

Microstructural Characterization of Multi-Component Systems Produced by Mechanical Alloying

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ABSTRACT

A series of binary to hexanary alloys (Ni, Co, Mo, Al, Fe, Cu) are produced by mechanical alloying. Formation of an FCC solid solution is observed in the binary system. For ternary to quinary systems the presence of an amorphous phase and a BCC solid solution is identified, and for the hexanary system a combination of BCC and FCC solid solutions is detected. There is a very small change in the lattice parameter of Mo, reflecting the limited solid solubility of other element in this structure. However, Mo induces the fast amorphization of other elements and the reduction of crystallite size.

INTRODUCTION

Multi-component systems are characterized by a high entropy and ability to form amorphous phases [1-5]. High entropy alloys (HEAs) are a new era of materials that consist of various major alloying elements; the system selected in each case is different, and each additional element changes the behavior of the final alloy. The HEAs are quite simple to analyze and control because they tend to form simple solid solution phases, mainly of FCC and BCC structures. They have numerous beneficial mechanical, magnetic, and electrochemical characteristics [6]. These systems can be processed by different routes, conventional casting, thin film deposition and milling process. The mechanical alloying (MA) process has been widely recognized as an alternative route for the formation of nanocrystalline materials, with unusual properties [7, 8]. In this investigation, a multi-component system formed by Ni-Co-Mo-Al-Fe-Cu is studied from the binary to hexanary alloy; the effect of each element and milling time is reported and discussed.

EXPERIMENTAL PROCEDURE

Ni, Co, Mo, Al, Fe and Cu powders with purity higher than 99.5% and particle size of -325 mesh are mechanically alloyed from binary Ni-Co to hexanary Ni-Co-Mo-Al-Fe-Cu systems in equiatomic ratio. Table 1 gives the nominal composition used in each system (identified as A, B, C, D, E series). The milling process is carried out from 0 to 30 h in a high energy shaker ball mill (SPEX-8000M). Hardened steel vials and balls are used as milling media. The milling ball-to-powder weight ratio is set at ~5:1. In order to avoid excessive welding of powders, methanol is added to the powders to act as a process control agent (PCA). The milled products are characterized by scanning electron microscopy (SEM) in a JEOL JSM-7401F microscope

supplied with an energy dispersive spectrometer (EDS), operated at 5 kV and 20 μ A. They are also analyzed by X-ray diffraction (XRD) in a Siemens D5000 diffractometer with Cu K α radiation ($\lambda=1.5406$ Å) and operated at 35 kV and 25 mA in the 2θ range of 20-110°. The step and acquisition time are 0.2° and 5 s, respectively.

Table 1. Nominal* and experimental chemical compositions of different systems studied (at. %).

System	Milling time (h)	Ni	Co	Mo	Al	Fe	Cu
A	0	*50.0	*50.0				
	10	50.9	49.1				
	20	51.5	48.5				
	30	51.0	49.0				
B	0	*33.3	*33.3	*33.4			
	10	36.9	36.0	27.1			
	20	37.6	34.6	27.8			
	30	37.5	35.0	27.5			
C	0	*25.0	*25.0	*25.0	*25.0		
	10	29.1	28.9	21.7	20.3		
	20	29.3	26.6	22.1	22.0		
	30	29.1	26.8	22.0	22.1		
D	0	*20.0	*20.0	*20.0	*20.0	*20.0	
	10	21.0	22.6	17.1	17.6	21.7	
	20	21.4	21.7	17.3	17.7	21.9	
	30	21.6	22.0	17.3	17.5	21.6	
E	0	*16.6	*16.6	*16.7	*16.7	*16.7	*16.7
	10	17.5	18.2	14.2	15.2	16.8	18.1
	20	16.1	18.3	14.6	16.4	16.9	17.7
	30	17.1	18.0	14.3	15.9	16.9	17.8

