

ASPECTS CONCERNING TERMINAL SOLID SOLUTIONS IN IRON - COBALT BINARY SYSTEM

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Abstract

The Fe–Co binary system features large solubility domains which are very useful for industrial applications. There appears an interesting problem concerning terminal compositions of the binary system. We investigate two terminal compositions 97% Fe, 3% Co and 5% Fe, 95% Co wt. % dosed from elemental powders. The mixtures were subjected to mechanical alloying process for several hours. The X – ray diffraction analysis was performed after each milling time, observing the phasic evolution of the powder mixtures. This shows that we achieved solid solution in both cases. In the case of 97% Fe, 3% Co compositions, there results a solid solution similar to the equilibrium one, and for 5% Fe, 95% Co results a solubility extension. Also we could notice the tendency to the nanocrystalline state of the powder mixture for both compositions.

Keywords: *Iron – Cobalt system, terminal solid solution, mechanical alloying*

INTRODUCTION

The binary Iron Cobalt system presents large regions of solubility [1], being an important factor for industrial purposes, because of high Curie temperature and corrosion resistance at high temperatures [2,3].

Analysing the binary equilibrium diagramme we observe there are two terminal solid solutions. One of them is reached in Co and represents a substitution solid solution of Fe atoms in Co (HCP). The existance domain for this solid solution is arround to 3 wt.% Fe, being limited by the hipoeutectoid domain around 5 wt.% Fe in Co (HCP). The other terminal solid solution is reached in Fe and represents a substitution solid solution of Co atoms in Fe (BCC). The domain of existence for this solid solution type is extended from 0 to 80 wt.% Fe. We notice that the cobalt reach solid solution domain is very short and the Fe reach solid solution is extended. Considering the information about terminal solid solution in the iron-cobalt binary system we assume that there will be no problem in mechanical alloying of iron rich content terminal solid solution, but the eutectoid involved at a higher cobalt content could affect mechanical alloying.

There were reported extensions of solubility in the other binary system with no solubility in solid state, and it is by mechanical alloying [4,5]. Taking into account those facts we select two compositions dosed from elemental powders for investigation: 97 wt.% Fe and 3 wt.% Co and 5 wt.% Fe and 95 wt.% Co to be subjected to mechanical alloying in the aim of achiving a solid solution. We must mention that at equilibrium the reach Fe composition provides solid solution and Co reach composition provides a hypereutectoid alloy.

EXPERIMENTAL PROCEDURE

For the experiment we selected the two compositions mentioned above according to phase diagramme to be at close range of terminal solid solutions. Those compositions are 5% Fe and 95% Co and 97% Fe and 3% Co all in weight percentage. The starting mixture is dosed from elemental powders of iron. Materials upon milling charge are powder mixture and balls. Table 1 presents the composition of milling charge for each vial.

Tab.1. Milling charge composition.

Composition [wt.%]	Mixture [wt.%]	Fe [wt.%]	Co [wt.%]	Number of balls	Balls [wt.%]	Total [wt.%]
97 Fe 3 Co	150	145	5	60	480	630
5 Fe 95 Co	150	7.5	142.5	60	480	630

Each composition was introduced into a steel vial on the planetary mill. The planetary ball mill's characteristics are plate radius 250 mm and rotation speed 1200 rpm. Vials are placed at the opposite position for mechanic system equilibration.

Powder mixtures were milled for 1, 2, 4, 8, and 12 hours. There was taken 5 g of powder mixture for analysis at the end of each milling time. The resulting powders were investigated by x-ray diffraction for determination of the phasic composition.

RESULTS AND DISCUSSION

X-ray diffraction analysis was done on a Dron 3 diffractometer, using $\text{Cu}_{k\alpha}$ radiation and a x-ray data table [6]. Using ASTM data collection we determined the phasic composition and Miller indices (hkl) corresponding to X-ray data [7].

As reference for the evolution of powder mixtures it is necessary to present the results of X – ray diffraction performed on the initial elemental powders, see Table 2 and 3.

Tab.2. X-ray diffraction data of Fe initial powder.

Cr. Nr.	2 theta [degree]	d/n [pm]	Integral intensity [a. u.]	b [degree]	Element (hkl)
1	44.60	203.16	30.16	0.34	Fe (110)
2	64.97	143.54	10.89	0.31	Fe (200)
3	82.43	117.00	20.25	0.49	Fe (211)
4	99.34	101.12	11.09	0.58	Fe (220)
5	116.50	90.65	29.72	0.83	Fe (310)

Tab.3. X-ray diffraction data of Co initial powder.

