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Structural evolution during mechanical alloying of stainless steels under nitrogen

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Abstract

Mechanical alloying of Fe-based powders under a nitrogen atmosphere has been recently converted into the subject of many researches. This paper reviews aspects of mechanical alloying of stainless steels under a nitrogen atmosphere. Nitrogen incorporation from the viewpoints of infusion mechanism, supersaturation, and kinetics is considered. The structural refinement, leading to nanocrystallization, and phase transformations, consisting of austenitization and amorphization, are outlined. Particularly, it is noted that nitrogen intensifies grain refinement and proceeds ferrite-to-austenite phase transformation and amorphization during mechanical alloying.

Keywords: Stainless steels; Mechanical alloying; Nitrogen; Nanostructures; Amorphization

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1. Introduction

It is well established that mechanical alloying (MA) is a capable process to synthesize a wide variety of equilibrium and non-equilibrium structures, including supersaturated, metastable crystalline, quasicrystalline, intermetallic, nanostructured, and amorphous alloy powders [1,2]. Milling atmosphere is one of the most important variables of MA, which considerably affects contamination, structure, and accordingly properties of the products. Generally, milling is conducted under an inert gas like argon or helium to prevent undesirable oxidation and contamination. On the contrary, ammonia, hydrogen, and oxygen atmospheres, apart from nitrogen, can be employed to produce nitrides, hydrides, and oxides, respectively [3–8]. Particularly, milling of reactive powders, such as titanium, aluminum, iron, and their alloys in the presence of a nitrogen ambience introduces nitrogen into the matrix via a solid–gas reaction. Nitrides formation and nitrogen-induced amorphization during MA under a nitrogen atmosphere have been frequently reported in non-ferrous powders, for example Refs. [9–14]. The absorption rate of nitrogen during MA increases with the increase in the chemical affinity of powder elements for nitrogen [15].

Nickel-free stainless steels are potential substitutes for traditional stainless steels, due to biocompatibility, low cost, good mechanical and corrosion properties [16–21]. Nitrogen in stainless steels is a strong austenite stabilizer and significantly improves their properties [22–28]. Recently, to synthesize these alloys, solid-state processes like MA have been regarded as an alternative to liquid-state methods.

Nitrogen alloying through MA can be accomplished by either milling under a nitrogen atmosphere or milling with proper nitride powders. MA of stainless steels with iron and chromium nitrides under an argon atmosphere has been frequently studied [29–37]. Concerning MA of pure Fe under a nitrogen atmosphere, studies conducted by El-

Eskandarany et al. [38] and Rawers et al. [39–42] are worthy of mention. This paper aims to outline last findings on MA of stainless steels under a nitrogen atmosphere, consisting of nitrogen incorporation, grain refinement, and phase transitions during MA.

2. Nitrogen incorporation

2.1. Infusion mechanism

It has been frequently reported that milling of Fe-based powders under a nitrogen atmosphere gives rise to the infusion of nitrogen into the matrix [38–55]. The nitrogen atmosphere can be provided by either a continuous flow of nitrogen gas or milling inside a sealed container filled with nitrogen gas. Since the powder particles are subjected continual fracturing and plastic deformation due to action of the milling media, very clean or fresh oxygen-free active surfaces from the atomistic viewpoint are created [1,2,38–42]. These fresh surfaces are very prone to react with any active species presented in the environment. When milling is conducted under nitrogen gas, molecular nitrogen was absorbed by the first atomically clean surfaces of the metallic ball-milled powders, was dissociated, and consequently penetrates atomically into the matrix via cold welding of the particles and diffusing down to interstitial sites, grain boundaries, dislocations, and other defects [43–55]. The chemisorption of nitrogen onto the clean surfaces created by milling is the essential step governing the solid–gas reaction [56,57]. However, a more detailed mechanism governing the aforementioned reaction is still far from understood, since the solid-gas reactions usually consist of a set of complex microprocesses.

