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1 **Phase Formation and Magnetic Properties of Nanocrystalline Ni₇₀Co₃₀ Alloy**
2 **Prepared by Mechanical Alloying**

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15

16 **Abstract**

17 Nanocrystalline Ni₇₀Co₃₀ alloy was synthesized by high energy ball alloying from elemental pure
18 Ni and Co powders as function of milling time. The changes in structural, morphological and
19 magnetic properties of the processed powders during mechanical alloying were characterized
20 respectively by X-ray diffraction, scanning electron microscopy and vibrating sample
21 magnetometer. X-ray diffraction analysis suggested the formation of two fcc nanostructured solid
22 solutions fcc-Co(Ni) and fcc-Ni(Co), where the crystallite size decreases reaching 4.7 – 8.0 nm
23 while the microstrain increases up to 0.39 - 0.42%, due to the severe plastic deformations and the
24 structural defects introduced by milling. Morphological observations indicated a progressive
25 refinement of the particles size with milling time. For longer milling, a narrow particle size
26 distribution with irregular shape was observed. Milling process induced some important changes
27 in the magnetic properties, whereas the variation of the saturation magnetization and coercivity
28 was associated mainly to the particle size refinement, accumulation of microstrain and formation
29 of solid solutions Co(Ni) and Ni(Co).

30

31 **Keywords:** *Mechanical alloying; Nanostructures; Ni₇₀Co₃₀, Solid solution; Magnetic properties.*

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35 **1. Introduction**

36 Nanomaterials (NMs), described as non-equilibrium materials with new performances, have
37 become the most developed and promising field of materials science and engineering. Compared
38 to traditional counterparts, NMs of similar compositions display enhanced and superior properties,
39 which offers possibilities for modern technological applications in everyday products [1-2]. In
40 fact, the combination of grains/particles at the nanometer size, the high surface area, and the
41 superior directionality enables nanostructures to access into interesting ranges of mechanical,
42 electronic, optical or magnetic properties [3]. It has been reported that these properties depend
43 mainly on the individual crystalline particles and particle boundaries including chemical
44 composition, structure, size and shape [3]. Therefore, extensive researches have been conducted
45 in order to understand their behavior and consequently to control their properties using advanced
46 characterization techniques and modeling.

47 Soft magnetic nanomaterials (SMNs) have known increasing attention in the past years due to their
48 common and unique characteristics to both amorphous and crystalline materials that provide many
49 exciting opportunities in magnetic applications. SMNs exist in different forms, including
50 nanoparticles, nanostructured thin films, nanowires, nanocrystalline ribbons, and so on. They can
51 be employed in a variety of devices such as transformers, motors and generators conversion of
52 electrical energy [4]. Such applications require a combination of high magnetic flux density, high
53 permeability, and a reduced coercive force [5]. It is well-known that the decrease of grain size to
54 the order of the domain wall exchange length lowers the coercivity towards a value controlled by
55 the random anisotropy model [6]. The production of such forms of SMNs was possible, via
56 chemical synthesis, plasma processing, or mechanical alloying (MA) [4].

57 Recently nanocrystalline soft magnetic materials synthesized by MA have experienced a large
58 development [7]. The reduction of particle size by MA to the nanoscale usually accompanied by
59 important modifications in the magnetic behavior and properties of powders that remain strongly
60 correlated to both phase and chemical composition as well microstructure such as particle size
61 distribution, internal tension, and the anisotropically shaped particles [8].

62 It has been noted that with MA it is easier to obtain the materials far from their thermodynamic
63 equilibrium. In particular, extended solid solutions, nanocrystalline, quasicrystalline, and
64 amorphous alloys with a large difference in melting temperatures of its ingredient can be obtained
65 via MA. Because of the chemically randomizing nature of MA, it can force heterogeneous
66 elements into a homogeneous amorphous alloy at room temperature [9].

67 During MA process, particles are subjected to severe plastic deformations. It consists of a repeated
68 fracturing and cold-welding of particles leading to significant size refinement of the powder
69 particles and a change in their shape [10].

70 Co-Ni nanoalloys were synthesized by different methods such as MA, polyol reduction and sol-
71 gel methods have been widely reported in the literature [11]. They showed a typical soft
72 ferromagnetic behavior because of their new anisotropic shape. Aymard et al. [12] synthesized and
73 characterized the microstructural and magnetic properties of Co-Ni alloys prepared by MA with
74 various compositions; the milling was carried out in a SPEX 8000 mill under an argon atmosphere.
75 The analysis of X-ray diffraction showed: (i) an allotropic transformation of Co from hcp form to
76 fcc during the first stage of milling, (ii) a mutual diffusion of Ni and Co into each other leading to
77 the formation of two phases with fcc structure. The obtained milled powders exhibited a
78 nanocrystalline character with a high rate of micro deformations. The measurement of the
79 saturation magnetization and the coercivity performed for $\text{Co}_x\text{Ni}_{100-x}$ alloys ($x = 30, 50, 70$)

80 indicated that the oxygen contamination decreases the value of the saturation magnetization by
81 15%. Over the past decade, Loudjani et al. devoted numerous studies about Co-Ni alloys during
82 high energy milling [10, 13-15]. The obtained results indicated the formation of homogeneous
83 solid solutions (SS) with a high rate of microstrain. The solid solution structure was either fcc, hcp
84 or mixed fcc and hcp. It was found that the structure depends essentially on the shape and the size
85 of milled particles as well as the percentage of Co in the alloy. The intensive generated energy
86 during milling process induces the diffusion of Co and Ni atoms in the SS phases and the allotropic
87 transformation of Co. It was also found that milling affects significantly the magnetic properties.
88 In fact, the variation of coercivity (H_c) and saturation magnetization (M_s) of CoNi alloys could not
89 be predicted; i.e. $Ni_{50}Co_{50}$ [14] and $Ni_{20}Co_{80}$ [10] showed different behaviors: $Ni_{50}Co_{50}$ alloy
90 reached H_c of 34.5 Oe and M_s of 150.3 emu/g [14] while $Ni_{20}Co_{80}$ exhibited higher H_c (60 Oe) and
91 lower M_s (125 emu/g) [10]. The common conclusion was that the alteration of the magnetic
92 parameters was related to crystallite size, phase and chemical composition, microstrain, and the
93 formed solid solutions.

