EFFECT OF COMPOSITION AND MILLING TIME ON THE SYNTHESIS OF NANOSTRUCTURED Ni-Cu ALLOYS BY MECHANICAL ALLOYING METHOD

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Abstract: *Ni and Cu elemental powder mixtures containing 25, 50, and 75% at Cu were subjected to mechanical alloying in a planetary ball mill under various milling times. Structural evolution was analyzed by means of X-ray diffraction and scanning electron microscopy. Experimental results indicated that nanostructured solid solution alloy powders having homogeneous distribution of Ni and Cu were formed by milling-induced interdiffusion of the elements. Average crystallite size of the as-milled powders was decreased with increasing Ni content and milling duration, and found to be in the order of 15-40 nm after 30 h of milling for all powder compositions. Moreover, lattice parameter and lattice strain of solid solutions were increased with the time of MA, which was more intense for nickel-rich alloys.*

Keywords: *Ni-Cu binary alloys, Mechanical alloying, High-energy ball milling, Nanostructured alloys.*

1. INTRODUCTION

Ni-Cu alloys generally exhibit good resistance to corrosion and stress corrosion cracking in a variety of environments, which depending on the copper content, have excellent ductility, moderate strength and high toughness [1]. These alloys are commonly fabricated in bulk by melting processes. However, by the use of mechanical alloying (MA) process, a nanostructured powder product can be produced with a low cost [2].

Mechanical alloying, a solid-state powder processing technique, was developed in the 1970's to produce oxide-dispersion strengthened nickel- and iron-base alloys [3]. More recently, it is well known that MA of elemental mixtures can generate equilibrium and non-equilibrium structures. In this process, the grinding components transfer a great amount of energy to the powder by welding and fracture cycles, giving a high chemical homogeneity to the processed material [4]. In the last two decades, it has been shown that nanostructured materials can be synthesized by MA.

In this research, Ni-Cu solid solution alloy powders with a wide compositional range are synthesized by MA, and the evolutions of structural characteristics with the milling time are reported and discussed.

2. EXPERIMENTAL PROCEDURE

Mixtures of elemental nickel and copper powders (>99.9% purity) having an average particle size of 10 μm and <60 μm, respectively, with three different molar ratios of 1:3, 1:1 and 3:1 were ball milled in a planetary ball mill operated at 300 rpm. The powder was charged into a chrome steel vial and sealed under an argon atmosphere. The ball to powder weight ratio (BPR) was 30:1. In each experiment, 1 mL of ethanol as a process control agent was added to the mixture to prevent agglomeration and oxidation of powders at room temperature. The accumulated milling times were 1, 3, 16 and 30 h.

The milled powder was collected from the vials after the desired milling time, and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

SEM apparatus operating at an accelerating voltage of 20 KV coupled with energy-dispersive X-ray spectrometer (EDS), was used for imaging the morphologies of the milled powders and for checking the compositional homogeneity and any possible contamination of samples by Fe from grinding media, respectively.

XRD apparatus equipped with Cu-Kα radiation (λ=1.540598 Å) and germanium monochromator was used to characterize the

phases present after different milling time. The lattice parameter has been determined after different milling times using Cohen's method by solving the following two equations [5]:

$$\sum \alpha \sin^2 \theta = A\sum \alpha^2 + C\sum \alpha\delta \quad (1)$$

$$\sum \delta \sin^2 \theta = A\sum \alpha\delta + C\sum \delta^2 \quad (2)$$

where 2θ is the Bragg angle (in rad) of reflection i (given by the centroid of the profile), $\alpha = (h^2 + k^2 + l^2)$, $A = \lambda^2 /4a_0^2$, λ is the wavelength (in nm), $\delta = 10\mathrm{Sin}^2\, 2\theta_i$, and C is a constant.

