

FULL PAPER

## Study of molybdenum effect on synthesis behavior of nanocrystalline NiAl intermetallic during mechanical alloying

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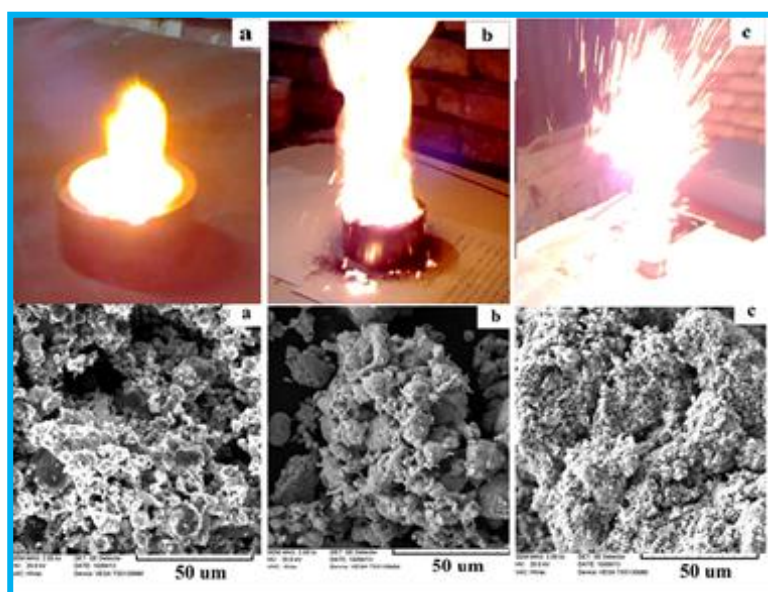
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**ABSTRACT:** The mechanical alloying (MA) procedure was used to synthesize the Ni<sub>50</sub>Al<sub>50</sub> and Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> nanocrystalline intermetallic compound using the pure Ni, Al and Mo elemental powders under in an argon atmosphere for different times (8, 16, 48, 80 and 128 h) in a planetary ball mill with hardened steel balls (12 balls-1cm and 4 balls-2cm in diameter). The mechanical alloying was carried out in the attendance of various Mo contents as a micro-alloying element for various milling times. Microstructural characterization and structural changes of powder particles during mechanical alloying were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Outcomes confirmed that the synthesis behavior of NiAl intermetallic depends on the milling time and Mo content. The results show that after than 80 h of milling, the intermetallic phase is produced after opening the vial lid. X-ray map shows that, in the fixed milling time, enhancing the Mo content leads to acceleration in the NiAl formation in air atmosphere. The mechanical alloyed powders have a microstructure consisting of nanometer size particles. Mo enhance has a considerable effect on the lowering of crystallite size. The TEM image showed that the Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> nano-particles were less than 10 nm. The average grain size is smaller than those sizes obtained in the NiAl (25–35 nm) alloy.

**KEYWORDS:** Mechanical alloying; nanocrystalline; intermetallic; Ni<sub>50</sub>Al<sub>50</sub>; Mo.

### GRAPHICAL ABSTRACT:



## 1. Introduction

The NiAl intermetallic compound offers a combination of attractive properties similar in high specific strength, high melting point, excellent oxidation resistance up to 1573K and good thermal conductivity [1, 2]. These attractive properties make the NiAl compound a potential candidate for structural applications.

Nonetheless, low ductility at room temperature is the major limitation for the structural applications of this material. One way for improving its ductility is to diminish the crystallite size to the nanometer scale [3].

Mechanical alloying is a solid state procedure which can be employed for the synthesis of nanocrystalline intermetallics. Synthesis of nanocrystalline nickel aluminide by MA elemental powders has been reported in several works [1, 4, 5].

