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Structural and Magnetic Properties of Nanostructured $Ni_{80}Co_{17}Mo_3$ Alloy Powder

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Mechanical alloying (MA) with a high-energy planetary ball mill is used to create nanostructured $Ni_{80}Co_{17}Mo_3$ -alloy samples from pure elemental powders. The powders obtained are analysed using x-ray diffraction, scanning electron microscopy, and vibrating-sample magnetometry techniques to investigate the microstructure, morphology, particle-sizes' distribution, and

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magnetic properties as functions of milling time. The results show that x-ray diffraction analysis suggests the formation of nanostructured f.c.c. solid solutions, f.c.c.-NiCo(Mo), which become the dominant phase after 6 h of MA, with decreasing crystallite sizes ranging from 15.1 nm to 9.78 nm and increasing microstrain (0.41–0.66%) with increasing milling time to 72 h. Morphological observations utilizing scanning electron microscopy validate the production of nanocomposite and reveal a progressive refinement in particle size with milling time and a narrow particle-sizes' distribution with an irregular shape for longer milling. The milling process induces significant changes in the magnetic properties, where the magnetism of the combination is lost due to the combined effects of crystallite-size reduction. After milling, the remanence ratio $M_r/M_s (\cong 4.1 \cdot 10^{-3})$ and coercive field ($\cong 10.87$ Oe) are found to be declining. The findings indicate that the alloy has reached its maximum level of magnetization and displays a very weak magnetic response.

Для створення наноструктурованих зразків стопу Ni₈₀Co₁₇Mo₃ з чистих елементарних порошків використовували механічне леґування за допомогою високоенергетичного планетарного кульового млина. Одержані порошки аналізували за допомогою методів рентґенівської дифракції, сканівної електронної мікроскопії і магнетометрії з вібрувальним зразком для дослідження мікроструктури, морфології, розподілу частинок за розміром і магнетних властивостей як функцій часу помелу. Результати показують, що рентґенівська дифракційна аналіза припускає утворення наноструктурованих ГЦК-твердих розчинів (ГЦК-NiCo(Mo)), які стають домінувальною фазою після 6 год механічного леґування, зі зменшенням розмірів кристалітів у діяпазоні від 15,1 нм до 9,78 нм і збільшенням мікродеформації (0,41-0,66%) зі збільшенням часу помелу до 72 год. Морфологічні спостереження з використанням сканівної електронної мікроскопії підтвердили виробництво нанокомпозиту та виявили проґресивне подрібнення розміру частинок із часом помелу та вузький розподіл розмірів частинок із неправильною формою для тривалого помелу. Процес помелу викликає значні зміни в магнетних властивостях, де магнетизм комбінації втрачається через комбінований ефект зменшення розміру кристалітів. Після подрібнення було виявлено, що коефіцієнт залишкової напруги M_r/M_s ($\cong 4,1.10^{-3}$) і коерцитивне поле ($\cong 10,87$ Ое) зменшуються. Висновки показали, що стоп досяг максимального рівня намагнетованости та демонструє дуже слабкий магнетний відгук.

Key words: nanomaterials, mechanical alloying, particles' morphology and size, x-ray diffraction, magnetic properties.

Ключові слова: наноматеріяли, механічне леґування, морфологія та розмір частинок, рентґенівська дифракція, магнетні властивості.

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1. INTRODUCTION

The field of nanomaterials has expanded rapidly due to their supe-

rior properties compared to traditional materials. These properties arise from their high surface area and unique directional properties, which allow them to exhibit enhanced mechanical, electronic, optical, or magnetic properties [1]. Among the various types of nanomaterials, soft magnetic nanomaterials (SMNs) have gained considerable attention due to their distinctive characteristics, offering exciting possibilities in magnetic applications [2].

One group of SMNs that has been receiving a lot of attention in recent years is 3*d*-transition metal alloys. Owing to their unique physical and chemical properties, these metals have garnered significant interest in various fields. Notably, elements such as nickel (Ni) and cobalt (Co) possess exceptional ferromagnetic, quantum, and electrical resistance properties [3]. Furthermore, when combined with molybdenum (Mo) or other non-ferromagnetic elements, these transition metals offer the desired characteristics at a substantially lower cost compared to their rare-element counterparts [4]. This cost-effective advantage has led to a surge in researchers' interest in studying and characterizing nanostructured metal alloys in recent years.

