MECHANICAL ALLOYING OF THE Fe-Cr MIXTURE AND STABILIZATION OF THE SINTERED NANOSTRUCTURE BY CARBON ADDITION

Saïfi AMIROUCHE[1, 2*], Boudjema BEZZAZI[2], Mustapha NECHICHE[3] and Said AZEM[4]

The present work concerns the mechanical alloying of the iron-chromium mixture (Fe20% Cr) and the evolution of the crystallite size before and after sintering at high temperature. A study was conducted on the stability of the nanostructure of the sintered material. The effect of adding carbon on the structure and the crystallite size was studied for the sintered material. The X-ray diffraction technique was used to identify the new phases and measure the crystallite size as well as the microstrains induced by mechanical alloying. Scanning electron microscopy revealed structural changes in the milled and sintered material.

Keywords: Mechanical alloying; Nanostructure; Fe-Cr alloys; nanocrystallite; sintering; chromium carbides

1. Introduction

High-energy mechanical alloying is a process which makes it possible to obtain nanostructured [1] or even amorphous powders [2] by gradual reduction of the crystallite size. It also results in a considerable change in the reactivity of the powders, which allows to obtain solid materials with better properties. A wide variety of materials can be produced by mechanical alloying [3-5], generally the nanometric powders, more precisely nanocomposites [6, 7], intermetallics [8] or cermets [9].

The sintering of these powders generally leads to solid materials whose properties are superior to those of conventional materials. Much research has focused on the different mechanical alloying parameters and their influence on the properties of materials product [3, 4].

_____

[1] PhD, Center for Scientific and Technical Research in Physico-chemical Analysis (CRAPC), Bou Ismail, Tipasa, Algeria, *Corresponding author,E-mail address: sa.amirouche@univ-boumerdes.dz

[2] Prof., Materials, Processes and Environment Research Unit (M.P.E.R.U.), Boumerdes University, Algeria

[3] PhD, Mechanical Engineering department, Mouloud Mammeri University of Tizi-Ouzou, Algeria

[4] Prof., Mechanical Engineering department, Mouloud Mammeri University of Tizi-Ouzou, Algeria

On the other hand, due to the magnification of grains, a partial or total loss of the nanocrystalline character of the powder is often observed during the

sintering operation. However, it is quite difficult to obtain massive high-density parts by powder metallurgy while retaining the nanostructure.

Indeed, the densification mechanisms during sintering are governed by diffusion, which is also at the origin of grain growth. Although the heat treatment promotes the cohesion of the particles, it decreases the nanocrystallinity and the properties which are linked to it. Thus, a particular interest is therefore reserved for the conservation of the nanostructure on which the characteristics of the final product strongly depend. In recent decades, great attention has been paid to nanomaterials in several fields, such as magnetism, optics, catalysis, etc. Gleiter [10] studied the methods of making nanomaterials and their properties. Recent work has been devoted to nanoparticles for environmental remediation [11].

The aim of this work is to obtain nanostructured powders of Fe-Cr mixtures by mechanical alloying and to follow the crystallite size evolution, before and after sintering, using X-ray diffraction. The carbon additions are used to mitigate the loss of nanocrystallinity and to develop a massive nanostructured material.

2. Experimental procedure
2.1. Raw materials

Fig. 1 shows the morphology of the powder particles of iron, chromium and graphite, the purities of which are 99.5%. The iron powder (Fig.1a) shows aggregates of small rounded particles. Chromium powder particles (Fig.1b) are almost polyhedral in shape while those of graphite (Fig.1c) are angular and flat in shape.
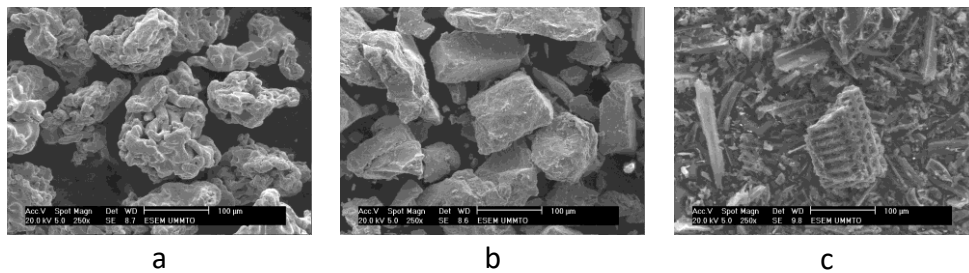

