Ultrafast Particle Size Reduction of $\text{Fe}_{73.9}\text{Si}_{15.5}\text{Cu}_1\text{Nb}_3\text{B}_{6.6}$ by High-Energy Milling: Nb_2O_5 as a Marker of Permeability Enhancement and Magnetic Hardening

Jesús López-Sánchez,^{*a} Elena Navarro,^{a,b} Aída Serrano,^c Cecilia Granados-Miralles,^c Adolfo del Campo,^c Adrián Quesada,^c and Pilar Marín,^{a,b}

^aInstituto de Magnetismo Aplicado, UCM-ADIF, 28230 Las Rozas, Spain

^bDepartamento de Física de Materiales, Universidad Complutense de Madrid (UCM), 28040 Madrid, Spain

^cDepartamento de Electrocerámica, Instituto de Cerámica y Vidrio, ICV-CSIC, 28049 Madrid, Spain

Corresponding author: jesus.lopez@ucm.es

KEYWORDS soft magnetic materials, amorphous magnetic materials, ultrafast particle size reduction, permeability enhancement, high-energy ball milling, confocal Raman microscopy

ABSTRACT

This work is conceived to provide a reproducible and fast method to obtain optimal particle sizes for competitive ultrasoft magnetic applications based on $\text{Fe}_{73.9}\text{Si}_{15.5}\text{Cu}_1\text{Nb}_3\text{B}_{6.6}$ nanostructured particles. In this scenario, partial nanocrystallization of the $\alpha\text{-Fe}_3\text{Si}$ compound is promoted by annealing and subsequent high-energy ball milling processes. The milling is performed in this material, for the first time, by a combination of mixer, vibratory, and planetary ball milling motions. Under these conditions, structural and magnetic properties are tuned as a function of milling time with reduced particle size distributions and maintaining the ultrasoft magnetic character. In addition, drastic electronic and structural changes are observed after a few minutes of milling where the saturation magnetization and initial permeability are strongly influenced by the percentage of the $\alpha\text{-Fe}_3\text{Si}$ nanocrystallites formed. Above 30 minutes of ball milling time, the formation of a low concentration of Nb_2O_5 clusters is detected by confocal Raman microscopy. This identification is essential since the rejection of the Nb from the amorphous matrix rich in Fe-Nb-B atoms acts as a marker of the seed mechanism that causes the deterioration of the softness character of these nanostructures. Therefore, on the one hand, this work introduces a successful procedure by combined milling processes to optimize the saturation magnetization and permeability with sub-micron particle sizes and, on the other hand, the detection of Nb_2O_5 clusters is implemented as an influential marker on the magnetic properties of these soft nanostructured particles.

1. Introduction

The major role of soft magnetic materials is to produce a stable high density magnetic flux in a specified spatial region with polarization switches at low applied magnetic field values.¹ Their applications encompass an enormous range of interdisciplinary technological purposes as highly efficient microwave absorbers,²⁻⁹ sensor microwires,^{10,11} hard/soft magnetic nanocomposites for improved permanent magnets,^{12,13} 3D nanoengineered composite multilayers,¹⁴ nanowires for magnetic sensing devices,^{15,16} polymers-coated multicore nanoparticles for sensing and drug delivery,¹⁷ microwires for high heating efficiency in magnetic hyperthermia,¹⁸ health monitoring,^{19,20} and soft magnetic ferrites for excellent diagnostic imaging applications.²¹ Therefore, a continuous and necessary demand of technological development exists with the objective of improving their functional properties by tuning the particle size, morphology, and chemical stability.^{22,23}

Within this context, those soft magnetic materials with high permeability, high Curie temperature, high saturation magnetization values, low coercivities, and zero magnetostriction are considered the best suitable candidates to cover the widest range of multifunctionality. Specifically, the amorphous $\text{Fe}_{73.9}\text{Si}_{15.5}\text{Cu}_1\text{Nb}_3\text{B}_{6.6}$ alloy stands out with such properties which are even improved by subsequent heat treatments performed at temperatures above 500 °C.²⁴⁻²⁸ In that thermal range, the alloy transforms into an ultrasoft magnetic material by promoting partial crystallization of the $\alpha\text{-Fe}_3\text{Si}$ nanocrystallites.²⁴⁻²⁸ Cu nanoclusters serve as nucleation points²⁹ and their growth is controlled by the presence of Nb atoms in the amorphous matrix since their high atomic radius causes a considerably reduced diffusion in the material.²⁴ Regarding the B atoms, these are incorporated into the alloy to favor the stability of the amorphous structure. This compositional puzzle results in a nanostructured material with amazing features composed by $\alpha\text{-Fe}_3\text{Si}$ nanocrystallites embedded in a stable magnetic amorphous matrix rich in Fe-B-Nb atoms.³⁰ The nanocrystallites are strongly exchange coupled within the matrix,^{25,26,31} decreasing their magnetocrystalline anisotropy without losing high values of saturation magnetization.³² However, the crystallization of the Fe-B compounds inevitably entails a magnetic hardening (coercivity increase) at temperatures above 640 °C. The Fe-Si-Cu-Nb-B alloy starts to leave behind the soft magnetic character and studies are performed as a function of the annealing temperature.³³

The most widely used and efficient method to obtain large quantities of this amorphous material is by melt-spinning as ribbon form.^{30,34,35} However, further processing on the ribbons is required to reduce their size to powder form for conferring a desired shape for a particular application. This procedure can be accomplished by ball milling processes in controlled atmosphere. For that, most studies employ planetary milling,³⁶ with low impact energy (< 750 rpm)^{36–39} and long execution times (tens of hours)^{39–42} to reduce both particle distribution and sizes, attempting to keep the physical properties of the starting material from being devalued. However, during these processes the permeability, the coercivity and the saturation magnetization are highly modified mainly due to the absence of shape anisotropy of the ribbons, the occurrence of undesirable phases such as FeB and/or the excessive crystallization of α -Fe₃Si compound which reduces the exchange coupling due to the reduction of the amount of amorphous matrix.⁴³ Therefore, the development of new methodologies or the optimization of the existing ones is necessary to achieve high-performance nanostructured materials.

This work is focused on developing a reproducible method to optimize the crystal domain and particle sizes to obtain competitive magnetic properties of the Fe_{73.9}Si_{15.5}Cu₁Nb₃B_{6.6} alloy in powder form with a fast and high-energy ball milling system.⁴⁴ For that, Emax apparatus combining mixer, vibratory and planetary ball milling motions at the same time is employed with a maximum frequency of 2000 rpm. The consolidation of these motions at this high-energy implies a generalized solid state diffusion accompanied by a reduction in particle size, obtaining particles below 100 nm in relatively short times of the order of a few hours.⁴⁵ To our best knowledge on the subject, this is the first work carried out at such high-energy for this composition, obtaining functional structures in a few minutes. In addition, despite the vast scientific literature related to this alloy, no systematic studies have been carried out to determine how the physical properties of samples are changing maintaining the same chemical composition. This means non-inducing other compounds such as FeB or FeCu₄ clusters which modify the hardening character of the samples.⁴³ Therefore, the main goal of this work is to "monitor" the evolution of the structural and magnetic properties as a function of the milling time to unveil the origin mechanisms that precede and to provide a new insight into their evolution as the milling time progresses. Moreover, an interesting structural point of view is provided by confocal Raman spectroscopy (CRM). The local formation of Nb₂O₅ clusters is identified and this observation determines the operational high-energy ball milling time range where the softness character of the powder starts to deteriorate.

2. Experimental Techniques

2.1. High-Energy Ball Milling of Nanocrystalline Magnetic Ribbons

$\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ amorphous ribbons are grown with a thickness of 20 μm by ultrafast melt spinning cooling technique by Vacuumschmelze GmgH & Co®. They are ensuing cut from their original coil of 50 mm width into small ribbons of approximately 17 x 60 mm² with a thickness of 20 μm . A thermal treatment is carried out at 550 °C in a nitrogen atmosphere for 1 h with a temperature ramp of 7 °C/min to promote the controlled growth of $\alpha\text{-Fe}_3\text{Si}$ nanocrystallites within the matrix.^{24–28} This makes the material more brittle, which favors the effectiveness of the subsequent milling process.⁹ For this milling, a Retsch® Emax high-energy mill is used with control temperature limits (water cooling refrigeration), set to prevent the temperature from overstepping the range 35–60 °C. The direction of rotation is reversed every effective minute of milling (full speed). These conditions enhance the particle size homogeneity, decrease the formation of agglomerates and prevent the formation of undesirable phases due to overheating. High-energy milling is performed at a frequency of 2000 rpm with 2 mm diameter balls as milling bodies, filling 2/3 of the volume of the milling jar. The jar has a capacity of 50 ml and, like the milling bodies, is made of tungsten carbide (WC). The annealed ribbons are subjected to different milling times up to 180 minutes, opening the system and scratching the residual powder agglomerates from the jar walls every 2 minutes of effective milling (one per direction of rotation).