Mechanical alloying (MA) is one of the most effective methods for producing nanocrystalline SMNs. This process involves severe plastic deformation of particles leading to particle size refinement and shape changes [5]. It is effective in producing materials far from their thermodynamic equilibrium, including amorphous alloys and extended solid solutions. In recent years, nanocrystalline SMNs synthesized through MA have gained significant development.

Nanocrystalline SMNs offer several advantages over their conventional counterparts, including lower power loss, higher magnetic permeability, and higher saturation magnetization [6]. These properties make them highly desirable for use in various magnetic applications such as magnetic sensors, magnetic data storage, and magnetic refrigeration [7].

One such nanomaterial that has been studied in recent years is NiCoMo. Produced through mechanical alloying, this nanomaterial offers promising possibilities for magnetic applications. Investigations into the influence of milling time on its properties are currently underway [8].

In 2011, the nanostructure CoNi was examined at various time intervals, observing the transformation of cobalt structure from hexagonal close-packed (h.c.p.) one to face-centred cubic (f.c.c.) one. As was completed, it was that refinement of particle size and the formation of Co(Ni) and Ni(Co) solid solutions, alloy powder exhibits a soft ferromagnetic property, where the magnetic parameters are susceptible to milling time [9].

In another study, the researchers employed the electrodeposition

technique to fabricate effectively Ni–Co alloys, featuring various morphologies, on porous Ni substrates. The results demonstrated that the nanocone Ni–Co alloys supported on porous Ni outperformed other morphologies in terms of edge structures, surface oxidation, and metallic states [10].

In a study conducted by Hossein Raanaei and colleagues in 2020 [11], a nanostructured Fe-Co-Mn-Ti-B alloy was synthesized using the ball milling method. The smallest grain size was observed after 80 hours of milling, while an increase in grain size values was noted between 80 and 100 hours of milling time. A sharp decline in saturation magnetization after 60 hours of milling could potentially be attributed to the diffusion of non-ferromagnetic atoms into the iron or cobalt structures.

In a study by Tuncay Şimşek *et al.* in 2021 [12], nanocrystalline NiFeCoMo alloys were successfully synthesized through mechanical alloying using elemental powders of Fe, Co, Ni, and Mo. Milling all elements together in stoichiometric quantities for 60 hours resulted in the formation of 95Mo5 and 90Mo10 alloys. In the first set of alloys, it was observed that an increase in Mo content led to a reduction in crystallite size and lattice strain. The addition of Mo in the alloy appeared to modify the particle morphology, transforming particle shapes from irregular to layered one. As expected, Mo also decreased the alloy saturation magnetization, with the saturation magnetization of the alloy diminishing as the proportion of Mo increased [12, 13].

In a study by M. Triki and colleagues in 2022, nanostructured powder of the Ni₂MnCo ternary alloy was successfully synthesized using the mechanical alloying process. Structural analysis revealed the formation of a solid solution within the face-centred cubic structure phase. Furthermore, it was noted that milling for 24 hours did not influence the particle size, suggesting that the mixture had achieved homogeneity by this point. Magnetic characterizations conducted at room temperature led to the observation of a newly emerged paramagnetic phase, which was influenced by the antiferromagnetic behaviour of manganese [14].

In this work, we present an investigation of the production of magnetic nanomaterials through mechanical alloying (MA), which is an advantageous method to produce solid solutions and new nanostructured materials [15]. the impact of the milling time on the microstructure and magnetic properties of the mechanically alloyed powder mixtures by tracking the development of its microstructure, analysing the impact of crystallite size reduction on magnetic characteristics, and observing the dissolution of an antiferromagnetic element (Mn) [16]. To accomplish this, we used x-ray diffraction (XRD) to identify precisely the formed phase and the crystal structure, followed by the development of the morphology and microstructural changes of the particle powder by SEM-EDX, evaluated the particle size distribution by laser diffraction, and, finally, examined the magnetic properties using a vibrating-sample magnetometer (VSM).