RESULTS AND DISCUSSION

Figure 1 presents the XRD spectra from binary to hexanary systems mechanically alloyed for different times. In general, elemental characteristic peaks disappear as the milling time increases while peaks corresponding to the crystallization of a single solid solution appear. For all systems, this solid solution appears from 10 h of milling time. It is important to mention that for initial powders (0 h of milling) Co has an HCP structure, which transforms to an FCC structure after the milling process due to particle size reduction and the accumulation of structural defects, as reported elsewhere [9, 10]. Thus, in figure 1a, peaks from Co HCP disappear after 10 h of milling. Ni peaks (FCC structure) are broadened and shortened as the milling time is increased; additionally the position of the Ni diffraction lines is shifted to lower angles after 10 h of milling. This displacement of the peaks remains for all milling times and it is assumed to be an indication of the formation of a FCC solid solution by MA.

The XRD patterns as a function of milling time for the NiCoMo system are presented in figure 1b. Mo characteristic reflections decrease in intensity and become broader, but they are

detected even after 30 h of milling, suggesting that this element is not dissolved in Ni or Co. By comparing figures 1a and 1b, an apparent effect of Mo on the amorphous phase formation is observed; for example, in figure 1a the two first peaks of Ni –in solid solution with Co– remain even after 30 h of milling, whereas in figure 1b Ni and Co reflections become too broad or disappear after 10 h of milling.

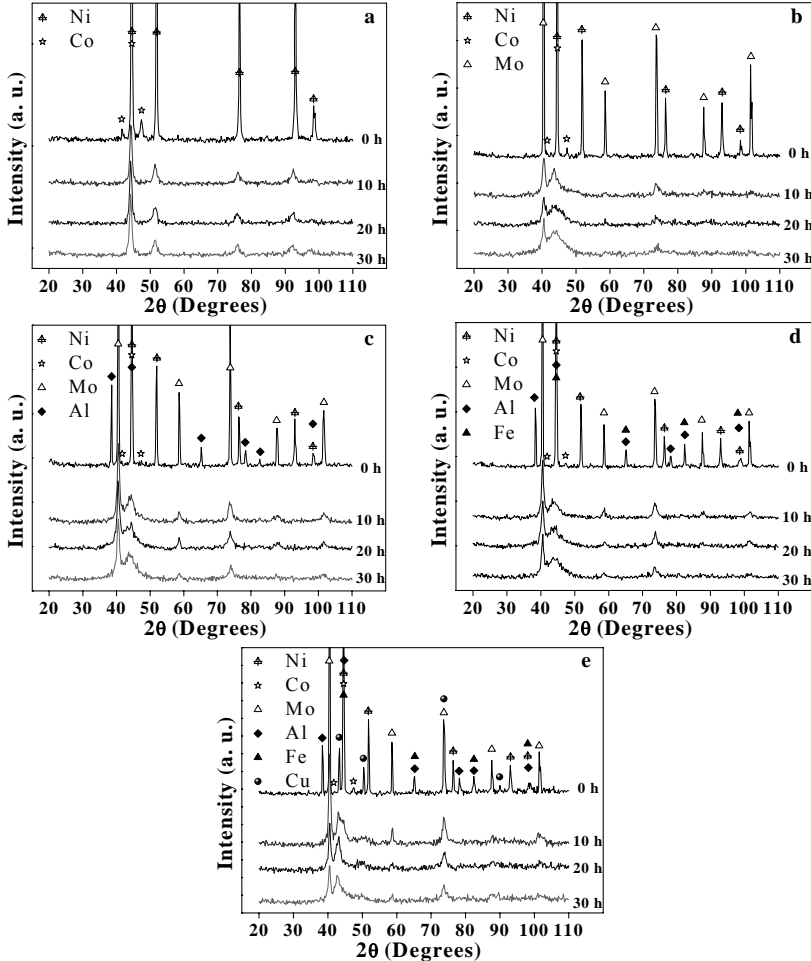


Figure 1. XRD spectra of the equiatomic (a) binary NiCo, (b) ternary NiCoMo, (c) quaternary NiCoMoAl, (d) quinary NiCoMoAlFe, and (e) hexanary NiCoMoAlFeCu systems as a function of milling time.