| a | b | c |

Fig. 1: SEM images of the starting powders: (a) Fe, (b) Cr and (c) C

Fig.2 shows the particle size distribution of these powders, which are monomodal for iron and chromium, the average size of each one is approximately 110 μm. On the other hand, carbon has an average size of 50 μm, with a small quantity of particles whose size is close to 150 μm, which results in a shoulder of the particle size curve.
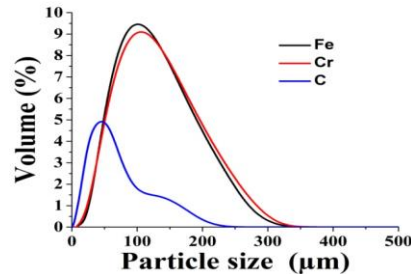
Fig. 2: Particle size distribution of the starting powders

2.2. Samples preparation

To prepare the nanostructure, a mixture of Fe-20wt%Cr powders was prepared and homogenized for 30 minutes in a Turbula type stirrer. Mechanical alloying was carried out using a planetary mill of the Fritch P5 type, under an argon atmosphere, for periods of up to 50 hours and a ball/powder mass ratio of 10/1.

A quantity of the mixture was ground for 50 hours and then cold compacted under a pressure of 380 MPa using a cylindrical die with 13 mm in diameter. The pellets were sintered at 1100, 1200 and 1300 °C under a dynamic argon atmosphere for one hour in a tube furnace.

In order to study the stability of the nanostructure at high temperature, quantities of 1 and 2% by weight of C were added to the initial mixture. Mechanical alloying during 50 hours was carried out in order to obtain the nanostructure in the two mixtures of Fe-20Cr-1C and Fe-20Cr-2C. The nanostructured powders thus obtained were compacted and sintered under the same conditions as the Fe-20Cr mixture.

2.3. Characterization techniques

The studied mixtures were the subject of a characterization of the crystal structure, the microstructure and the particle size. The microstructural analysis was carried out on a scanning electron microscope of the Philips ESEM XL30 type with tungsten filament.

The particle size distribution was carried out on a laser granulometer of the Coulter LS 1100 type.

X-ray diffraction was used to follow the crystallographic structure evolution as a function of milling durations and heat treatment. The device used is a PanalyticalX'Pert PRO (Cu-Kα radiation) diffractometer equipped with a rapid detector. The diffractograms were recorded from 30 to 120 ° with a step of 0.016 ° and a time of 8 seconds per step.

The calculation of the crystallite size and the microdeformations was carried out according to the Williamson-Hall method [12] using relations (1) and (2).

$$\beta^D = \frac{\lambda}{D.\cos\theta} \tag{1}$$

$$\beta^M = 2\varepsilon.\tan\theta \tag{2}$$

Where β^D is the integral width of the diffraction line due to the crystallite size, λ is the wavelength of the radiation used, D is the apparent size of the crystallites, θ diffraction angle, while β^M represents the integral width due to microdeformations whose rate is denoted by ε. The integral widths were measured using X'PertPRO software.

The instrumental contribution to the widening of the diffraction peaks was previously corrected according to the form factor of each peak and by using the Caglioti polynomial [13] given by equation 3. This expression describes the evolution of the integral width of the peak as a function of the diffraction angle. The plot of this polynomial, represented in FIG.3, is obtained by analyzing a standard sample under the same analysis conditions as the studied mixtures.

$$\beta^2 = U.\tan^2\theta + V.\tan\theta + W \tag{3}$$

Where β is the integral width of the standard sample peaks; U, V and W are the intrinsic parameters of the diffractometer used and θ diffraction angle.