2. EXPERIMENTAL PROCEDURE

In an argon atmosphere at room temperature, Ni-Co-Mo polycrystalline samples were produced using a planetary ball mill (Fritsch Pulverisette 7). As starting materials, high-purity elemental powders of nickel (99.999%), cobalt (99.99%), and molybdenum (99.98%) were purchased from Sigma Aldrich Chemical Company, Inc., USA, by atomic weight calculations, these powders were weighed and combined in a stoichiometric ratio using balls and jars of hardened steel. The ball/mass ratio of the powder was about 15:1, and the rotation speed was 350 rpm. The synthesis was done in 30-minute cycles of milling with 15-minute breaks to avoid an excessive rise in temperature inside the vials. For each milling time, the jars are opened only after a cooling period of 20 to 60 min. X-ray diffraction (XRD) was used to track the microstructural and structural evolution of the mixture using a high-resolution diffractometer model, the Bruker D8, in a geometry of (-2) Bragg-Brentano and with CuK radiation (= 0.15406 nm). The ICDD-PDF 4 + database and the PANalytical X'Pert HighScore Plus software were used to identify the phases. Using the Williamson-Hall method, the crystallite size (Cs) and internal microstrains (ε) of the samples were determined, followed by Rietveld refinement. The morphology and chemical composition of the milled powder mixture were investigated using a JEOL 6300 scanning electron microscope (SEM) operating at voltage of 20 kV and equipped with an electron dispersion spectrometer (EDS, also abbreviated EDX or XEDS) for chemical composition [14]. The magnetic measurements were performed at room temperature using a PCM MicroMag 3900 vibrating-sample magnetometer (VSM) with a magnet of 1 Tesla.

3. RESULTS AND DISCUSSION

3.1. Structural and Microstructural Analysis

X-ray powder diffraction (XRD) examined samples' phase structures. Figure 1 shows the XRD patterns made of typical $Ni_{80}Co_{17}Mo_3$ alloy without any impurities. The process was carried out in highpower planetary ball mill. Diffraction peaks, where 11 initially



Fig. 1. Evolution of the XRD patterns of $Ni_{80}Co_{17}Mo_3$ powdered mixture as a function of milling time.

sharp peaks were found for the composite samples at 37.231° , 40.486° , 44.475° , 51.828° , 65.433° , 68.665° , 73.740° , 75.846° , and 76.348° , 92.890° , 98.384° , can be indexed well for (111), (110), (111), (200), (220), (531), (211), (220) and (220), (311), (222) Ni₈₀Co₁₇Mo₃ aircraft with cubic hull centre (JCPDS No. 00-004-0850 and 00-015-0806). We observe the presence of overlapping peaks originating from the fact that f.c.c. Ni, Co, and Mo phases have similar lattice parameters.

It is evident that a solid-state reaction takes place as the milling time progresses. Additionally, the diffraction peaks are observed to broaden and their relative intensity diminishes with an increase in milling time. This is attributed to the persistent reduction in particle size and the introduction of lattice strain. Consequently, all elemental diffraction peaks vanish following the solid-state substitution process, wherein Mo and Co atoms replace their positions within the Ni host lattice.

The vanishing of the Mo peaks becomes increasingly apparent after 24 hours of milling, while the solid Ni–Co phase starts to emerge distinctly at the locations of the diffraction peaks at 20: 44.319° , 51.671° , 76.161° , 92.521° , and 97.920° . These peaks correspond to the Miller indices of (111), (200), (220), (311), and (222), respectively. Through continuous observation, the diffraction peak's position reveals a progressive shift towards smaller angles, accompanied by a reduction in intensity and a broadening of the peak. This evolution is attributed to the conversion of a heterogeneous microcrystalline blend into a homogeneous nanocrystalline mixture, ultimately yielding a uniform single-phase Ni80Co17Mo3 alloy. This alloy exhibits a face-centred cubic (f.c.c.) structure and belongs to the Fm3m (No. 225) space group.

In Figure 2, it is clear that the lattice modulus (a) increases with milling time from 2.673 Å initially before milling to 3.539 Å. This is justified by the progressive formation of a homogeneous NiCo alloy during milling a process characterized by an increase in the lattice parameter of the f.c.c. structure because of an increase in the degree of the solid solution of Mo and Co atoms in the Ni host lattice. The growth of the lattice parameter is reflected by the shift of the diffraction peaks towards small angles. Moreover, this is clear from Mo being an element with a larger atomic radius and, a low amount of in alloy system. The dissolution of Mo in the Ni lattice is more stable. This is the most probable reason why the solid solution process showed gradual peak shifts to lower angles as the milling continued [14, 18].

The crystal size and lattice strain in the milled powders were determined jointly from the diffraction spectra related to the different milling times using the famous Williamson-Hall equation, which is expressed as follows: $\beta \cos \theta = K \lambda D^{-1} + \varepsilon \sin \theta$, where λ is the wavelength of the x-rays used, K is a constant whose value is approximately 0.9, θ is the Bragg angle, β is the full width at half



Fig. 2. Evolution of the lattice parameter a of the f.c.c. cubic lattice for each (hkl) as a function of milling time.

maximum (FWHM) of a diffraction peak (usually, the most intensive peak).