Cr. Nr.	2 theta [degree]	d/n [pm]	Integral intensity [a. u.]	b [degree]	Element (hkl)
1	44.39	204.07	35.41	0.68	Co (111)
2	47.39	191.83	5.07	0.37	Co (101)
3	53.63	170.89	14.67	0.57	Co (200)
4	62.48	148.64	6.87	0.43	Co (102)
5	76.22	124.91	18.48	0.40	Co (110)
6	84.45	114.71	7.94	0.63	Co (103)

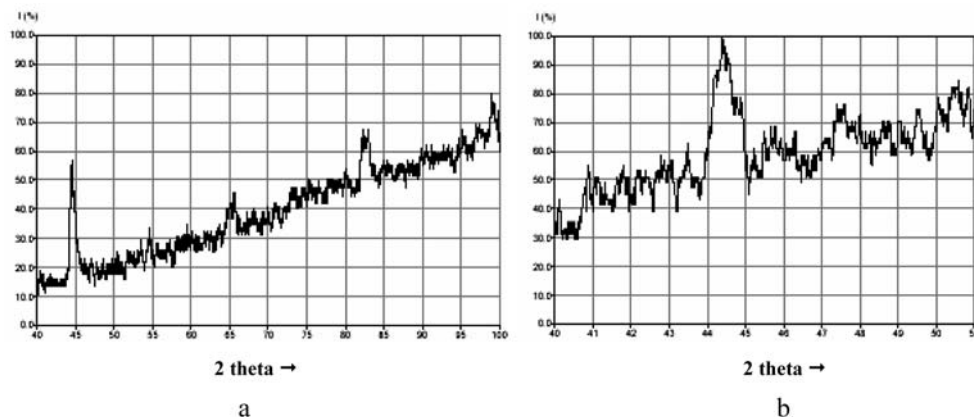


Fig.1. X ray spectra for initial powders: a) iron elemental powder, b) cobalt elemental powder.

The data in Tables 2 and 3 correspond to X – ray diffraction spectra in Fig.1a and b. We notice that values corresponding to the iron and cobalt peaks are in accordance with ASTM data. This situation is to be changed after several milling times due to the mechanical alloying process.

On the other hand, we notice that for representative peaks the full width at half height is 0.34 for iron and respectively 0.68 for cobalt, a fact corresponding to the annealed state of the powder. We could consider those values as reference for grain size determination.

In Table 4 we present the X-ray diffraction data for 5 wt.% Fe and 95 wt.% Co at each milling time, and the most relevant X - ray diffraction spectra for this composition, at one hour of milling and at 12 hours of milling, Fig.2.

Tab.4. X ray data for 97 Fe 3 Co weight composition function of milling time.

Milling time [h]	1		2		4		8		12	
	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]
Fe (110). Co	201.7	0.48	201.8	0.48	202.1	0.65	201.6	0.69	201.8	0.77
Co (200)	177.0	1.42	-	-	-	-	-	-	-	-
Co (102)	148.4	1.42	-	-	-	-	-	-	-	-
Fe (200)	142.66	0.86	142.79	0.63	143.2	0.65	143.2	0.66	-	-
Fe (211)	116.71	0.57	116.8	0.72	116.7	0.83	116.6	0.63	116.4	0.77
Fe (220)	101.16	0.34	101.3	0.66	101.3	0.37	-	-	-	-

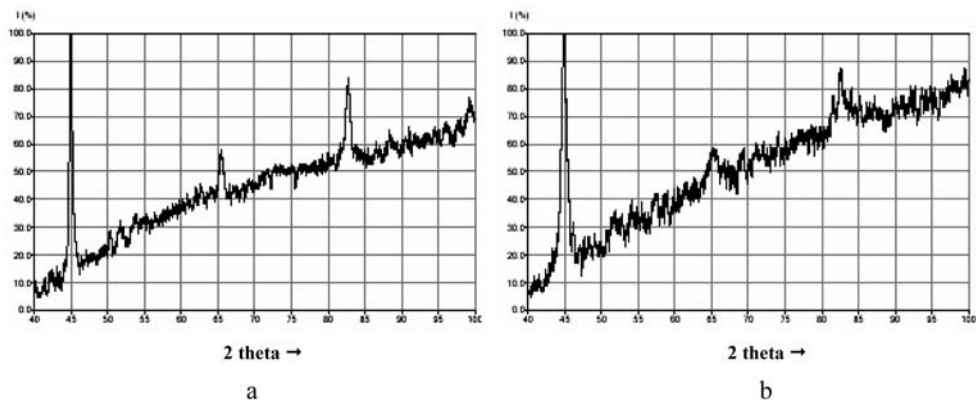


Fig.2. X ray spectra for 97 Fe 3 Co mixtures: a) after 1 hour of milling and b) after 12 hours of milling.

