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Microstructure of NiCoAlFeCuCr multi-component systems synthesized by mechanical alloying

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ABSTRACT

The present study uses the mechanical alloying method to produce series of binary to senary alloys based on Ni, Co, Al, Fe, Cu, Cr. Milling times are 0, 10, 20 and 30 h and experiments are performed in a high energy ball mill. The results of this investigation show that an FCC solid solution is formed in all the studied systems, but a different phase formation response is presented in each system. A mixture of FCC and BCC solid solutions in quaternary to senary systems, is formed for short milling times. Apparently, the dissolution rate of Fe and Cr into the FCC solid solution, is low. Moreover, it is observed that additions of these elements promote the formation of BCC solid solution, which is stable at temperatures up to −1273 K. Finally, it is observed that the heat treated products present a mixture of FCC and BCC solid solutions with lattice parameters close to those found in the milled products.

1. Introduction

Within traditional alloy concept, most alloys are composed of one principal metallic element. As the amount of alloying element increases, intermetallic compounds are typically formed due to the limited solid solubility of the element in the alloy, which leads to enhanced strength at the expense of accompanying embrittlement. This traditional strategy induces some difficulties in the processing and gives rise to complexity in microstructure analyses and generally, the deterioration of mechanical properties. High-entropy alloys (HEAs) are a new generation alloys that are different from conventional alloys based on one or two elements. HEAs contain at least five principal elements with concentrations between 5 and 35 at.% of each one, preferably in equiatomic ratio. The configurational entropy of HEAs increases with increments in the number of elements in the system and it is maximized at equiatomic composition. Making difficult the formation of intermetallics and leading to the formation of simple FCC and/or BCC solid solutions rather than complex phases [1–5]. With proper composition design, HEAs can achieve excellent mechanical and physical properties such as high strength and ductility, and good wear, oxidation and corrosion resistance. Therefore, these promising properties offer the potential to be used in many applications [6]. Some different methods such as: rapid solidification, chemical and physical vapor deposition, and mechanical alloying (MA), have been used to prepare many HEAs systems. However, the first three processes can only prepare limited quantities of sample, which will definitely restrict the practical applications of these alloys. In contrast, MA has been widely recognized as an attractive alternative route for the production of nanocrystalline materials, with unusual properties [7,8]. During this process, the solid solubility extension (introduced by the non-equilibrium state of the process) enhances the general formation mechanism of HEAs. The grain size of the elemental components decreases down to nanometer range and then a substantial amount of enthalpy can be stored in nanocrystalline alloys due to the large grain boundary area. In this investigation, multi-component systems (from binary to senary alloys) based on Ni–Co–Al–Fe–Cu–Cr are studied. Finally, the effect of the alloying elements and milling time is reported and discussed.

2. Experimental procedure

Commercial pure elemental powders of Ni, Co, Al, Fe, Cu and Cr (purity higher than 99.5%, −325 mesh) are used as the starting materials. The powders are mechanically alloyed from binary (Ni–Co) to senary (Ni–Co–Al–Fe–Cu–Cr) systems in equiatomic ratio. Table 1 lists the nominal composition used in each system. Milling is performed in a high energy ball mill (SPEX-8000M). Milling times are 0, 10, 20, and 30 h. The millings are performed under argon atmosphere using hardened steel vials and balls.

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Table 1
Nominal* and experimental chemical compositions of the different systems.

System	Milling time (h)	At.% Ni	At.% Co	At.% Al	At.% Fe	At.% Cu	At.% Cr
Binary (A)	0	*50.0	*50.0				
	10	50.9	49.1				
	20	51.5	48.5				
	30	51.0	49.0				
Ternary (B)	0	*33.4	*33.3	*33.3			
	10	36.3	35.7	28.0			
	20	35.3	35.8	28.9			
	30	35.6	35.3	29.1			
Quaternary (C)	0	*25.0	*25.0	*25.0	*25.0		
	10	25.1	27.6	22.0	25.3		
	20	24.6	27.8	22.3	25.3		
	30	23.3	27.5	23.3	25.9		
Quinary (D)	0	*20.0	*20.0	*20.0	*20.0	*20.0	
	10	19.2	23.2	16.8	21.6	19.2	
	20	19.8	21.4	17.9	20.9	20.0	
	30	19.5	21.1	19.0	20.8	19.6	
Senary (E)	0	*16.7	*16.7	*16.7	*16.7	*16.6	*16.6
	10	17.2	17.1	16.3	16.8	17.5	15.1
	20	16.4	16.5	17.3	16.8	16.6	16.4
	30	17.3	17.5	15.6	16.5	16.4	16.7

The milling ball-to-powder weight ratio is ~5:1. Methanol is added to the powders to avoid excessive welding and acting as process control agent (PCA). On the other hand, to evaluate the powder structural stability, some milled products are heat treated from room temperature to 1273 K; held at this temperature 5 min and then cooled down. The heating and cooling rate is 10 K/min and an argon atmosphere is used through the heat treatments. The 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 μA. EDS semi-quantitative analyses were carried-out in 100 μm × 100 μm square. The products are also analyzed by X-ray diffraction (XRD) in a Siemens D5000 diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm). Analyses are performed 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.

