Dependence of magnetic properties with structural/microstructural parameters of ball-milled Fe$_{15}$Co$_2$P$_3$ powder mixture

Hanane Berkani$^{1,2}$ · Rachid Siab$^1$ · Wassila Tebib$^1$ · Locif Redouani$^1$ · Saida Boukeffa$^1$ · Mohamed Bououdina$^3$

Received: 1 July 2021 / Accepted: 16 November 2021 / Published online: 2 December 2021
© The Author(s), under exclusive licence to Springer-Verlag London Ltd., part of Springer Nature 2021

Abstract
This research work aims to investigate the mechanical alloying of Fe$_{15}$Co$_2$P$_3$ powder mixture in terms of phases’ formation, microstructural parameters, and magnetic properties as function of milling time. Parametric Rietveld refinement method, of the obtained X-ray patterns, was performed for qualitative and quantitative phase analysis alongside the determination of structural, microstructural, and mechanical properties. The ball-milled powder mixture crystallized within the face-centered cubic α-Fe(P) solid solution in equilibrium with Co$_{75}$Fe$_{25}$ phase. The crystallite size decreases reaching 100 and 200 nm respectively after 3 h of milling. The highest values of the dislocation density, microstrain, and stored energy are registered for the α-Fe(P) solid solution. The studied mechanical properties manifest the brittle nature of the α-Fe(P) solid solution compared to the Co$_{75}$Fe$_{25}$ phase. The squareness ratio $M_s/M_r$ and the coercivity values of the milled powders increase with increasing milling time and reach steady state after 2 h. The hysteresis loss energy and maximum permeability reach minimal values of $45 \times 10^{-4}$ W/m$^3$ and $49 \times 10^{-3}$ H/m respectively, after 1 h of milling at the opposite of the switching field distribution. The obtained results demonstrate the formation of nanostructured Fe$_{15}$Co$_2$P$_3$ ternary alloy with optimum characteristics as promising candidate for diverse applications primarily in the biomedical field for diagnostics and therapeutics such as magnetic hyperthermia and vector probes for future imaging technologies.

Keywords Fe$_{15}$Co$_2$P$_3$ · Ball milling, XRD · Rietveld · Mechanical · Magnetic

1 Introduction

The magnetic nanoparticles Fe-Co-based alloys have been the subject of many researches due to their potential applications such as medical hyperthermia and targeted drug delivery [1].

When entered cancer cells, an external source applied to activate these magnetic nanoparticles leads to the destruction of pathological cells by physic-chemical effect [2]. Moreover, iron oxides and derivative nanoparticles act as an agent for the advancement of clinical regenerative medicine and magnetoresponsive therapy using magnetic resonance imaging tracking or multimodal imaging [3, 4]. Other studies reveal that calcium phosphate CaP and indium phosphides InP based alloys have an influence on biocompatibility property [5, 6]. The magnetic hyperthermia is a type of thermal treatment of cancer; the ferromagnetic nanoparticles once localized in cancer cells, under external magnetic field will heat up resulting in the death (burn out) of cancer cells. Thus, heat can be used as a support of the therapeutic effects of other treatments by reducing the covering of cancer cells from anti-cancer activities [7, 8]. Hence, magnetic Fe-Co-P alloys due to their interesting properties, are considered as promising candidates for wide range of applications, including from media storage as the Fe-Co-P/C [9] to magnetic memory devices to vector probes in the biomedical research and clinical diagnostics and therapeutics [10, 11].

Most of Fe-Co-P alloys were produced as amorphous and/or crystalline nanowires by electrochemical deposition process [12] whereas in the biomedical field powder is recommended for the preparation of suspensions that can subsequently be easily administered to the human body. For this purpose, in this study Fe-Co-P alloys will
be prepared in the form of powder by mechanical milling technique, which was used frequently to mix powders to achieve a homogeneous alloy through successive welding, fracturing, and re-welding processes [13].

Similarly, binary systems such as Fe–P- and Fe–Co-based alloys were also prepared by mechanical alloying and exhibited interesting properties [14, 15]. In one hand, Fe–Co alloys attracted great attention due to their excellent soft magnetic and mechanical properties, which are found to be strongly dependent on the adopted fabrication method and subsequent heating treatment [16, 17]. They are widely known by their high specific saturation magnetization, low coercivity, high permeability, and high Curie temperature, making them promising for high temperature applications besides being competitive candidates with other highly magnetic materials [18, 54]. In the other hand, the transition metal phosphide alloys and their solid solutions demonstrated interesting magnetic properties which are greatly influenced by both the type of the crystal structure and the chemical composition; for instance, it was reported that the lattice parameters and Curie temperature of Fe$_{2-x}$P system changes significantly with the presence of small amount of impurities and the deviation of stoichiometry [19]. The role of the compound on the structure stability, phase composition, and properties was mostly studied on binary Fe–P alloys that depend on P concentration with a ferromagnetic ground state [14, 20]. In recent years, great attention has been given to the thermal stability of transition metal phosphide nanomaterials [21, 22]. Others studies of Co$_2$P encapsulated in N, P-doped grapheme, CoMnP nanoparticles, nanostructured Fe$_{25}$P$_8$ and Fe–Co, MnFe$_{1-x}$As$_x$, (Fe$_{1-x}$Mn$_x$)$_2$P, Li–Fe–P, and FeP alloys report a robust catalytic activity [23, 24], interesting magnetic [25, 26], electronic and mechanical properties [27, 28], and a good storage energy capacity [29, 30]. These properties can be altered by changing the chemical composition, type of crystal structure, and grain size. These nanostructured materials formed by mixing a metal with phosphorus are well-known by their metalloid characteristics with good electrical conductivity [31], which is important for electrochemical applications. In fact, such materials could be used as anode without binder and other conductivity additive and achieved high-performance sodium ion batteries. Furthermore, the interesting properties of FeCoP magnetic nanoparticles can be utilized as superior magnetic resonance contrast agents, magnetic separation vectors to magnetic memory devices, vector probes as future imaging technologies in the biomedical research, as well as clinical diagnostics and therapeutics. They are also widely used in diverse industrial applications such as films in soft area of corrosion protection, as robust nanotubes with high structural stability and excellent long-term stability and durability, as a highly effective oxygen evolution reaction catalyst material, as well as a promising catalyst candidate for the hydrogen evolution reaction.