2.2. Structural and Magnetic Characterization

Composition and structure of the samples were examined by X-ray diffraction (XRD) with a PANalytical X-ray diffractometer in a Bragg-Brentano configuration using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Subsequent Rietveld analyses were performed in the XRD patterns using FullProf Suite.⁴⁶ Morphological aspects were studied by scanning electron microscopy (SEM) with a JEOL JSM6400 instrument. Crystal structure of $\alpha\text{-Fe}_3\text{Si}$ compound were examined by high resolution transmission electron microscopy (HRTEM) with a JEOL 3000 system. Particle (from SEM images) and nanocrystallite (from TEM images) size distributions were analyzed using the ImageJ software.

Due to the high-energy of the milling process, significant structural variations are expected at short-order range of the material. Therefore, X-ray absorption near edge structure (XANES) and

extended X-ray absorption fine structure (EXAFS) experiments were carried out at the Fe K-edge (7112 eV) in the range between 6900 and 8000 eV at the SpLine beamline of The European Synchrotron (ESRF). The energy resolution given by the monochromator was 1.2 eV. A few milligrams of sample were dispersed in a cellulose matrix and pressed into pellets at 5 tons for 2 minutes to optimize the absorption edge signature in transmission mode. The X-ray absorption spectroscopy (XAS) spectra were measured at room temperature and for the analysis an average of 5 XAS scans was carried out. Reference data from an Fe foil were used for the energy calibration. XANES and EXAFS data were interpreted following standard procedures using the Athena and Artemis program packages.^{47,48} Complementary compositional phase information was performed from CRM measurements with a Witec ALPHA 300RA instrument equipped with a Nd:YAG laser (532 nm) taking an average of 6 Raman spectra with 3 seconds of integration time in selected areas. Raman data were analyzed using the Witec Project Plus software.

Magnetic properties of the milled powders were studied with a vibrating sample magnetometer attached to a physical property measurement system (PPMS model 6000 controller – Quantum Design). Magnetic hysteresis loops were obtained at room temperature with a maximum applied magnetic field of 5 T.

3. Results and Discussion

3.1. Structural Characterization of the Nanostructured Particles

Figure 1b shows a detailed scheme of the milling process carried out on annealed $\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ ribbons where large friction and impact zones are present due to the oval shape of the jars. This innovative milling is performed for the first time for the alloy at a frequency of 2000 rpm, which is combined with mixer mill, vibratory disc mill, and planetary mill.⁴⁴ The consolidation of the motions offered by the Emax system promotes a much higher homogeneity in the particle size distribution in relatively short periods of time, yielding values below 10 μm after only 12 min (Figure 1a1). For this specific time, the particle size distribution resulting from the analysis of 400 particles follows a log-normal function with a mode close to 1 μm . Large particle sizes between 30 and 50 μm are residually observable at the tail of the distribution (Figure 1a1). Although the amorphous ribbons have a thickness of 20 μm , the lateral dimensions are of the order of centimeters. Therefore, the enormous potential of this revolutionary milling system is evident.

Figure 1a1–a4 show the SEM images and particle distributions obtained for 30, 60, and 110 min of ball milling time. As milling time advances, the particle size continues diminishing reaching values below ~ 200 nm, for a milling time of 110 min with no evidence of formation of large particles due to agglomeration of smaller particles (Figure 1a4). For these selected times, the particle size distribution remains with log-normal character whose mode values are progressively reduced from 0.710 (13) > 0.578 (22) > 0.185 (11) μm for $30 < 60 < 110$ min of milling respectively. After 60 min, no particles above $10 \mu\text{m}$ are detected in the studied areas (Figure 1a3–a4). An additional indication of the significant decrease in particle size is the sample color turning from grey to black as the milling time increases (bottom part in Figure 1b).⁴⁹

Figure 1: SEM images and particle size distribution (overlapped) obtained by 400 particle sampling for milling times of (a1) 12, (a2) 30, (a3) 60, and (a4) 110 min respectively. The bin size for the distributions of the Figures a1 and a2 is 1000 nm and for the Figures a3 and a4 is 200 nm. The mode for each case is shown at the maximum of the distribution; (b) Schematic illustration of the milling process of annealed Fe_{73.9}Cu₁Nb₃Si_{15.5}B_{6.6} ribbons using an Emax system. At the bottom of the Figure b pictures of the annealed ribbons and powders obtained for milling times of 12, 90, and 180 min are displayed.

The evolution of structural properties, microstructure and composition of all samples are investigated by XRD measurements. Figure 2a shows the diffraction patterns collected for selected samples as a function of milling time. In all cases, the diffraction peaks could be assigned to the α -Fe₃Si phase.³⁶ Numerous studies have shown the emergence of new compositional phases such as iron silicides (i.e. FeSi₂)⁵⁰ and iron borides (i.e. Fe₃B)³⁸ with planetary mill systems as the milling time increases. In this work, this scenario does not occur and the same compounds found in the annealed sample are preserved throughout the milling time range investigated.

A Rietveld model was constructed for the α -Fe₃Si phase (space group: *Fm-3m*, bulk lattice parameter $a=5.665(3)$ Å)⁵¹ and this model was fitted to the XRD data collected for all samples. The broad line profile is modelled as a convolution of two individual effects: the small size of the α -Fe₃Si nanocrystallites, and the microstrain induced in the crystallites by the milling process (see Figure S1 in the Supporting Information for additional details and plots of the Rietveld analysis). The fit is substantially improved by including in the model the contribution of a “near-amorphous” α -Fe₃Si phase. To make the refinements more stable, the latter contribution has been considered strain-free and its crystal domain size was fixed at 0.6 nm for all samples. No significant evolution is noted as the milling time progresses.

Figure 2b shows the progression of the lattice parameters calculated for the two phases. For the “near-amorphous” α -Fe₃Si phase, variations in the lattice parameter occur with a non-visible trend as a function of the milling, but in all cases, the values slightly higher than the crystalline α -Fe₃Si phase (~ 0.2 Å higher). On the contrary, a monotonic cubic trend is observed for the crystalline phase with a final increase of the a -lattice parameter of 1.1%, comparing annealed ribbons with the powder obtained after 180 min of milling. The influence of milling time over the microstructure of the crystalline phase is shown in Figure 2c. The evolution of the crystal domain size of the crystalline phase shows an abrupt drop from 8.75 to 5.25 nm after 40 min of milling. This is followed by a slight linear increase up to 100 min and above this value, a stabilization at 7.75 nm is observed up to 170 min. For the evolution of the induced strain, an expansion zone and a strain mitigation zone are identified, with a turning point at 100 min (Figure 2c). In the expansion zone, the microstrain has an approximately linear progression from 25%% (0 min) to 110%% (100 min), excluding a region between 6 and 20 min where it remains almost constant. In the mitigation zone, it decreases linearly to 87%% at 180 min.

Figure 2: (a) Evolution of XRD patterns for milling times from 0 (annealed ribbons) to 180 min. Structural parameters derived from Rietveld analysis: (b) refined a -lattice parameter for crystalline and “near-amorphous” α -Fe₃Si phases, (c) crystallite size and strain induced for crystalline α -Fe₃Si phase, and (d) compositional percentage of the two contributions.

With these structural results, two conclusions are drawn to this discussion. First, the high impact energy of the milling process up to 40 min reduces the crystal domain size previously formed by annealing at 550 °C. Trend change above this value is not directly related to the microstrain and/or the relaxation of the lattice parameter (strain-spreading zone) (Figure 2b–c). In that zone, the decrease in particle size (Figure 1a1–a2) is accompanied by an increase in the microstrain on the crystalline α -Fe₃Si phase (Figure 2c). The second conclusion is that the strain mitigation region from 100 min of milling time results in a stabilization of the crystal domain size at ~7.5 nm. This effect could be the manifest that the crystal domain sizes of the crystalline α -Fe₃Si phase are interacting with the Nb atoms that inhibits its growth, in favor of mitigating defects in its crystalline

lattice. In addition, the lattice parameter has undergone a relaxation of 0.9% at 100 min. Compared to 1.1% calculated for 180 min, this means that the material is energetically more stable after 100 min and although the lattice continues to expand, this expansion occurs to a lesser degree (Figure 2b). Therefore, the material finds a tunable structurally stable situation to such high energetic milling processes and there is no transition towards the generation of other undesirable compounds. This would imply a potential transfer to industry with physical size reductions below 100 nm while maintaining the chemical composition of the starting material in relatively short period of time.