Mechanical alloying can provide all the above-mentioned points simultaneously; therefore, this technique has been extensively applied to synthesize NiAl

intermetallic. Though extensive researches have been carried out on these alloys, new investigations still continue to disclose attractive properties of the NiAl alloy system [6-8]. Mechanical alloying has been successfully applied for making nanocrystalline materials. Many researchers have reported making nanocrystalline NiAl intermetallic compound by mechanical alloying [9-12]. Atzmon [13] was the first to report the occurrence of mechanically produced self-propagating reaction (MSR) during the mechanical alloying of Ni and Al powders. Joardaret al. [5] also reported the obtaining of the NiAl compound without the occurrence of a MSR; also, the authors specified the optimum milling parameters and energy domains for synthesis of nanocrystalline nickel aluminide by mechanical alloying in planetary mill. Kubaski et al. [14] also verified that the occurrence of a MSR, and the NiAl intermetallic compound was found in

specimens after about 40 min of milling in a shaker mill. Recently, great attention has been paid to the investigation of ternary systems by mechanical alloying. As already mentioned mechanical alloying is known as a suitable tool for synthesis of nanocrystalline NiAl-x intermetallics. It has been verified that in the nanocrystalline materials obtained by mechanical alloying, due to the extensive deformation, the internal energy of the particle lattice increases and consequently their reactivity is increased. The basic factors that affect the mechanisms occurring during the mechanical alloying procedure are fractured and cold welding repetition of particles followed by an enhance in their reactivity [15].

The purpose of this work is to explore the formation mechanism of Ni<sub>50</sub>Al<sub>50</sub> intermetallic compound was studied by applying a planetary ball mill and the effect of Mo additions and different milling times on structure of Ni<sub>50</sub>Al<sub>50</sub> and

Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> intermetallic manufactured by MA method was investigated.

## 2. Materials and Methods

The starting materials used in this study include high purity Ni, Al and Mo powders with particle size of <10, <200 and <150 μm, respectively. MA was done in a Fritsch-P5 planetary-type ball mill with hardened steel balls (12 balls-1cm and 4 balls-2cm in diameter) and under argon atmosphere to prevent sample oxidation. Different ball sizes with their more accidental collisions [16] gave more energy to the powder particles [17]. In all MA runs the ball to powder weight ratio was 15:1 and the vial rotation speed was 250 rpm. Various elemental blend with the composition of Ni<sub>50</sub>Al<sub>50</sub> and Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> have been studied in the present investigation. Small amount (3 wt%) of ethanol was added to prevent exorbitant welding of the powders to the steel balls and container. The milling times were 8, 16, 48, 80 and 128 h.

Crystallite size (D) in the milled samples were calculated from the XRD with Cu-K $\alpha$  ( $\lambda = 0.15405$  nm) radiation over 20–100  $2\theta$  using the Scherrer formula [18]:

$$D = k\lambda / (\beta \cos\theta) \quad (1)$$

Where k is the Scherrer constant, which is 0.9,  $\lambda = 0.1542$  nm,  $\beta$  is the peak breadth in mid height and  $\theta$  half of the diffraction angle. Microstructure of powder particles which was investigated by SEM in a Philips XL30 CamScan MV2300. X-ray mapping was also done to see the repartition of the different elements in the milled powders. To see the distribution of the different elements in the milled powders, XRD mapping was used. The morphology and the average particle size of Ni<sub>50</sub>Al<sub>50</sub> and Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> nano-particles were further investigated by a transmission electron microscope (TEM, PHILIPS CM20). Bright and dark field images and also high-resolution images were obtained.

### 3. Results and discussion

The following aspects can be interpreted from the X-ray diffraction patterns of milled Ni<sub>50</sub>Al<sub>50</sub> and Ni<sub>50</sub>Al<sub>45</sub>Mo<sub>5</sub> powder mixtures after different milling times:

1. All X-ray diffraction patterns illustrate that the nickel aluminide intermetallic diffraction peak as the only phase existence in the final product.
2. The X-ray diffraction patterns just vary together in (a): peaks intensity and (b): change in peaks positions.

Table 1 illustrates the initial powder mixtures chosen for milling procedure and the surroundings in which the nickel aluminide compound is formed pursuant to Table 1, after stopping the milling procedure, two feasibility can be viewed in relation to nickel aluminide synthesis as the milling product: (a) the NiAl phase has been synthesized under Ar atmosphere through milling operation, in effect, before reaching the significant milling time. These specimens were marked with ★ symbol in Table 1. (b) The nickel aluminide

compound would be produced after stopping the milling procedure and opening the vial lid, in effect, by an exothermic reaction in the air atmosphere followed by a flame. These specimens are marked with ■ and ▲ symbols in Table 1. As Table 1 represents, the mentioned possibilities depend on milling time as well as the Mo contents. According to Table 1, 16 and 48 h of milling outcomes in the possibility of (b)

for all Mo contents, 128 h of milling outcomes in the possibility of (a) for all Mo contents and the formation manner of nickel aluminide for 80 h of milling time depends on the Mo content. It can be viewed that the peaks of that low Mo contents (specimens 1-80 up to 3-80) will culminate in the possibility of (b) while enhancing the Mo values (specimens 4-80 and 5-80) resulting in the possibility of (a).