Moreover, numerous studies report on the fabrication of Fe–Co–P alloys by different techniques such as reacting low-reactive metal-olates (Co$^{2+}$ and Fe$^{3+}$) with trietylphosphine [32], electrodeposition [12, 33, 34], drop synthesis method [35], organic phase reaction [36, 37], phase-solution method [38], and electroless plating method [39].

Herein, it is important to highlight that phosphorus was added to FeCo alloy to improve the soft magnetic performance of the mixture of the magnetic permeability as well as provides strengthening to the solid solution within the matrix [40, 41].

The present work aims to study the elemental (Fe, Co, and P) powder mixture through atomic diffusion during the mechanical alloying process. Particular emphasis will be devoted to the evolution of structural and microstructural as function of milling time, and subsequently the correlation with the mechanical and magnetic properties. This study primarily focuses on the fabrication of nanostructured powder by optimizing their manufacturing protocol and analysis for a future preformulation of active nanosuspensions.

2 Materials and methods

2.1 Materials synthesis

Pure elemental powders of iron, Fe (97%, average particle size ~ 325 mesh), cobalt, Co (99.90% average particle size ~ 150 µm), and amorphous red phosphorus, P (99.9%), were mixed in a high energy planetary ball mill Retsch PM 400. The milling process was performed at room temperature under an inert atmosphere using hardened steel balls and vials. The milling speed was fixed at 350 rpm with a ball-to-powder weight ratio of 10:3 while the milling time was varied from 1 to 3 h with a pause of 30 min/h.

2.2 Materials characterization

The structure of the milled powder was checked by X-ray diffraction (XRD) using a Bruker-D8 advanced diffractometer in a (θ–2θ) Bragg–Brentano geometry equipped with Cu-Kα radiation source (λ$_{Cu}$ = 0.15406 nm). Qualitative and quantitative phase analysis of XRD patterns was investigated by the Rietveld method [42] using the MAUD program [43]. The magnetic measurements were carried out at 300 K using the vibrating sample magnetometer (VSM) MicroSence-EZ7 under an applied magnetic field of 20 kOe.
The phase composition, structural, microstructural, and mechanical parameters were determined by the refinements of XRD patterns by means of MAUD program [42]. The effective crystallite size and root mean square (r.m.s) of microstrain were obtained by fitting the peaks profile using the pseudo-voigt function, which is a combination of a Gaussian and a Lorentzian peaks shape [44]. The refinement program minimized, by an algorithm based on the least squares method, the function $M$ called residue where its absolute value is defined by [45]:

$$M = \sum_i w_i (y_i - y_{ci})^2$$  \hspace{1cm} (1)

where $y_i$ and $y_{ci}$ are, respectively, the observed and calculated intensity; $w_i = 1/y_i$ is the weight associated to the $i$th observed count.

The calculated intensity is obtained by summing different contributions of Bragg diffraction peaks and the background [46]:

$$y_{ci} = y_{bi} + \sum_{\varnothing=1}^{\text{phase}} S_\varnothing \cdot \sum_{K=1}^{\text{pics}} \frac{1}{K} \cdot \sum_{i} \left( L_{PK} \cdot O_{\varnothing K} \cdot A_i \cdot F_{\varnothing K} \right)^2 \cdot \Omega_{\varnothing K}$$  \hspace{1cm} (2)

With $K$ the Miller’s indices for a reflection $(h,k,l)$; $y_{bi}$ the continuous background intensity; $S_\varnothing$ the scale factor, proportional to the volume fraction of each refined phase; $O_{\varnothing K}$ the multiplicity factor of the $k$th reflection peak; $L_{PK}$ the Lorentz-Polarization factor; $O_{\varnothing K}$ the correction factor describing the preferred orientation; $A$ the absorption factor; $F_{\varnothing K}$ the structure factor; and $\Omega_{\varnothing K}$ the profile shape function.

The quality of the refinement with the MAUD program is characterized by the reliability weighted, $R_w$, and expected factor, $R_{exp}$, or just by the goodness of fit, $\chi^2$, defined as follow:

$$R_w = \sqrt{\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i (w_i y_i)^2}}$$  \hspace{1cm} (3)

$$R_{exp} = \left( \frac{N - P}{\sum_i (w_i y_i)^2} \right)^{1/2}$$  \hspace{1cm} (4)

$$\chi^2 = \frac{R_w}{R_{exp}}$$  \hspace{1cm} (5)

where $N$ and $P$ are the number of experimental points and refined parameters, respectively.

The dislocation density, $\rho$, is one of the important parameter influencing the final microstructure, is calculated by [47]:

$$\rho = 2\sqrt{\frac{3}{2}} \frac{\langle \sigma^2 \rangle}{\langle L \rangle B}$$  \hspace{1cm} (6)

where $B$ is the Burger’s vector, which is equal to $(\sqrt{2}/3)$ for the $<110>$ direction of the bcc structure, $<L>$ the crystal lattice size, and $<\sigma^2>/2$ the root mean square (r.m.s) microstrain, obtained by the Rietveld refinements.