3. Results

XRD spectra corresponding to the mechanically alloyed systems (from binary to senary) during different times (0–30 h) are shown in Fig. 1. In general, it is observed that the intensity of the elemental characteristic peaks disappears as the milling time increases. In contrast, the peaks that indicate the formation of the single solid solution appear. Furthermore, the formation of the two solid solutions (FCC and BCC) is evident in all systems, from 10 h of milling. It is important to mention that the crystal structure of Co powders in the as-received condition (0 h of milling), is HCP. However, after milling, the HCP structure transforms to FCC. For this reason, the peak corresponding to Co HCP disappears after the 10-h milling (see Fig. 1a). This can be explained by the reduction on the particle size and accumulation of structural defects, as reported elsewhere [9,10]. On the other hand, the peaks corresponding to Ni FCC become broadened and shortened with increments in the milling time. In addition, the position of the Ni diffraction lines suffers a slightly shift to lower angles, for all milling times. Therefore, it is assumed that FCC solid solution formation is induced by MA. The shift observed in the position of the main Ni peak is attributed to that Ni and Co have similar atomic radii.

Fig. 1b presents the XRD patterns of the NiCoAl alloy system as a function of the milling time. As can be observed, the Co and Al characteristic peaks disappear after the 10-h milling, remaining broad and short Ni-type peaks without any evident shift. After 20 h of milling, an incipient shoulder formation on broad principal Ni-type peak is observed, while the intensity of the secondary peaks almost disappears. With increments in the milling time (30 h), only the most intense Ni-type peak is observed and an apparent mixture of two FCC solid solutions is evidenced, this is in agreement with the secondary peaks position. Moreover, the Ni-type peak shifts slightly to lower angles.

In the case of the NiCoAlFe alloy system (Fig. 1c), after 10 h of milling, the Co and Al characteristic peaks are not observed. Short and broad signals of BCC solid solution are present mixed with FCC solid solution signals. FCC solid solution peaks are present in accordance with the Ni positions. However, a slightly shift to lower angles of the main Ni-type characteristic peak is observed. Additionally, it is observed an asymmetry in the main FCC solid solution. This is related probably to the presence of two peaks from solid solutions. After 20 h of milling, the BCC solid solution peaks are not observed, and only those corresponding to the FCC solid solution are presented. It is observed that two peaks are overlapped with the main peak. It can be related to an incipient variation in the FCC solid solution lattice parameter, or to a secondary phase formed from the first one (crystallized during 10 h of milling). In contrast, for 30 h of milling, only a short and broad FCC signal is observed. The lattice parameter measured in this peak (1 1 1), is 0.360 nm, which is similar to that found in the ternary system after 30 h of milling. On the other hand, aluminum is expected to be the main factor that favors the growth of lattice parameter since Fe has smaller atomic size than Ni and Co.

Fig. 1d presents the XRD patterns of the NiCoAlFeCu alloy system in the as-mixed and as-milled conditions. After 10 h of milling, the Co and Al characteristic peaks are not observed. As can be seen, only short peaks that correspond to the typical FCC and BCC structures are distinguished over the background noise. Additionally, a broad and short peak with two maximums, which correspond possibly to the FCC and BCC phases, is observed. The lattice parameters calculated for these two phases are 0.360 and 0.289 nm, respectively. However, after 20 h and 30 h of milling, only FCC phase signals are observed and the lattice parameter is stabilized at 0.362 nm.

For the NiCoAlFeCuCr system (Fig. 1e), there is no evidence of Co and Al peaks after 10 h of milling. It is observed that the peaks corresponding to the BCC phase are overlapped with the Cr and Fe peaks. An incipient FCC phase formation is noticed by a signal at $2\theta = 43.60$, which is in agreement with the last XRD spectra (Fig. 1d). With increments in the milling times until 20 h, the intensity of the FCC phase increases and the BCC phase decreases. According to the peaks position, this FCC solid solution presents a higher lattice parameter (0.359 nm) than that found in the binary Ni–Co system (0.354 nm, Fig. 1a).