Figure 1c presents XRD patterns of the NiCoMoAl alloy. In this case, 10 h of milling considerably reduce the intensity of the diffraction peaks corresponding to Ni, Co or Al. Apparently 10 and 20 h of milling induce the formation of an FCC solid solution, but a longer milling time produces an amorphous phase. Nevertheless, the XRD patterns always show Mo reflections regardless of the milling time. In this alloying system, it is appreciated a small variation of Mo peaks to higher 2θ values as the milling time increases; this denote the incipient formation of a BCC solid solution.

In the case of the NiCoMoAlFe alloy, the XRD patterns are shown in figure 1d. There is a similar behavior as compared to the quaternary system. The reflections belonging to Co, Al and Fe disappear. Apparently, an amorphous phase formation is produced at long milling times while the reflections of Mo are still retained in the XRD pattern. However, in a similar case as the quaternary system, Mo reflections are shifted to higher angles as the milling time is increased, denoting the formation of a BCC solid solution.

For the NiCoMoAlFeCu system (Fig. 1e), there is no evidence of Co, Al, Fe and Cu peaks even after 10 h of milling. Milling produces only short and broad peaks near the original Mo peak positions and an apparent FCC solid solution. According to the peaks position, this FCC solid solution presents higher lattice parameter than that found in the binary system (Ni-Co system, Fig. 1a). Mo characteristic reflections present shortening, broadening and shifting to higher angles denoting crystal refining and the formation of a BCC solid solution.

Crystallite size and lattice strain of the alloys have been calculated from the diffraction peaks at 2θ positions near the first Ni and Mo peaks by using an algorithm included in the X'Pert Data Viewer software, based in the Scherrer formule; instrumental correction has been performed employing a silicon standard. Figure 2 shows the evolution of these parameters as a function of the milling time; each point corresponds to the average of 5 measurements and the error bars indicate the standard deviation. For all the series, a decrease in crystallite size and an increase in lattice strain are found as the milling time increases. This is attributed to the mechanical deformation introduced in the powders. Severe plastic deformation can lead to variation in crystallite size and the accumulation of internal stresses. Due to the precision achieved in our evaluations (5-15 Å), difference in crystallite size between samples B, C, D and E (Fig. 2a) could be negligible.

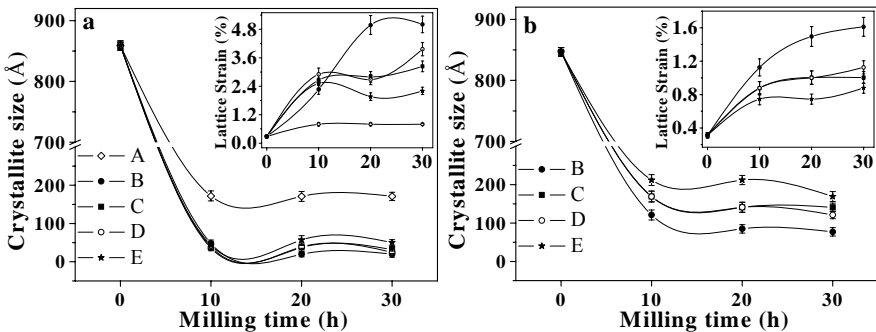


Figure 2. Crystallite size and lattice strain versus milling time for (a) first Ni-type and (b) first Mo-type reflections. A-E indicate the different investigated multi-component alloys.

Figure 3 shows the powder cross section microstructure of quaternary and hexanary alloys after 10 and 30 h of milling. For lower milling times a quasi-lamellar structure is observed, which is typical in the early stages of MA for ductile components [7]; during the SEM observations at higher magnifications, a bright phase is observed, which is identified as a Mo-rich phase by means of EDS microanalyses (Figs. 3a and 3c). With further milling, a more uniform microstructure (Figs. 3b and 3d) is observed, but some bright particles are still noted. These results are in accordance with the XRD analysis, where Mo reflections are detected in all systems containing this element (Figs. 1b-1e). General microanalyses by EDS show that the chemical composition of all systems is homogeneous after longer milling times (Table 1); oxygen signal is not detected, indicating that the oxidation during the milling process is very low.