2.2. Nitrogen supersaturation

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Obviously, by increasing milling time, the nitrogen infusion increases progressively. A review on the amounts of nitrogen infused during MA under nitrogen (Table 1) suggests that the incorporated nitrogen is several orders of magnitude in excess of the equilibrium contents. The equilibrium solubility limit of nitrogen in iron at room temperature is less than 0.1 wt.% [48,51]. The addition of such alloying elements as Cr, Mn, and Mo which are located in the left of Fe in the periodic table enhances the nitrogen solubility compared to the Fe–N system. However, this fact cannot alone rationalize the observed supersaturation. Extension of equilibrium solid solubility limits has been pointed out in other alloy systems by non-equilibrium processing routes like MA [1]. During milling due to severe plastic deformation, high amounts of structural defects like point defects, dislocations, and nanograin boundaries are generated. Since the mismatch strain of solute nitrogen is reduced in the defects, a high proportion of nitrogen atoms are diffused down to the defects. In other words, the dislocations and nanograin boundaries formed during MA provide additional interstitial sites, decrease diffusion paths, and increase diffusivity, leading to supersaturation.

It would be worth mentioning that Mossbauer studies of high-nitrogen iron powders prepared by MA have verified that a considerable amount of infused nitrogen accumulates at grain boundaries [55,58]. In addition, the development of an amorphous phase during MA with an enhanced solubility for nitrogen is another source for supersaturation [1,43,48]. A novel quantitative analysis based on X-ray diffraction, thermogravimetry, and differential scanning calorimetery has implied that the amorphous phase formed during MA of stainless steel powders milled under nitrogen plays a crucial role in the nitrogen supersaturation [59–61]. Typically, in Fe–18Cr–8Mn–2.5N alloy powder synthesized by MA under nitrogen, about 4, 21 and 75 percent of nitrogen is distributed among the crystal interstitial sites, defects, and amorphous phase, respectively [59].

2.3. Infusion kinetics

The kinetics of the nitrogen incorporation through MA is related to the evolution of size, morphology, and accordingly surface area of the particles exposed to the nitrogen atmosphere. This correlation is in accordance with the nitrogen infusion mechanism described above. Cisneros et al. [48] have observed that the rate of the nitrogen infusion follows an exponential trend with milling time (Fig. 1a). This is due to a continuous increase in the surface area per volume of the powders with time. In contrast to Refs. [48,53] in which the particle size progressively decreases, the average particle size of Fe–18Cr–11Mn powders milled under nitrogen in a planetary ball mill increases by milling time [51]. This has been attributed to the domination of austenite phase that is ductile, increasing cold welding than fracturing during MA. On the other hand, it has been pointed out that at high milling times when the density of defects almost saturates, the rate of the nitrogen incorporation is reduced [51]. The nitrogen absorption rate by Fe–18Cr–11Mn–5Mo powders milled under nitrogen has been reported to show different behaviors with time (Fig. 1b), attributed to variations of size and morphology of the powders [50]. Ref. [52] has found a linear relation between the nitrogen content and milling time during MA of nickel-free stainless steels under a flowing nitrogen atmosphere, in which the particles morphology tends to spherical by increasing milling time. Indeed, these antitheses between the results are due to the fact that employed milling conditions have been different, providing different size and morphological evolutions.

3. Structural refinement

Regarding MA of stainless steels under nitrogen gas, it has been reported that the grain size approaches about 7 nm after 60 h [51], 6 nm after 120 h [49], 5 nm after 144 h [43], and

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3.3 nm after 170 h of milling [48]. These severe grain refinements are regarded from two viewpoints:

3.1. The role of mechanical milling

During MA, the powder particles are subjected to severe plastic deformation, increasing the density of dislocations and forming shear bands containing a high dislocation density. Dislocation cells and subgrains separated by low-angle grain boundaries are formed to decrease the lattice strain. Consequently, the transformation of the low-angle to high-angle grain boundaries takes place by grain rotation, giving nanostructures, which is a typical and well-established mechanism [1].

3.2. The role of nitrogen

The X-ray diffraction (XRD) pattern of Fe–18Cr–8Mn powder milled under argon and nitrogen is presented in Fig. 2. Based on these traces, XRD peak profile analyses suggested that the grain refinement in stainless steel powders milled under nitrogen occurs more rapidly and more significantly than in those milled under argon (Fig. 3). Diffused nitrogen atoms are segregated at dislocations and grain boundaries, fixing the dislocations and stabilizing the grain boundaries [7]. Afterward, the trickling down of mobile dislocations on the fixed dislocations contributes to the nucleation of new boundaries and severe grain refinement [43,62].