94 In the case of polycrystals, in order to improve the properties of Co-Ni alloys, other elements are
95 added to the binary alloys such as Fe, Ga, and Cu. For example, the Co-Ni-Ga alloy has been
96 investigated; the study was devoted to the magnetic properties of $Co_{36.4+x}Ni_{33.3-x}Ga_{30.3}$ system
97 obtained by melting under controlled Argon atmosphere [16]. The magnetic hysteresis cycles
98 obtained for four compositions ($0 \leq x \leq 3.1$ at.%) exhibited very narrow hysteresis loops. From the
99 above studies, it can be highlighted that the maximum magnetization of the studied alloys increases
100 with the amount of Co. Likewise, the coercivity increases with the content of Co; it has a greater
101 value for compositions with Co above 39.5 at.%. This behavior has been attributed to the increase

102 in magnetic anisotropy with the proportion of Co. Similar results have been also observed on
103 nanocrystalline alloys obtained by mechanical grinding of the ternary alloys CoNiFe [17].
104 This research work aims to investigate specifically the binary Ni₇₀Co₃₀ alloy prepared by high
105 energy ball milling, since to the best knowledge of the authors, no studies are reported in the
106 literature. Particular emphasis will be devoted to the effect of milling on structural and magnetic
107 properties of this alloy as well as the influence of Ni that favors the development of metastable
108 structures at low milling times. This paper presents the evolution of phase formation and
109 composition, structural and microstructural parameters as well magnetic properties of
110 mechanically alloyed Ni₇₀Co₃₀ powder mixture as function of milling time.

111 **2. Experimental details**

112 **A. Mechanical alloying of Ni₇₀Co₃₀ powder mixture**

113 The preparation of Ni₇₀Co₃₀ powders was carried out by mechanical alloying using a planetary
114 mill type Pulverisette P5. The synthesis was performed by cycles of 30 min of milling at 250 rpm
115 followed by 15 min pause to avoid an excessive rise in temperature inside the vials. For each
116 powder, a mass of 8 g was crushed under an argon atmosphere, in vials containing 36 instrumented
117 steel balls of 1 mm in diameter, the ratio of the mass of the balls and the mass of the powder being
118 equal to 17: 1.

119 **B. Characterization of mechanically alloyed Ni₇₀Co₃₀ samples**

120 The samples were characterized by X-ray diffraction (XRD) using a Philips PANalytical X'Pert
121 (PW1820) diffractometer equipped with Cu K_{α1} radiation source ($\lambda=1.5418 \text{ \AA}$). The amount of
122 each phase was estimated from XRD refinement using EVA software.

123 The average crystallite size (D) and microstrain (ϵ) were determined by using the following
124 equations [9]:

$$125 \quad D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

$$126 \quad \epsilon = \frac{\beta}{4 \tan \theta} \quad (2)$$

127 where λ is the wavelength of the X-ray radiation, θ is the diffraction peak's position, and β is the
128 full width at half maximum (FWHM). Instrumental broadening corrections were performed using
129 a LaB6 standard.

130 Morphology observations of the milled powder mixture (changes in shape, size, particle size
131 distribution) were carried out by scanning electron microscopy (SEM) using a Zeiss DSM 960A
132 microscope operating at voltage of 20 kV and equipped with electron dispersive X-ray (EDS)
133 detector for chemical analysis.

134 Magnetic measurements were carried out at room temperature using a vibrating sample
135 magnetometer (VSM) MicroMag model 3900 with a maximum magnetic field of 10 kOe (1 Tesla).

136 **3. Results and Discussion**

137 ***3.1 XRD Analysis***

138 ***3.1.1 Evolution of Phase Composition***

139 The evolution of XRD patterns with milling time is displayed in Fig. 1. The XRD pattern of the
140 un-milled powder mixture shows the presence of characteristic peaks of face centered cubic Cobalt
141 (fcc-Co), hexagonal close packed Cobalt (hcp-Co) and face centered cubic Nickel (fcc-Ni). The
142 main peaks are indicated by the planes (111), (200) and (220) for fcc phase as well (100), (002) and
143 (101) for hcp phase (Fig. 2). As a consequence of their close lattice parameters, the resolution of
144 both elements was prevented. In addition to the identified peaks belonging to both Co and Ni, few

145 additional minor peaks with low intensity probably related CoO and/or NiO oxides are detected.
146 The observed slight shift of the main Ni and/or Co diffraction peaks towards smaller 2θ angles can
147 be correlated to the lattice distortion of Ni and/or Co arising from their interdiffusion.

148 As a result of the progressive mixing of cobalt (Co) and nickel (Ni) powders as well due to the
149 severe plastic deformations caused by the high energy ball milling, many phenomena take place.
150 As milling proceeds, the crystallite size decreases while the atomic level of strains rises
151 continuously. A variety of crystal defects such stacking faults, dislocations, vacancies and grain
152 boundaries are introduced promoting the mutual diffusivity of both elements during the milling
153 process. The effect of such phenomena can be observed clearly on the diffraction peaks illustrated
154 in Fig. 1. The intensity of diffraction peaks reduces gradually although their width increases with
155 the milling time, indicating the evolution of phases besides grain refinement and higher defects
156 density.

157 After 1h of milling, the same peaks are observed as in the un-milled mixture (0h) with a small
158 decrease in intensity especially for (101) line of hcp Co phase (Fig. 2). This line disappears
159 completely after 4 h of milling while the peaks related to the lines (111) and (200) of fcc Co phase
160 remain present with a notable decrease in their intensity. This can be attributed to several reasons
161 such as reduction in particle size, the dissolution of Co into Ni lattice or the reverse allotropic
162 phase transformation of Co from hcp to fcc [14].

163 One of the most important features of the binary CoNi alloys is the appearance of the reversible
164 phase transition of Co phases as shown in the phase diagram [18, 19]. The temperature of this
165 phase transformation decreases when the rise in Ni content. The allotropic transformation of Co
166 during the mechanical alloying of elements has been reported in the literature [13-15]. At ambient

167 temperature, Co phase is considered as a metastable structure and due to external energy either
168 mechanical or thermal [19]. Besides, the milling time and intensity are considered as major factors
169 of the allotropic phase transformation of Co [20]. It has been deduced that for short milling time
170 and higher milling intensity, this transformation is faster [21]. Many studies also [10,23] confirmed
171 that while milling time increases, a large amount of stacking faults accumulated within the hcp-
172 Co lattice inducing the hcp-Co phase transformation into fcc-Co phase. Further, this phase
173 transition can be favored by the contamination of the hcp-Co powder by Fe originating from bowl
174 and balls, leading to the stabilization of the fcc-Co form [22].

175 In their study; Cardellini et al. [20] pointed out that it is essential to take into consideration Fe
176 contamination during the transition of cobalt structures; Fe stabilizes the fcc-phase of Co at room
177 temperature up to 5 at.% content following the standard phase diagram.

178 For longer milling times (5, 10, 15 and 25 h), a significant reduction of diffraction peaks intensity
179 is observed. It is obvious that the line profiles are almost symmetrical which is related to the
180 formation and the stabilization of a new phase, identified as a solid solution of two fcc structures
181 of Ni and Co. The phase diagram of Co and Ni alloys [18] indicates that at temperatures between
182 the solidus and the allotropic transformation, Co and Ni can form a complete solid solution with
183 an fcc structure; this transformation takes place at a temperature close to 300°C [18]. One of the
184 most known fcc high-temperature phase is the $\text{Co}_{84.43}\text{Ni}_{15.57}$ alloy [22].