The planar defects expressed in terms of stacking faults probabilities, $SFP$, are given by [48, 49]:

$$SFP = [1.5(\alpha' + \alpha'') + \beta]$$  \hspace{1cm} (7)

where $\alpha'$, $\alpha''$ are the intrinsic and extrinsic deformation faults probabilities, respectively, and $\beta$ is the twin faults one.

To calculate the stored energy, $E_s$, the following formula is used [50]:

$$E_s = \left[ 3E/2(1+2v^2) \right] \langle \sigma^2 \rangle$$  \hspace{1cm} (8)

where $E$ is Young’s modulus and $v$ is Poisson ratio.

### 3 Results and discussion

#### 3.1 XRD Rietveld refinement

The best Rietveld refinements of XRD patterns of the powder mixture $Fe_{15}Co_2P_3$ as function of milling time have been obtained using an isotropic fitting model with the combination of different phases. For the un-milled powder mixture, the starting structural model is based on the elementary powders of $sc-P$, $bcc-\alpha-Fe$, and $Co-hexagonal$. However, for the $XRD$ pattern of the milled powder mixture, the best Rietveld refinements has been found with two $bcc$ phase sonly; an $\alpha-Fe(P)$ solid solution and a binary $Co_{22}Fe_{25}$ phase with Im-3 m space group. Figure 1 displays the XRD refined patterns of the un-milled and ball-milled $Fe_{15}Co_2P_3$ powder mixture using the MAUD program [43], manifesting the evolution of the alloying as a function of milling time. From Fig. 1, one can observe that the variation of peaks relative intensity with milling time indicates the corresponding change of phase’s composition, whereas peaks’ broadening indicates the occurrence of grain refinement and accumulation of microstrain induced by severe plastic deformations during the milling process.

The initial mixture displays the diffraction peaks characteristics of pure $bcc-\alpha-Fe$ and $Co-hep$ in addition to $P$, whereas the latter disappears after milling evidenced by the dissolution of $P$ into the $\alpha-Fe$ host lattice by solid state reaction accompanied by the formation of the $\alpha-Fe(P)$ solid solution. Similarly, $Co$ atoms will diffuse and incorporate into $\alpha-Fe$ host lattice leading to the formation of $Co_7Fe_{25}$ phase after 1 h of milling. The formation of
this phase is due to its higher thermodynamic stability under the experimental milling conditions compared to other phases present in the binary Fe-Co phase diagram. In fact, it is important to highlight that this phase has been obtained under an ultrahigh-vacuum chamber at a low pressure by molecular beam epitaxy (MBE) [51] and synthesized by DC magnetron sputtering deposition on top of a tunneling barrier of AlOx [52]. Accordingly, the presence of P atoms in the studied mixture facilitates the precipitation of Co_{75}Fe_{25} into an α-Fe(P) solid solution with lesser energy. This is probably due to the small difference between the atomic radii of the host metal, Fe, and the dissolved P \( (r_{Fe} = 0.125 \text{ nm}, r_{P} = 0.128 \text{ nm}) \), hence preferring a substitutional site within the Fe crystal lattice [53]. The α-Fe(P) solid solution was also obtained at much higher milling time of 9, 12, and 21 h [54] with subsequent annealing at 210 °C under argon for 30 min [55].

### 3.2 Structural properties

The relative deviation of the unit cell volume from that of the perfect crystal \( V_0 \), as defined by \( \Delta V/V_0 = (V - V_0)/V_0 \), is found to be nearly constant after 1 h of milling (Fig. 2a). The deviation increases after the first hour of milling is due to the deformation of the crystal structure of both α-Fe(P) and Co_{75}Fe_{25} phases, associated with the repeated fracturing, cold welding, and re-welding processes of the newly formed powdered particles and the diffusion of both P and Co atoms within the host lattice of Fe. The obtained results reveal that

![XRD refined patterns with a zoom on sub-spectra of Co_{75}Fe_{25} and α-Fe(P) phases in the Fe_{15}Co_{2}P_{3} compound. (a) Un-milled and (b, c, d) milled for 1, 2, and 3 h, respectively](image-url)
the unit cell volume expansion of the newly formed Co$_{75}$Fe$_{25}$ phase is higher than that of the $\alpha$-Fe(P) solid solution. In fact, after 3 h of milling, $\Delta V/V_0$ of Co$_{75}$Fe$_{25}$ is in the order of 5.26±0.02%, which is two times higher than 2.5±0.02% for $\alpha$-Fe(P), signifying that the structure of the Co$_{75}$Fe$_{25}$ phase is more deformed than that of the $\alpha$-Fe(P) solid solution. These results can be correlated with the values of the internal microstrain $<\sigma^2>^{1/2}$ deduced from the Rietveld refinements of the XRD patterns; i.e., $0.4 \times 10^{-3} \pm 0.0002$ for Co$_{75}$Fe$_{25}$ compared to $0.2 \times 10^{-3} \pm 0.0002$ for $\alpha$-Fe(P) solid solution, after 3 h of milling.

Figure 2b illustrates the variation of phase proportions as a function of milling time. The percentage of the formed Co$_{75}$Fe$_{25}$ phase increases rapidly, in the first milling hour, at the expense of pure Co and Fe elements reaching ~60%. In fact, pure $\alpha$-Fe has the highest percentage before milling of ~75% then varies with milling time to reach 35% after 3 h milling.