The addition of a second degree polynomial trend curve allows the determination of the quantities U, V, W intrinsic to the diffractometer. Equation (4) is determined with a correlation coefficient of 0,996 as shown in Fig. 3.

$$\beta^2 = 0{,}035\tan^2\theta - 0{,}023\tan\theta + 0{,}028 \tag{4}$$

The evolution of the lattice parameter a_{Fe} of the solid solution as a function of the milling duration is calculated by applying equation 5 for the most intense peaks.

$$d_{hkl} = \frac{a_{Fe}}{\sqrt{h^2+k^2+l^2}} \tag{5}$$

Where d_{hkl} is the inter-reticular distance calculated from the diffractogram using the Bragg relation. The numbers *h*, *k* and *l* represent the Miller indices of the diffracting planes.
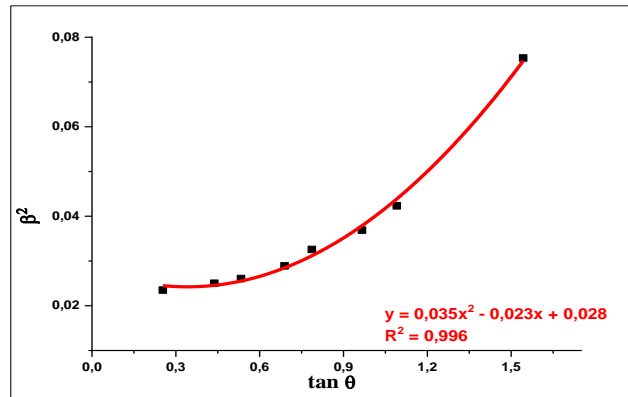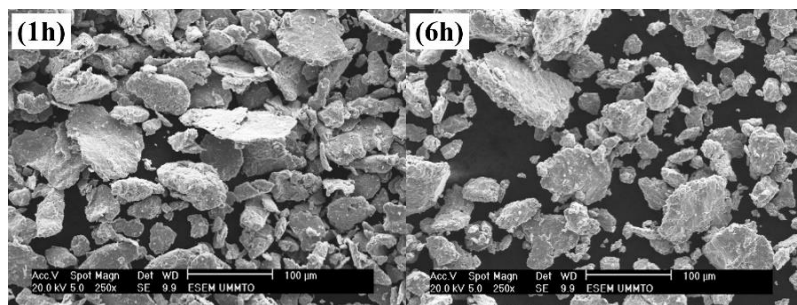
Fig.3: Evolution of the square of the integral width as a function of tan θ

3. Results and discussion

3.1. Milling of the Fe-20Cr mixture
3.1.1. Morphology and particle size

The Fe-20Cr mixture is subjected to mechanical alloying and then examined with a scanning electron microscope (SEM) in order to follow the evolution of the microstructure as a function of the milling time. The micrographic observations are shown in Fig.4. It appears that at short milling times the particles are agglutinated and have undergone plastic deformations under the effect of the milling energy which gives them a flat shape. The accumulation of plastic deformations causes these agglomerates to disintegrate into fine particles with long milling times [14]. Indeed, Fig.4 reveals the formation of particles with dimensions close to 1 µm after 50 hours of milling.
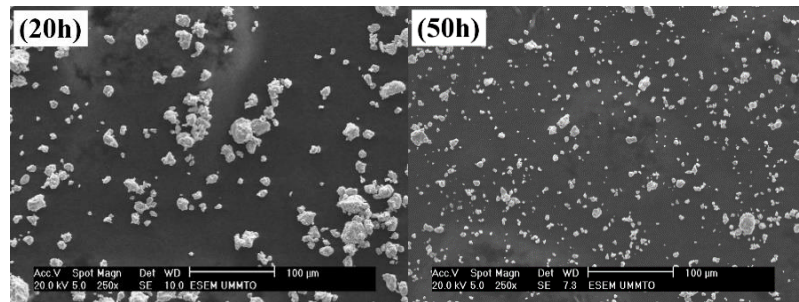
Fig.4: SEM observations of the Fe-20Cr mixture as a function of the milling time