185 According to Hume-Rothery rules, a solid solution is favorable following 4 conditions: (i) the
186 difference in atomic radii is less than 15 %; (ii) both elements have same crystal structures; (iii)
187 close electronegativity; and (iv) same valence. For the $\text{Ni}_{70}\text{Co}_{30}$ alloy, the above criteria are
188 fulfilled, therefore the formation of heterogeneous solid solution is likely occur: very close atomic

189 radii of Ni and Co (0.124 nm and 0.125 nm respectively), fcc-Ni and of course the Co-fcc obtained
190 after phase transformation, both Ni and Co have an electronegativity of 1.9 and same valence of
191 +2. Therefore, Co-Ni alloy formation occurs simultaneously during the conversion of hcp-Co form
192 into fcc form and the mutual diffusion of Co and Ni in the two fcc phases. The existence of the
193 fcc-Ni(Co) and the fcc-Co(Ni) solid solutions is confirmed by the important decrease of Ni and
194 Co peaks intensities after 5 h. It is important to mention that because of the larger diffusivity of
195 Co into Ni lattice ($D = 2.51 \times 10^{-8} \text{ m}^2/\text{s}$ at $T=800^\circ\text{C}$) than that of Ni in Co ($D = 1.02 \times 10^{-8} \text{ m}^2/\text{s}$ at
196 $T=800^\circ\text{C}$) [23], the proportion of the fcc-Ni(Co) solid solution is found more noticeable than that
197 of fcc-Co(Ni).

198 Many previous studies reported that during MA a non-homogeneous solid solution can be formed
199 by the diffusive mixing process in binary alloys [7,15,24]. As it was confirmed by XRD patterns
200 [10,13-15], the Co-Ni alloys prepared by MA are nanocrystallized solid solutions. In the $\text{Co}_{50}\text{Ni}_{50}$
201 alloy [13, 14], the formation of grain boundaries in the milled elements facilitates the diffusion of
202 Co and Ni into each other region, resulting in the creation of two main solid solutions: dominant
203 fcc-Ni(Co) and fcc-Co(Ni). For the $\text{Co}_{80}\text{Ni}_{20}$ alloy [10], several solid solutions with different
204 structures were detected through XRD analysis. In addition to the two fcc solid solution phases
205 detected in $\text{Co}_{50}\text{Ni}_{50}$ powder mixture, a new solid solution with an hcp structure (hcp-Co(Ni)) was
206 identified. The same mixture of fcc and hcp solid solutions was observed in the milled $\text{Co}_{90}\text{Ni}_{10}$
207 [25].

208 **3.1.2 Microstructural Study**

209 The formation of solid solution (SS) as confirmed by the change in XRD peaks broadening has
210 been accompanied by particle size reduction (grain refinement) and the increase of lattice
211 microstrain. Both parameters are essential to follow the phase constitution and transformation

212 characteristics during high energy milling. Both microstructural parameters have been calculated
213 using the widening of XRD peaks by taking into consideration instrumental contribution. Fig. 3
214 depicts the evolution of crystallite sizes $\langle L \rangle$ and internal microstrain $\langle \sigma^2 \rangle^{1/2}$ for the two solid
215 solutions fcc-Co(Ni) and fcc-Ni(Co) along various (hkl) planes as function of milling time.

216 It has been reported that, the progress of microstructural parameters $\langle L \rangle$ and $\langle \sigma^2 \rangle^{1/2}$ in mechanically
217 alloyed materials peruse two main stages [26]: (i) during the first stage, particles refinement occurs
218 accompanied by an increase in microstrain; while (ii) the second stage is defined by a steady-state
219 for both parameters. Clearly, after the first 4 h of milling, the crystallite size for both SS phases
220 decreases rapidly from 31.85 nm (0h) to 7.60 nm (4 h) for the SS of fcc-Ni(Co) and from 27.34
221 nm (0 h) to 6.41 nm for the fcc-Co(Ni) SS. The important grain refinement occurs with a
222 progressive rise in microstrain level as milling time is prolonged. The rapid reduction indicates the
223 effect of repeated collisions in flattening the grains. MA process was known by the ability to reduce
224 particle size to the range of nanometer in a short time [27]. In fact, the higher the shock intensity
225 is, the narrower the grain size. In this stage, the severe plastic deformation leads to a developing
226 number of matrix dislocations. The created dislocations are multiplied in the shear zones. As a
227 result of their rearrangement and interactions [28], new surfaces are established leading to the
228 phenomenon of polygonization [15]. Thus, the size of crystallites declines and the value of lattice
229 microstrain rise. Since the rise in the local temperature during milling process has been reduced
230 by applying a pause repeatedly, hence the effect of grain growth does not appear in this study, in
231 contrary to similar work in the literature [29].

232 At longer milling above 5 h, the variation of crystallite size and microstrain is gradually reduced.
233 The rise of surface temperature during MA process could be the origin associated with this modest
234 variation of both parameters [30].

235 The evolution of crystallite size afterward remains stable; reaching about 8 nm and 4.67 nm after
236 25 h for fcc-Ni(Co) SS and fcc-Co(Ni) SS, respectively. It is important to mention that for
237 prolonged periods of milling (15 and 25 h); the sub-grains are disoriented one to another. Thus,
238 the deformation occurs mainly on grain boundaries. This phase stabilization can be associated with
239 the constraint of the crystallites deformation σ_p defined by Hall-Petch relation [31, 32], which
240 becomes much superior to that caused by milling. The new surfaces created previously cannot be
241 formed again considering that grains attain their size limit improving the inversely proportional
242 relation between strength and crystallite size as described by Hall-Petch relation. The reached
243 value of $\langle L \rangle$ can be correlated with an equilibrium state of the Ni₇₀Co₃₀ mixture. The possible
244 explanation is that when this critical value is achieved, the required energy to create further
245 deformations, new grain boundaries and interfaces appears to be too high [33].

246 On the other hand, the increment of microstrain level continues moderately until reaching a
247 maximum value of 0.39% for fcc-Ni(Co) SS and 0.42 % for fcc-Co(Ni) SS. This is due to the high
248 density of dislocations produced by severe plastic deformations of high energetic nanoparticles for
249 longer milling times, which shows the anisotropic behavior [14].

250 The calculated microstrain values are comparable to those found for other ball-milled metals and
251 alloys. In particular, the fcc-Ni(Co) phase of the milled Co₅₀Ni₅₀ alloy showed a microstrain rate of
252 0.31% after 24 h of milling which is close to that of Ni₇₀Co₃₀ alloy while the fcc-Co(Ni) phase of
253 the same alloy [14] displayed twice (0.85%) the microstrain rate of that in Ni₇₀Co₃₀ alloy. From
254 this comparison, one can conclude that due to the fragile nature of Co particles comparable to that
255 of Ni, Co(Ni) phase possesses the highest deformation values, hence the smallest crystallite size
256 [34,35].