### 3.3 Microstructural properties

To better understand the pure element diffusion within the host lattice and subsequently the formation mechanism occurring by the mechanical milling process, primarily well-defined planar crystallographic defects playing a key role in solid state reactions has been chosen carefully. Thus, Fig. 3a illustrates the evolution of the antiphases’ presence probability during the milling in both $\alpha$-Fe(P) solid solution and Co$_{75}$Fe$_{25}$ structures deduced from the XRD Rietveld refinements. The highest probability values are recorded for the newly formed Co$_{75}$Fe$_{25}$ phase, which corroborate with the variation of its unit cell volume.
Alternatively, the stacking fault probability, $SFP$, is found to be very weak in the binary $Co_{75}Fe_{25}$ phase but increases with milling time for the solid solution (Fig. 3b). The increase of $SFP$, intimately related to the creation and reaction of dislocations, with extensive milling time reflects an important increase in the dislocations density in Fe crystalline lattice (Fig. 3c). These results highlight the pathway of the solid state reactions in this compound, occurring by diffusion of both elemental $P$ and $Co$ within Fe host lattice through stacking faults as well as dislocations induced by the milling process into the solid solution and $Co_{75}Fe_{25}$ phase. As a host, the bcc $\alpha$-Fe phase can dissolve $P$ atoms thereby creating lattice defects such as dislocations and grain boundaries. The increase of the SFP after 2 h of milling can be attributed to the annihilation of dislocations to minimize their energy. It is clear that the dislocations density of $Co_{75}Fe_{25}$ phase is steady and reaches the smallest value of about $2.22 \times 10^{16}$ m$^{-2}$.

The accumulation of lattice defects induced during milling, manifested by the variation of the microstrain rate $<\sigma^2>^{1/2}$, has a direct influence on the evolution of the crystallite size $<L>$ of the obtained phases in the milled $Fe_{15}Co_{2}P_{3}$ powder mixture (Fig. 3d). Accordingly, for $\alpha$-Fe(P) solid solution, the crystallite size decreases drastically from 483 nm to reach an average value of about 100 nm from 1 to 3 h of milling. Meanwhile, the crystallite size of $Co_{75}Fe_{25}$ phase is found to be nearly stable with milling time and reaches a mean value of 193 nm.

### 3.4 Mechanical properties

The evolution of the simulated mechanical properties, such as Young modulus and Poisson ratio, has been deduced from the XRD Rietveld refinements. The highest value of Young modulus, $E$, in the milled $Fe_{15}Co_{2}P_{3}$ powder mixture is $\sim$200 GPa, which is close to that of coarsed metals but higher than that of other nanomaterials such as FeCoP nanoglass films, i.e.,138.85 GPa [56]. However, this estimated value is slightly smaller compared to that of $Fe_{60}Co_{40}$ alloy of 250 GPa [57] but almost three times lower than the monolithic FeCo alloy setting in the range 611–536 MPa [58]. The results obtained in this study reflect the influence of the addition of $P$ powder to the Fe-Co system; as consequence, a dramatic decrease in the Young modulus values compared to Fe-Co binary alloys. This can be attributed to the precipitation of the $Co_{75}Fe_{25}$ particles embedded in the $\alpha$-Fe(P) solid solution during the milling process, resulting in the weakness and rigidity of final powder mixture because the initial powder mixture is ductile (Co, Fe)—brittle (P) type. The Poisson ratio (Fig. 4a) of the $Co_{75}Fe_{25}$ phase reaches a nearly stable mean value during the milling while for the $\alpha$-Fe(P) solid solution, it has lower values and decreases gradually with milling time. The above results expose the brittle nature of the $\alpha$-Fe(P) solid solution in comparison with the $Co_{75}Fe_{25}$ phase. Moreover, the evolution of the calculated stored energy as a function of milling time (Fig. 4b) shows that the prevalent value of the stored energy is observed for the $\alpha$-Fe(P) solid solution after 1 h of milling. The values of the stored energy in the $Co_{75}Fe_{25}$ phase are very weak and nearly equal to $83 \times 10^{-6}$ J/mol. These results may be attributed to the high rate of microstrain and dislocations density in the nanometric $\alpha$-Fe(P) grains compared to those of $Co_{75}Fe_{25}$ phase.

### 3.5 Magnetic properties

The magnetization-field hysteresis (M-H) curves of the $Fe_{15}Co_{2}P_{3}$ powder mixture at room temperature are displayed in Fig. 5a, with the inset representing M-H curves at low fields. All M-H curves exhibit similar soft magnetic features of the powder mixture with an extremely thin hysteresis loops, irrespective of the milling time. This shape is determined by the domain state which can be distinguished by several parameters such as the coercive field, $H_c$; the squareness ratio, $M_r/M_s$; the switching field distribution, $SFD$; magnetic permeability, $\mu_{max}$; and loss energy, $Q_h$.

The maximum energy loss of the hysteresis loop in the 2$^{nd}$ and 4$^{th}$ quadrant of the hysteresis loop is presented in Fig. 5b. A very small hysteresis loss is implied by the resulting narrow of the hysteresis loop. This type of loss
strongly depends on the crystallite size, residual stresses, and density of the material. According to the obtained results, for the \( \text{Fe}_{15}\text{Co}_2\text{P}_3 \) compound, the hysteresis loss shows a higher value of \( 6.94 \times 10^{-3} \text{ W/m}^3 \) in un-milled powder mixture due to the large crystallite size. The hysteresis loss decreases for the first hour of milling following an important reduction of the crystallite size [59] and then increases with further milling to reach a steady state between 2 and 3 h.