The particle size distribution curves show a significant change in the particle size during milling (Fig.5).
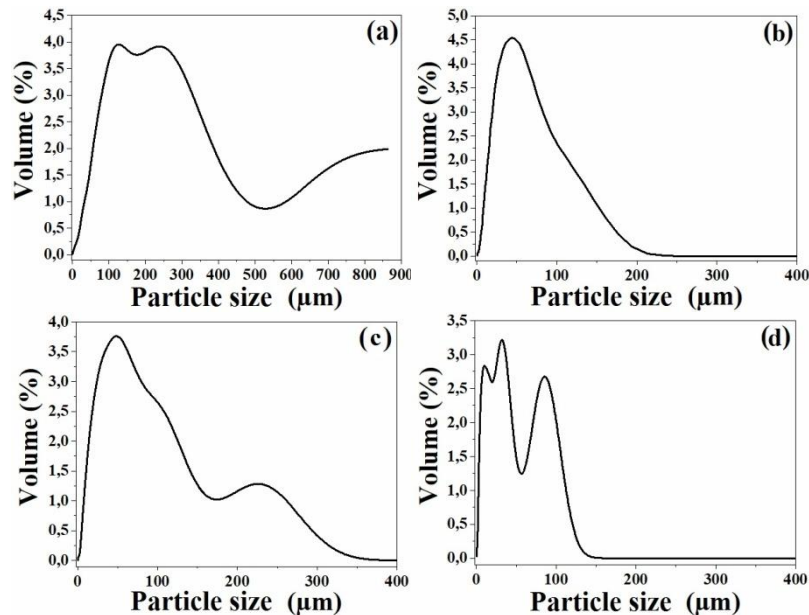

Fig.5: Laser particle size analysis of Fe-20Cr milled mixtures a) 1h, b) 6h, c) 10h and d) 50h

After one hour of milling, we notice the formation of agglomerates of different sizes of 200 and 800 µm. However, for 6 hours of milling, a large part of the powder mixture acquires an average size around 50 µm. After 50 hours of milling, it appears that the volume of fine particles becomes significantly larger and the particle size distribution interval is relatively reduced. This phenomenon is the result of a mechanism alternately associating a deformation/rupture process. This mechanism is observed in the case of ductile materials as reported in the literature [14].

3.1.2. XRD analysis

The milled mixtures are analyzed by X-ray diffraction in order to highlight the changes caused in the crystal structure of the mixture. The diffractograms in figure 6 show the formation of a solid solution of chromium in iron. Indeed, the zoom of the iron peak (110) (Fig.6b) highlights a gradual disappearance of the chromium diffraction peaks and a shift of the iron peak towards the small angles. It appears that this offset is all the greater the longer the milling time. This is explained by a dissolution of the Cr atoms in the iron lattice under the effect of the milling energy and consequently an increase in the lattice parameter of the iron. The evolution of the lattice parameter of the solid solution is shown in Fig.7, which in fact reveals a gradual increase in the parameter and a tendency to stabilize it over long milling times. In addition, there is a widening of the solid solution peak as a function of the milling time. This enlargement is a consequence of the simultaneous effects of microdeformations and the reduction in the crystallite size. It has been reported by several researchers that the duration of milling causes an increase in microstrains and a reduction in the crystallite size [14].
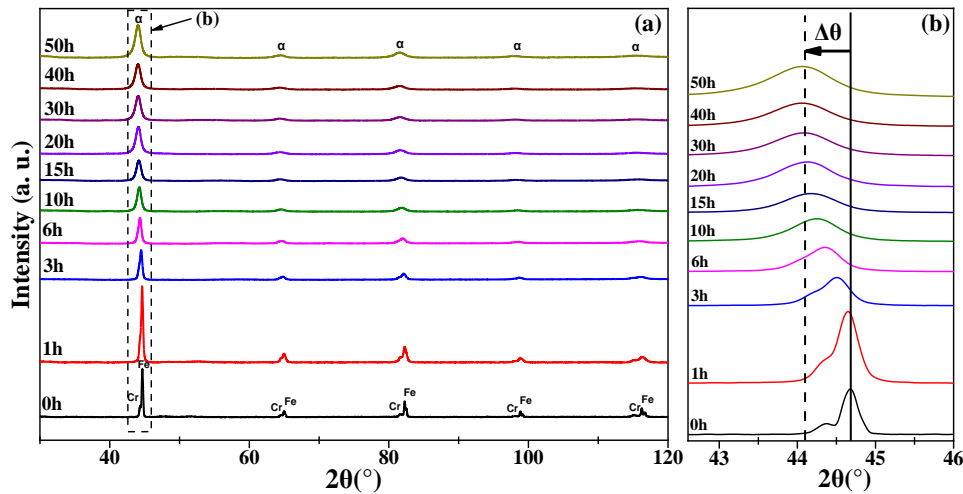