The observed contribution of nitrogen to the grain refinement is in good agreement with the dislocation-based model proposed by Mohammad [63] estimating the minimum grain size achievable through MA. In accordance with this model, the normalized minimum grain size (d_{min}/b) achieved by milling is related to structural properties, particularly hardness (H), self-diffusion activation energy (Q), stacking fault energy (SFE) (γ), shear modulus (G), and milling temperature (T) as:

$$d_{min}/b \equiv (e^{-\beta Q/4RT})\,(1/T)^{0.25}\,(G)\,(\gamma)^{0.5}\,(1/H)^{1.25} \qquad (1)$$

where b, R, and β are the Burgers vector, the gas constant, and a constant less than unity, respectively. It has been reported that nitrogen enhances the self-diffusion activation energy and hardness, in contrast, reduces the stacking fault energy and shear modulus in this alloy system [53], intensifying the structural refinement based on the Mohammad's model.

4. Phase transformations

Phase transformations occurring in the course of MA is one of the most studied topics in the MA field. In the first stages of MA of stainless steels under nitrogen, elemental powders are dissolved into the matrix, leaving a nanostructured BCC ferrite phase. Typically, the milling time required for this dissolution event has been reported to be 26.5 h for Fe–18Cr–11Mn [48] and 24 h for Fe–18Cr–11Mn–5Mo powders [50]. The high-resolution transmission electron microscopy (HRTEM) micrograph and corresponding selected area diffraction (SAD) patterns of Fe–18Cr–4Mn powder milled under nitrogen for different durations are provided in Fig. 4. At a short milling time, ferrite and austenite nanocrystals are dominant. By progression of the MA process to an intermediate time (72 h), a featureless amorphous matrix with a halo SAD pattern can be clearly recognized. Finally, milling for a sufficiently prolonged time (126 h) leads to the development of a fully amorphous structure. Table 2 tabulates the evolution of the austenitization and amorphization transformations during MA of Fe–18Cr–8Mn powder under nitrogen and argon gases, based on XRD studies [43], suggesting the key contribution of nitrogen species to the transitions.

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4.1. Austenitization

By progression of MA of stainless steel powders under nitrogen, the ferrite-to-austenite transformation proceeds [43,44,46–54]. On the one hand, it results from the nitrogen incorporation and the fact that nitrogen is a strong austenite stabilizer element. Nitrogen atoms diffuse into interstitial sites of ferrite crystallites and produce mismatch strains. Austenite has larger interstitial sites than ferrite, implying that nitrogen atoms in austenite create less distortion and volume mismatch. In addition, austenite has smaller interfacial energy compared to ferrite [43]. Apart from the nitrogen effect, refinement of the structure to the nanometric scale favors the austenitization transition during MA [51,62]. The grain refinement increases the volume fraction of interfaces (grain boundaries), where the density of grain boundaries reaches 10^{19} cm^{-3} [64]. In this case, the enthalpy or strain energy of the materials is such high as high-temperature phase transformations like austenitization are promoted at room temperature [65,66].

Cisneros et al. [49] have found that a fully austenitic nanostructure is obtained after 120 h of milling in a high-energy SPEX mill. Furthermore, milling times of 80 h [51] and 96 h [52] have been reported for the development of a fully austenitic structure, albeit according to XRD studies where amorphization was not considered. Meanwhile, one should not expect that by increasing milling time, the austenite content increases progressively, as shown in Table 2. It should be considered that in parallel with the ferrite-to-austenite transition, amorphization of both ferrite and austenite occurs. This contributes to decrease the amount of austenite, when amorphization prevails over the ferrite-to-austenite transformation. This behavior has been reported at sufficiently milling times when the dissolved nitrogen approaches considerable values [43].

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4.2. Amorphization

As well as austenitization, evidences for amorphization in stainless steels during MA under nitrogen have been found [43–47,49–51]. According to a quantitative amorphous phase analysis approach that is based on the Rietveld refinement of XRD data (detailed in Ref. [43]), by increasing milling time and consequently nitrogen content, the amorphous content increases [43–47]. For instance, Fe–18Cr–8Mn powders milled under nitrogen for 144 h in a shaker mill possess about 83.7 % amorphous phase, 14.9 % austenite, and 1.4 % ferrite [43]. The TEM and HRTEM micrographs and SAD patterns of this sample are indicated in Fig. 5, reflecting that the dark regions are a combination of the nanocrystalline ferrite and austenite phases and the bright matrix is a featureless amorphous phase. Amorphization has been indentified to be completed for Fe–18Cr–4Mn–*x*N alloys after 126 h of milling in a planetary ball mill [45,46].