257 **3.2 SEM Analysis**

258 SEM micrographs of Ni₇₀Co₃₀ alloys obtained at various milling durations (0 – 25h) are shown in
259 Fig.4. It can be noted the existence of gradual grains refinement with milling time. The morphology
260 presented in Fig.4. Ni₇₀Co₃₀ powder mixture before milling shows two different types of particles:
261 smooth rounded spherical particles belonging to Ni powder and rough bulky particles consist of
262 several smaller particles belonging to Co powder. In view of the magnetic nature of both Co and
263 Ni, many blocks of agglomerated particles can be observed in the unmilled Ni₇₀Co₃₀ alloy
264 morphology.

265 After the first hour of milling (1 h), notable microstructural modifications occur and new surfaces
266 are formed. This is can be related mainly to the different mechanical properties of both metals: Ni
267 is a rigid, ductile and malleable metal so the atoms tend to enter new positions without destroying
268 the metallic boundary, while Co is hard and fragile. Consequently, the particles are smashed and
269 transformed into an irregular shape with a heterogeneous size distribution. Therefore, a mixture of
270 large and small particles is observed along this phase of MA (Fig. 4). The variation of morphology
271 and particle size originates from combined three principal mechanisms: plastic deformation, cold
272 welding, and fracturing. The particles are agglomerated, fractured progressively into fragile flakes
273 by the compressive forces generated during the balls-powders collisions, and then they are cold-
274 welded, agglomerated and de-agglomerated. During MA, these mechanisms compete and control
275 the morphology of powders during different alloying periods. Because of the ductility of both Co
276 and Ni, the diffusivity of their particles in each other lattice is favored and the particle size rises in
277 early milling stages (5 h). According to Suryanarayana [27], particles of ductile-ductile alloyed
278 systems can be plastically deformed smoothly; they are flattened, cold-welded, fractured then they
279 rewelded.

280 Besides, the soft particles activated by the newly created surfaces tend to aggregate and create
281 larger particles by cold welding. Thus, the welding process is dominant at this stage of milling.
282 The Ni₇₀Co₃₀ alloy presents a structure of large sharp edges particles as it is shown in Fig. 4.

283 For relatively longer milling time (10 h), fracturing becomes the most predominating process
284 assuming the brittle property of Co particles. Thus, the mechanism of fracture tends to generate
285 fragments of powder particles that continue to decrease gradually in size because of the lack of
286 active agglomerating forces.

287 Milling extended up to longer durations (15 and 25 h) results in the formation of more homogenous
288 powders mixture with irregular shape and reduced particle size.

289 One can notice that the edges are gradually fractured and particles share and size become more
290 refined (Fig. 4). The nearly uniform size distribution of particles is a result of severe deformations
291 and cold welding; the large particles are fractured into small ones although the smaller particles
292 are welded to each other [36, 37]. In addition, the powder morphology is characterized by a matrix
293 of thin layers of highly deformed particles randomly welded. Therefore, one can deduce that the
294 lamellar-type microstructure formed between Co and Ni is mechanically preferred. Considering
295 that this lamellar phase is very reactive, the diffusivity of Co and Ni elements is enhanced. Many
296 studies [38-40] confirmed that these lamellar multilayer structures are usually formed in ductile-
297 ductile mechanically alloyed systems, as a result of the combination of frequent mechanical
298 deformations and cold welding. The micrograph of milled powders for 25h illustrates the
299 competition between the two mechanisms of hard deformations and welding. As it is observed,
300 both fine particles and agglomerates coexist. Thus, a relative equilibrium of cold welding and
301 fracturing is reached at this point of milling. However, several regions possess a modest growth of

302 particles. This can be justified by the incorporation of fine particles into the layered matrix and/or
303 the welding of fragments together.

304 ***3.3 Magnetic Properties***

305 In order to examine the effect of MA on the magnetic behavior as well the evolution of magnetic
306 properties of Ni₇₀Co₃₀ alloy selected samples, the hysteresis loops have been recorded as illustrated
307 in Fig. 5. The nanostructured Ni₇₀Co₃₀ milled alloys show similar and sigmoidal small hysteresis
308 cycle which indicates their typical ferromagnetic order. Generally, fine soft magnetic materials
309 possess a small coercive domain (narrow hysteresis loops) [41]. This behavior can be related
310 mainly to the microstructural internal deformations. The magnetization-field (M-H) loops have
311 been used to determine the values of the coercive field (H_c) and the saturation magnetization (M_s)
312 at various milling durations. The evolution of H_c and M_s with alloying time is displayed in Fig. 6.
313 Since, the magnetization process depends essentially on the movement of domain walls and the
314 rotation of spin; hence it can be strongly influenced by the grain refinement. Thus, the following
315 reasons can be the origin of the variation of coercivity and magnetic saturation: crystallite size, the
316 lattice internal strain, the density of defects, the domain walls displacement and the redistribution
317 of elements during phase evolution [6].

318 The curve of coercivity H_c shown in Fig. 6a can be divided into three main stages.

319 The first stage shows a slight increase in coercivity from 62.65 Oe to 76.65 Oe after 1 h of milling.

320 A high value of H_c indicates the existence of micro-deformations, impurities, pores and various
321 defects that can appear during the milling process. Actually, as the magnetization reverses, the
322 severe plastic deformations and the various defects generated by the repeated collisions ball-
323 powder and/or ball-powder-wall of the milling bowl serve to trap the walls of magnetic domains

324 during their movements [42,44]. Hamzaoui et al. [45] followed the evolution of H_c as function of
325 collision power. It was deduced that the introduction of high internal stains caused the increase of
326 this magnetic parameter. The magnetic domain walls can be pinned to another anisotropic
327 ferromagnetic particle and/or non-magnetic inclusions causing the increase of H_c [46]. This modest
328 increase of coercivity can be also caused by the simultaneous diffusion mechanism, the allotropic
329 transformation of Co as well the formation of solid solution at the same time. Further, it can be
330 resulted by the irregularities of the newly created surfaces and/or the random shape of particles
331 [47-48]. Similar rise in H_c was observed for the $Ni_{60}Cr_{40}$ alloy upon 3 h of milling; from 19 to 60
332 Oe [49].