Fig.6: (a) XRD patterns of Fe-20Cr powder after different milling times and (b) displacement of the (1 1 0) iron peak.
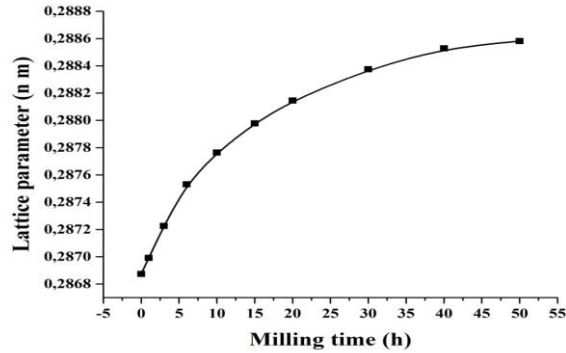
Fig.7: Lattice parameter of the solid solution in the crystallographic direction [1 1 0]

3.1.2.1. Deconvolution of the diffraction peak (110)

Fig. 8a shows the peak (110) of iron which includes the peak of the Cr appearing as a shoulder on the left. The deconvolution of the peaks indeed shows that it is a covering of the iron and Cr peaks. It appears that the shoulder disappears completely after 10 hours of milling (fig.8d).
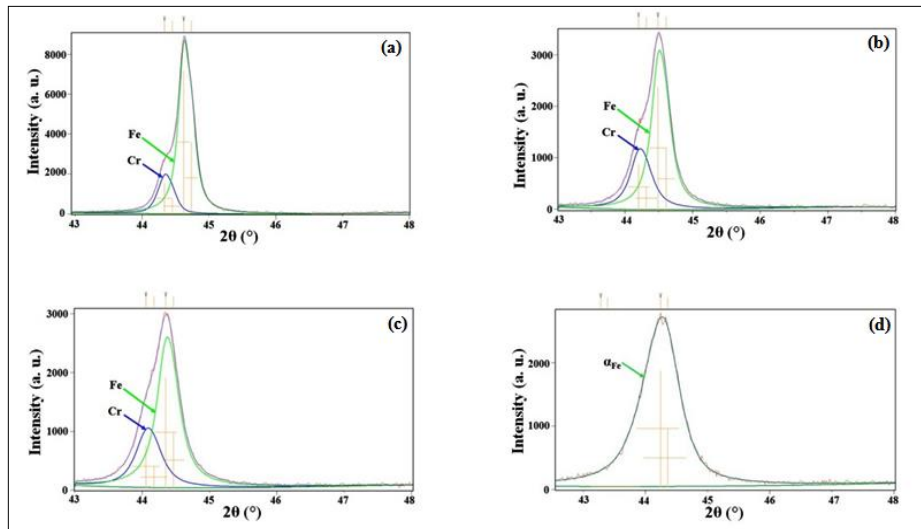

Fig.8: Diffraction peaks deconvolution

This confirms the dissolution of Cr in the iron lattice by forming a solid solution. As a result, a gradual increase in the lattice parameter of the solid solution was observed (Fig.7). This also results in an offset of the iron diffraction peak towards the small angles as shown in Fig.6b. A similar result has been reported in the literature [5].