For calculation of the crystal parameter there was used the relation between interplanar distances. Miller indices and crystal parameter are given by following equation [6].

$$a = d(h^2 + k^2 + l^2)^{1/2} \tag{1}$$

where: a – is crystal parameter.
 h. k. l. - Miller indices.
 d – interplanar distance.

For the values obtained for each set of crystal parameters we use the function in equation (2) to extrapolate the value at 2 theta 90 degree. Results are presented in Table 5.

$$f = \cos^2 \theta / \sin \theta + \cos^2 \theta / \theta \tag{2}$$

Tab.5. Crystal parameter. a_0 . for each milling time

T_m . [h]	1	2	4	8	12
a_0 . [pm]	286.25	286.31	286.10	286.09	285.64

Representing the crystal parameter versus milling time, we achieve a mechanical alloying evolution diagramme which represents the powder mixture state. We must take account of the crystal parameter for initial iron powder, $a = 286.68$.

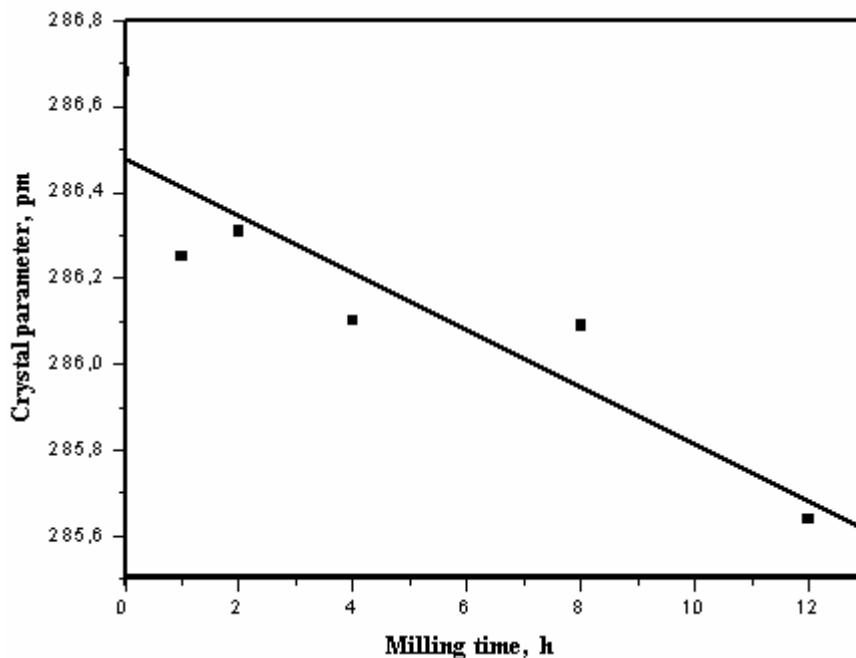


Fig.3. Crystal parameter versus milling time for 97 Fe 3 Co compositions.

The atomic radius of iron has 126 pm and respectively cobalt has 125 pm [8,9]. By mechanical alloying the mixture, evolution presents three stages where the atom's radii have a major influence. The first stage is the mixing of powder particles combined with string deformation resulting in a mixed sandwich structure of iron and cobalt. That was observed by X-ray diffraction spectra at one hour of milling, identifying distinct iron and cobalt peaks. The second stage is the formation of solid solution by strong deformation of particles and structural defects caused by cold hardening. The structural defects and high energy of impact caused diffusion of Co atoms into Fe lattice. The third stage corresponds to the fragmentation of particles and consolidation of new-formed solid solution.

The cobalt atom is smaller than the iron atom and we expect that the crystal parameter of iron decrease in order of replacing some atoms in its crystal lattice with cobalt atoms. Calculating the crystal parameter for iron at each milling time we observe a decreasing tendency. Figure 3 confirms achievement of solid solution. After 4 hours of milling the crystal parameter value decreases slowly, meaning that the solid solution is completely formed.