333 The second interval exhibits a rapid reduction of coercivity up to 4 h, from 76.68 Oe (1h) to 31.21
334 Oe (4 h). During this milling period, the shape of particles changes gradually from a lamellar to a
335 spherical, leading to the reduction of the anisotropy related to the shape [47, 50, 51]. Due to the
336 progressive powders diffusivity, the mixture becomes more homogeneous and the grains are
337 refined. As a consequence, the magnetocrystalline anisotropy is reduced. In fact, it was deduced
338 that for soft nanocrystalline magnetic materials, when the grain size is reduced to about 6 nm, to
339 the order of the ferromagnetic exchange length, the magnetic anisotropy level became average and
340 the coercive field H_c decreases proportionally with the grain size [52]. Therefore, the magnetic
341 characteristics become softer. The milled $Ni_{70}Co_{30}$ alloy was identified previously by the allotropic
342 transformation of Co which can affect the coercivity because of the continuous disappearance of
343 the hcp-Co phase in favor of the fcc-Co phase. It was well established that the Co-fcc structure
344 possesses smaller magnetocrystalline anisotropy than Co-hcp [53]. Thus, this reduction of
345 coercivity occurs simultaneously with the formation of the alloy. The dislocation density as well
346 was considered as a principal parameter influencing the coercivity [54]. The entanglements of

347 dislocations generate barriers that prevent the plastic flow of the material and tend to interact
348 strongly with the walls of the magnetic domain in ferromagnetic materials [55]. The discontinuous
349 movement of domain walls which are fixed by dislocations tangles and other inhomogeneities
350 create a change in the magnetic flux density [55]. The decrease of particle size resulting from the
351 competition between fracture and welding can be also related to the coercivity. Similar behavior
352 was observed in FeNbB alloy obtained by mechanical milling [56]. Both, Co₈₀Ni₂₀ [10] and
353 Co₅₀Ni₅₀ [14] milled alloys showed a rapid decrease in coercivity after 3 h of milling.

354 In the third region, a slight increase to 32.35 Oe is noted followed by a steady state on prolonged
355 milling time, which can be related to the effect of the very small crystallite size. In this case, the
356 high level of microstrain impacts the coercive field much more than the crystallite size, hence
357 confirming the theory of soft magnetic materials [14, 57,58]. The crystallites are very small at this
358 level and the nanostructured alloy transformation is completed, leading to a decrease in coercivity.
359 Because of their important density in the particles during this milling stage, dislocations are
360 annihilated and H_c is reduced. Another explanation is the minimization of surface irregularities as
361 function with milling time [47]. The values of H_c obtained after 25 h for milling is comparable to
362 the value 34 Oe found in the Co₅₀Ni₅₀ powders prepared by MA [14].

363 The change of saturation magnetization M_s with milling time as shown in Fig. 6b exhibits an
364 antagonistic behavior. The value of M_s increases gradually from 76 emu/g up to a maximum of
365 107 emu/g after 15h of milling, then decreases sharply to 87 emu/g after 25h. The milled Co₅₀Ni₅₀
366 [14] and Fe₅₀Co₄₀Ni₁₀ [59] alloys showed similar trend for 24 and 90 h of MA respectively while
367 the Co₈₀Ni₂₀ [10] alloy had an opposite trend up to 12 h of milling. After the first 3 h of milling,
368 M_s decreased from 147 to 130 emu/g and then increased to 135 emu/g for 12 h. Up to 48 h of
369 milling, the M_s of Co₈₀Ni₂₀ continued to decrease until reaching a value of 127 emu/g.

370 The increase of M_s during the first 15 h of milling process can be attributed to the combined effects
371 associated with the formation of solid solutions and the refinement of microstructure. In fact, in
372 correlation with XRD analysis (Fig.1), the formation of two different solid solutions fcc-Co(Ni)
373 and fcc-Ni(Co) by diffusion mechanism has been confirmed during early hours of MA. This
374 diffusion induces the transformation of charges between the atoms of the two ferromagnetic
375 elements [59].

376 Further, the diminution in the anisotropy of magneto-crystalline caused by the gradual reduction
377 of crystallite size tends to facilitate the rotation of the magnetic vector [10]. At this stage of milling,
378 the averaging impact of the magnetization dominates the random orientation of nanocrystalline
379 powder and the possibility of considering each grain as a single magnetic domain eliminates the
380 magnetic wall effect [10, 14, 60]. It is important to mention that for the $Ni_{70}Co_{30}$ alloy, the
381 continuous substitution of Ni atoms in the solid solutions improves the alloying completion and
382 particles refinement, as confirmed in several studies in the literature [10,61,62].

383 Moreover, the change in the lattice parameter of milled alloys was considered also as a factor of
384 the observed increase in M_s value. This contribution can be caused by the alloy formation, the
385 created order-disorder and the high level of defects especially antisites that generate several
386 alterations in the electronic band arrangements [63].

387 Along the milling process, a large disorder of atoms is generated resulting in a significant
388 modification in the magnetic moment. Because of the change in the configuration of the magnetic
389 elements (Ni and Co), the magnetic atoms are arranged in the highly disordered grain boundaries.
390 In fact, the disordered imperfections such as dislocations and grain boundaries accompanied by
391 the important internal strain induced by MA block the movement of magnetic domain walls.

392 Hence, the magnetic saturation decreases. The fact that M_s reduces with particles refinement can
393 be ascribed to the existence of an inert or no-functional surface layer that has a small magnetization
394 [14, 64]. It is probable that after 15h of milling, the formation of a non-magnetic intermetallic alloy
395 can contribute in the decrease of magnetization saturation.

396 One can conclude that the saturation magnetization increases with longer milling time, while the
397 coercivity decreases. By comparison with XRD analysis, this result can be attributed to the
398 crystallite size refinement as consequence of milling. This variation with crystallite size is also
399 explained on the basics of domain structure, mean size of particles and crystal anisotropy.

400 Since milling time causes changes by decomposition or transformation of phases, as consequence
401 there is an increase in the crystallite size, decrease of microstrain and subsequently a reduction in
402 the value of coercivity [10, 14].

403

404

405 **4. Conclusion**

406 The effect of MA on the evolution of structural, morphological and magnetic properties of
407 mechanically alloyed $Ni_{70}Co_{30}$ alloy prepared from elemental Ni and Co powders has been
408 investigated. XRD analysis indicates the formation of two main solid solutions Co(Ni) and Ni(Co)
409 with a face centered structure. This phenomenon was confirmed by the progressive decrease of
410 peaks' intensity as well as the remarkable peak broadening with milling time. The powder-ball
411 collisions generated severe plastic deformations and high level of crystal defects promoting the
412 mutual diffusivity of elements. The allotropic structural transformation of Co from hcp to fcc has

413 been identified; hcp-Co peaks completely disappear after 4 h. Prolonged milling time procured a
414 maximum value of accumulated strain (0.42% for fcc-Co(Ni) and 0.39% for fcc-Ni(Co)). Unlike
415 the level of microstrain, crystallite size gradually decreases reaching 4.67 nm for fcc-Ni(Co) and
416 8 nm for fcc-Co(Ni). The competition between cold welding and fracturing phenomena for longer
417 milling durations, as illustrated by SEM micrographs reveals irregular shaped particles and
418 homogeneous size distribution with an important effect of the ductile-ductile mixture property.
419 Magnetic measurements of the milled Ni₇₀Co₃₀ alloy powder exhibit a soft ferromagnetic character
420 where the magnetic parameters are sensitive to the milling time, mainly due to the particle size
421 refinement as well as the formation of Co(Ni) and Ni(Co) solid solutions. Both the saturation
422 magnetization (Ms) and coercivity (Hc) are found to decrease with milling time, attaining the
423 values of Ms = 87 emu/g and Hc = 30 Oe after 25 h of milling.