To conclude with the results obtained from Rietveld analyses, the evolution of the crystalline and “near-amorphous” phases percentage is represented in Figure 2d. These percentages are dependent on each other and inversely correlated. At low milling times, the crystalline phase percentage increases from 45% (0 min) to 60% (40 min) and is accompanied by a decrease in crystal domain size. This increase in percentage is interpreted as a result of the progressive transformation of the “near-amorphous” phase into the crystalline one. As the milling continues, there is an interesting region from 40 to 100 min where both percentages look constant. This effect may be understood as an atomic rearrangement resulting in an increase in the size of the crystalline domains, but the introduction of strain persists. Above 100 min, the evolution of the crystalline α -Fe₃Si phase percentage starts to increase again from 60% (100 min) to 75% (180 min). However, the crystal domain size is virtually constant on this occasion, probably due to the interaction with the Nb atoms. The effect of increasing the crystallinity of the α -Fe₃Si compound as the milling time advances is observed by other studies and would confirm the results revealed in the present investigation.^{28,52} Specifically, the preferential increase of α -Fe₃Si nanocrystallites is examined by TEM analysis in this work (Figure 3a–d).

Figure 3a–c shows the α -Fe₃Si nanocrystallite distribution embedded in the amorphous matrix rich in Fe, B and Nb atoms for milling times of 30, 110, and 180 min respectively. The particles studied are relatively thick and a quantitative percentage value of nanocrystallites present in the samples is rather difficult to determine. However, an increase in the amount of nanocrystallites is observed comparing the 30 min sample with the other two selected samples with 110 min and 180 min of milling. At the edges of the particles, high resolution images can be performed where the amorphous matrix is distinguished and several α -Fe₃Si nanocrystallites are detected for 180 min

(Figure 3d). As an example, an oriented α -Fe₃Si nanocrystallite with a size of ~10 nm along the axis of zone $[11\bar{1}]$ is displayed in Figure 3e and its crystal structure is simulated in the real space oriented in that direction in Figure 3f. As an interesting observation, nanocrystallites are not found at the edges of particles, a sign that the collisions between particles at 2000 rpm are quite virulent and the degree of crystallization increases in the inner part of the particles, probably due to an atomic diffusion mechanism.

Figure 3: TEM images of the particles prepared at (a) 30, (b) 110, and (c) 180 min of milling time. (d) HRTEM image of 180 min sample where α -Fe₃Si nanocrystallites (delimited with dashed white lines) are observed embedded in the amorphous matrix (delimited with dashed grey line). (e) Fast Fourier transform (FFT) image calculated from the yellow square region depicted in Figure d, where various reflections and interplanar distances associated with the α -Fe₃Si compound are marked. (f) Schematic representation of atomic positions in the α -Fe₃Si crystal structure in $[010]$ orientation.

In-depth studies are performed to determine the oxidation state and the short-range order of the samples by XAS experiments. The normalized XANES spectra at Fe K-edge for amorphous $\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ ribbons, annealed with different subsequent milling times and Fe foil added as a reference, are shown in Figure 4a. The average valence of transition metals is ascertained from the absorption edge position corresponding to the first maximum in the first derivative of the XANES experimental curves (labelled as **i** for these Fe-based compounds in Figure 4a–b).^{53,54} Here, no evidences of oxidizing in the Fe-based compounds are detected during the annealing and subsequent milling processes, obtaining a valence of ~ 0 in all cases as for the Fe foil standard. Besides the large intensity changes of the Fe absorption edge (**i**), several near edge fine structure resonances with different intensities are also distinguished (labelled as **ii** and **iii**). The **i** region arises from the transitions from 1s states to unoccupied states having admixed 4s-4p-3d symmetry, whereas the **ii** region arises from the transitions to the Laporte-allowed states of nearly pure 4p symmetry.^{55–57} In turn, the **iii** region shows a maximum of absorption intensity, corresponding to the transitions from 1s to np with $n = 5, 6, 7$, etc. The region marked with an asterisk (*) undergoes an intensity decrease since a threshold between pure s and p character is established (Figure 4a–b).^{55,56} This point is the most sensitive to disruptions in crystalline lattice when a thermal and/or pressure experiment is performed.⁵⁸ When the material exhibits an amorphous state order a broadening is observed in this region showing strong resemblances to the liquid phase γ -FCC around 2600 K.⁵⁸ Therefore, the potential of this technique is demonstrated to monitor different amorphous and crystalline states of the samples at the Fe K-edge. As milling time increases, an enhancement of the degree of crystallization causes a resemblance of the XANES and EXAFS spectra features to BCC structure of metallic α -Fe⁵⁹ and the region (*) becomes more pronounced (Figure 4a–b).

A localized singularity between **i** and **ii** transitions is detected in Figure 4b for milling times comprised between 2 and 30 min. This is reflected in the XANES region with an increase in absorption in the range between 7115 and 7118 eV, showing similarities with the XANES spectrum of α -Fe₃Si compound.^{59–61} This phenomenon can be interpreted as p-type electron unoccupied states formed around Fe atoms during the annealing process.⁶⁰ As the milling time increases, this density of unoccupied states evolves towards the fine structure of the α -Fe BCC-type structure and could have its influence on the magnetic properties.

Figure 4: (a) Normalized XANES spectra and (b) their derivative curves for amorphous $\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ ribbons and these annealed with a subsequent ball milling times ranging from 2 to 170 min. Three near edge fine structure transitions are marked as **i**, **ii** and **iii**. The plateau region indicated as * represents the limit between s and p character transitions in Figures a and b. The continuous red oval line in Figure b shows the influence of Fe-Si coordination in the XANES region. (c) Weight percentage of the crystallinity degree calculated from a linear combination taking into account Fe foil reference and amorphous $\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ ribbons. (d) FT magnitude (open circles) of Fe K-edge EXAFS (k^3 -weighted) and fits (continuous lines) carried out in the R range comprised between 1.5 and 3.0 Å. The colour code is the same of Figure a.

An estimation of the crystallinity degree as the milling time progresses is calculated for each sample by a linear combination of the derivative of the XANES spectra from those of the amorphous ribbons and Fe foil (Figure 4c). For 2 min of milling, the percentage of α -Fe BCC-type structure is close to 10% and for 170 min of milling a value of about 40% is obtained. This increase of 30% is similar to that one calculated by Rietveld analyses (Figure 2d). Therefore, XAS analyses can become a good alternative for calculating the crystalline percentage achieved by the milling influences in this kind of compounds.

Figure 4d displays the modulus of the FT of the EXAFS signal. The FT is performed in the $k^3 \chi(k)$ weighted EXAFS signal between 2.5 and 11.5 $\text{\AA}^{-1}$. Experimental EXAFS results are fitted in R-space in the range 1.5-3.0 $\text{\AA}$ (first neighbors) using the FEFFIT code.^{47,48} The fitting is carried out fixing the energy shift which is previously calculated from the Fe foil signal. The coordination number N, the interatomic distance R and the Debye-Waller (DW) factor σ^2 for the two first shells (within the first peak in Figure 4d) are used as free parameters for each fitting. Obtained values from the fitting of EXAFS signal are presented in Table 1.

Table 1. N, R, and σ^2 EXAFS Parameters of First and Second Coordination Shell Obtained from Experimental EXAFS Results for the Fe foil and $\text{Fe}_{73.9}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_{6.6}$ Samples (Amorphous Ribbons and as a Function of the Milling Time 2 min $\rightarrow$ 170 min).