**Table 1.** Formation behavior of NiAl after the considered milling time: (★) Formation of NiAl in vial under Ar atmosphere; (■&▲) Formation of NiAl in air.

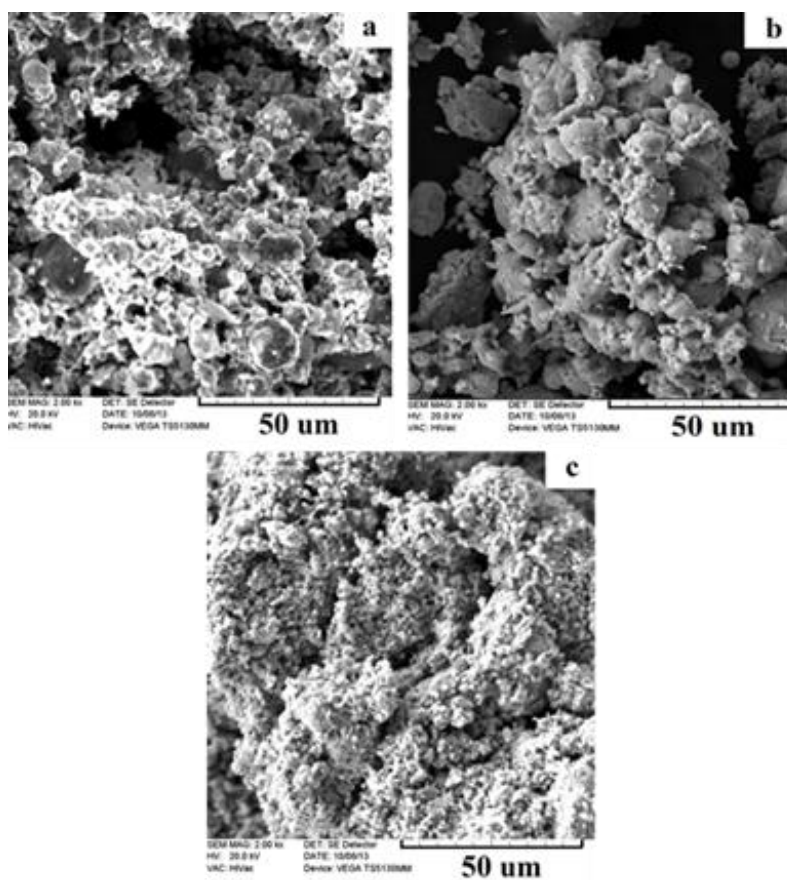
Number	Composition	16 h	48 h	80 h	128 h
1	Ni <sub>50</sub> Al <sub>50</sub>	■	■	▲	★
2	Ni <sub>50</sub> Al <sub>49.5</sub> Mo <sub>0.5</sub>	■	■	▲	★
3	Ni <sub>50</sub> Al <sub>49</sub> Mo <sub>1</sub>	■	■	▲	★
4	Ni <sub>50</sub> Al <sub>47.5</sub> Mo <sub>2.5</sub>	■	■	★	★
5	Ni <sub>50</sub> Al <sub>45</sub> Mo <sub>5</sub>	■	▲	★	★

After opening the vial lid of the specimens marked with (■ and ▲), mixed powders are exposed to air atmosphere and a reaction takes place which is followed by a flame for a little duration of time. It was viewed that the reaction in the specimens 1-80 up to 3-80 took place significantly faster than the ones in the specimens with 16 and 48 h of milling. This

observation can be related to decreasing the particle size which consequently enhances the surface region during the mechanical alloying procedure. Fig. 1 illustrates a SEM micrograph of the mixed powders in the specimens 1-16 (Fig. 1a), 1-48 (Fig. 1b) and 1-80 (Fig. 1c). It can be easily viewed that the specimen with longer milling time (1-80) includes finer and more homogenous

particles with attention to the ones with lesser milling time. Therefore, the specimens milled for 80 h are more ready to react with the air atmosphere with attention to the specimens milled at 16 and 48 h. To investigate nickel aluminide synthesis manner more indepth, study of the structural changes of Ni and Al lattice during mechanical alloying in the attendance of Mo as micro-alloying element was attempted.