424

425

426 **References**

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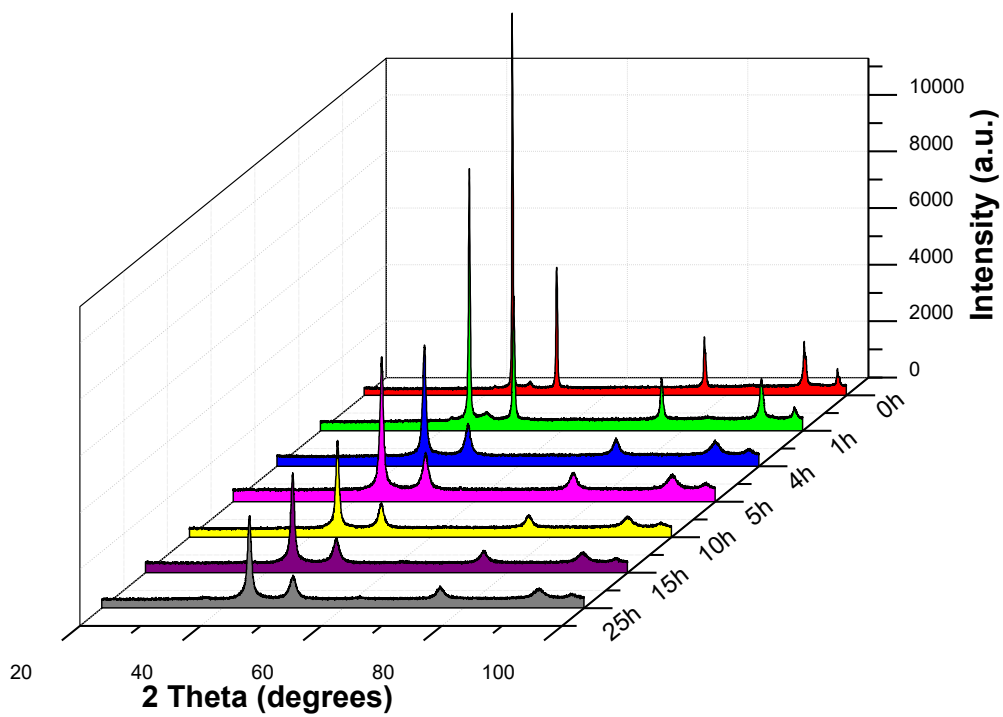
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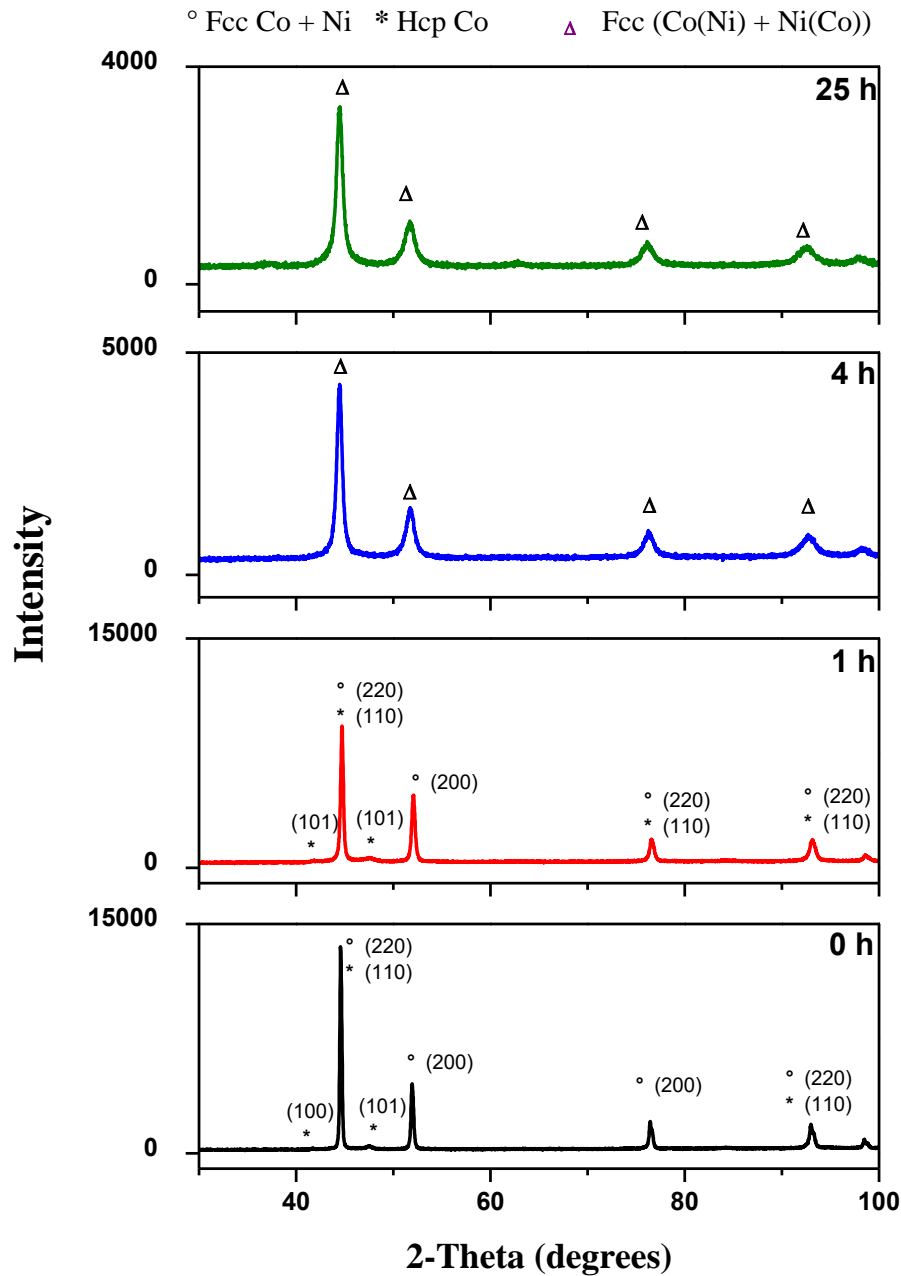
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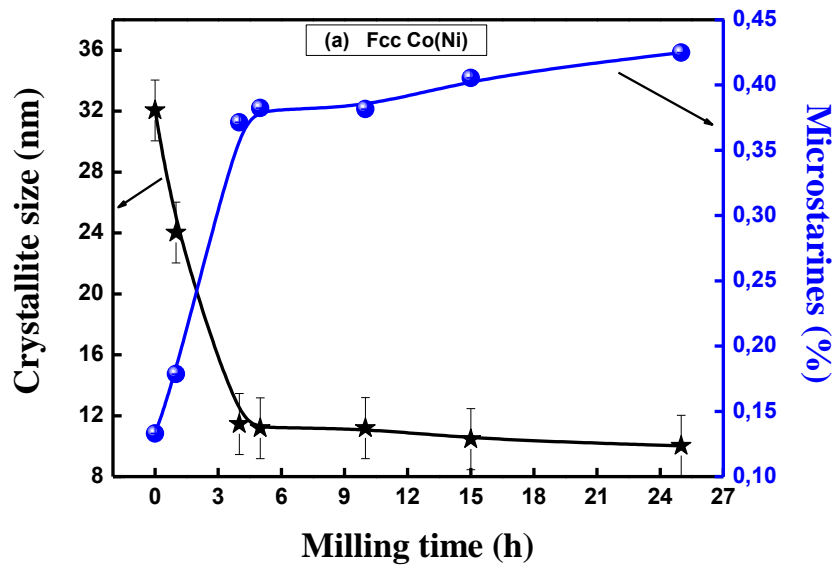
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Figure 1. Evolution of XRD patterns of MA Ni₇₀Co₃₀ powder as function of milling *time*.