Indeed, the evolution of the coercive field \( H_c \) vs. the average grain size of the \( \text{Fe}_{15}\text{Co}_2\text{P}_3 \) powder mixture, as a function of milling time (Fig. 5c), manifests a gradual increase up to 2 h of milling while the average grain size decreases then reaches a steady state. The increase of the coercive field is related to the growth of the microstrain ratio introduced during milling and can be explained through the theory of soft magnetic materials [60]. Additionally, one can observe the evolution of the nucleation field \( H_n \) of the \( \text{Fe}_{15}\text{Co}_2\text{P}_3 \) powder mixture \( H_n \), which means that a magnetization state becomes unstable and the change in the magnetization configuration begins. However, the nucleation field is nearly close to the coercive field \( H_c (H_n \approx H_c) \), indicating that the milled powder mixture is nearly a perfect magnet.

The squareness ratio \( M/M_s \) (Fig. 5d) increases gradually with the milling time and then reaches stability up to 2 h. The rise of the \( M/M_s \) ratio can be associated with the crystallization process that leads to the increase in the magnetic anisotropy. From the values of the squareness ratio \( M/M_s \), it is possible to differentiate between single domain and multi-domain particles. Thus, the obtained values of \( M/M_s \) ratio in the range of 0.07 to 0.09 are much lower than the expected values [61], which reached 0.95 for the ferromagnetic \( \text{Co}_{75}\text{Fe}_{25} \) alloy [62].

The switching field distribution, \( SFD \), is an important micromagnetic characteristic curve depending on the degree of alignment of particles along the easy axis. It is supposed...
that the extracted SFD from macroscopic measurements rely on separating the contributions to the measurements of the intrinsic SFD, the extrinsic effects of magnetostatic and exchange interactions. The characteristic features of interphase exchange coupling are illustrated by switching field distribution via $dH/dH_c$ vs. the milling time (Fig. 5e), where $dH$ is the field between $0.5 M_r$ and $-0.5 M_r$, whereas $H_c$ is the coercivity. The distribution of the switching field shows one peak at 1 h of milling a typical characteristic of soft phases, indicating the magnetization reversal is completed in one step for this powder mixture. Consequently, the width of the $dH/dH_c$ peak can be interpreted as an estimation of the efficiency of hard/soft interphase exchange coupling.

Figure 5f shows the maximum magnetic permeability $\mu_{\text{max}}$ of the Fe$_{15}$Co$_2$P$_3$ powder mixture as a function of milling time. It can be seen that the maximum permeability decreases after 1 h of milling compared with its value before milling then increases with milling time to reach a maximum permeability value of about $65 \times 10^{-3}$ H/m after 3 h of milling. This can be attributed to the presence of a nonmagnetic P element within the α-Fe(P) solid solution in the powder mixtures which acts like an air gap, as a source of demagnetizing field causing the existence of very mobile domain walls. As consequence, the maximum permeability value increases, since it is reported that the permeability is sensitive to the microstructure and thereby can be affected by the shape of the particles, density, porosity, and strongly depends on the grain size [63, 64]. It is well-known that addition of P increases the permeability while decreases the coercivity [65, 66]. This, as suggested by the above magnetic results, is due to the higher phosphorus concentration ~15 (wt.%) in the α-Fe(P) solid solution.

The observed variation in the magnetic properties of the milled Fe$_{15}$Co$_2$P$_3$ powder mixture may also be correlated indirectly with the fabrication parameters, for instance milling atmosphere, milling speed, rise of the local temperature, and so on. Indeed, it is well established that the effect of temperature on ferromagnetism is very important. When the temperature increases, the thermal energy tends more and more to break the spontaneous alignment of atoms. The increase of the local temperature during the milling process can modify the magnetic properties of materials mainly by an irreversible change in their local chemical composition and homogeneity.

4 Conclusion

In this study, a soft magnetic Fe$_{15}$Co$_2$P$_3$ nanocrystalline alloy with optimum properties was successfully prepared by mechanical alloying from elemental Fe, Co, and red P powders. The Rietveld refinements of the XRD patterns revealed that, irrespective of the milling time, only bcc-type structures are formed and present Lorentizien Bragg diffraction peaks, with grain refinement and accumulated microstrain. After 1 h of milling, the phase mixture is composed of 60% Co$_{75}$Fe$_{25}$ phase with the highest anti-phases boundaries and deformed grains. The crystallite size decreased to 100–200 nm after 3 h of milling. The high values of the SFP reflected an important increase in the dislocations density in Fe host lattice and manifested the solid state reaction pathway which takes place through dislocations and stacking faults. The value of Young modulus in the Fe$_{15}$Co$_2$P$_3$ powder mixture was found smaller than that obtained in binary Fe-Co alloys, reflecting the effect of P addition. A narrow hysteresis loop suggested a very low hysteresis loss. The coercivity was found to increase with milling time while the average grain size decreases, which is accompanied by an enhancement of the microstrain ratio. The obtained results highlight that different magnetic properties such as hysteresis loss energy, magnetic susceptibility, and switching field distribution were determined as function of milling time, which help in defining the manufacturing protocol with a better preformulation of active magnetic nanosuspensions for biomedical applications.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s00170-021-08397-1.

Acknowledgements This work was supported by the Algerian Directorate for Scientific Research and Technological Development (DGRSDT). The authors warmly thank Dr. Ali Hafs for VSM characterization.

Author contributions Hanane Berkani (PhD student): validation, investigation, resources, writing—original draft, writing—review and editing, visualization. Prof. Rachid Siab (supervisor): conception, methodology, resources, supervision. Prof. Wassila Tebib (co-supervisor): conception, methodology, resources, review and editing, visualization, supervision, validation. Dr. Locif Redouani (XRD manager): XRD measurements and data base, visualization. Saïda Boukëffa (PhD student): XRD refinement, visualization. Prof. Mohamed Bououdina (research collaborator): validation, writing—review and editing, visualization.