Sample	First coordination shell Fe-Fe			Second coordination shell Fe-Si/Fe		
	N	R ($\text{\AA}$)	σ^2 ($\text{\AA}^2$)	N	R ($\text{\AA}$)	σ^2 ($\text{\AA}^2$)
Fe foil	8	2.460 (2)	0.0048 (2)	6	2.845 (3)	0.0072 (4)
170 min	3.91 (2)	2.465 (2)	0.0051 (2)	3.66 (6)	2.842 (4)	0.0120 (6)
140 min	3.76 (3)	2.465 (2)	0.0051 (2)	3.42 (2)	2.843 (3)	0.0123 (6)
110 min	3.17 (1)	2.464 (2)	0.0050 (2)	2.83 (6)	2.839 (5)	0.0131 (7)
80 min	2.83 (3)	2.465 (2)	0.0055 (3)	2.6 (1)	2.832 (6)	0.0141 (9)
60 min	2.48 (1)	2.460 (2)	0.0049 (2)	2.38 (7)	2.832 (6)	0.0156 (8)
30 min	2.37 (8)	2.457 (2)	0.0054 (2)	2.35 (1)	2.822 (8)	0.0147 (9)
12 min	1.73 (1)	2.454 (2)	0.0050 (2)	2.00 (7)	2.819 (6)	0.0173 (9)
2 min	1.55 (3)	2.457 (3)	0.0055 (4)	1.7 (1)	2.824 (8)	0.017 (1)
Amorphous ribbons	2.64 (8)	2.378 (4)	0.0110 (5)	-	-	-

A general observation for all samples is their relative low amplitude of the oscillations displayed in the R signature compared to those observed in the Fe foil (Figure 4d). Theoretical studies simulated at the Fe K-edge for metallic α -Fe and for α -Fe₃Si compounds show how the combination of these signals result in destructive oscillations and thus the reduced signal.⁶¹

Going into semiquantitative analysis for the Fe_{73.9}Cu₁Nb₃Si_{15.5}B_{6.6} amorphous sample, the EXAFS signature is fitted considering one Fe-Fe shell. Short-range ordering at larger distance is not appreciable (other shells), likely to the amorphous character of the sample. The most significant modification of the amorphous sample after the annealing and milling processes is the emergence of a new coordination shell (Figure 4d) located at the first peak. This shell may be related to the Fe-Si/Fe bonds. The different XANES signature of the samples with respect to the Fe foil is indicative of other coordination type (Figure 4a), suggesting an Fe-Si coordination in the second shell for the samples instead an Fe-Fe bond as for the Fe foil. This results in a crystallization of the α -Fe₃Si structure when the sample is annealed at 550 °C and evolves as a function of milling time as happens in the XANES region (Figure 4a–b). In addition, the number of coordination is progressively rising to values around half of the coordination of the Fe foil (Table 1). This behavior is also identified at larger coordination shells up to ~5 Å (Figure 4d). A few studies can be found related with the application of the EXAFS technique to study the evolution of the short-range ordering around Fe atoms in this kind of materials. In the case of Fe₈₆Zr₇Cu₁B₆ alloys, the EXAFS spectra also show the evolution from a disordered Fe environment to the BCC crystalline arrangement.⁶²

Regarding both the first and the second coordination shells an increase of the radial distances and a decrease in the DW factors of the α -Fe₃Si nanocrystallites are noted when milling processes advance. This result is consistent with the increase of the lattice parameter observed by XRD data up to approximately 100 min (Figure 2b), and tends to stabilize at higher milling times. Therefore, an evolution of the crystalline structure is evidenced as a function of the ball milling time going to larger coordination from the EXAFS signal, including the emergence of one second shell (not detectable in Fe_{73.9}Cu₁Nb₃Si_{15.5}B_{6.6} amorphous sample) with lower crystal disorder degree reflected in the DW factor calculations.

3.2. Influence of the High-Energy Ball Milling Time Performed in $\text{Fe}_{73.9}\text{Si}_{15.5}\text{Cu}_1\text{Nb}_3\text{B}_{6.6}$ on the Magnetic Applications

All electronic and structural changes arising as a function of the milling time may have an influence on the magnetic properties. In the case of nanocrystalline magnetic materials with randomly oriented easy axes in which the structural correlation length D (grain size) is smaller than the ferromagnetic exchange length L_{ex} , the magnetization does not follow local magnetic anisotropy axes, but instead, it is forced to align parallel due to the exchange interaction.⁶³ Thus, the effective anisotropy value is averaged over several grains and its magnitude is thereby reduced. In nanocrystalline systems based on Fe-alloys, the exchange correlation length is between 30 and 50 nm.⁶³ To ensure the applicability of this anisotropy average model^{25,26} in this particular system, the nanocrystallite size distribution is calculated using TEM image processing for 30 and 180 min milling time samples (Figure 5a–b). The sizes obtained are confined below 20 nm and their distribution is fitted to a log-normal function with mode values of 4 nm and 8 nm for 30 min and 180 min respectively. Compared with the results obtained by Rietveld refinement depicted in Figure 2c (6 nm for 30 min and 8.5 nm for 180 min), these ones are similar. As a consequence, the $\alpha\text{-Fe}_3\text{Si}$ nanocrystallites are single crystal and their magnitudes are below the ferromagnetic correlation length proving the applicability of this anisotropy model.^{25,26,36,63}

To unveil the magnetic behavior of these nanostructured particles, hysteresis magnetic loop measurements are carried out for the annealed samples as a function of the milling time (see Figure S2 in the Supporting Information). The saturation magnetization and coercivity values obtained are represented in Figure 5c. The saturation magnetization values are within the ranges reported the literature involving mechanical milling processes.^{28,38} However, several studies show no significant variation in saturation magnetization as milling time increases.²⁸ In this work, a sharp jump is detected from 128.5 (value obtained for annealed ribbons) to 141.2 emu/g obtained for 20 min. Afterward, there is a "ball milling time window" where the saturation magnetization remains almost stable between 141 and 147 emu/g and then decreases to 136 emu/g at 180 min with a linear trend (Figure 5c).

Figure 5: Nanocrystallite size distribution obtained from TEM analyses performed for 30 min (a) and 180 min (b) of milling time samples. The distributions (200 particle sampling) follow a log-normal function in both cases. The bin size for the distributions is 1.25 nm. The mode for each case is shown at the maximum of the distribution. (c) Evolution of the saturation magnetization and coercivity as a function of the ball milling time. Inset of Figure c shows a magnification of the area delimited by the black rectangle, showing a close look of coercivity evolution. (d) Calculated initial permeability and effective anisotropy taking into account the random anisotropy model.^{25,26,63} Three different magnetic behavior regions are distinguished: (1) Temperature-induced α -Fe₃Si nanocrystallites emergence region (red color), (2) initial permeability enhancement region (light blue color), and (3) magnetic hardening region (dark blue color).

In this kind of materials, the saturation magnetization results from a competition between the percentage of nanocrystallized α -Fe₃Si compound and the Fe-Nb-B atom-rich amorphous matrix. The amorphous matrix is ferromagnetic but exhibits a lower saturation magnetization compared to the nanocrystallized one.⁶⁴ In Figure 2d, an increase of the crystalline α -Fe₃Si percentage was observed up to 40 min ($\sim +15\%$) and up to 100 min remains approximately constant ($\sim +0\%$). This area of study corresponds to the strain-spreading zone (Figure 2c) and the correlation between the

percentage of crystalline α -Fe₃Si phase and saturation magnetization is evidenced. In addition, no significant variations in saturation magnetization should be observed with the progressive rise of the domain size from 5.25 (40 min) to 7.75 nm (100 min) in the same range (Figure 2c). As this situation occurs, the rearrangement of the atoms in favor of increasing the crystal domain size is assumed.

This same approach becomes inconsistent in the strain mitigation zone as the crystalline phase percentage increases (Figure 2d) and the saturation magnetization decreases (Figure 5c). This effect could be due to the formation of superparamagnetic (SPM) particles as occurs in other works with long milling times (>100 h).^{41,65} However, no decrease in the crystal domain size is detected after 100 min of milling at ~7.75 nm (Figure 2c) and therefore the formation of SPM particles seems unlikely. An alternative possibility is the formation of secondary phases that have a lower saturation magnetization than crystalline α -Fe₃Si (such as the formation of FeB-based compounds).³⁸

In contrast, the evolution of coercivity (Figure 5c) does not follow the trend of the crystal domain size as observed in other works.^{25,28} The coercivity values of amorphous and annealed ribbon precursor are 0.8 (blue point) and 0.2 Oe (red point) respectively. When the milling process starts, a value of 20 Oe is obtained (0 min_pre-milling sample). Afterwards, the coercivity has a parabolic behavior as the milling time increases and an anomalous behavior is noted from 2 to 20 min (*soft magnetic region* in Figure 5c) where its value decreases to 2.1 Oe at 12 min. This ultrasoft value, combined with the narrow particle size distribution with a mode of ~0.96 μ m (Figure 1a1), results in an alternative potential to break down the technological barrier of obtaining large quantities of this material with highly competitive magnetic properties in powder form.