At 2 hours of milling the Co peaks disappear completely, meaning that Co disappears as distinct phase in powder mixture. At crystal lattice the Co atoms take random places, and after that, need to be distributed equally in all Fe composition and this fact corresponds to the fragmentation of particles due to the cold hardening effect up to 4 hours of milling.

It is obvious that the formation of solid solution starts at 2 hours of milling and ends at 4 hours of milling. After 4 hours of milling the powder mixture enters into another process caused by mechanical milling, the amorphisation process which sets the tendency toward the nanocrystalline state. This process will be analysed after investigation of cobalt reach composition from the mechanical alloying point of view.

Tab.6. X ray data for 5Fe 95Co weight composition function of milling time.

Milling time [h]	1		2		4		8		12	
	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]	d/n. [pm]	b. [deg.]
Co (100)	-	-	-	-	216.5	0.49	215.9	0.25	214.6	0.46
Co (111). Fe	202.9	0.52	202.3	0.51	202.6	0.48	202.5	0.40	202.5	0.75
Co (101)	190.5	0.91	190.7	0.91	191.1	0.49	189.5	0.60	191.1	0.63
Co (110)	124.6	0.37	125.2	0.83	125.1	0.28	125.1	0.26	-	-
Fe (211)	116.9	0.34	-	-	-	-	-	-	-	-

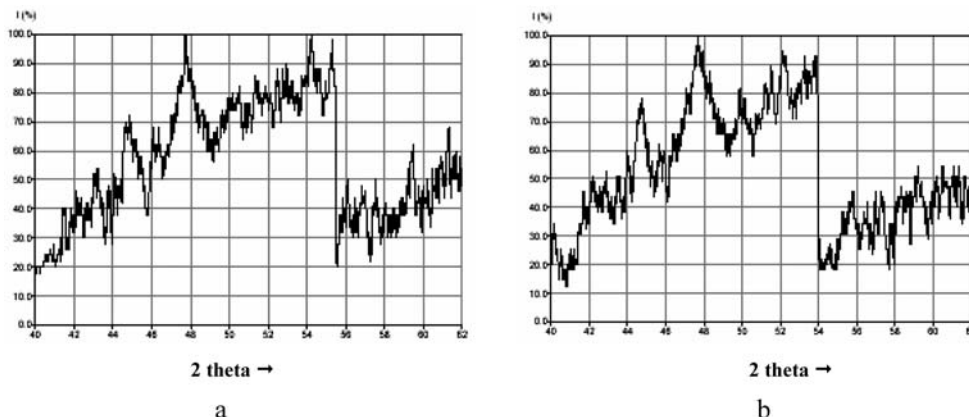


Fig.4. X ray spectra for 5 Fe 95 Co mixture: a) after 1 hour of milling and b) after 12 hours of milling.

In Table 6 there are presented X- ray data for 5Fe 95Co composition for each milling time. Figure 4 represents the most important X – ray spectra for this composition. In this composition the excedentary element is Co having HCP structure. The equilibrium composition is hipoeutectoide. and by mechanical alloying we expect to achieve a solid solubility extension.

A rough analysis of the X-ray data shows us that for this composition we obtain a HCP solid solution of Fe in Co. This results in a disappearing of Fe peaks in X-ray diffraction spectra after 1 hour of milling. For more accuracy it needs crystal parameter calculation and c based on the Bragg relation:

$$\sin^2 \theta = A(h^2 + hk + k^2) + Cl^2 \tag{3}$$

where: $A = 2 \lambda^2/3 a^2$ and $C = \lambda^2/2 c^2$.

h. k. l. - Miller indices.

θ – Bragg angle.

Calculating results HCP crystal parameter a and c according to relations (4):

$$a = (2/3)(\lambda / (A)^{1/2}) \text{ and } c = (1/2)(\lambda / (C)^{1/2}) \tag{4}$$

To observe the evolution of the powder mixture during milling it is useful to observe the evolution of c/a rapport, for the initial Co powder $c/a = 1.41$. In Table 5 there are presented calculated values for c/a rapport at each milling time and in Figure 5 is plotted the graph for this variation.

Tab.5. Crystal parameter. a_0 . for each milling time.