For this purpose, it is necessary to investigate the X-ray diffraction pattern of some milled specimens before production of nickel aluminide phase. Therefore the specimens (2-16 and 5-16) in which the nickel aluminide phase is not formed under Ar are chosen and their X-ray diffraction pattern is achieved before reacting with air atmosphere.



**Fig. 1.** The SEM micrograph of NiAl particles without Mo content generated in air atmosphere for the samples 1-16, 1-48 and 1-80.

A cross-sectional X-ray diffraction pattern related to the most intense peak of Ni is drawn in Fig. 2. This figure discloses the structural variations of Ni lattice during mechanical alloying before production of nickel aluminide phase. Three peaks are represented in this figure: the lesser peak is related to as received the Ni powder and other peaks illustrate the X-ray diffraction patterns of Ni milled together with the Al powder for 16 h in the attendance of Mo as micro-alloying element. The intermediate and high peaks are related to the powder blend including 0.5 and 5.0 at% Mo, respectively. The intermediate and high peaks are related to the specimen in which there is not any nickel aluminide intermetallic yet. It is obvious from Fig. 2 that the intermediate and high peaks are a little shifted toward higher  $2\theta$  angles with attention to the lesser peak. As an outcome, the peak of Ni for the specimen with higher Mo contents (high peak) moves less than the

one with lesser Mo contents (intermediate peak).

Due to the atomic size of the elements existed in the powder blend (Ni = 124 pm, Mo = 136 pm and Al = 143 pm), the manner viewed in Fig. 2 is being described as follows:

It is clear that during mechanical alloying, heavy deformation, welding and fracturing are introduced into the particles. This is manifested by the attendance of a variety of crystal defects similar stacking faults, dislocations, vacancies and enhanced number of grain boundaries. The attendance of this defect structure enhances diffusivity of solute elements into the matrix. Furthermore, the refined microstructural features reduce the diffusion distances. Furthermore, it is obvious that a little increase in the temperature during milling further aids the diffusion behavior. Change in Ni peaks positions is caused by the stress induced by the structural defects such as vacancies created during mechanical

alloying. Since, the Mo atomic size is approximately close to the Ni atomic size, situation of Mo in some of the Ni vacancies diminishes the stress induced by mechanical alloying. In the other words, solution of Mo in the Ni lattice compensates the stress stored in the Ni lattice raised by the defects induced during mechanical alloying. For this Cause, the peak of Ni for the specimen with higher Mo contents (high peak in Fig. 2) has been displaced less than the specimen with lesser Mo contents (intermediate peak in Fig. 2). However, the

amount of Mo is not sufficient to compensate the stress stored in the Ni lattice fully. It has been reported that Mo dissolution in Ni is an exothermic procedure. The heat released from this reaction speeds up the reaction of Ni with Al. Therefore, enhancing the Mo content speeds up the formation of nickel aluminide. This is the Cause for the viewed difference in the formation behavior of nickel aluminide at the 80 h milling time (view Table 1).