In addition, an observation with SEM in backscattered electrons (Fig.9) shows a chemical contrast which decreases and disappears completely for 10 hours of milling. The micrographs show a clear zone rich in Cr and a dark zone less rich in this element. The dark area narrows with the milling time to disappear completely at 10 hours of milling. The micrograph in Fig.9d effectively shows a single phase representing the solid solution of Cr in iron.
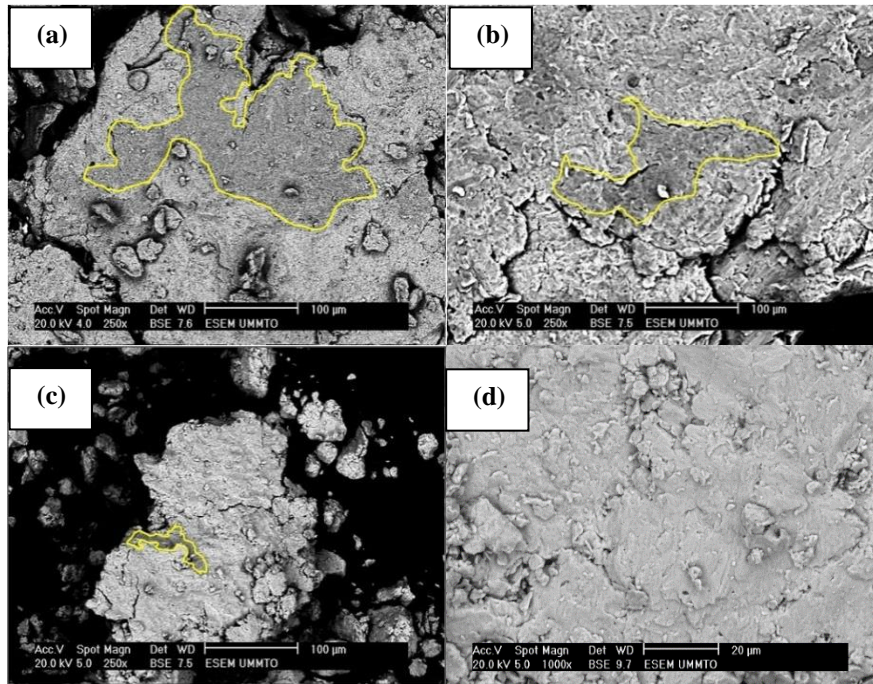

Fig.9: SEM micrographs in backscattered electron mode (BSE) of Fe20%Cr milled mixture, (a) 1h, (b) 3h, (c) 6h and (d) 10h

3.1.2.2. Crystallite size and microstrains calculation

Mechanical alloying also causes a change in the size of the crystallites and an induction of microstrains in the crystal lattice. The effect of these two phenomena results in a widening of the X-ray diffraction peaks. The measurement of the peak width made it possible to calculate the crystallite size and the microstrain rate using the Williamson-Hall method [12]. Fig.10 shows a reduction of the crystallite size with the milling time.
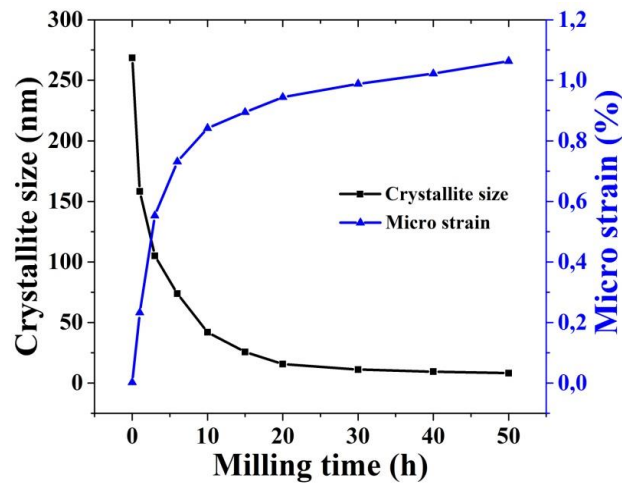
Fig.10: Evolution of the crystallite size and the rate of microstrains as
a function of the milling time

In fact, there is a sudden decrease of the crystallites size from the first hours of milling and after 20 hours a nanometric size is reached (20 nm) with a tendency to stabilize over long periods. On the other hand, an increase in microstrains is recorded as a function of the milling time. These results are in agreement with those reported in the literature on the milling of ductile products [15].