Declarations

Ethics approval Not applicable.

Consent to participate All authors agreed with the consent to participate.

Consent for publication All authors read and gave their consent for the publication of this article.

Conflict of interest/competing interests The authors declare no competing interests.
References

1. Najafi A, NematiPour K (2007) Synthesis and magnetic properties of monosized Fe-Co alloy nanoparticles through microemulsion method. J Super cond Nov Magn 30(9):2647–2653. https://doi.org/10.1007/s10948-017-4052-2

2. Marcel L, Patrick B, Philippe H (2007) Les Nanosciences. Tome 3. Nanotechnologie et Nanobiologie, Belin

3. Mahmoudi M, Hosseinkhani H, Hosseinkhani M, Boutry S, Simchi A, JournayWsh SK, Laurent S (2011) Magnetic resonance imaging of tracking stem in cells vivo using iron oxide nanoparticles as a tool for the advancement of clinical regenerative medicine. Chem Rev 111:253–280. https://doi.org/10.1021/cr1001832

4. Lee N, Cheon J, Yoo D, Ling D, Cho MH, Hyeon T (2015) Iron oxide based nanoparticles for multimodal imaging and magnetoresponsive therapy. Chem Rev 115:10637–10689. https://doi.org/10.1021/acs.chemrev.5b00112

5. Shekhar N, Rajesh T, Bikramjit B (2009) Understanding phase stability, microstructure development and biocompatibility in calcium phosphate–titania composites, synthesized from hydroxyapatite and titanium powder mix. Mater Sci Eng C 29:97–107. https://doi.org/10.1016/j.msec.2008.05.019

6. Giulia V, Maria M, Hiram CM, Lucia M, Giada O, Karl DW, Wai LL, Peter R, Claudia T (2019) In vivo biotransformations of indium phosphate quantum dots revealed by X-ray microspectroscopy. ACS Appl Mater Interfaces 11:35630–35640. https://doi.org/10.1021/acs.chemmater.9b05133

7. Herget R, Dutz S, Müller R, Zeisberger M (2006) Magnetic particle hyperthermia: nanoparticle magnetism and materials development for cancer therapy. J Phys Condens Matter 18:S2919-S2934. https://doi.org/10.1088/0953-8984/18/38/S26

8. Noh SH, Moona SH, Shin TH, Lim Y, Cheon J (2017) Recent advances of magneto-thermal capabilities of nanoparticles: from design principles to biomedical applications. Nano Today 13:61–76. https://doi.org/10.1016/j.nantod.2017.02.006

9. Li X, Qian X, Xu Y, Wu H, Dan Y, Chen L, Yu Q (2019) Fe-Co-P/C with strong coupling interaction for enhanced sodium ion batteries and oxygen evolution reactions. Electrochim Acta 321:134646. https://doi.org/10.1016/j.electacta.2019.134646

10. Cheon J, Lee JH (2008) Synergistically integrated nanoparticles as multimodal probes for nanobiotechnology. Acc Chem Res 41(12):1630–1640. https://doi.org/10.1021/ar800045c

11. Cheon J, Jun YW, Seo JW, Jinwoo Ch (2008) Nanoscaling laws of magnetic nanoparticles and their applicabilities in biomedical science. Acc Chem Res 41:179–189. https://doi.org/10.1021/ar70121f

12. Xue DS, Fu JL, Yan ZJ, Xu Y, Fan LX (2007) Effects of annealing temperature on structure and magnetic properties of amorphous Fe52Co18P11 nanowire arrays. J Phys Chem Solids 68:2221–2226. https://doi.org/10.1016/j.jpcs.2007.06.023

13. Grigorieva TF, Barinova AP, Lyakhov NZ (2008) Mechanosynthetic synthesis in mechanochemical systems. Parallel, Novosibirsk, pp 1–311 [in Russian]

14. Tebib W, Alleg S, Bensalem R, Grenèche JM (2010) Structural study of the mechanically alloyed Fe-P. Int J Nanoparticles 3:237–245. https://doi.org/10.1504/IJNP.2010.035879

15. Chakka VM, Aluntcevahir B, Jin ZQ, Li Y, Liua JP (2006) Magnetic nanoparticles produced by surfactant-assisted ball milling. J Appl Phys 99:08E912. https://doi.org/10.1063/1.2170593

16. Manh DH, Tung DKh, Nam DH, Hong LV, Phong PhTh, Phuc NX (2014) Magnetic properties of annealed Fe52Co18P11 powders prepared by mechanical alloying. IEEE T MAGN. 50:1–4. https://doi.org/10.1109/TMAG.2014.2303078

17. Zeng Q, Baker I, McCrearyn V, YanZ, (2007) Soft Ferromagnetism in nanostructured mechanical alloying Fe-Co based powders. J Magn Magn Mater 318:28–38. https://doi.org/10.1016/j.jmmm.2007.04.037

18. Sundaram K, Dhanasekaran V, Mahalingam T (2011) Structural and magnetic properties of high magnetic moment electrodeposited CoNiFe thin films. Ionics 17:835–842. https://doi.org/10.1007/s11581-011-0580-0

19. Pfeifer F, Radeloff C (1980) Soft magnetic Ni-Fe and Co-Fe alloys—some physical and metallurgical aspects. J Magn Magn Mater 19:190–207. https://doi.org/10.1016/0304-8853(80) 90592-2