The evolution curve (see Fig. 3) of crystallite size refers to the changes in the crystal structure and properties of a material over time as it undergoes grinding or other forms of processing. In this case, the material being studied is a Ni₈₀Co₁₇Mo₃ powder mixture, and the size of the crystals and the value of the microstrain are being tracked over time. As can be seen, the crystallite size sharply decreased during the initial period of milling and then increased and stabilized due to the predominant crushing and welding processes, which were often used in repeated grinding [16]. The value of the microstrain (ε) is also being tracked, and it is stated that the value of ε initially decreased, as the powder mixture was ground, suggesting a more uniform crystal structure was being formed.

After the milling process, the crystal size of the face-centred cubic (f.c.c.) phase NiCo(Mo) was found to be of 9.78 nm. This reduction in size is associated with an increase in microstrain, which is a



Fig. 3. Evolution of crystallite size and microstrain of $Ni_{80}Co_{17}Mo_3$ powder mixture as functions of milling time.

Milling time, h	R_p	R_{wp}	R_{exp}	Chi-square (GOF)
0	1.811	2.696	1.835	1.468
2	0.606	0.9	0.900	1.000
6	0.697	0.934	0.915	1.020
12	1.581	3.176	1.706	1.861
24	1.606	3.113	1.830	1.700
48	1.586	3.089	1.838	1.680
72	2.192	3.588	3.109	1.153

TABLE 1. Rietveld refinement *R*-factors of Ni₈₀Co₁₇Mo₃ powdered mixture.

result of the high-energy collisions between the balls and the recurring events of cold welding, fracturing, and re-welding. In summary, the crystal evolution curve for the Ni₈₀Co₁₇Mo₃ powder mixture demonstrates that the milling process substantially influences the materials' crystal structure and properties, leading to alterations in crystal size, volume, and microstrain. The specific consequences of the observed changes in the materials' properties depend on the intended use of the Ni₈₀Co₁₇Mo₃ powder mixture. The Rietveld refinement technique was employed to analyse x-ray diffraction (XRD) patterns using the PANalytical X'Pert High Score Plus software [19]. The refinement procedure was as follows. The background, displacement of the specimen, and scale factor were all considered. The dimensions of unit cells, atomic coordinates, and procedural parameters were then considered. The quality of the Rietveld fitting was assessed (Table 1) after each iteration using reliability R-factors, including the expected R-factor (R_{exp}) , profile *R*-factor (R_p) , and weighted profile *R*-factor (R_{wp}) [20].

The initial cell parameters, space group, and atomic coordinates are obtained by matching reference patterns generated using a crystallographic database. The Fourier series involves twelve refinable coefficients, and the profile sharp refinement is characterized by the pseudo-Voigt function. The pseudo-Voigt function, which is a linear combination of Lorentzian and Gaussian functions, is employed to determine peak shapes. This function is particularly useful for resolving strain and size contributions to peak broadening, as it can effectively model a range of peak shapes that arise due to various factors influencing the diffraction patterns. A good refining model should accurately reproduce the matched peak positions and intensities. As illustrated in Fig. 4. There is a strong agreement between the observed and computed patterns. The goodness of fit is evaluated based on peak shape, peak position, structure, and background, as shown in Table 1. The effectiveness of the refinement process is further validated by comparing the current and refined models, in line with the findings reported by various researchers [19, 21].

3.2. Morphology Observation of Particles by SEM

The examination of powder particles was conducted using scanning electron microscopy, which provided insights into particle morphology, shape, size, and distribution, as illustrated in Fig. 5. It was determined that the repetitive milling and welding actions involved in the milling process tend to increase the contact surface between the two components being ground, resulting in the formation of solid solutions at lower temperatures.



Fig. 4. Rietveld refinements of $Ni_{80}Co_{17}Mo_3$ powdered mixture as a function of milling time.

Prior to milling, the nickel powder particles exhibit a spherical shape, while cobalt particles appear smoother, and molybdenum particles are highly round and fine. After 72 hours of intermittent milling, the composite particles ($Ni_{80}Co_{17}Mo_3$) display a distinct shape, featuring a cap structure with some white regions. This cap structure is a well-known characteristic of nickel particles. Additionally, the emergence of $Fe_{1-x}Cr_x$ crystal powders is observed after



Fig. 5. SEM micrographs of $Ni_{80}Co_{17}Mo_3$ powdered mixture at a different time of milling.

other formulations, which are produced by high-energy milling processes.