3.2. Influence of carbon on the mechanical milling of the Fe-20Cr-C mixture

The Fe-20% Cr-X% C mixtures (X = 1 or 2) were ground under the same conditions for 50 hours and are analyzed by X-ray diffraction. The results show that carbon reacts with iron and chromium under the effect of milling energy. In fact, the diffractograms in Fig.11 show the formation of Fe_3C and Cr_7C_3 carbide. The literature has reported several works having focused on the synthesis of carbides by mechanical alloying [16].
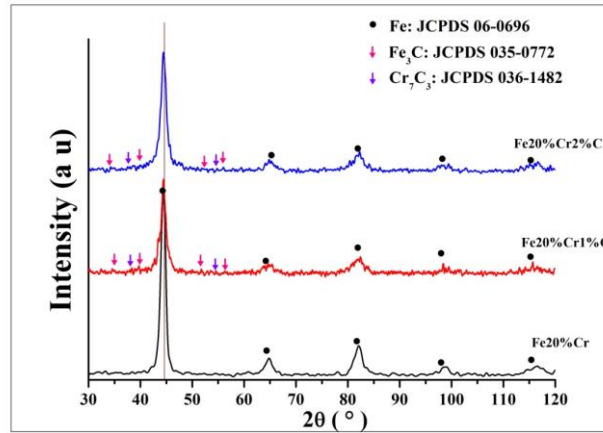
Fig.11: XRD patterns of 50h milled powders mixtures

3.3. Evolution of the nanostructure as a function of temperature

The mixtures ground for 50 hours are compacted and sintered at temperatures of 1100, 1200 and 1300 ° C. The sintered materials are analyzed by X-ray diffraction in order to reveal the new phases formed during sintering. The diffractograms are shown in Fig.11 and 12 for mixtures with and without the carbon addition.
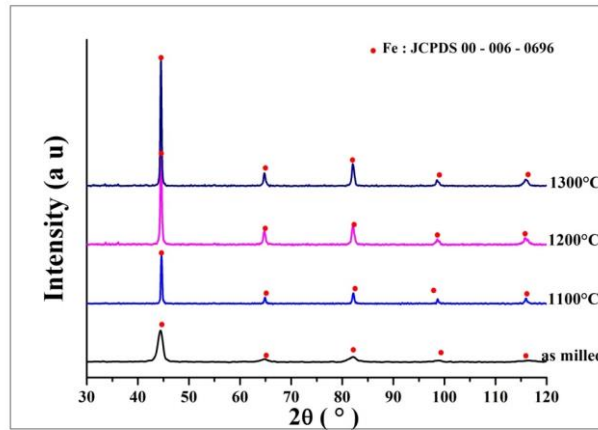

Fig.12: XRD patterns of Fe-20Cr powder after different annealing temperature: (a) as milled; (b) at 1100°C; (c) at 1200°C and (d) at 1300°C.
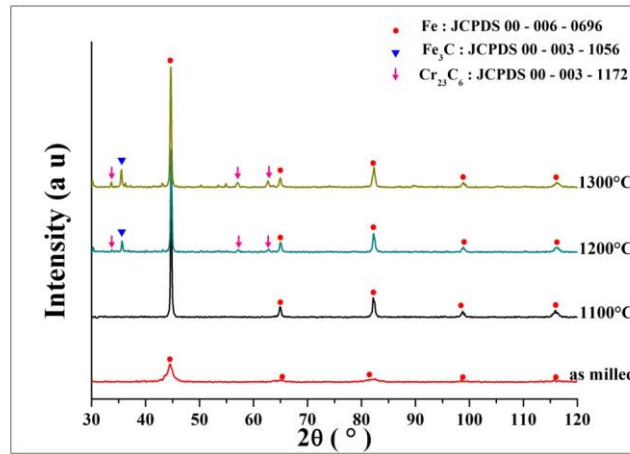
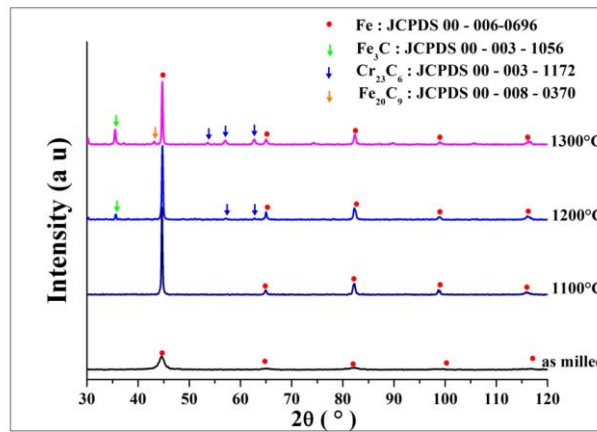Fig.13: XRD patterns of Fe-20Cr-1C mixture milled 50h and sintered