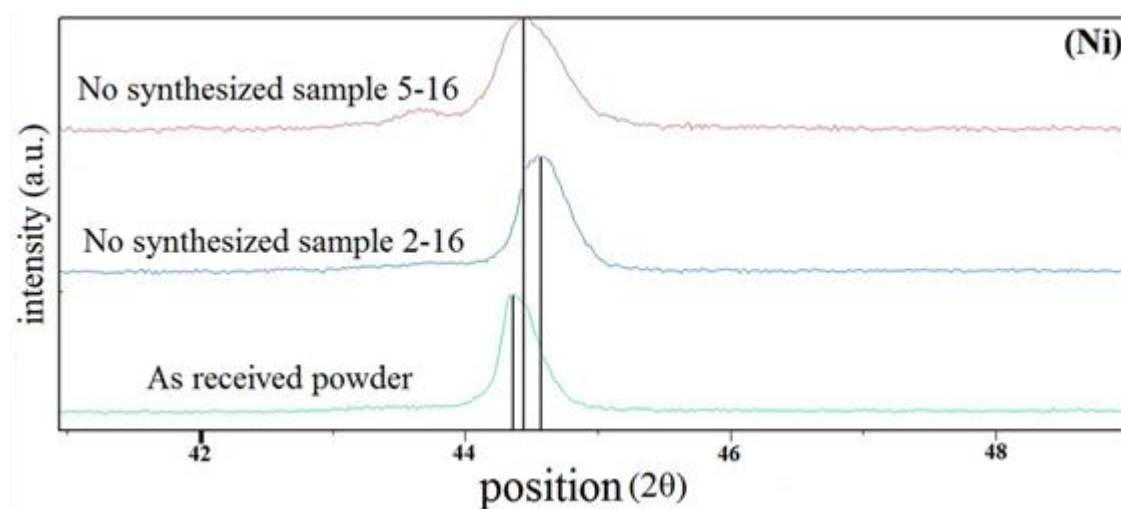


Fig. 2. Comparison between three most intense Ni peaks (the XRD pattern provided before generation of nickel aluminide phase in samples 2-16 and 5-16).

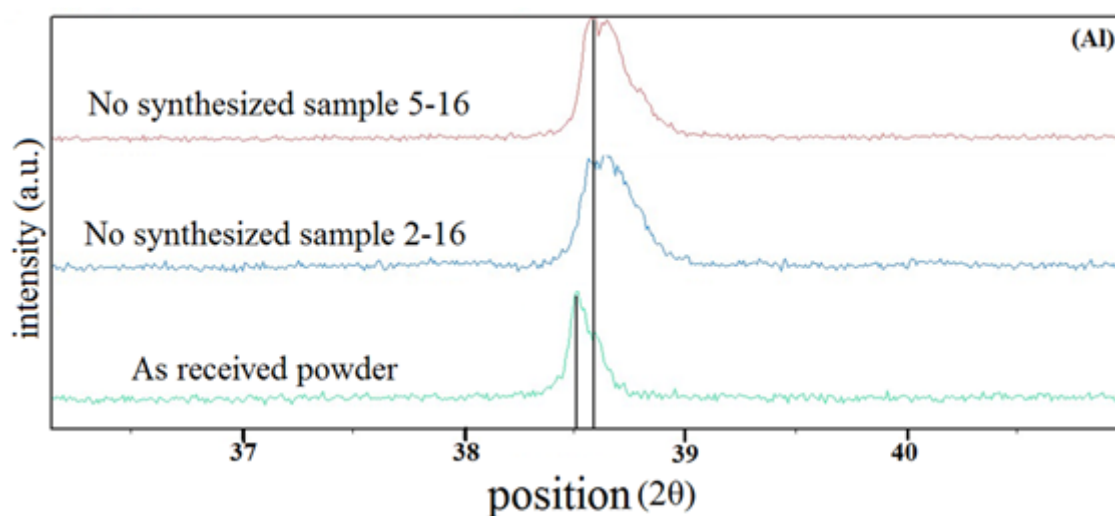
The highest peaks of elemental Al outcomes by X-ray diffraction analysis of the powder-

blend milled for 16 h illustrates in Fig. 3 and can be used to study the structural variations



of Al lattice during mechanical alloying before production of nickel aluminide phase. Resemble to Fig. 2, there exist three peaks in Fig. 3: the lesser peak is related to as received Al powder and other peaks illustrate the X-ray diffraction patterns of Al milled together with the Ni and Mo powder for 16 h. The intermediate and high peaks are related to the Al in the powder-blend including 0.5 and 5.0 at% Mo, respectively. These peaks are related to the specimen in which there is not any nickel aluminide intermetallic yet. According to Fig. 3, both intermediate and high peaks have been moved toward higher  $2\theta$  angles with

attention to the lesser peak (no milled peak). In contrast to the contrariwise Ni peaks, the high peaks of Al have been moved equivalent to the intermediate peak. This means that the Mo which existed in the powder-blend does not have any effect on the change in Al peaks positions. As the solubility of Mo in Al lattice is low; the Mo cannot compensate the stored stress in Al lattice induced by the defects which was created during mechanical alloying. Therefore, change in Al peaks positions is only due to severe plastic deformation and the production of many defects resulted from milling media.