Figure 6 illustrates the evolution of the morphology of $Ni_{80}Co_{17}Mo_3$ powder particles as a function of milling time. During the initial two hours, the powder particles exhibit various dimensions, indicating the presence of two processes: welding and fracturing. The fracturing occurs due to ball-powder-ball and ball-ball powder-wall collisions. During the milling process, welding is likely as the powder particles appear large, which can be attributed to their high plasticity, softness, and low-pressure shape, resulting in a propensity to fuse and form larger particles.

Moreover, the presence of a laminar structure is observed. This lamellar microstructure is typically seen in Ni-based compounds produced by high-energy mechanical milling, and it arises from the intermingling of pure elements and the relatively large proportion of nickel, which is known for its flexible structure.

After 6 hours of milling, the powder particles display various irregular shapes and sizes. The presence of large particles suggests that the welding process is more dominant than the fracturing process. As the milling time increases to 12 hours, a reduction in particle size is observed, with some coarse particles remaining. This change indicates the predominance of the fracturing process and a significant decrease in particle size. Milling after 24 hours reveals that the welding process is suppressed, and some fractured powder particles exhibit inclusions. Following an additional 48 hours of milling, the particle shapes become relatively homogeneous, reaching a stable state characterized by a balance between fracturing and welding. After intermittent milling for 72 hours, the welding process is observed at this stage, where the powder particles appear polished and regular, with an average size of approximately 22 μ m, as shown in Fig. 7, displaying semi-oval forms.



Fig. 6. SEM micrographs and corresponding histograms of particle-sizes' distribution of Ni₈₀Co₁₇Mo₃ powdered mixture as functions of milling time.



Continuation Fig. 6.

3.3 ANALYSIS BY EDS

Table 2 presents the evolution of the weight percentage of the nickel-cobalt-molybdenum alloy in the FeSoNiZo system after several intermittent milling sessions. It is observed that additional peaks appear after 24 hours of milling, attributed to iron and chromium. However, these peaks disappear after 48 hours, suggesting that their presence may be due to impurities introduced during the milling process. Subsequently, no other peaks are detected, except for those corresponding to the elements initially present in the powder.



Fig. 7. Average particle size of $\rm Ni_{80}\rm Co_{17}\rm Mo_{3}$ powdered mixture as a function of milling time.

TABLE 2. Evolution of the chemical composition of $Ni_{80}Co_{17}Mo_3$ powdered mixture as a function of milling time.

Milling time	Mass, %	σ	Element
2	73.7	0.1	$Ni(K_{\alpha 1})$
	22.7	0.1	$Co(K_{\alpha 1})$
	3.6	0.1	$Mo(L_{\alpha 1})$
6	77.9	0.2	$Ni(K_{\alpha 1})$
	19.6	0.1	$Co(K_{\alpha_1})$
	2.5	0.1	$Mo(L_{\alpha 1})$
12	78.1	0.2	$Ni(K_{\alpha 1})$
	19.6	0.1	$Co(K_{\alpha 1})$
	2.3	0.1	$Mo(L_{\alpha_1})$
24	78.4	0.2	$Ni(K_{\alpha 1})$
	19.2	0.1	$Co(K_{\alpha 1})$
	2.4	0.1	$Mo(L_{\alpha 1})$
48	78.5	0.1	$Ni(K_{\alpha 1})$
	19.2	0.1	$Co(K_{\alpha_1})$
	2.4	0.1	$Mo(L_{\alpha 1})$
72	78.8	0.2	$Ni(K_{\alpha 1})$
	19.0	0.1	$Co(K_{\alpha 1})$
	2.2	0.1	$Mo(L_{\alpha_1})$
	2.2	0.1	$Mo(L_{\alpha_1})$

The quantitative spectrometry results depicted in Fig. 8 reveal that the chemical composition of the $(Ni_{80}Co_{17}Mo_3)$ powders closely resembles the starting composition, with a 5% increase in nickel content and a slight decrease in the other elements. This observa-



Fig. 8. EDS mapping of $Ni_{80}Co_{17}Mo_3$ powdered mixture of (a) milled for 2 h and (b) milled for 72 h.

tion indicates the absence of impurities and the minimal possibility of contamination during the milling process, either from the milling balls or from the internal walls of the jars. Therefore, the final composition obtained after 72 h of milling closely represents the quantities initially introduced into the mill.