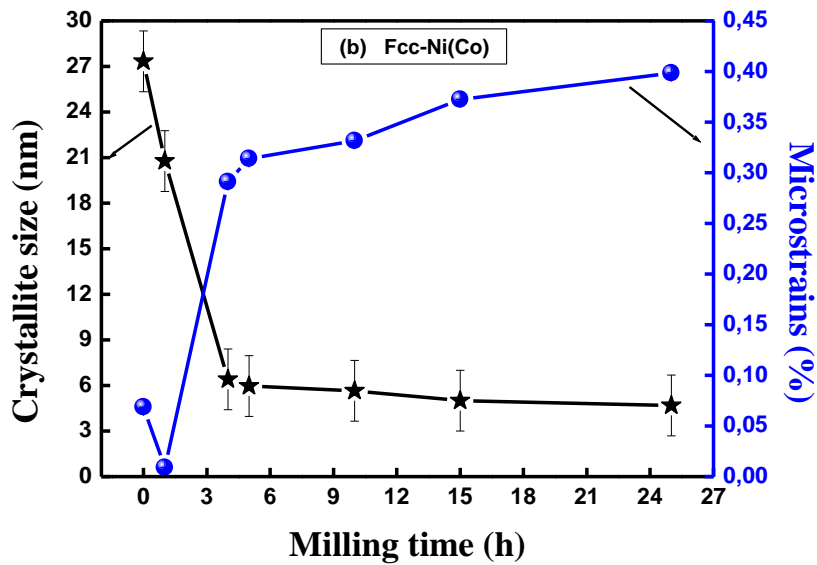
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610 *Figure 2. XRD patterns of Ni₇₀Co₃₀ powders for different milling time (0 h, 1 h, 4 h and 25 h).*



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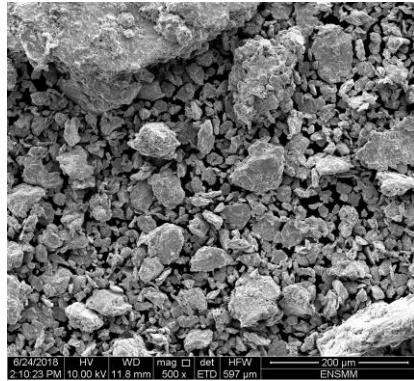
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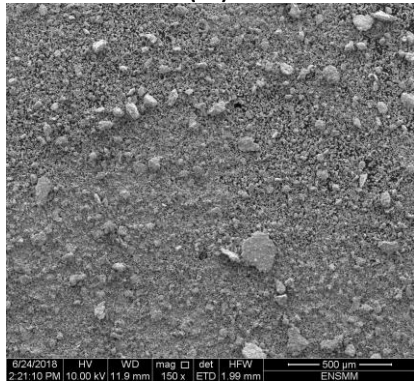
616 **Figure 3.** Variation of crystallite size and microstrain with milling time: (a) fcc-Co(Ni) phase; (b)
 617 fcc-Ni(Co) phase.



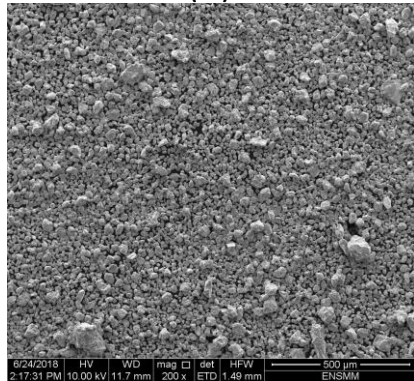
(0h)