20. Liu XB, Ping LJ, Zhang Q, Altounyan Z (2013) Fe magnetic moment formation and exchange interaction in Fe3P: a first-principles study. Phys Lett A 377:731–735. https://doi.org/10.1016/j.physleta.2013.01.019

21. Tebib W, AllegG SJ, FuoliJJ (2018) Thermal stability of the nanocrystalline Fe-S8 (wt. %) powder produced by ball milling. Phosphorus. Sulfur Silicon Relat Elem 193:500–506. https://doi.org/10.1016/j.ijnsns.2018.1452233

22. Tebib W, Chenouanga I (2018) Effects of substitutional site in mechanical behavior of highly reactive nanostructured iron phosphides alloys. J Physics and Engineering 2:26–30

23. Zhuang M, Ou X, Dou Y, Zhang L, Zhang Q, Wu R, Ding Y, Shao M, LuoZh (2016) Polymer-embedded fabrication of Co2P nanoparticles encapsulated in N, P-doped graphene for hydrogen generation. Nano Lett 16:4691–4698. https://doi.org/10.1021/acs.nanolett.6b02033

24. Li D, Baydoun H, Verani CN, Brock SL (2016) Efficient water oxidation using CoMnP nanoparticles. J Am Chem Soc 138:4006–4009. https://doi.org/10.1021/jacs.6b01543

25. Bensalem R, Tebib W, Alleg S, Safioli JJ, Bessais L, Grenèche JM (2009) Magnetic properties of nanostructured Fe3P14 powder mixture. J Alloy Compd 471:24–27. https://doi.org/10.1016/j.jallcom.2008.03.138

26. Alleg S, Bentayeb FZ, Bensalem R, Djebbari C, Bessais L, Grenèche JM (2008) Effect of the milling conditions on the formation of nanostructured Fe-Co powders. Phys Status Solidi A 205:1641–1646. https://doi.org/10.1002/pssa.200824040

27. Bachmann M, Soubeyroux JL, Barrett R, Fruchart D, Zach R, Nizioł S, Fruchart R (1994) Magneticetoelastic transition and antiferro-ferromagnetic ordering in the system MnFeP14As9. J Magn Magn Mater 134:59–67. https://doi.org/10.1016/S0304-8853(94)00073-6

28. Broddelfalk A, James P, Liu HP, Kalska B, Andersson Y, Granberg P, Nordblad P, Häggström L, Eriksson O (2000) Structural and magnetic properties of (Fe1-xMnx)14P(x<0.25). Phys Rev B 61:413–421. https://doi.org/10.1103/PhysRevB.61.413

29. Silva DCC, Crosnier O, Ouvrard G, Gredian J, Safa-Sefat A, Nazar LF (2003) Reversible lithium uptake by FeP2. Electrochem. Solid State Lett. 6:A162–A165. https://doi.org/10.1149/1.1588112

30. Tang J, Zhang Zh, Lu B, Hao J, Yang W (2014) FeP nanoparticles grown on graphene sheets as highly active nonprecious-metal electrocatalyst for hydrogen evolution reaction. Chem Commun 50:11554–11557. https://doi.org/10.1039/C4CC05285D

31. Oyama ST, Gott T, Zhao H, Lee YK (2009) Transition metal phosphide hydrosprocessing catalysts: a review. Catal Today 143:94–107. https://doi.org/10.1016/j.cattod.2008.09.019

32. Han MY, Ye E, Zhang ShY, Lim SH, Bosman M, Zhang Zh, Win KhY (2011) Ternary cobalt–iron phosphide nanocrystals with controlled compositions, properties, and morphologies from nanorods and nanorice to split nanostructures. Chem Eur J 17:5982–5988. https://doi.org/10.1002/chem.201002698

33. Wei J, Feng E, Hao L, Cao D, Wang J, Liu Q (2013) The influence of magnetic heat treatment on morphology, structure, magnetic properties of Fe-Co-P alloy films. Appl Phys A 115:359–363. https://doi.org/10.1007/s00339-013-7840-y

34. Huang GF, Huang WQ, Liang B, Xie CL (2009) Magnetic properties of CoFeP films prepared by electroless deposition. J Magn
Magn Mater 321:1177–1181. https://doi.org/10.1016/j.jmmm.2008.10.028

35. Liu HP, James P, Broddealka A, Andersson Y, Granberg P, Eriksson O (1998) Structural and magnetic properties of (Fe1-xCo)xP compounds: experiment and theory. J Magn Magn Mater 189:69–82. https://doi.org/10.1016/S0304-8853(98)00203-0

36. Mendoza-Garcia A, Zh H, Yu Y, Li Q, Zhou L, Su D, Kramer MJ, Sun Sh (2015) Controlled anisotropic growth of Co-Fe-P from Co-Fe-O nanoparticles. Angew Chem Int Ed 54:9642–9645. https://doi.org/10.1002/anie.201503386

37. Chen J, Liu J, Xie JQ, Ye H, Fu XZ, Sun R, Wonge CHP (2018) Co-Fe-P nanotubes electrocatalysts derived from metal-organic frameworks for efficient hydrogen evolution reaction under wide pH range. Nano Energy 56:225–233. https://doi.org/10.1016/j.nanoen.2018.11.051

38. Li D, Arachchige MP, Kulikowski B, Lawes G, Seda T, Brock SL (2016) Control of composition and size in discrete Co3Fe2P nanoparticles: consequences for magnetic properties. Chem Mater 28:3920–2937. https://doi.org/10.1021/acs.chemmater.6b01185