In detailed discussion, during the mechanical process the material is first hardened probably by the formation of defects in the crystalline structure due to the high-energy impact processes (0 min_pre-milling stage). This value (20 Oe) is in agreement with common values obtained in the scientific literature.^{25,36,42} In the present work, the interesting breakthrough is the *soft magnetic region* with the progressively decreasing trend until 20 min of milling time. The observation could be due to an increase in the percentage of the α -Fe₃Si phase with no influence of structural defects on coercivity (inset in Figure 5c). The effect obtained is analogous to that caused by annealing at 550 °C the amorphous ribbons, although produced by mechanical milling in the first stage. To

evaluate the influence of the increased degree of crystallization on the initial permeability and average anisotropy of nanocrystallites, the anisotropy average model⁶⁴ is used to calculate their values through the following expressions:

$$H_c = p_c \frac{\langle K \rangle}{J_s} \quad (1)$$

$$\mu_i = p_\mu \frac{J_s^2}{\mu_0 \langle K \rangle} \quad (2)$$

where H_c is the coercivity, $\langle K \rangle$ is the average effective anisotropy, J_s is the average saturation magnetization, μ_i/μ_0 are the initial and vacuum permeabilities respectively, and p_c/p_μ are dimensionless pre-factors close to unit. The representation of the calculated average effective anisotropy and initial permeability is depicted in Figure 5d. Here, average effective anisotropy has a similar trend to coercivity. The evolution of the initial permeability has a significant sharp enhancement with a maximum value of 6000 for a milling time of 12 min (Figure 5d). Therefore, the pronounced decrease in the crystal domain size combined with the increase of the crystallization percentage, leads to a considerable increase of both the initial permeability and the saturation magnetization (*soft magnetic region* in Figure 5c–d)). With these results, reduction of one order of magnitude in coercivity (up to 2.1 Oe) is achieved under these 12 min of milling conditions, maintaining its ultrasoft magnetic character in powder form and encouraging its potential transfer to industry.

Above 40 min of milling (*magnetic hardening region* in Figure 5c–d), despite the relatively high saturation values, the initial permeability decreases (Figure 5d) while the coercivity start to progressively increase (Figure 5c). The effect of decreasing the particle size could change the reversal processes of magnetization from domain wall to rotation motions⁶⁵ and may influence coercivity, average anisotropy and initial permeability. However, this behavior would also be associated with the formation of secondary residual phases with milling time.

Between the *soft* and *magnetic hardening regions*, an *intermediate region* exists which exhibits transitional properties. Although the percentage of α -Fe₃Si crystallites is still growing and the crystal domain size is decreasing, both the saturation magnetization and the coercivity remain constant. On the other hand, the permeability undergoes a drastic subsequent decrease accompanied by an increase of the α -Fe₃Si crystalline strain.

3.3. Nb₂O₅ as a Marker of Permeability Enhancement and Magnetic Hardening

Aiming to delve deeper into the reasons for these remarkable changes in the *intermediate region* (Figure 5c–d), CRM measurements are made since this technique can provide compositional information with local character in samples with a low degree of crystallinity. Generally speaking, to observe Raman modes through interaction with a laser irradiance requires polar bonds between atoms. Most metals (including the α -Fe₃Si phase) do not have a well-defined Raman spectrum and fluorescence phenomena may occur due to excitation with a laser.^{66–68} Raman spectra for different milling times from 2 to 170 min are illustrated in Figure 6a. Surprisingly, the emergence of new bands for milling times above 2 min is observed in isolated reduced areas, evolving an intensity increase as the ball milling time progresses. Exploring in the scientific literature the nature of these bands, they have similarities with the Raman spectrum corresponding to niobium dioxide (Nb₂O₅) compound.^{69,70}

The Raman bands are located at 121 cm⁻¹ (V1, vibrations of NbO₆ octahedrons as a whole), 232 and 310 cm⁻¹ (V2 and V3, bending modes of Nb–O–Nb linkages located inside the octahedrons and tetrahedrons), 690 cm⁻¹ (V4, stretching modes of Nb–O bonds), and 820 cm⁻¹ (V5, symmetric stretching modes of Nb=O).^{69,70} If it is compared with a Raman spectrum acquired from commercial reference powder, its determination is verified and the differences found between them are probably due to size effects confined to the nanoscale.^{71–73} This is a broadening of the bands accompanied by an increase in the position of the bands towards higher Raman frequencies for smaller particle sizes. In addition, the band located around 960 cm⁻¹ (V5) is magnified in intensity with respect to the reference powder (Figure 6b). This band is associated with stretching modes of Nb=O surface groups and it is indicative of the amorphous degree.⁶⁹ Therefore, this magnification highlights the low crystalline order of this phase. It should be noted that Nb₂O₅ compound is only detected by this technique in very isolated zones and the overall percentage is negligible with respect to the phases present in the alloy.

Figure 6: (a) Evolution of the Raman spectra of selected areas as ball milling time increases from 2 to 170 min. The emergence of Nb₂O₅ compound is clearly detected from 30 min; (b) Comparison between 170 min sample and Nb₂O₅ powder reference for indexation; (c) Evolution of the relative intensity between M (680 cm⁻¹) and B (475 cm⁻¹) points and between D (960 cm⁻¹) and M points.

The formation of this phase may be related to the higher molecular weight that Nb atoms have with respect to the other constituent elements of the matrix. If the relative intensity of the background (point B) with respect to the intensity of the band located around 680 cm⁻¹ (point M) is taken as a reference in Figure 6a, a parabolic trend formation of this compound is observed as a function of the milling time (Figure 6c). Furthermore, the degree of structural disorder characteristic of this system is also evaluated by the intensity ratio of point D (960 cm⁻¹) and point M, showing an increase of it with the same trend as the intensity ratio between M and B points (Figure 6c). Therefore, the growth of the Nb₂O₅ phase is accompanied by a high structural disorder degree.

Figure 7: Schematic representation of the evolution of the physical properties of the nanostructured particles as a function of the milling time. Step **i**) represents the pre-milling stage (0 min). After 12 min of milling, the magnetic properties are optimized with high initial permeability and reduced coercivity in powder form (step **ii**). The influence of Nb₂O₅ clusters becomes important and the coercivity starts to increase (step **iii**). At 100 min (step **iv**), stabilization of the crystal domain size is achieved accompanied by a change of the trend of the crystalline α-Fe₃Si strain (Figure 2c). In step **v**, the sample is magnetically hardened after 180 min of milling.

To conclude, a scenario of the evolution of the structural and magnetic properties as a function of the milling time is shown in Figure 7. When the high-energy milling processes occur (step **i**), Nb atoms have the highest kinetic energy and in the early stages of milling (up to 30 min), its diffusion does not seem to influence the structural properties of the alloy (steps **i-iii**). In addition, the matrix has no oxygen in its structure and these solid-diffused Nb atoms are suggested to reach the surface of the particles oxidizing. However, its progressive emergence (Figure 6c) may be related to the increase observed in the strain of α-Fe₃Si nanocrystallites up to 100 min (step **iv** and Figure 2c) and the stabilization of its crystal domain size up to 180 min (step **v** and Figure 2c). Regarding the magnetic properties, the optimized magnetic properties are achieved after 12 min

of milling (step **ii**). Afterward, this preferential segregation of the Nb atoms from the matrix is no longer fulfilling its function to ensure the ultrasoft character of these alloys (steps **iii-v** in Figure 7). As a result, the magnetic properties from 100 min of milling time on become devalued even with the increase of the percentage of crystalline α -Fe₃Si phase (Figure 2d). The trend of the Nb₂O₅ formation (Figure 6c) could be associated with the observed ones for coercivity and average effective anisotropy after 30 min of milling (Figure 5c–d), where this compound clearly begins to be detected by CRM.

4. Conclusions

Numerous efforts have been made with limited success to transfer the excellent properties of Fe_{73.9}Si_{15.5}Cu₁Nb₃B_{6.6} amorphous ribbons grown by melt spinning to powder form to cover the widest range of technological applicability. This work shatters this technological barrier through an innovative milling process that combines mixer, vibrating, and planetary mills at the same time under a frequency of 2000 rpm. For an effective milling time of 12 min, nanostructured particles with sizes below the micron are obtained with magnetic properties that are highly competitive compared to those from ribbon precursors. In addition, for milling times below 20 min a decrease in coercivity is obtained coinciding with an increase of the initial permeability. This outcome is obtained for the first time in mechanical milling processes and represents a major breakthrough in the optimization and tunability of the magnetic properties of these nanostructured particles. Furthermore, other purpose of this work is to introduce the CRM technique as a method to determine the deterioration of the magnetic properties, since secondary phases arising during the high-energy ball milling processes may be detected. As a result, the formation of Nb₂O₅ clusters are identified only by this local character technique. Their progressive formation with milling time records the evolution of the Nb atoms rejected from the amorphous matrix towards the surface of the particles where they are oxidized. This observation determines the operational range where the magnetic properties of the alloy in powder form start to deteriorate.

