led to increased defects in the material, especially dislocations. As a result, strain rate of the material increased compared to NiAl compound. Increasing Mo not only reduced the final crystallite size, but also had an important effect on modifying microstructure. Variations in crystallite size were very severe at first and decreased later when reaching saturation. Crystal size in the NiAl molybdenum-free sample was 26 nm and increasing Mo to 5 at.% reduced it to 10 nm. Mo increase to 1% intensely increased microhardness rate to 690 Hv. Broadening peaks of X-ray diffraction pattern due to molybdenum increase was mainly due to decreased crystallite size and increased lattice strain. In the presence of molybdenum, the produced alloy's lattice parameter showed higher values.

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