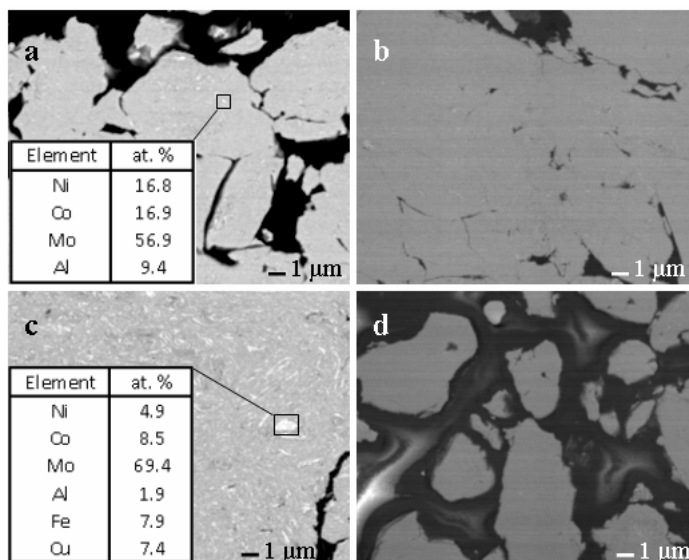


Figure 3. Powder cross section backscattered electron images of the quaternary NiCoMoAl alloy after (a) 10 h and (b) 30 h and the hexanary NiCoMoAlFeCu alloy after (c) 10 h and (d) 30 h of milling.

From the above results, a different answer is observed in all the alloying systems studied. Binary NiCo system shows the preference to form FCC solid solution. Ternary NiCoMo system shows a sequence Crystalline \rightarrow BCC + FCC solid solution \rightarrow BCC + Amorphous. Quaternary NiCoMoAl and quinary NiCoMoAlFe systems show the sequence Crystalline \rightarrow BCC solid solution + Amorphous. Finally, the hexanary NiCoMoAlFeCu system shows the preference to form a BCC + FCC solid solution. For the binary system, despite the fact that for initial powder Co presents an hexagonal structure, the final phase formed is an FCC solid solution, whose reflections correspond with Ni peaks positions. From ternary to quinary systems, the apparent amorphous phase formation after longer milling time is present. For ternary system, Mo shows

an apparent inertness to combine with Ni or Co; Mo peaks shifting is not observed. However additions of Al (quaternary system) and Al-Fe (quinary system) have an effect in the Mo peaks positions, they are shifted to higher values. Mo effect on the amorphous phase formation could be attributed to the *i*) atomic size factor, as reported by Miedema [11], *ii*) difference in crystal structure, and *iii*) difference in melting point. In the case of the FCC solid solution peak measurements (Fig. 2a), the presence of Mo in systems B, C, D and E induces the reduction of the crystallite size, giving rise to the formation of an apparent amorphous phase, and the increment of the lattice strain, in comparison to the NiCo system (series A). For the BCC solid solution peak measurements (Fig. 2b), the reduction of crystallite size and lattice strain increase are due just to the milling effect [7]. In both FCC and BCC solid solution peak measurements, higher values in lattice strain can be seen for the alloy system B. From figure 2b, quaternary to hexanary systems have a larger BCC solid solution crystallite size than the ternary (NiCoMo) system. The crystal size refinement and micro-tensions increment are normal answers in powder mechanically alloyed.

CONCLUSIONS

The binary to hexanary equiatomic high entropy alloys in Ni-Co-Mo-Al-Fe-Cu system have been successfully synthesized by mechanical alloying in a high energy ball mill. Formation of an FCC solid solution structure after longer milling time was observed in binary and hexanary systems. After 10 h of milling, it was observed that the Mo presence improves the amorphous phase formation in ternary and quaternary systems. Mo presence favored the BCC solid solution structure formation.

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