ASSOCIATED CONTENT

Supporting Information. Rietveld analyses of the XRD data and hysteresis magnetic loops of selected samples annealed and as a function of the milling time.

AUTHOR INFORMATION

Corresponding Author

*Dr. Jesús López-Sánchez, Instituto de Magnetismo Aplicado (UCM-ADIF) Ctra. A-6, Km. 22,5
Vía de Servicio - 28231 Las Rozas, Spain, jesus.lopez@ucm.es

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

The authors acknowledge the Spanish Ministry of Industry, Economy and Competitiveness for financing the project MAT2015-65445-C2-1-R, MAT2017-86450-C4-1-R, MAT2015-67557-C2-1-P, the Comunidad de Madrid by S2013/MIT-2850 NANOFRONTMAG, and the European Commission under H2020 frame by AMPHIBIAN Project ID: 720853. The authors are also grateful for the financial support from the Spanish Ministry of Science, Innovation and Universities (MICIU) and The Spanish National Research Council (CSIC) under Grant no. PIE 2010-6OE-013, A. S. acknowledges the financial support from the Comunidad de Madrid for an “Atracción de Talento Investigador” contract (no. 2017-t2/IND5395). C.G.-M. and A.Q. acknowledges financial support from MICINN through the “Juan de la Cierva” Program (FJC2018-035532-I) and through the Ramón y Cajal Contract RYC-2017-23320.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The ESRF- The European Synchrotron, MICIU and CSIC are acknowledged for provision of synchrotron radiation facilities. The authors are also grateful to the BM25-SpLine staff for their valuable technical support beyond their duties.

REFERENCES

- (1) McHenry, M. E.; Willard, M. A.; Laughlin, D. E. Amorphous and Nanocrystalline Materials for Applications as Soft Magnets. *Prog. Mater. Sci.* **1999**, 44, 291–433, 10.1016/S0079-6425(99)00002-X.
- (2) Zhang, T.; Huang, D.; Yang, Y.; Kang, F.; Gu, J. Fe₃O₄/Carbon Composite Nanofiber Absorber with Enhanced Microwave Absorption Performance. *Mater. Sci. Eng. B* **2013**, 178, 1–9, 10.1016/j.mseb.2012.06.005.
- (3) Hou, Y.; Zhang, Y.; Du, X.; Yang, Y.; Deng, C.; Yang, Z.; Zheng, L.; Cheng, L. Flexible Fe₃Si/SiC Ultrathin Hybrid Fiber Mats with Designable Microwave Absorption Performance. *RSC Adv.* **2018**, 8, 33574–33582, 10.1039/C8RA06941G.
- (4) Xu, W.; Pan, Y. F.; Wei, W.; Wang, G. S. Nanocomposites of Oriented Nickel Chains with Tunable Magnetic Properties for High-Performance Broadband Microwave Absorption. *ACS Appl. Nano Mater.* **2018**, 1, 1116–1123, 10.1021/acsanm.7b00293.
- (5) Bai, G.; Jin, J.; Wu, C.; Yan, M. Ultrafine FeCo Nanoparticles Isolated by Ultrathin Dielectric Shells for Microwave Application. *ACS Appl. Nano Mater.* **2019**, 2, 3570–3576, 10.1021/acsanm.9b00537.
- (6) Bhattacharyya, R.; Prakash, O.; Roy, S.; Singh, A. P.; Bhattacharya, T. K.; Maiti, P.; Bhattacharyya, S.; Das, S. Graphene Oxide-Ferrite Hybrid Framework as Enhanced Broadband Absorption in Gigahertz Frequencies. *Sci. Rep.* **2019**, 9, 1–12, 10.1038/s41598-019-48487-5.
- (7) Marín, P.; Cortina, D.; Gorriti, A.; Hernando, A. Electromagnetic-Radiation Attenuator and Method for Controlling the Spectrum Thereof, International Patent Number: WO 2010/029193, 2011.
- (8) Marín, P.; Cortina, D.; Hernando, A. Electromagnetic Wave Absorbing Material Based on Magnetic Microwires. *IEEE Trans. Magn.* **2008**, 44, 3934–3937, 10.1109/TMAG.2008.2002472.
- (9) Gueye, P. G. B.; López-Sánchez, J.; Navarro, E.; Serrano, A.; Marín, P. Control of the Length of Fe_{73.5}Si_{13.5}Nb₃Cu₁B₉ Microwires to Be Used for Magnetic and Microwave Absorbing Purposes. *ACS Appl. Mater. Interfaces* **2020**, 12, 15644–15656, 10.1021/acsami.9b21865.

- (10) Vázquez, M.; Hernando, A. A Soft Magnetic Wire for Sensor Applications. *J. Phys. D. Appl. Phys.* **1996**, 29, 939–949, 10.1088/0022-3727/29/4/001.
- (11) Zhukova, V.; Ipatov, M.; Zhukov, A. Thin Magnetically Soft Wires for Magnetic Microsensors. *Sensors* **2009**, 9, 9216–9240, 10.3390/s91109216.
- (12) Granados-Miralles, C.; Saura-Múzquiz, M.; Andersen, H. L.; Quesada, A.; Ahlburg, J. V.; Dippel, A. C.; Canévet, E.; Christensen, M. Approaching Ferrite-Based Exchange-Coupled Nanocomposites as Permanent Magnets. *ACS Appl. Nano Mater.* **2018**, 1, 3693–3704, 10.1021/acsanm.8b00808.
- (13) Lee, J.; Lee, G.; Hwang, T.; Cho, H.; Kim, J.; Choa, Y. Phase- and Composition-Tunable Hard/Soft Magnetic Nanofibers for High-Performance Permanent Magnet. *ACS Appl. Nano Mater.* **2020**, XXXX, XXX, XXX-XXX, 10.1021/acsanm.9b02470.
- (14) Zhang, J.; Quintana, A.; Menéndez, E.; Coll, M.; Pellicer, E.; Sort, J. Electrodeposited Ni-Based Magnetic Mesoporous Films as Smart Surfaces for Atomic Layer Deposition: An “All-Chemical” Deposition Approach toward 3D Nanoengineered Composite Layers. *ACS Appl. Mater. Interfaces* **2018**, 10, 14877–14885, 10.1021/acsaami.8b01626.
- (15) Zhang, M.; Wang, M.; Zhang, M.; Maimaitiming, A.; Pang, L.; Liang, Y.; Hu, J.; Wu, G. Fe₃O₄ Nanowire Arrays on Flexible Polypropylene Substrates for UV and Magnetic Sensing. *ACS Appl. Nano Mater.* **2018**, 1, 5742–5752, 10.1021/acsanm.8b01386.
- (16) Remadevi, A.; Kesavapillai Sreedeviamma, D.; Surendran, K. P. Printable Hierarchical Nickel Nanowires for Soft Magnetic Applications. *ACS Omega* **2018**, 3, 14245–14257, 10.1021/acsomega.8b01422.
- (17) Von Der Lühe, M.; Weidner, A.; Dutz, S.; Schacher, F. H. Reversible Electrostatic Adsorption of Polyelectrolytes and Bovine Serum Albumin onto Polyzwitterion-Coated Magnetic Multicore Nanoparticles: Implications for Sensing and Drug Delivery. *ACS Appl. Nano Mater.* **2018**, 1, 232–244, 10.1021/acsanm.7b00118.
- (18) Morales, I.; Archilla, D.; de la Presa, P.; Hernando, A.; Marin, P. Colossal Heating Efficiency via Eddy Currents in Amorphous Microwires with Nearly Zero Magnetostriction. *Sci. Rep.* **2020**, 10, 1–14, 10.1038/s41598-020-57434-8.