There is a competition between the formation of an amorphous phase and the precipitation of crystallites. Apparently, when the Gibbs free energy of the amorphous phase is lower than that of the crystallites, solid-state amorphization takes place. The amorphization reaction can be explained by high energies given to the powders during milling. The severe plastic deformation and extreme structural refinement which have occurred during milling increase the density of defects and the constraints of neighboring crystallites, decreasing the stability of the crystalline structure and promoting amorphization [1,43]. Nonetheless, the study of milling under argon has reflected that the contribution of nitrogen to amorphization is very significant [43,46]. Notice that milling of Fe–18Cr–8Mn powders under an argon atmosphere provides only 3.2 % amorphous phase after 144 h processing [43].

According to the Inoue’s empirical rules [67,68], the amount of the amorphous phase formed depends on (i) the number of the constituent elements, (ii) the atomic size mismatch,

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and (iii) the heat of mixing among the constituent elements. To have a considerable amorphous phase, the powder mixture should consist of more than two elements, disturbing the crystal formation by imposing a chemical disorder [45]. This condition is satisfied for both the Fe–Cr–Mn–N and Fe–Cr–Mn alloy systems. On the other hand, a large atomic size mismatch among the elements prevents formation of a crystalline solid solution. Moreover, a large negative heat of mixing among the elements provides the driving force for amorphization [50] and increases the viscosity of the supercooled liquid [45], suppressing atomic diffusions required for precipitation of crystals. Since N is far from Fe, Cr, and Mn elements in the periodic table, the addition of nitrogen to Fe–Cr–Mn alloys leads to a considerable increase in the atomic size differences and the negative heats of mixing, encouraging amorphization significantly. It is worthwhile to note that the amorphous phase nucleates at grain boundaries and grows by interdiffusion reaction under metastable equilibrium during MA [43,50,69]. Finally, it is noted that last findings on physical properties of theses mechanically alloyed stainless steel powders, consisting of their nitrogen distribution, thermal, magnetic, indentation, and grain growth behaviors have been reviewed in Ref. [61].

5. Summary

Aspects of MA of stainless steels under a nitrogen atmosphere were outlined. MA under these conditions introduces nitrogen into the matrix, through a solid–gas reaction. The kinetics of the nitrogen incorporation by MA developing nitrogen-supersaturated alloys was explained by considering variations of the powder particle size with milling time. It was noted that MA under nitrogen intensifies grain refinement compared to MA under argon.

Ferrite-to-austenite phase transformation and amorphization occur during MA, leading to the development of nanostructured-amorphous powders.

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Tables

Table 1. Amounts of nitrogen infused through MA under a nitrogen atmosphere.

Composition (wt.%)	Type of mill	Milling time (h)	Nitrogen content (wt.%)	Reference
Fe–18Cr–8Mn	Shaker mill	144	2.54	[43]
Fe–18Cr–12Mn	Planetary ball mill	144	4.31	[44]
Fe–18Cr–4Mn	Planetary ball mill	162	3.95	[45]
Fe–18Cr–4Mn	Planetary ball mill	144	3.62	[46]
Fe–18Cr–4Mn	Planetary ball mill	153	3.76	[47]
Fe–18Cr–11Mn	Attritor	170	2.47	[48]
Fe–18Cr–11Mn	Attritor	144	5.00	[49]
Fe–18Cr–11Mn	SPEX mill	120	4.39	[49]
Fe–18Cr–11Mn–5Mo	Attritor	192	1.60	[50]
Fe–18Cr–11Mn	Planetary ball mill	100	0.65	[51]

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Table 2. Results of a quantitative phase analysis on Fe–18Cr–8Mn powder milled under nitrogen and argon [43,59,60].