Fig. 1f shows the effect of milling time on the intensity of FCC and BCC solid solutions. It can be established from this figure that, FCC phase is more stable at longer milling times (30 h). Lattice parameters are included in the graph.

Crystallite size and lattice strain have been calculated from the broadening of the diffraction peaks, using the X'Pert Data Viewer software, which has an algorithm based on the Scherrer's formula. Instrumental correction has been possible using a standardized silicon sample. Fig. 2 shows the effect of milling time on the crystallite size and lattice strain, for each system. Each point represents the average value obtained from 5 measurements, while the error bars indicate its standard deviation. As can be seen, the crystallite size decreases and the lattice strain increases with milling time. This is attributed to the plastic deformation of powders caused by ball collisions during the milling. Severe plastic deformation can lead to variations in the crystallite size and accumulation of internal stresses. Considering the accuracy and precision of the measurements (0.5–1.5 nm), the difference in the crystallite size between samples B, C and E (Fig. 2), could be ignored.

Fig. 3 displays the effect of milling time (10 and 30 h) on the microstructure of quaternary and quinary alloys. As can be observed, a quasi-lamellar structure is presented after short-time millings (10 h). This microstructure is typically observed in the early

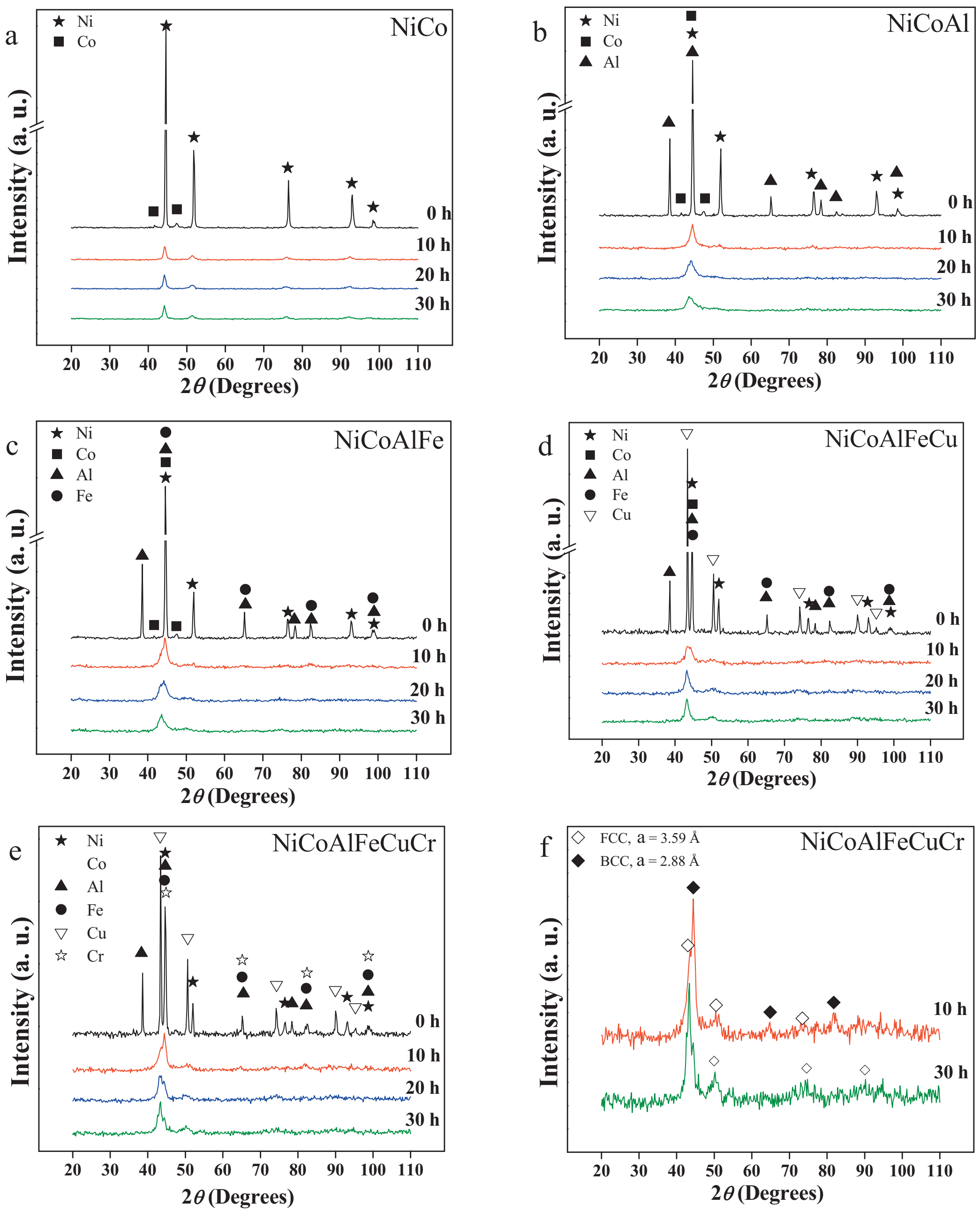

Fig. 1. XRD patterns of the equiatomic (a) binary NiCo, (b) ternary NiCoAl, (c) quaternary NiCoAlFe, (d) quinary NiCoAlFeCu, (e) senary NiCoAlFeCuCr systems as a function of the milling time and (f) senary NiCoAlFeCuCr system with two different milling times showing FCC and BCC phases.

stages of MA for ductile components [7]. The results of SEM analyses show the presence of a bright phase (indicated by the white arrow), which has been identified by EDS microanalyses as a Co-rich phase (Fig. 3a). In contrast, for the quinary alloy, the bright region corresponds to a Ni-rich phase (Fig. 3c).