3.4. Magnetic Properties

Figure 9 presents hysteresis loops obtained from vibrating-sample magnetometer (VSM) studies, or M-H-loop studies, for the milled Ni₈₀Co₁₇Mo₃ powder as a function of milling time. The evaluation of saturation magnetization, coercivity, and retentivity at room temperature using a vibrating sample reveals hysteresis. The value increases after two hours of milling and then gradually decreases. This change can be attributed to structural distortions within the particles. The weak ferromagnetic behaviour indicates the presence of a small amount of Mo phase in the sample, which is not clearly visible in the XRD pattern. The presence of molybdenum in a material can influence magnetic hysteresis by modifying the magnetic properties of the material. Mo can interact with the magnetic domains, causing alterations to magnetic anisotropy and magnetic saturation. This interaction can result in changes to the shape and



Fig. 9. Evolution of M-H-hysteresis loops as a function of milling time recorded at T = 300 K. The inset is enlargement of low-filed region.

size of the hysteresis loop, as well as modifications to other magnetic properties, such as magnetic permeability and magnetism. The precise effect of molybdenum on magnetic hysteresis depends on various factors, including the type of material, the concentration of molybdenum, and the processing conditions. In some instances, Mo can enhance the magnetic properties of a material, such as steel, by increasing magnetic saturation and permeability. In other cases, molybdenum can influence magnetic hysteresis, leading to reductions in magnetic saturation and magnetic permeability [22, 23]. Generally, small hysteresis losses are desirable properties for materials used in magnetic applications.

Figure 10 illustrates the variations in coercivity force as a function of the ball milling time. The coercivity curve for the $Co_{50}Ni_{50}$ alloy exhibits a peak value of 214.07 Oe after two hours of milling, followed by a rapid decline from 131.65 Oe to 10.87 Oe. The decrease in H_c reaches its minimum value after 72 hours of milling. This reduction is attributed to the influence of small crystal size, which supersedes the impact of microstrains as the powder particles increase in size.

The particle size, observed by SEM to increase with milling time, may also contribute to the low H_c values. Coercivity (H_c) can be influenced by numerous factors, including magnetic domain motion, exchange interaction, magnetic anisotropy, demagnetization effects, surface conditions, and material structure [24, 25]. These parameters are influenced by crystalline alloys, microstrain, grain size, dislocation density, and grain boundaries, as well as amorphous alloys' residual stresses, free volumes, and microstructure [26, 27]. Furthermore, the substantial deformation of powder particles leads to the formation of numerous nanocrystalline defects (primarily



Fig. 10. Evolution of magnetic properties of powdered mixture as functions of milling time: (a) coercivity; (b) saturation magnetization; (c) remanent magnetization; (d) remanence-to-saturation ratio M_r/M_s .

stacking faults) within the primary structure, which subsequently reduces coercivity [14, 28]. Loudjani *et al.* [9] made a similar note-worthy observation following a magnetic study on the $Ni_{50}Co_{50}$ binary alloy produced through mechanical alloying.

Figure 10, a, b display the progression of saturation magnetization (M_s) and remanent magnetization (M_r) as functions of milling time. In the initial stage of the curve for both M_s and M_r , it is observed that M_s increases in value and then stabilizes. This trend can be attributed to the reduction in magnetocrystalline anisotropy caused by the refinement of crystallite size, which facilitates the rotation of the magnetic vector and suggests the formation of a crystalline magnetic phase. Meanwhile, M_r remains relatively constant throughout the process. In the first hours of milling, M_r increases after 24 hours, reaching a value of 321.686 emu/g, accompanied by a decrease in the value of M_s to 19 emu/g after 48 hours of milling. This reduction in M_s may be attributed to the decrease in crystallite size, as suggested by previous research [29, 30]. Amils et al. demonstrated that the ball-milling process generates a high density of defects [31]. In our study, the decrease in the coercive field as a function of milling time could be ascribed to the influence of the extremely small grain size. Subsequently, the value of M_s is increasing to 78.382 emu/g after 72 hours of milling that may be associated with the crystallite size resulting from the milling process, by correlating this finding with the XRD results. The variations in domain structure, average particle size, and crystal anisotropy can also be employed to elucidate the difference in crystallite size. Figure 10, d presents M_r/M_s , another important magnetic parameter, as a function of milling time. During the initial hours of milling, M_r/M_s experiences a slight increase and subsequently decreases, attaining a value of approximately 0.004 after 72 hours of milling.