Milling time (h)	Relative phase content (wt. %)					
	Milling under nitrogen			Milling under argon		
	Amorphous	Austenite	Ferrite	Amorphous	Austenite	Ferrite
24	29.0	19.3	51.7	1.5	1.4	97.1
48	39.3	37.8	22.9	1.9	1.6	96.5
72	43.7	38.6	17.7	2.2	1.7	96.1
96	54.4	33.9	11.7	2.5	2.0	95.5
120	67.4	27.3	5.3	2.8	2.2	95.0
144	83.7	14.9	1.4	3.2	2.3	94.5

Figures

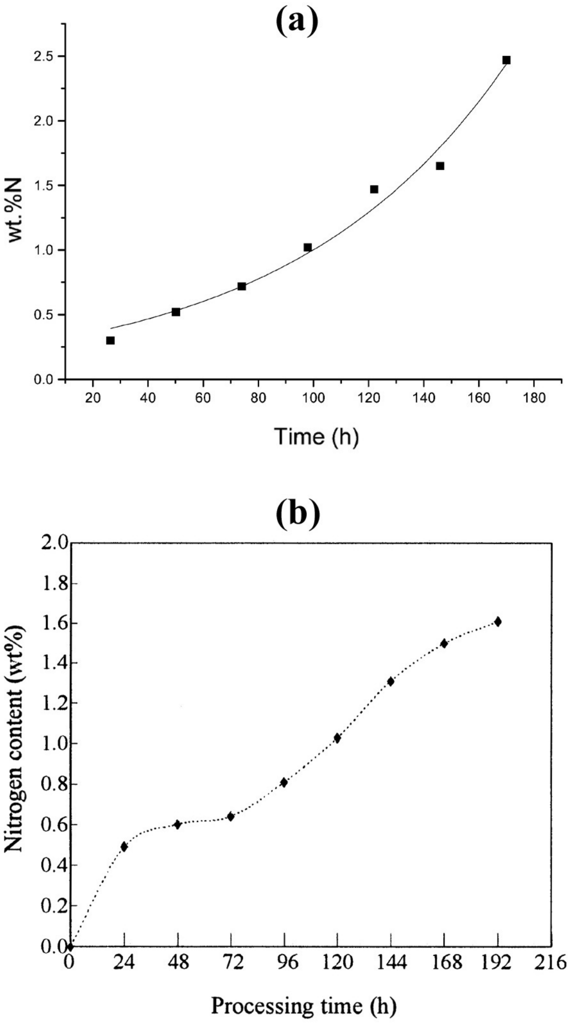

Fig. 1. Nitrogen absorption of Fe–18Cr–11Mn [48] and Fe–18Cr–11Mn–5Mo [50] powder mixtures as a function of milling time.