Further milling results in more uniform microstructures with some bright spots (Fig. 3b and d). EDS semi-quantitative analyses reveal that chemical composition of all systems is homogeneous after further milling time (Table 1 and Fig. 3). Besides, the presence of oxygen is not detected, which indicates that oxidation during milling process and manipulation steps is minimal.

Fig. 4 shows XRD spectra of the quinary system after heating to 1273 K. A single mixture of FCC and BCC solid solutions is observed after this thermal treatment. The FCC phase formed during the milling process is stable up to 1273 K. Crystallization or growing of the BCC solid solution during heat treatment is observed. Milling time has no effect on the crystallized phases. As can be seen, the XRD spectra of the samples milled during 10, 20 and 30 h are practically the same. Furthermore, the lattice parameters of the FCC and BCC phases are 0.360 and 0.289 nm, respectively. These values present a slight deviation compared with the lattice parameters calculated from milled samples without thermical treatment.

4. Discussion

From the above-mentioned results, a different response is observed in each investigated alloying system. FCC solid solution is formed in the binary NiCo and ternary NiCoAl systems. However, the quaternary NiCoAlFe, quinary NiCoAlFeCu and senary NiCoAlFeCuCr systems present the following sequence: crystalline phases → FCC + BCC solid solutions → FCC solid solution. Also, it is observed that, although the initial Co powder has an hexagonal

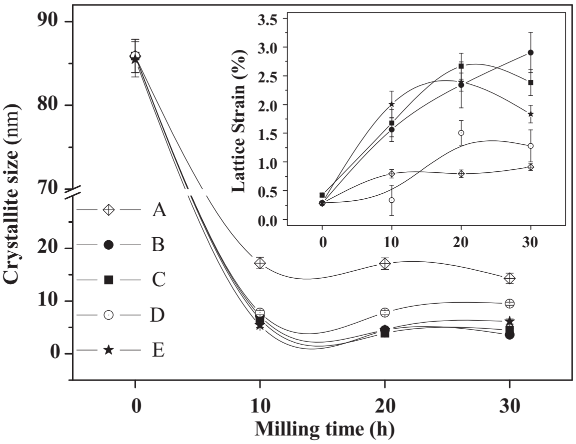

Fig. 2. Effect of milling time on the crystallite size and lattice strain. Parameters have been calculated from main Ni peak.

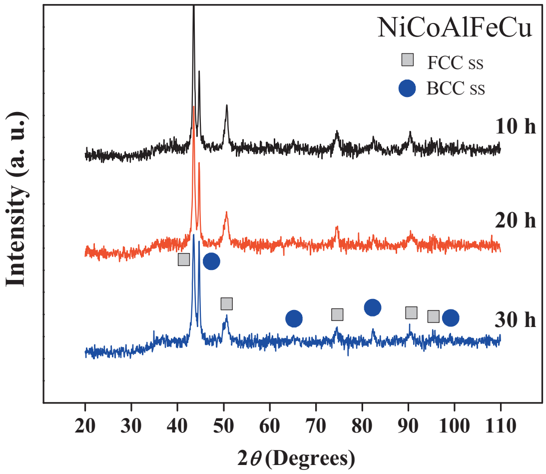

Fig. 4. XRD patterns of the equiatomic NiCoAlFeCu system after milling for a selected time and heated to 1273 K.

crystal structure, the resulting phase is a FCC solid solution, whose diffraction peaks transpose with the Ni solid solution peaks positions. Besides, it is evident that the presence of BCC elements favors the formation of BCC phases from quaternary to senary systems with short milling time (10 h). However, they are not stable with further milling time (30 h).