The observed behaviour, which is contrary to what is typically expected in polycrystalline materials, may likely be attributed to the small magnetic particles that are generally single domains. These particles exhibit an extremely low remanence ratio and nearly zero coercive field [14]. This intriguing observation has also been reported in previous studies [32]. From these findings, it can be inferred that the nanostructured Ni₈₀Co₁₇Mo₃ alloy demonstrates highly soft magnetic behaviour. Such materials are commonly utilized in electronic components where low coercive fields and superior magnetic permeability are desired, such as inductors, transformers, and electric motors [33].

4. CONCLUSION

In this research, $Ni_{80}Co_{17}Mo_3$ nanostructured powder mixtures were produced through high-energy mechanical alloying (MA) at different times, and subsequently analysed using XRD, SEM, and VSM techniques. The structural investigation unveiled the formation of the solid solution, which was achieved after 24 hours of milling, resulting in the development of a face-centred cubic structure phase. The SEM and EDS analysis confirmed the refinement of the milled particles as a consequence of the milling time, demonstrating that a homogenous mixture is formed from uniformly sized and rounded agglomerations of grains. This study observed a notable reduction in particle and crystallite size, along with an increase in lattice parameter and microstrain, as the milling time increased.

As a result of magnetic characterizations carried out at room temperature, a new paramagnetic phase emerged, influenced by the antiferromagnetic activity of manganese. On the other hand, it was found that the reduction in grain size also affected the magnetic behaviour of the mixture due to a significant increase in magnetic disorder states and the appearance of single domains. Based on these findings, the magnetic properties and behaviour of the nanostructured $Ni_{80}Co_{17}Mo_3$ become magnetically saturated as a function of milling time, which is essential in magnetic materials processing for potential large-scale industrial production in the future.

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REFERENCES

- 1. M. Amiri, M. Salavati-Niasari, and A. Akbari, *Advances in Colloid and Interface Science*, **265**: 29 (2019); https://doi.org/10.1016/J.CIS.2019.01.003
- 2. Y. Zhao, Z. Zhang, Z. Pan, and Y. Liu, *Wiley Online Library*, **1**, No. 3: 0089 (2021); https://doi.org/10.1002/EXP.20210089
- 3. H. Ahmadian Baghbaderani, S. Sharafi, and M. Delshad Chermahini, *Powder Technology*, 230: 241 (2012); https://doi.org/10.1016/J.POWTEC.2012.07.039
- 4. K. H. J. Buschow, *Reports on Progress in Physics*, 40, No. 10: 1179 (1977); https://doi.org/10.1088/0034-4885/40/10/002
- 5. N. Abu-warda, M. V. Utrilla, M. D. Escalera, E. Otero, and M. D. López, *Powder Technology*, **328**: 235 (2018); https://doi.org/10.1016/J.POWTEC.2018.01.028
- 6. X. Mao, J. Xu, and H. Cui, Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology, 8, No. 6: 814 (2016); https://doi.org/10.1002/WNAN.1400
- 7. V. Franco, J.S. Blázquez, B. Ingale, and A. Conde, *Annual Review of Materials Research*, **42**: 305 (2012); https://doi.org/10.1146/ANNUREV-MATSCI-062910-100356
- S. Chandrasekaran, L. Yao, L. Deng, C. R. Bowen, Y. Zhang, S. Chen, Z. Lin, F. Peng, and P. Zhang, *Chemical Society Reviews*, 48, No. 15: 4178 (2019); https://doi.org/10.1039/C8CS00664D
- 9. N. Loudjani, N. Bensebaa, S. Alleg, C. Djebbari, and J. M. Greneche, *physica status solidi (a)*, 208, No. 9: 2124 (2011); https://doi.org/10.1002/PSSA.201026723
- X. Zhang, Y. Li, Y. Guo, A. Hu, M. Li, T. Hang, and H. Ling, International Journal of Hydrogen Energy, 44, No. 57: 29946 (2019); https://doi.org/10.1016/J.IJHYDENE.2019.09.193
- 11. H. Raanaei, M. Rahimi, and V. Mohammad-Hosseini, Journal of Magnetism and Magnetic Materials, 508: 0166870 (2020); https://doi.org/10.1016/J.JMMM.2020.166870
- T. Şimşek, Ş. Akgül, Ö. Güler, I. Özkul, B. Avar, A. K. Chattopadhyay, C. A. Canbay, and S. H. Güler, *Materials Today Communications*, 29: 102986 (2021); https://doi.org/10.1016/J.MTCOMM.2021.102986.
- 13. R. R. Shahi and R. K. Mishra, *High Entropy Alloys* (CRC Press: 2020); https://doi.org/10.1201/9780367374426-22
- M. Triki, H. Mechri, H. Azzaz, and M. Azzaz, Journal of Magnetism and Magnetic Materials, 541: 168514 (2022); https://doi.org/10.1016/j.jmmm.2021.168514