Average crystallite size and lattice strain of the phases were evaluated by means of XRD line-broadening analysis. Apart from the instrumental effect, the XRD pattern of nanocrystalline materials exhibits considerable peak broadening with reduced intensity due to changes in structural parameters like crystallite size and internal strains, caused by the lattice distortion. Williamson-Hall (WH) method represented by Eq. (3) was employed to calculate the latter two parameters [6].

$$B\cos\theta_i = \frac{K\lambda}{D} + 2\varepsilon \sin\theta_i \quad (3)$$

where D is the coherent scattering length (crystalline size in nm), K is a constant whose value is approximately 0.9, ε is the inhomogeneous internal strain (in %), and B is integral width of sample (in rad) calculated by Eq. (4):

$$B^2 = \beta_{\exp}^2 - \beta_{ins}^2 \quad (4)$$

where β_{exp} is the integral breadth (= peak area/peak height) and β_{ins} is the instrumental broadening (in rad) and it was determined by using National Institute for Standards and Technology (NIST) standard 640c (polycrystalline silicon powder) [7]. A plot of Bcosθ versus sinθ should result in a straight line, and the values for crystallite size and strain can be obtained from the intercept and the slope, respectively.

3. RESULTS AND DISCUSSION

3. 1. X-ray Diffraction Analysis

Figure 1 shows XRD patterns of mechanically alloyed powders under different milling durations and alloy compositions. It can be seen that, for all compositions, the sharp pair-wise diffraction

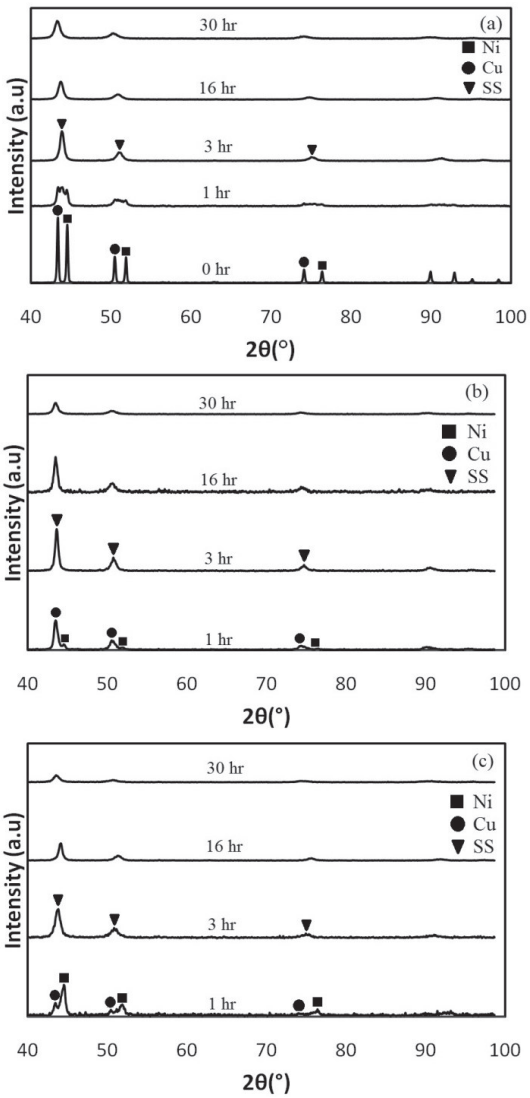

Fig. 1. The evolution of XRD patterns of the milled powders with milling time: (a) $Ni_{50}Cu_{50}$, (b) $Ni_{25}Cu_{75}$ and (c) $Ni_{75}Cu_{25}$.

peaks of the initial copper-nickel powder mixtures broaden and lose intensity after 1 h of intensive milling. With increasing milling time, in-between peaks progressively emerge, indicating the formation of Ni-Cu solid solution (SS) alloy. For the 3 h ball milled powder, three distinct diffraction peaks can be clearly seen, which indicate the complete formation of solid solution structure.

According to the Ni-Cu binary phase diagram, the Cu-Ni system includes complete solubility of its constituents in the liquid and solid state. Hence, continuous equilibrium FCC solid solutions can be formed in the whole compositional range. Therefore, the peaks in the XRD pattern of the samples after 3 h of milling could be attributed to $Ni_{25}Cu_{75}$, $Ni_{50}Cu_{50}$ and $Ni_{75}Cu_{25}$ compositions, corresponding to 1:3, 1:1 and 3:1 molar ratios of Ni-Cu mixture in the starting material, respectively.