- (19) Hernando, M.; Marín, P.; Aragón-Sánchez, A. M.; Bravo, E.; López-Domínguez, V.; Martínez, I.; Fernández, C.; Bilbao, A.; Serrano, F. J.; Vega, R.; Hernando, A. Development of a Telemetric System for Postoperative Follow-up of Vascular Surgery Procedures: In Vitro Model. *J. Am. Heart Assoc.* **2016**, 5, 1–12, 10.1161/JAHA.116.003608.
- (20) Rivero, G.; García-Páez, J. M.; Alvarez, L.; Multigner, M.; Valdés, J.; Carabias, I.; Spottorno, J.; Hernando, A. Sensor System for Early Detection of Heart Valve Bioprostheses Failure. *Sensor Actuat. A-Phys.* **2008**, 142, 511–519, 10.1016/j.sna.2007.09.010.
- (21) Nandwana, V.; Zhou, R.; Mohapatra, J.; Kim, S.; Prasad, P. V.; Liu, J. P.; Dravid, V. P. Exchange Coupling in Soft Magnetic Nanostructures and Its Direct Effect on Their Theranostic Properties. *ACS Appl. Mater. Interfaces* **2018**, 10, 27233–27243, 10.1021/acsami.8b09346.
- (22) Hasegawa, R. Applications of Amorphous Magnetic Alloys. *Mater. Sci. Eng. A* **2004**, 375–377, 90–97, 10.1016/j.msea.2003.10.258.
- (23) Lachowicz, H. K. Modern Soft Magnetic Materials. *Mater. Sci. Forum* **2003**, 414–415, 139–146, 10.4028/www.scientific.net/MSF.414-415.139.
- (24) Marín, P.; Vázquez, M.; Olofinjana, A. O.; Davies, H. A. Influence of Cu and Nb on Relaxation and Crystallization of Amorphous FeSiB(CuNb) Wires. **1998**, 10, 299–310, 10.1016/S0965-9773(98)00070-1.
- (25) Herzer, G. Grain Size Dependence of Coercivity and Permeability in Nanocrystalline Ferromagnets. *IEEE Trans. Magn.* **1990**, 26, 1397–1402, 10.1109/20.104389.
- (26) Herzer, G. Grain Structure and Magnetism of Nanocrystalline Ferromagnets. *IEEE Trans. Magn.* **1989**, 25, 3327–3329, 10.1109/20.42292.
- (27) Willard, M. A.; Daniil, M. *Handbook of Magnetic Materials: Volume 21: Nanocrystalline Soft Magnetic Alloys Two Decades of Progress*, 1st ed.; Elsevier B.V., **2013**, 10.1016/B978-0-444-59593-5.00004-0.
- (28) Raja, M. M.; Chattopadhyay, K.; Majumdar, B.; Narayanasamy, A. Structure and Soft Magnetic Properties of Finemet Alloys. *J. Alloys Compd.* **2000**, 297, 199–205, 10.1007/978-3-642-10764-1_27.

- (29) Vázquez, M.; Marín, P.; Davies, H. A.; Olofinjana, A. O. Magnetic Hardening of FeSiBCuNb Ribbons and Wires during the First Stage of Crystallization to a Nanophase Structure. *Appl. Phys. Lett.* **1994**, 64, 3184–3186, 10.1063/1.111333.
- (30) Gheiratmand, T.; Hosseini, H. R. M. Finemet Nanocrystalline Soft Magnetic Alloy: Investigation of Glass Forming Ability, Crystallization Mechanism, Production Techniques, Magnetic Softness and the Effect of Replacing the Main Constituents by Other Elements. *J. Magn. Magn. Mater.* **2016**, 408, 177–192, 10.1016/j.jmmm.2016.02.057.
- (31) Herzer, G. Soft Magnetic Nanocrystalline Materials. *Scr. Metall. Mater.* **1995**, 33, 1741–1756, 10.1016/0956-716X(95)00397-E.
- (32) Hernando, A.; Marín, P.; Vázquez, M.; Herzer, G. Thermal Dependence of Coercivity in Soft Magnetic Nanocrystals. *J. Magn. Magn. Mater.* **1998**, 177–181, 959–961, 10.1103/PhysRevB.58.366.
- (33) Kulik, T.; Hernando, A.; Vázquez, M. Correlation between Structure and the Magnetic Properties of Amorphous and Nanocrystalline $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{22.5-x}\text{B}_x$. **1994**, 8853, 2–5, 10.1016/0304-8853(94)90554-1.
- (34) Gomez-Polo, C.; Pascual, L.; Ghannami, M. E.; Marin, P. Optimisation of Rapidly Quenched FeSiBCuNb Alloys through the Control of the Quenching Rate. *Sensor. Actuators. A.* **1997**, 59, 261–265, 10.1016/S0924-4247(97)80185-9.
- (35) Gheiratmand, T.; Hosseini, H. R. M.; Davami, P.; Ostadhossein, F.; Song, M.; Gjoka, M. On the Effect of Cooling Rate during Melt Spinning of FINEMET Ribbons. *Nanoscale* **2013**, 5, 7520–7527, 10.1039/C3NR01213A.
- (36) Hernando, A.; Marín, P.; López, M.; Kulik, T.; Varga, L. K.; Hadjipanayis, G. Size Dependence of Coercivity in Nanostructured Soft Alloys. *Phys. Rev. B* **2004**, 69, 052501, 10.1103/PhysRevB.69.052501.
- (37) Sirvent, P.; Berganza, E.; Aragón, A. M.; Bollero, A.; Moure, A.; García-Hernández, M.; Marín, P.; Fernández, J. F.; Quesada, A. Effective High-Energy Ball Milling in Air of $\text{Fe}_{65}\text{Co}_{35}$ Alloys. *J. Appl. Phys.* **2014**, 115, 17B505, 10.1063/1.4862220.

- (38) Gheiratmand, T.; Hosseini, H. R. M.; Davami, P.; Gjoka, M.; Song, M. The Effect of Mechanical Milling on the Soft Magnetic Properties of Amorphous FINEMET Alloy. *J. Magn. Magn. Mater.* **2015**, 381, 322–327, 10.1016/j.jmmm.2015.01.016.
- (39) Reddi, P. D.; Mukhopadhyay, N. K.; Majumdar, B.; Singh, A. K.; Meena, S. S.; Yusuf, S. M.; Prasad, N. K. Synthesis of Fe-Si-B-Mn-Based Nanocrystalline Magnetic Alloys with Large Coercivity by High Energy Ball Milling. *Bull. Mater. Sci.* **2014**, 37, 815–821, 10.1007/s12034-014-0011-8.
- (40) Alleg, S.; Kartout, S.; Ibrir, M.; Azzaza, S.; Fenineche, N. E.; Suñol, J. J. Magnetic, Structural and Thermal Properties of the Finemet-Type Powders Prepared by Mechanical Alloying. *J. Phys. Chem. Solids* **2013**, 74, 550–557, 10.1016/j.jpcs.2012.12.002.
- (41) Kováč, J.; Petrovic, P.; Fečová, E.; Füzer, J.; Kollár, P. Magnetic Properties of the FINEMET Type Powder Prepared by Long Time Milling. *Phys. Status Solidi* **2002**, 189, 859–863, 10.1002/1521-396X(200202)189:3<859::AID-PSSA859>3.0.CO;2-G.
- (42) Marín, P.; Hernando, A.; López, M.; Kulik, T.; Varga, L. K.; Hadjipanayis, G. Influence of Mechanical Grinding on the Structure and Magnetic Properties of FeCuNbSiB Material. *J. Magn. Magn. Mater.* **2004**, 272–276, 1131–1133, 10.1016/j.jmmm.2003.12.133.
- (43) Herzer, G. Nanocrystalline Soft Magnetic Alloys. In *Handbook of Magnetic Materials*; Chapter 3, Volumen 10, 415–462, **1997**, 10.1016/S1567-2719(97)10007-5.
- (44) Kessler, M.; Woodward, R. T.; Wong, N.; Rinaldi, R. Kinematic Modeling of Mechanocatalytic Depolymerization of α -Cellulose and Beechwood. *Chem. Sus. Chem.* **2018**, 11, 552–561, 10.1002/cssc.201702060.
- (45) Benítez-Guerrero, M.; Valverde, J. M.; Perejón, A.; Sánchez-Jiménez, P. E.; Perez-Maqueda, L. A. Effect of Milling Mechanism on the CO₂ Capture Performance of Limestone in the Calcium Looping Process. *Chem. Eng. J.* **2018**, 346, 549–556, 10.1016/j.cej.2018.03.146.
- (46) Rodríguez-Carvajal, J. Recent Advances in Magnetic Structure Determination Neutron Powder Diffraction. *Phys. Rev. B* **1993**, 192, 55–69, 10.1016/0921-4526(93)90108-I.
- (47) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, 12, 537–541, 10.1107/S0909049505012719.