- 15. J. Schilz, M. Riffel, K. Pixius, and H. J. Meyer, *Powder Technology*, **105**, Nos. 1– 3: 149 (1999); https://doi.org/10.1016/S0032-5910(99)00130-8
- 16. A. Abuchenari and M. Moradi, *Journal of Composites and Compounds*, 1, No. 1: 10 (2019); https://doi.org/10.29252/JCC.1.1.2
- I. Constantinides, M. Gritsch, A. Adriaens, H. Hutter, and F. Adams, *Analytica Chimica Acta*, 440, No. 2: 189 (2001); https://doi.org/10.1016/S0003-2670(01)01061-3
- T. Gouasmia, N. Loudjani, M. Boulkra, M. Benchiheub, K. Belakroum, and M. Bououdina, *Applied Physics A*, **128**, No. 10: 935 (2022); https://doi.org/10.1007/s00339-022-06074-y
- T. Ramkumar, M. Selvakumar, R. Vasanthsankar, A. S. Sathishkumar, P. Narayanasamy, and G. Girija, *Journal of Magnesium and Alloys*, 6, No. 4: 390 (2018); https://doi.org/10.1016/J.JMA.2018.08.002
- 20. D. L. Bish and J. E. Post, American Mineralogist, 78, Nos. 9–10: 932 (1993).
- 21. S. Verma, S. Rani, S. Kumar, and M. A. M. Khan, *Ceramics International*, 44, No. 2: 1653 (2018); https://doi.org/10.1016/J.CERAMINT.2017.10.090
- 22. P. Tandon, R. Sahu, and A. Mishra, *Journal of Materials Science*, **57**, No. 41: 19631 (2022); https://doi.org/10.1007/s10853-022-07808-2
- 23. M. Hossain, B. Qin, B. Li, and X. Duan, *Nano Today*, **42**: 101338 (2022); https://doi.org/10.1016/j.nantod.2021.101338
- 24. Z. Hedayatnasab, F. Abnisa, and W. M. A. Wan Daud, *Materials & Design*, **123**: 174 (2017); https://doi.org/10.1016/J.MATDES.2017.03.036
- 25. J. Fidler and T. Schrefl, *Journal of Physics D: Applied Physics*, **33**, No. 15: R135 (2000); https://doi.org/10.1088/0022-3727/33/15/201
- 26. X. Fang, G. Jin, X. Cui, and J.-N. Liu, Surface and Coatings Technology, 305: 208 (2016); https://doi.org/10.1016/J.SURFCOAT.2016.08.042
- 27. A. L. Ortiz, J. W. Tian, J. C. Villegas, L. L. Shaw, and P. K. Liaw, *Acta Materialia*, 56, No. 3: 413 (2008); https://doi.org/10.1016/J.ACTAMAT.2007.10.003
- Y. Xu, Y. Sun, X. Dai, B. Liao, S. Zhou, and D. Chen, Journal of Materials Research and Technology, 8, No. 3: 2486 (2019); https://doi.org/10.1016/J.JMRT.2019.02.007
- M. D. Chermahini, M. Zandrahimi, H. Shokrollahi, and S. Sharafi, *Journal of Alloys and Compounds*, 477, Nos. 1–2: 45 (2009); https://doi.org/10.1016/J.JALLCOM.2008.10.163
- 30. R. Hamzaoui, S. Guessasma, O. Elkedim, and E. Gaffet, Materials Science and Engineering: B, 119, No. 2: 164 (2005); https://doi.org/10.1016/J.MSEB.2005.02.049
- X. Amils, J. Nogués, S. Suricach, and M. D. Bary, *Journal of Magnetism and Magnetic Materials*, 203, Nos. 1–3: 129 (1999); https://doi.org/10.1016/S0304-8853(99)00211-5
- 32. J. J. Sucol, A. González, J. Saurina, L. Escoda, and L. Fernández Barquín, Journal of Non-Crystalline Solids, 353, Nos. 8–10: 865 (2007); https://doi.org/10.1016/J.JNONCRYSOL.2006.12.108
- 33. William Hopkins, *The Davenport Electric Motor: A Look at How the First Electric Motor Can Teach the Fundamentals of Magnetism and Motion* (Ed. John A. Goulet) (Worcester Polytechnic Institute: 2022).

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