The milling time required for the formation of Ni-Cu alloys under different experimental conditions reported by other researchers [8,9] has been compared with that in the present investigation in Table 1. As seen, the shortest formation time (3 h) belongs to the present study that may be attributed to the more intense milling conditions. A higher BPR increases the number of impacts applied by the balls in the unit time. Moreover, various types of the mills used may generate different mechanical energies and thus alloying kinetics.

Lattice parameters of Ni, Cu and Ni-Cu solid solutions calculated by Cohen's method are shown in Table 2. It is observed that, in the course of MA and before the formation of a solid solution, the lattice parameters approach each other, which indicates an interdiffusive mode of alloying (interdiffusion mechanism) [10]. It also reveals that the lattice parameter of the solid solution increased after 3 hours with the progress of milling. This could be mainly ascribed to the increased amount of point defects, such as interstitial atoms and vacancies, which would expand the lattice [8]. Furthermore, it is interesting to note that the rate of change of the lattice parameter with milling time is significantly higher as the alloy composition getting richer in nickel. This, may be attributed to the fact that nickel is more work-hardenable than copper. Therefore, with applying a given amount of mechanical energy to Ni-rich particles, more defects and hence bigger lattice parameters are created when compared to Cu-rich alloys.

Figure 2 illustrates the variation of crystallite size and lattice strain of different Ni-Cu solid solution alloys as a function of milling time. The figure apparently shows that with increasing the time of milling, severe crystallite size reduction occurs toward the formation of nanostructure alloys while the lattice strain increases. The crystallite size of 30 h mechanically-alloyed powders is in the range of 15-40 nm depending on the composition. It is worth to note that the crystallite size refinement is mostly occurred in

Table 1. Effect of different mechanical alloying parameters on the formation time of Ni-Cu alloy

Type of mill	BPR	Rotational speed (rpm)	Formation time (hr)	Reference
Planetary	10:1	300	30	2
Vibration	10:1	Not reported	4	8
Attritor	9:1	1400	7.5	9
Planetary	30:1	300	3	Present study

Table 2. Variation of lattice parameter with the progress of MA

Milling time (hr)	Lattice parameter (Å)								
	$Ni_{25}Cu_{75}$			$Ni_{50}Cu_{50}$			$Ni_{75}Cu_{25}$		
	Cu	Ni	SS	Cu	Ni	SS	Cu	Ni	SS
0	3.6134	3.5250	-----	3.6134	3.5250	-----	3.6134	3.5250	-----
1	3.6042	3.5387	3.5866	3.6061	3.5283	3.5635	3.6067	3.5272	3.5433
3	-----	-----	3.5946	-----	-----	3.5708	-----	-----	3.5485
16	-----	-----	3.5977	-----	-----	3.5889	-----	-----	3.5809
30	-----	-----	3.6052	-----	-----	3.6044	-----	-----	3.5952

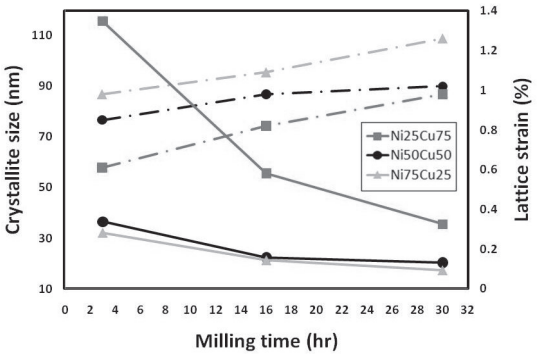

Fig. 2. Variation of crystallite size (solid lines) and lattice strain (dashed and dotted lines) of Ni-Cu solid solutions with different initial powder compositions as a function of the milling time.

the early stage of milling, while lattice strain increases steadily with the milling time. At a given milling time, these structural changes are apparently more intense for alloys containing 50 and 75 at% Ni. The mechanical deformation induced in the powder and the solid solution strengthening caused by increasing the Ni content might be responsible for this behavior [4].