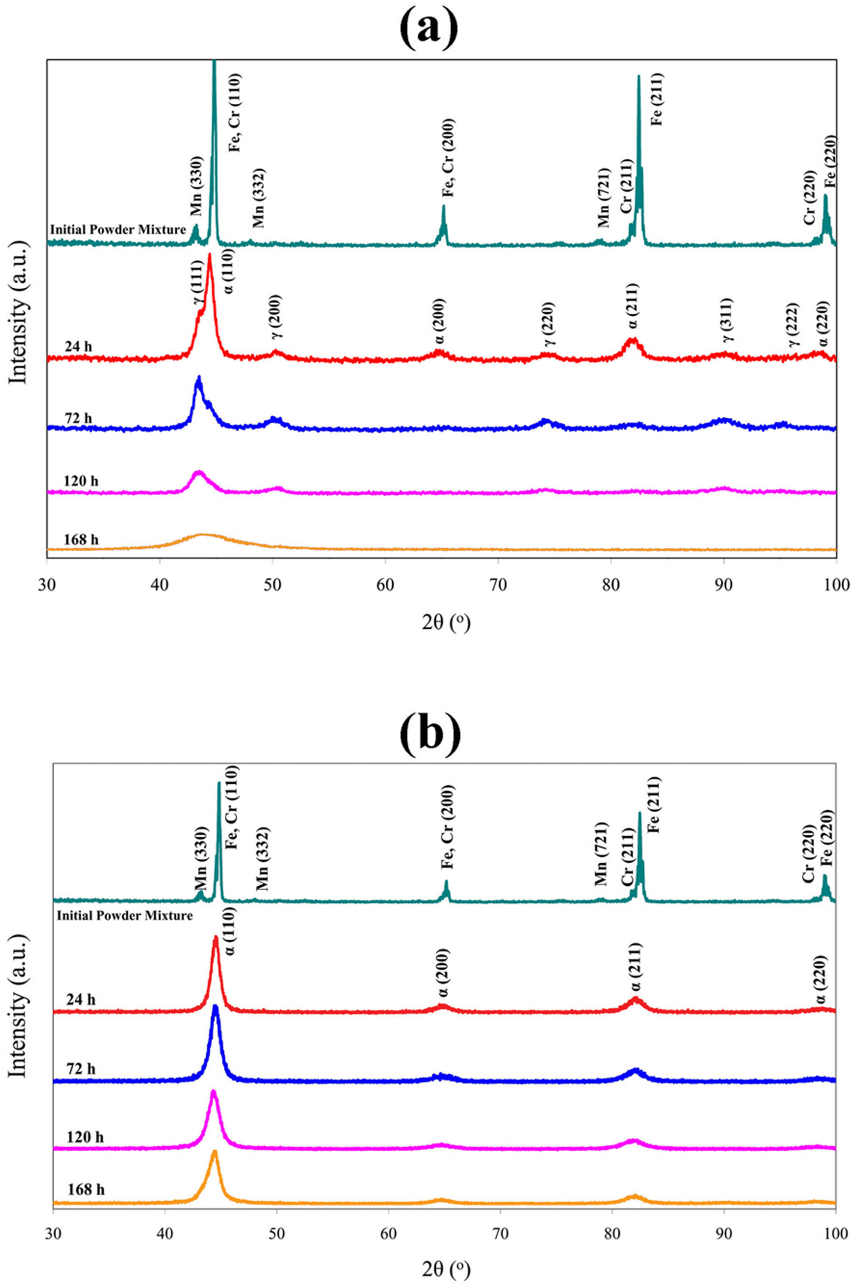

Fig. 2. XRD pattern of Fe–18Cr–8Mn powder milled under nitrogen (a) and argon (b) [59].

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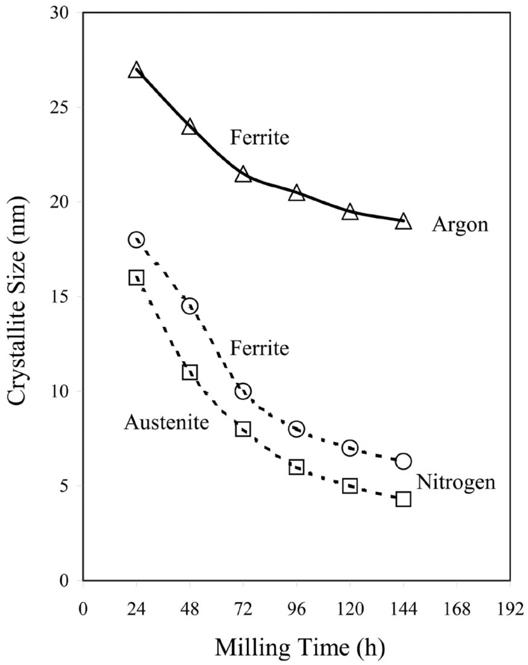

Fig. 3. Crystallite size of the austenite and ferrite phases in Fe–18Cr–8Mn powder milled under nitrogen and argon atmospheres, measured by XRD [43].