- (48) Newville, M. IFEFFIT: Interactive XAFS Analysis and FEFF Fitting. *J. Synchrotron Radiat.* **2001**, 8, 322–324, 10.1107/S0909049500016964.
- (49) Gueli, A. M.; Bonfiglio, G.; Pasquale, S.; Troja, S. O. Effect of Particle Size on Pigments Colour. *Color Res. Appl.* **2016**, 42, 236–243, 10.1002/col.22062.
- (50) Jang, J.; Kang, I.; Kim, M.; Kim, J.; Lee, Y.; Yi, K.; Cho, Y. W. Si/Iron Silicide Nanocomposite Anodes with Furfuryl-Alcohol-Derived Carbon Coating for Li-Ion Batteries. *J. Mater. Sci.* **2017**, 52, 5027–5037, 10.1007/s10853-016-0740-8.
- (51) Schütte, M.; Wartchow, R.; Binnewies, M. Shape Controlling Synthesis - Formation of Fe₃Si by the Reaction of Iron with Silicon Tetrachloride and Crystal Structure Refinement. *Zeitschrift für Anorg. und Allg. Chemie* **2003**, 629, 1846–1850, 10.1002/zaac.200300125.
- (52) Xu, H.; He, K. Y.; Qiu, Y. Q.; Wang, Z. J.; Feng, W.; Dong, Y. D.; Xiao, X. S.; Wang, Q. Intense Milling Nanocrystalline Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉: A Soft Magnetic Material in Powdered Form. *Mater. Sci. Eng. A* **2000**, 286, 197–200, 10.1016/S0921-5093(00)00713-9.
- (53) Abuín, M.; Serrano, A.; Chaboy, J.; García, M. A.; Carmona, N. XAS Study of Mn, Fe and Cu as Indicators of Historical Glass Decay. *J. Anal. At. Spectrom.* **2013**, 28, 1118–1124, 10.1039/C3JA30374H.
- (54) Rubio-Zuazo, J.; Chainani, A.; Taguchi, M.; Malterre, D.; Serrano, A.; Castro, G. R. Electronic Structure of FeO, γ -Fe₂O₃, and Fe₃O₄ Epitaxial Films Using High-Energy Spectroscopies. *Phys. Rev. B* **2018**, 235148, 1–9, 10.1103/PhysRevB.97.235148.
- (55) Kau, L. S.; Spira-Solomon, D. J.; Penner-Hahn, J. E.; Hodgson, K. O.; Solomon, E. I. X-Ray Absorption Edge Determination of the Oxidation State and Coordination Number of Copper: Application to the Type 3 Site in Rhus Vernicifera Laccase and Its Reaction with Oxygen. *J. Am. Chem. Soc.* **1987**, 109, 6433–6442, 10.1021/ja00255a032.
- (56) Gaur, A.; Shrivastava, B. D.; Nigam, H. L. X-Ray Absorption Fine Structure (XAFS) Spectroscopy – A Review. *Proc Indian Natn Sci Acad Spl. Issue, Part B* **2013**, 79, 921–966, 10.6084/m9.figshare.943499.v1.
- (57) Grunes, L. A. Study of the K Edges of 3d Transition Metals in Pure and Oxide Form by X-Ray-Absorption Spectroscopy. *Phys. Rev. B* **1983**, 27, 2111–2131, 10.1103/PhysRevB.27.2111.

- (58) Aquilanti, G.; Trapananti, A.; Karandikar, A.; Kantor, I.; Marini, C.; Mathon, O.; Pascarelli, S.; Boehler, R. Melting of Iron Determined by X-Ray Absorption Spectroscopy to 100 GPa. *Proc. Natl. Acad. Sci.* **2015**, 112, 12042–12045, 10.1073/pnas.1502363112.
- (59) Borrego, J. M.; Conde, C. F.; Conde, A.; Chadwick, A. V.; Morrison, G. X-Ray Absorption Studies of a FINEMET Alloy. *J. Non. Cryst. Solids* **1998**, 232–234, 352–357, 10.1016/S0022-3093(98)00420-7.
- (60) Swilem, Y.; Sobczak, E.; Nietubyc, R.; Slawska-Waniewska, A.; Doyama, M. X-Ray Absorption Studies of Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ Amorphous and Nanocrystalline Alloys. *Acta Phys. Pol. A* **1997**, 91, 883–886, ISSN 0587-4246.
- (61) Sobczak, E.; Swilem, Y.; Dorozhkin, N. N.; Nietubyc, R.; Dluzewski, P.; Slawska-Waniewska, A. X-Ray Absorption Studies of Fe-Based Nanocrystalline Alloys. *J. Alloys Compd.* **2001**, 328, 57–63, 10.1016/S0925-8388(01)01347-0.
- (62) Zhang, Y.; Wang, Y.; Makino, A. Structural and Magnetic Properties on the Fe-B-P-Cu-W Nano-Crystalline Alloy System. *AIP Adv.* **2018**, 8, 047703, 10.1063/1.4993711.
- (63) Suzuki, K.; Herzer, G. *Soft Magnetic Nanostructures and Applications*. In *Advanced Magnetic Nanostructures*; Sellmyer, D., Skomski, R., Eds.; Springer; 365–401, **2006**, 10.1007/b101199.
- (64) Herzer, G. Modern Soft Magnets: Amorphous and Nanocrystalline Materials. *Acta Mater.* **2013**, 61, 718–734, 10.1016/j.actamat.2012.10.040.
- (65) Fechova, E.; Kollar, P.; Fuzer, J.; Kovac, J.; Petrovic, P.; Kavecansky, V. The Influence of the Long Time Milling on the Structure and Magnetic Properties of the Fe–Cu–Nb–Si–B Powder. *Mater. Sci. Eng. B* **2004**, 107, 155–160, 10.1016/j.mseb.2003.10.102.
- (66) Serrano, A. *Modified Au-Based Nanomaterials Studied by Surface Plasmon Resonance Spectroscopy*; Springer, **2015**, 10.1007/978-3-319-19402-8.
- (67) Liu, Z.; Osamura, M.; Ootsuka, T.; Kuroda, R.; Fukuzawa, Y.; Otogawa, N.; Nakayama, Y.; Makita, Y.; Tanoue, H. Effect of α -Fe₃Si Buffer Layer for the Growth of Semiconducting β -FeSi₂ Thin Film on Stainless Steel Substrate. *J. Cryst. Growth* **2007**, 307, 82–86, 10.1016/j.jcrysgro.2007.06.007.

- (68) Butvinová, B.; Butvin, P.; Kadlečiková, M.; Malinovský, L. Raman Spectroscopy Used to Inspect Relationship between Surface and Magnetic Properties of Fe-Nb-Cu-B-Si(4.5) Nanocrystalline Ribbons. *Kov. Mater.* **2012**, 50, 145–152, 10.4149/km_2012_3_145.
- (69) Jehng, J. M.; Wachs, I. E. Structural Chemistry and Raman Spectra of Niobium Oxides. *Chem. Mater.* **1991**, 3, 100–107, 10.1021/cm00013a025.
- (70) Lopes, O. F.; Paris, E. C.; Ribeiro, C. Environmental Synthesis of Nb₂O₅ Nanoparticles through the Oxidant Peroxide Method Applied to Organic Pollutant Photodegradation: A Mechanistic Study. *Appl. Catal. B Environ.* **2014**, 144, 800–808, 10.1016/j.apcatb.2013.08.031.
- (71) López-Sánchez, J.; Serrano, A.; del Campo, A.; Abuín, M.; Salas-Colera, E.; Muñoz-Noval, A.; Castro, G. R.; de la Figuera, J.; Marco, J. F.; Marín, P.; Carmona, N.; Rodríguez de la Fuente, O. Self-Assembly of Iron Oxide Precursor Micelles Driven by Magnetic Stirring Time in Sol–Gel Coatings. *RSC Adv.* **2019**, 9, 17571–17580, 10.1016/j.actamat.2020.01.058.
- (72) López-Sánchez, J.; Muñoz-Noval, A.; Castellano, C.; Serrano, A.; del Campo, A.; Cabero, M.; Varela, M.; Abuín, M.; de la Figuera, J.; Marco, J. F.; Castro, G. R.; Rodríguez de la Fuente, O.; Carmona, N. Origin of the Magnetic Transition at 100 K in ϵ -Fe₂O₃ Nanoparticles Studied by X-Ray Absorption Fine Structure Spectroscopy. *J. Phys. Condens. Matter* **2017**, 29, 485701, 10.1088/1361-648X/aa904b.
- (73) López-Sánchez, J.; Muñoz-Noval, A.; Serrano, A.; Abuín, M.; de la Figuera, J.; Marco, J. F.; Pérez, L.; Carmona, N.; Rodríguez de la Fuente, O. Growth, Structure and Magnetism of ϵ -Fe₂O₃ in Nanoparticle Form. *RSC Adv.* **2016**, 6, 46380, 10.1039/C6RA01912A.

Structural and magnetic properties optimization of $\text{Fe}_{73.9}\text{Si}_{15.5}\text{Cu}_1\text{Nb}_3\text{B}_{6.6}$ particles by high-energy ball milling