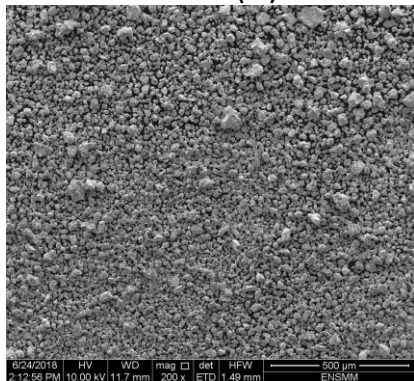
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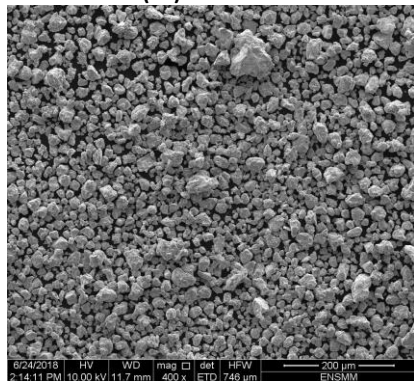
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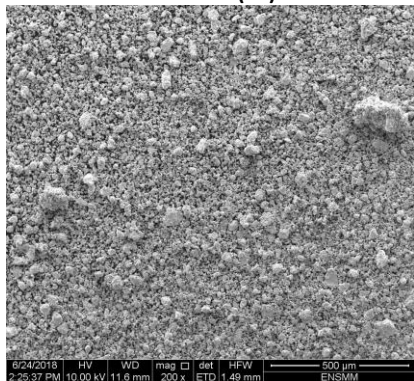
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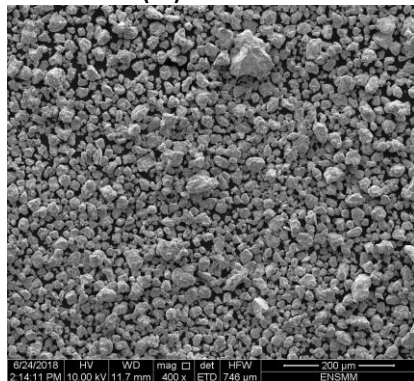
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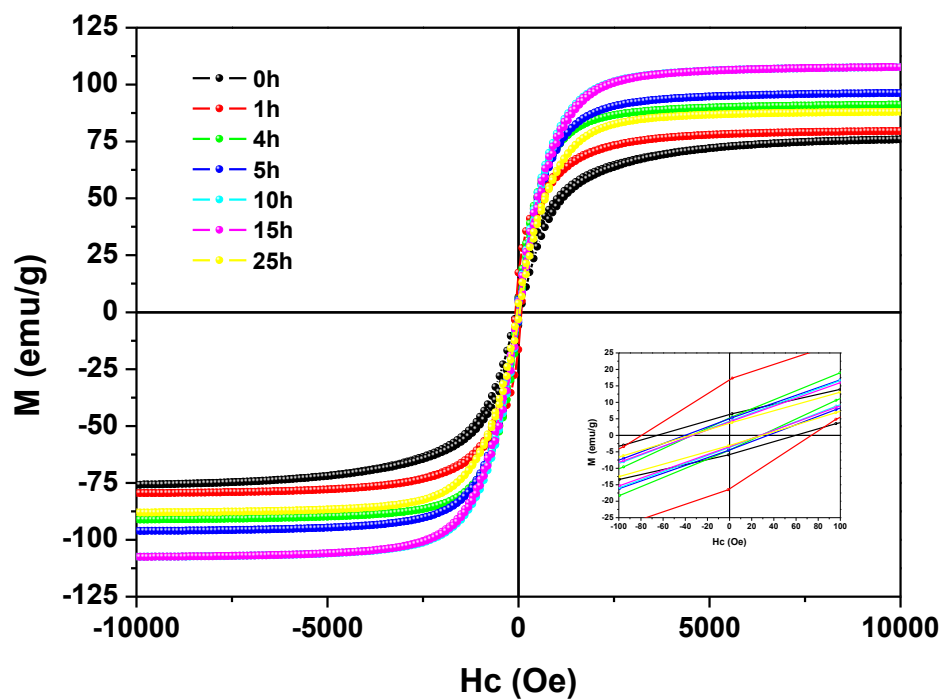
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Figure 4. SEM micrographs of MA Ni₇₀Co₃₀ powders.

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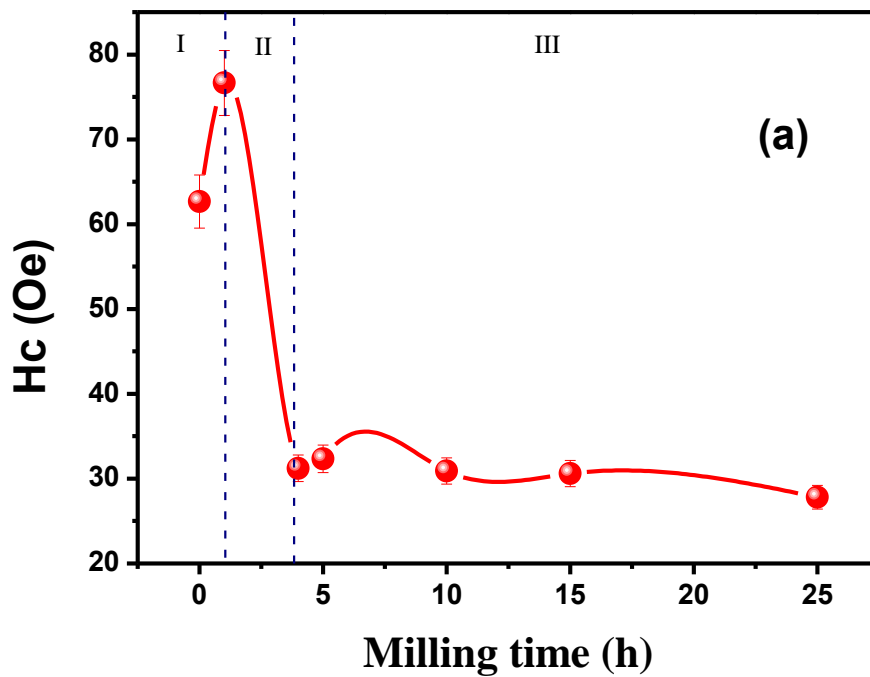
647 *Figure 5. Hysteresis loops recorded at T=300 K of MA Ni₇₀Co₃₀ powders as a function of milling*
648 *time.*

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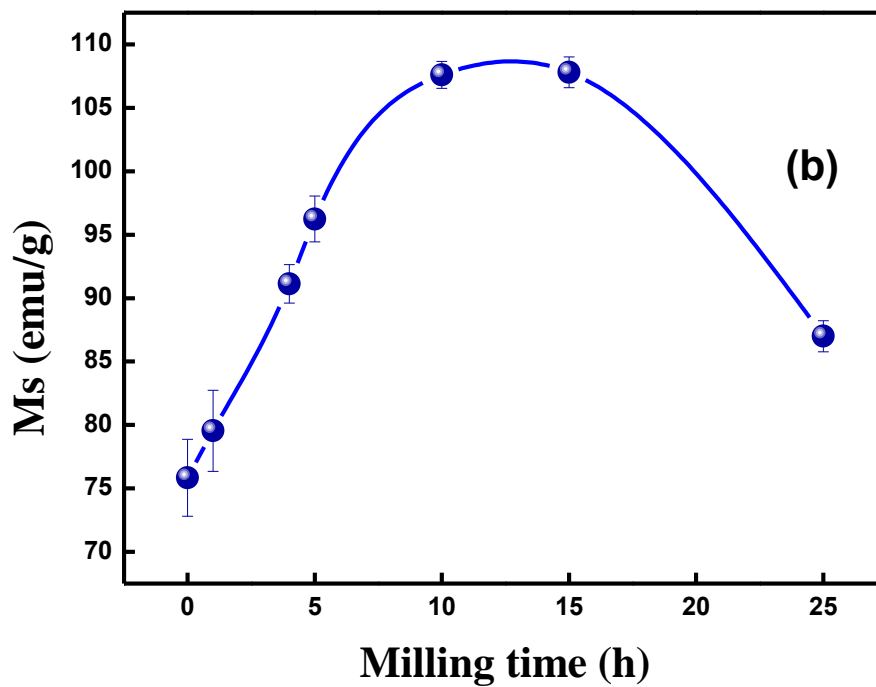
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Figure 6. Variation of (a) coercivity H_c , and (b) saturation magnetization of MA $Ni_{70}Co_{30}$ powders as a function of milling time.