**Fig. 3.** Comparison between three most intense Al peaks (the XRD pattern provided before the generation of nickel aluminide phase in samples 2-16 and 5-16).

Fig. 4 represents the basic X-ray diffraction peaks of nickel aluminide phase synthesized in the attendance of 0 and 0.5 at% Mo. The two highest peaks are related to the specimens 1-128 and 2-128 that were milled up to 128 h and the nickel aluminide compound which was fully formed in the Ar atmosphere before milling off. Other peaks illustrate the X-ray diffraction pattern of nickel aluminide phase produced after milling off in the air atmosphere (the specimens 1-16, 1-80 and 2-80).

As it can be viewed from Fig. 4:

1. The nickel aluminide peaks for the specimens 1-80 and 2-80 have been appearing in resemble angles. It means that when the produced nickel aluminide is milled under Ar, enhancing Mo from 0 up to 0.5 at% it does not have any effect on the peaks positions.
2. The nickel aluminide peaks for the specimens 1-16 and 1-80 have been appearing in resemble angles. It means that the milling time of the powder blend does

not have any effect on the diffraction manner of nickel aluminide compound synthesized after milling off (in the air atmosphere).

3. In relation to nickel aluminide phases produced in the specimens 1-16 and 1-80, though the intensities and diffraction angles are similar to each other, they have been a little displaced to lesser angles with attention to the specimens 1-128 and 2-128.

4. The basic peak of nickel aluminide phase formed in the specimen 2-80 appears in the lowest diffraction angles with attention to the one formed in the other specimens.

The above observations can be described as follows:

When the milling time is sufficient, the nickel aluminide intermetallic is synthesized under protective gas (here is Ar) before milling off. Continuing the milling procedure after the production of nickel aluminide causes an enhancement in the internal crystal stress in the nickel aluminide lattice. In the other words, the

nickel aluminide phases synthesized in the specimens 1-128 and 2-128 have been milled after production while those synthesized in the specimens 1-16 and 1-80 do not have any milling experience after production.

Therefore, the basic peak of nickel aluminide formed in the specimens 1-128 and 2-128 is located in the higher angles with attention to that one formed in the specimens 1-16 and 1-80.

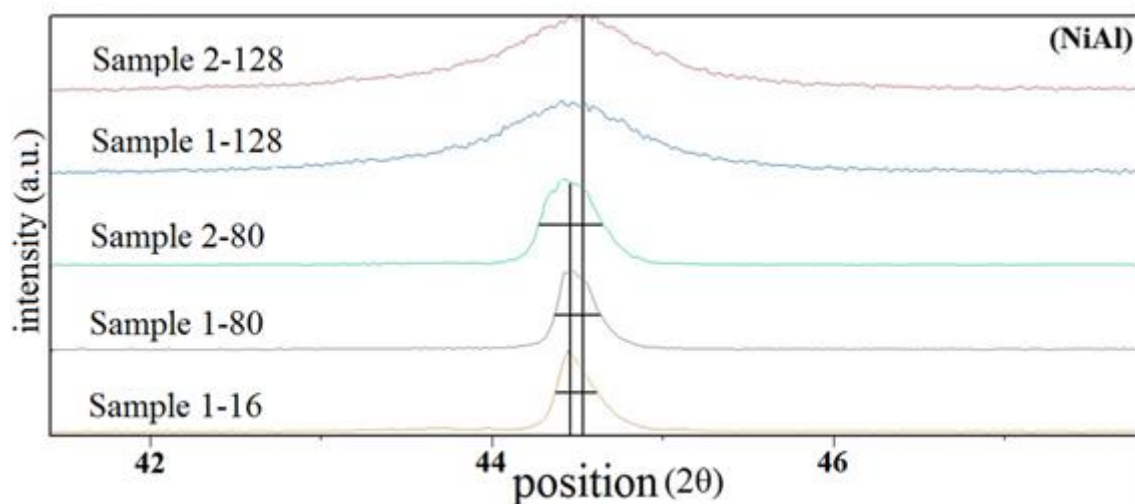


Fig. 4. Comparison between various most intense NiAl peaks formed on different milling times.