39. Sun K, Wang K, Yu T, Liu X, Wang G, Jiang L, Bu Y (2018) Xei G (2018) High-performance Fe-Co-P alloy catalysts by electroless deposition for overall water splitting. Int J Hydrogen Energy 23:206–296. https://doi.org/10.1016/j.ijhydene.2018.11.182

40. Weglinski B, Kaczmar J (1980) Effect of FeP addition on magnetic properties and structure of sintered iron. Powder Metall 23:210–216. https://doi.org/10.1179/pow.1980.23.4.210

41. Moyer KH (1998) Powder metallurgy and application; magnetic materials and properties for part applications. ASM International, ASM Handbook 7:1006–20

42. Young RA (1996) The Rietveld method, 1st edn. Oxford University, Oxford

43. Lutteroti L, Matthes S, Wenk HR (1999) MAUD: a friendly java program for material analysis using diffraction. IUCr: News letter of the CPD 21:1–15

44. Young RA (1993) The Rietveld method. Oxford University Press, Oxford

45. SenGupta SP, Chatterjee P (2002) Powder diffraction: proceedings of the II international powder diffraction: Proceedings of the II international school on powder diffraction. Allied publishers LTD, India. 63–76

46. Gravereau P (2012) Introduction à la pratique de la diffraction des rayons X par les poudres. Université Bordeaux, ICMCB-CNRS, p1

47. Hull D, Bacon D (1950) J. Introduction to dislocations, fourth ed. Pergamon press, Oxford

48. Warren BH, Averbach BL (1950) J Appl Phys 21:595

49. Warren BH (1969) X-ray diffraction. Addition-Wesley. 275

50. Stibitz GR (1937) Phys Rev 49:862

51. Easton SN, Kupper D, Ionescu A, Kurebayashi H, Barnes CHW (2010) Spin-engineering in the Co0.5Fe0.5Cu (110) system. J Magn Magn Magn 322:2493–2497. https://doi.org/10.1016/j.jmmm.2010.03.007

52. Joshua YJ, Bengston AK, Ji CX, Morgan D, Chang YA (2008) Crystal structure effect of ferromagnetic electrode on tunneling magnetoresistance. Acta Mater 56:1491–1495. https://doi.org/10.1016/j.actamat.2007.11.045

53. Gale B (1959) Lattice parameters of solid solutions of phosphorus in iron. Acta Metall 7:420–421. https://doi.org/10.1016/0001-6160(59)90053-7

54. Tchib B, Alleg M, Sengue R, Benbali B, Bentayeb FZ, Sunol JJ, Grenache JM (2008) Structural characterization of nanosized Fe-8P powder mixture. J Nanosci Nanotechnol 8:2029–2036. https://doi.org/10.1166/jnn.2008.056

55. Tchib B, Alleg M, Grenache JM, Sunol JJ (2018) Thermal stability of the nanocrystalline Fe-8P (wt. %) powder produced by ball milling. Phosphorus Sulfur Silicon Relat Elem 193:500–506. https://doi.org/10.1080/10426507.2018.1452233

56. Zhang M, Zhou P, Li Q, Gong P, Wang X (2020) Electrodeposition of FeCoPnanoglass films. Microelectron Eng 229:111363. https://doi.org/10.1016/j.mee.2020.111363

57. Vladyssav AV, James OR, Mark TK (2004) Structure, stress, and magnetic properties of high saturation magnetization films of FeCo. IEEE I MAG, 40:2335–2337. https://doi.org/10.1109/TMAG.2004.832256

58. Albaaja AJ, Castle EG, Reece MJ, Hall JP, Evans SL (2017) Effect of ball-milling time on mechanical and magnetic properties of carbon nanotube reinforced FeCo alloy composites. Mater Des 122:296–306. https://doi.org/10.1016/j.matdes.2017.02.091

59. Shokrollahi H, Janghorban K (2006) The effect of compaction parameters and particle size on magnetic properties of iron-based alloys used in soft magnetic composites. MSEE, 134:41–43. https://doi.org/10.1016/j.mseb.2006.07.015

60. Herzer G (1997) Nanocrystalline soft magnetic materials. Handb Magn Mater 10:415–462. https://doi.org/10.1016/S1567-2719(97)10007-5

61. Stoner EC, Wohlfarth EPA (1948) Mechanism of magnetic hysteresis in heterogeneous alloys. Soc Lond A 240:599–642. https://doi.org/10.1098/rsta.1948.0007

62. Naganuma H, Oogane M, Ando Y (2011) Exchange biases of Co, Py, Co0.5Fe1.3B0.5, Co0.5Fe50, and Co0.5Fe50 on epitaxial BiFeO3 films prepared by chemical solution deposition. Int J Appl Phys 109:07D736-1. https://doi.org/10.1063/1.3563061

63. Hamzaoui R, Elkedim O, Gaffet E, Grenèche JM (2006) Structure, magnetic and Mössbauer studies of mechanically alloyed Fe–20 wt.% Ni powders. J Alloys Compd 417:32–38. https://doi.org/10.1016/j.alcom.2005.09.064

64. Shokrollahi H (2009) The magnetic and structural properties of the most important alloys of iron produced by mechanical alloying. Mater Des 30:3374–3387. https://doi.org/10.1016/j.matdes.2009.03.035

65. Kordecki A, Węgliński B, Kaczmar J (1982) Properties and applications of soft magnetic powder composites. Powder Metall 25(4):201–208. https://doi.org/10.1179/pow.1982.25.4.201

66. Mann SK, Prabhu DB, Gopalan R, Srinivas V (2014) AC magnetic properties and core loss behavior of Fe-P soft magnetic sheets. IEEE Trans Magn 50(11):4–7. https://doi.org/10.1109/TMAG.2014.2331084

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.