T_m h	1	2	4	8	12
c/a	1.41	1.38	1.40	1.36	1.46

Analysing the evolution of c/a rapport as tendency we observe increasing of this rapport value. It is expected because of iron atoms which replace some atoms in the Co HCP lattice; a Fe atom being a little greater than Co atoms causes some increasing at the crystal parameter level. The most important fact is maintaining of HCP structure for composition during all milling times.

The iron diffraction peaks disappear after 1 hour of milling; giving us a clue that solid solution has been achieved. The effect of replacement of Co atoms with Fe atoms affects the Co HCP lattice by increasing the value of the crystal parameter as we could observe in Fig.5. We could affirm that at 4 hours of milling Fe atoms are well dispersed in Co the lattice, obtaining a solid solution.

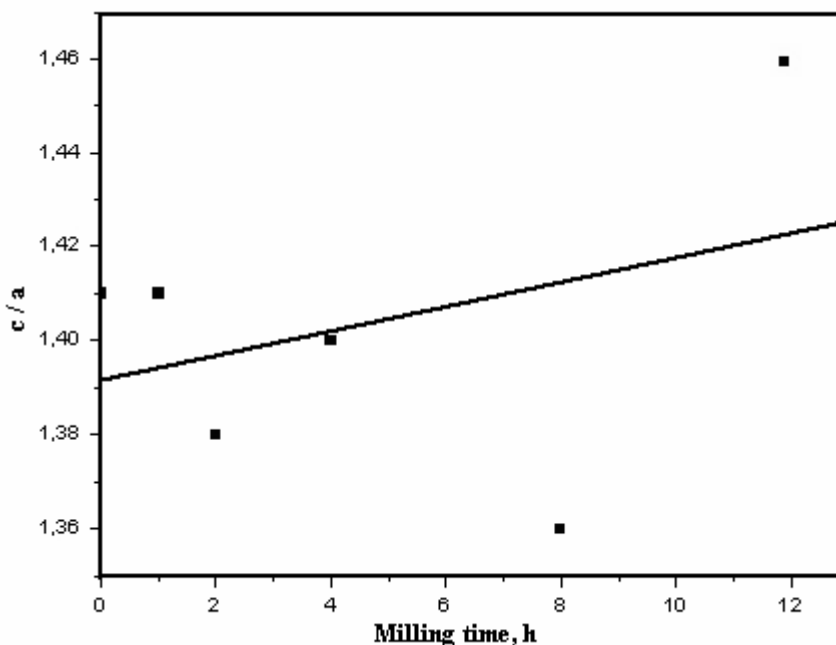


Fig.5. The c/a rapport versus milling time.

Achieving the solid solution for 5Fe95Co composition, there results a solubility extension by nonequilibrium processing. In equilibrium condition at this composition, 5Fe95Co, there is a hypoeutectoid mixture formed by Co (HCP) and FeCo (BCC) solid solution. We obtain by mechanical alloying a single phase for this composition.

As we notice previously, the amorphisation phenomenon appears during the mechanical milling process. To observe the influence of this phenomenon, we observe the full width at half height of the most significant diffraction peak at each milling time for both compositions. Qualitative information related to this value is the grain size, D , calculated from full width at half height using the Scherrer formula [10]. Resulting values are presented in Table 6.

Tab.6. Grain size evolution during milling time.

T_m h	1	2	4	8	12
$D_{97Fe3Co}$ [nm]	20.00	17.92	13.23	12.46	11.17
$D_{5Fe95Co}$ [nm]	16.52	16.86	17.90	21.49	13.64

We observe for 97Fe3Co composition that grain size decreases progressive with milling time and it is around 15 nm, we could affirm that after 12 hours of milling this powder mixture presents a nanocrystalline tendency. For 5Fe95Co composition, the grain size presents a maximum at 8 hours of milling, and after that decreases under initial value. Also we could affirm that this composition is in nanocrystalline tendency. For quantitative information about amorphisation effect on milled composition must be performed detailed calculations.

CONCLUSIONS

Both compositions: 97Fe3Co wt.% and 5Fe95Co wt.%, subjected to mechanical alloying resulted as solid solution. The solid solution for 97Fe3Co wt.% composition is formed after 1 hour of milling, and consolidated between 2 and 4 hours of milling. The 5Fe95Co wt.% composition formed a single phase after 1 hour of milling, and the consolidation of solid solution is achieved at 4 hours of milling. This solid solution represents a solid solubility extension. Calculating grain size by the Scherrer formula results a qualitative characterisation of both milled composition featuring nanocrystalline tendency.

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