3. 2. SEM Analysis

SEM micrographs showing the morphologies and elemental mapping of milled powders for different milling times and alloy compositions are presented in Fig. 3. It can be seen that mechanically alloyed powders get flattened and coalesce due to the high impact forces (ball-ball and ball-wall collisions) on ductile Ni and Cu starting powders that lead to cold welding. At longer milling times (Fig. 3b compared to 3a), powder particles begin to disintegrate due to welding and fracture cycles and the brittleness induced as a result of continuous milling and work/strain hardening [4].

Moreover, elemental mapping through EDS analysis of the as-milled powder shows an actual homogeneous distribution of Cu and Ni for all compositions, which again proves the formation of solid solution at micro-scale. Only very small iron contamination (less than 1 at%) was detected after 30 h MA.

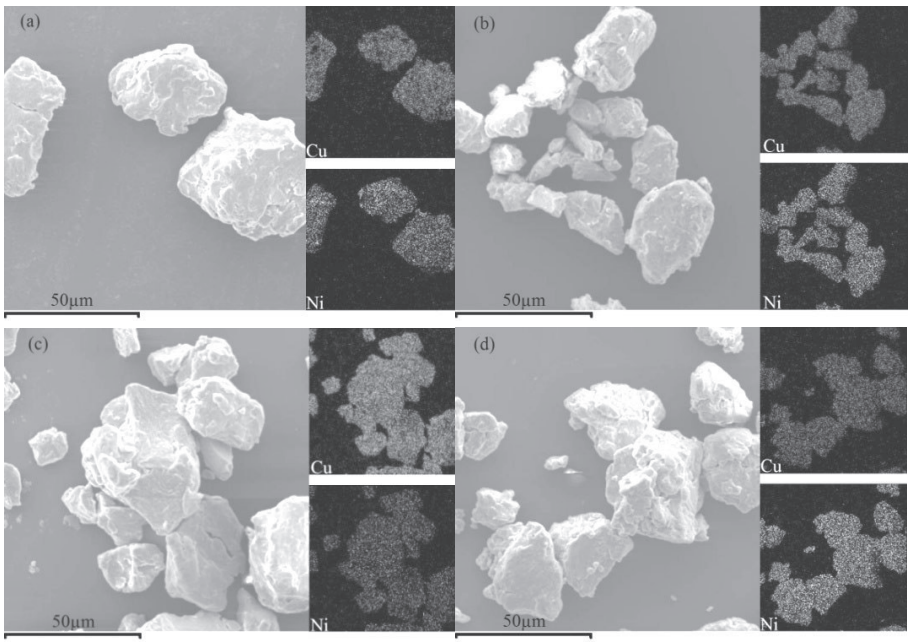

Fig. 3. SEM micrographs along with elemental mapping of Cu and Ni showing respectively the morphology and homogeneity for different powder compositions and milling times: (a) $Ni_{50}Cu_{50}$ for 1 h, (b) $Ni_{50}Cu_{50}$ for 30 h, (c) $Ni_{25}Cu_{75}$ for 30 h, and (d) $Ni_{75}Cu_{25}$ for 30 h.

4. CONCLUSIONS

The main findings of the present research are summarized as follow:

1. A relatively short-time MA treatment of nickel and copper elemental powders in a planetary ball mill could resulted in the formation of nanostructured Ni-Cu solid solution alloy powders with significant homogeneity.
2. Analysis of the XRD data of powders milled for different times revealed that copper and nickel are progressively alloyed through mutual diffusion of atoms into each other.
3. The structural characteristics, such as morphology, crystallite size and lattice strain, caused by heavy mechanical deformation are greatly influenced by the milling time as well as the composition.
4. Most of the crystallite size refinement occurs during the early stage of milling, while lattice strain increases steadily with the milling time.
5. It was found that the structural changes in a given milling time are apparently more intense for nickel-rich alloy compositions.
6. For nickel-rich alloys, the rate of change of the lattice parameter of the solid solution with the time of milling is also considerably higher.
7. The results of the study can be applied to the synthesis of homogeneous copper-nickel alloy powders with any desired composition in the whole range.

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