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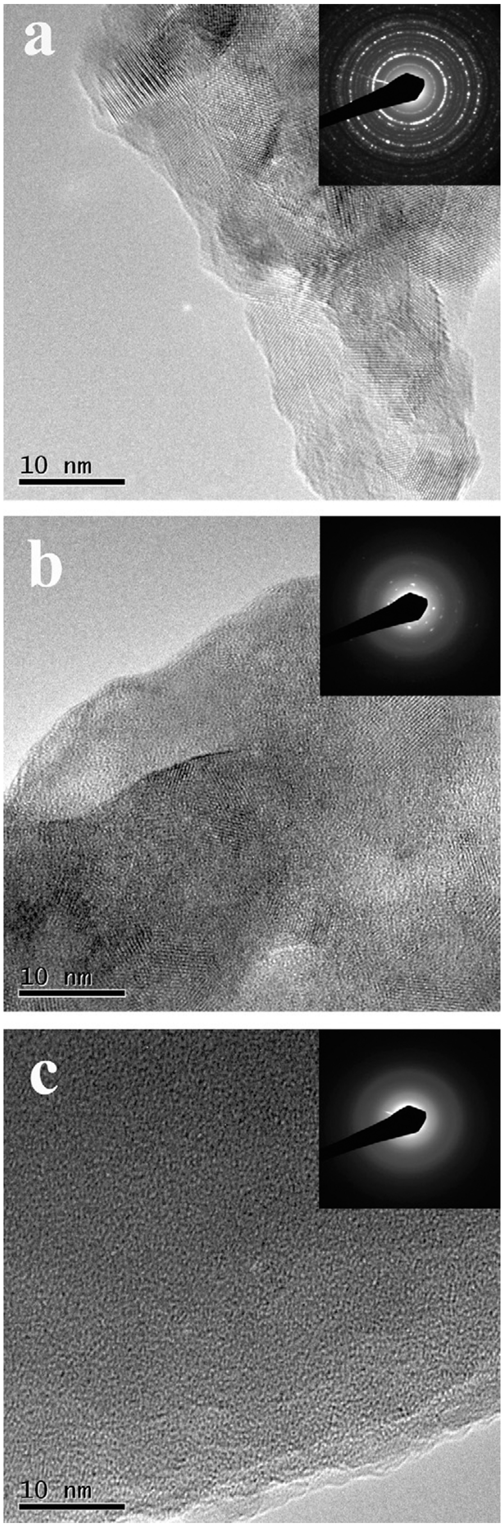

Fig. 4. TEM micrograph of the powder particles milled under nitrogen for (a) 18 h, (b) 72 h, and (c) 126 h [46].

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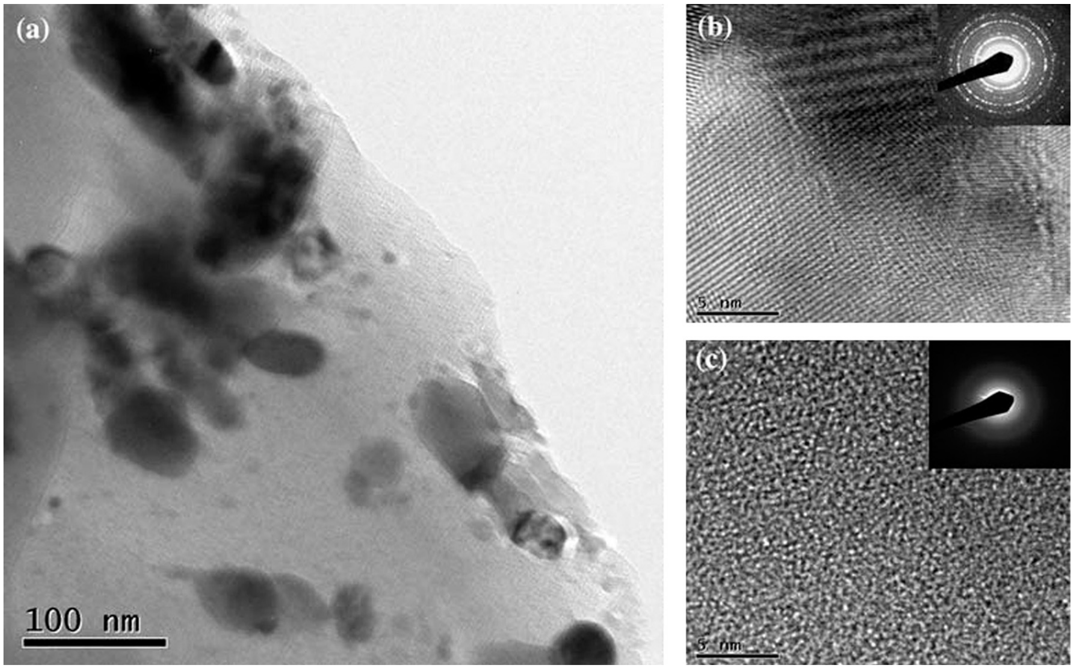

Fig. 5. TEM micrograph of Fe–18Cr–8Mn–2.54N as-milled powder (a); high-resolution picture and related SAD pattern of the dark regions (b); those of the bright matrix (c) [43].