Also, the FCC solid solution from binary to quinary systems is formed from the shorter milling time. In the case of the ternary system, a slight variation in the lattice parameter is observed. The main diffraction peak is shifted to lower 2θ values. On the other hand, for the quaternary system, additions of Fe favor the formation of a BCC solid solution for shorter milling time. Nevertheless, after longer milling times (30 h), only a FCC phase is detected by XRD analyses. Microstructural characterization by transmission electron microscopy is carried-out to corroborate the XRD results.

Apparently, the dissolution rate of Fe and Cr into the FCC solid solution is low. This can be attributed to: atomic size factor, difference in crystal structure, and difference in melting point. In the case of the FCC solid solution peak measurements (Fig. 2), the presence of Fe and Cr in the quaternary, quinary and senary systems causes the reduction of the crystallite size, giving rise to an increment of the lattice strain. However, compared with the NiCo system and according to the broad peaks for 20 and 30 h of milling, it seems that copper additions avoid the crystal refinement, which can be

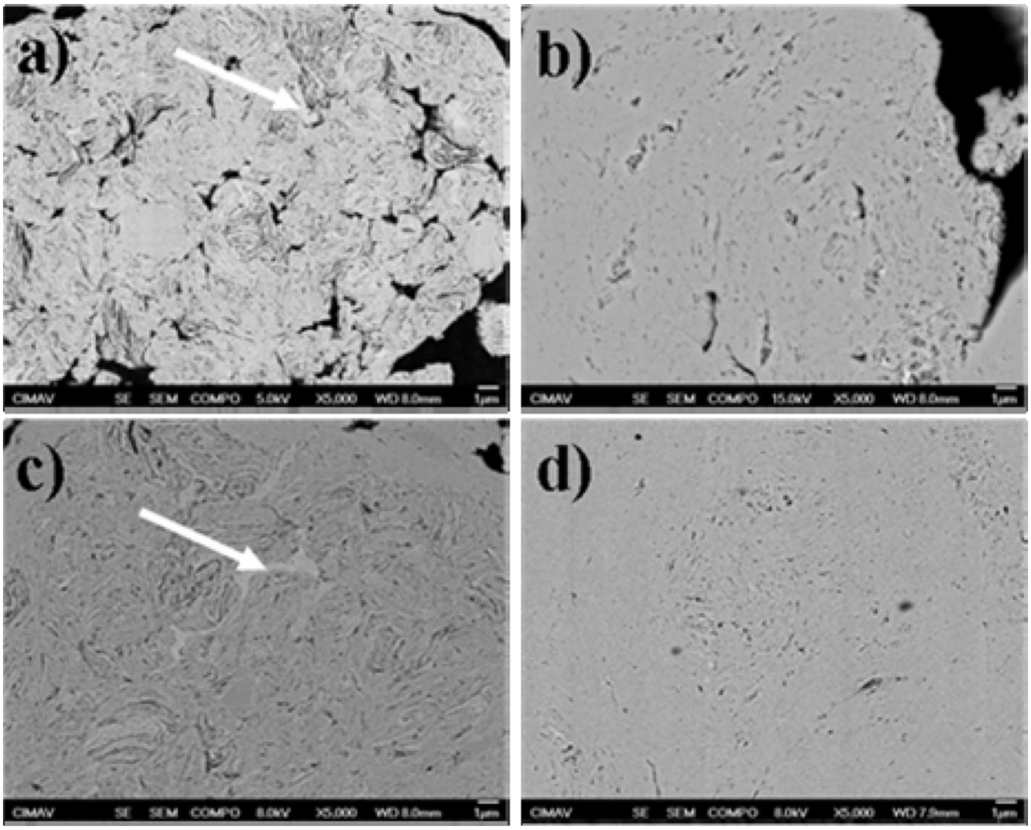

Fig. 3. Microstructure in cross-section of: quaternary NiCoAlFe alloy after milling for (a) 10 h and (b) 30 h, quinary NiCoAlFeCu alloy after (c) 10 h and (d) 30 h of milling.

related to the Cu ductility. By the countrary, this behavior is not observed with Al additions.

5. Conclusions

Binary to senary equiatomic high-entropy alloys in Ni–Co–Al–Fe–Cu–Cr system have been successfully synthesized by mechanical alloying in a high energy ball mill. The results show that the FCC solid solution is observed in binary and senary systems for milling times longer than 20 h. During short-time millings (10 h), the formation of BCC phase is favored by additions of Fe and Cr. Finally, it is observed that the FCC phase is thermally stable up to 1273 K, but there exist a BCC phase after heat treatment.

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