In relation to the specimens 1-16, 1-80 and 2-80 it can be expressed that the heat released during the formation of NiAl compound (in the air) causes recovery and annealing of the milled particles, hence, the peaks of nickel aluminide phase produced in the specimens 1-16 and 1-80 are independent of the milling time. For the specimens 1-80 and 2-80, it can be viewed that the peak of nickel aluminide formed in the specimen 2-80 appears in the lesser angles, while, as it

was already mentioned that enhancing Mo from 0 at% up to 0.5 at% does not have any significant effect on the peaks positions (view the peaks of 1-128 and 2-128). It can be described that the Mo enhances the slip systems and reduces the APB energy. Hence, as the critical shear stress for dislocation production would be reduced at the final step, the dislocation mobility is enhanced. Obviously, the new dislocations produced by the new activated slip systems

affect the recovery and annealing procedure, in effect, Mo can influence the recovery and annealing procedure of nickel aluminide phase. Hence, when the nickel aluminide intermetallic is synthesized in the air atmosphere, enhancing the Mo from 0 up to 0.5 at% has a significant effect on its crystal lattice. The stress is released due to recovery and annealing, therefore, the peak of nickel aluminide produced in the

specimen2-80 appears in the lesser angle with attention to the specimen1-80.

Fig. 5 illustrates a dark field TEM image of the  $\text{Ni}_{50}\text{Al}_{50}$  and  $\text{Ni}_{50}\text{Al}_{45}\text{Mo}_5$  alloys after the mechanical alloyed process. Fig. 5(a) clearly shows grain sizes in the 25 - 35 nm range. The average grain size is in the nanometric range less than 10 nm (Fig. 5(b)) and smaller than those sizes obtained in the NiAl (25–35 nm) alloy.

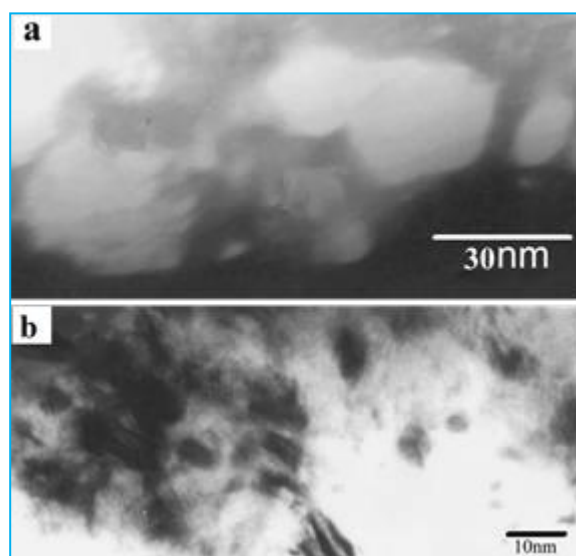


Fig. 5. Dark field image of the (a) NiAl (b)  $\text{Ni}_{50}\text{Al}_{45}\text{Mo}_5$  powders after the mechanical alloying process

#### 4. Conclusions

The mechanical alloying procedure was used to synthesize the  $\text{Ni}_{50}\text{Al}_{50}$  and  $\text{Ni}_{50}\text{Al}_{45}\text{Mo}_5$  nanocrystalline intermetallic compound using the pure Ni, Al and Mo

elemental powders in a planetary ball mill.

The mechanical alloying was carried out in the attendance of various Mo contents as a micro-alloying element for various milling times. In a sufficient milling time, the nickel

aluminide phase is produced during mechanical alloying under protective gas which here is Ar. The synthesis manner of nickel aluminide intermetallic depends on the micro-alloying of Mo contents and milling time. If the milling time is not sufficient, the nickel aluminide intermetallic is not produced during the milling procedure. Longer milling time speeds up the nickel aluminide formation in the air atmosphere. When the milling time is fixed, enhancing the Mo content speeds up the nickel aluminide formation in the air atmosphere. The Mo compensates the defects created in the Ni lattice during mechanical alloying. When the nickel aluminide phase is formed during mechanical alloying, the Mo content does not affect the peaks positions. Although, the peak of nickel aluminide produced in the air atmosphere is displaced by changing the Mo contents. In the fixed milling time, enhancing the Mo content leads to acceleration in the nickel aluminide

formation in the air atmosphere. Mo enhance has a considerable effect on the lowering of crystallite size.

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