Fig.14: XRD patterns of Fe-20Cr-2C mixture milled 50h and sintered

The crystallite size was determined as a function of the sintering temperature for the different compositions from the widths of the diffraction peaks. The results are shown in Fig.15 which reveals an increase in the crystallite size for all the mixtures. However, it appears that the addition of carbon decreases the evolution of the crystallite size in temperature. The inhibition of this evolution is all the more accentuated as the sintered material contains more carbon.
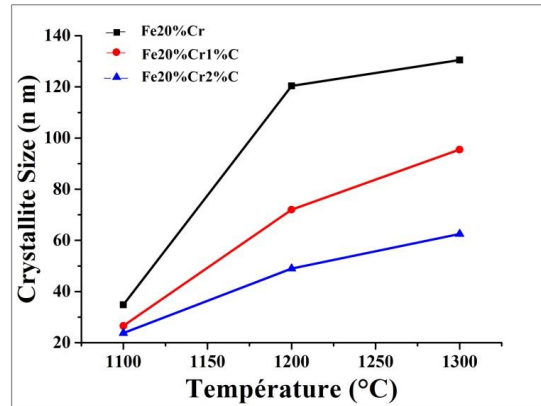
Fig.15: Influence of carbon and sintering temperature on the change in crystallite
size of sintered products

The figure shows that heating increases the crystallite size for all ground mixtures. The presence of carbon makes it possible to stabilize the nanostructure even at high temperatures. Indeed, the addition of carbon maintains the crystallite size at 90 and 60 nm respectively for mixtures which contain 1 and 2% C.

X-ray diffraction analysis identified iron and chromium carbides that formed during high energy mechanical alloying (Fe_3C and Cr_7C_3) and during sintering ($Cr_{23}C_6$). Similar results are reported in the literature [17, 18]

These carbides segregate at the grain boundaries and slow down the growth of the crystallite size. Thus these phases play the role of crystal growth inhibitors and stabilize the nanostructure. In addition, the high hardness of the carbides improves the resistance characteristics of the sintered material. The micrograph of Fig.16 shows, in fact, the carbides at the grain boundaries.
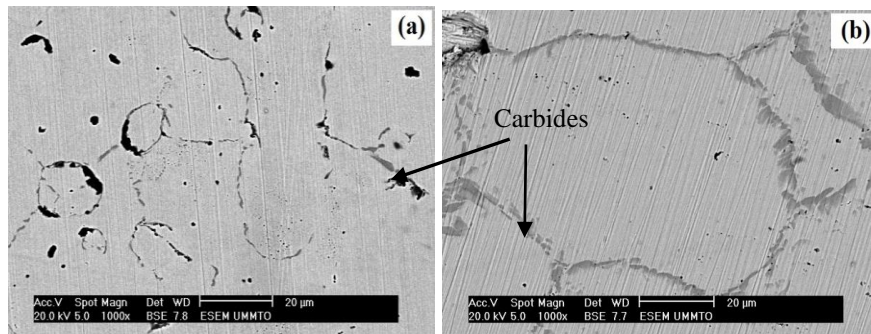

Fig.16: Micrographs of the sintered at 1200°C, (a) Fe20Cr1C, (b) Fe20Cr2C

4. Conclusions

The mechanosynthesis process made it possible to obtain nanostructured Fe-Cr powders by gradually reducing the crystallite size under the effect of high energy mechanical alloying. The reduction in crystallite size and the increase in

microstrains are related to the milling duration. The average crystallite size reaches 20 nm after 20 hours of milling and tends to stabilize at longer times. The rate of micro-deformations reaches nearly 1% after 50 hours of milling. The addition of 1 and 2% carbon to the Fe-Cr mixture allows an in situ reaction under the action of mechanical alloying which leads to the formation of Fe_3C and Cr_7C_3 type carbides identified by DRX. In addition, after high temperature sintering, $Cr_{23}C_6$ carbide is formed. The high temperature sintering of ground Fe-Cr mixtures leads to a loss of the nanostructured state due to grain enlargement. The crystallite size reaches nearly 130nm for sintering at 1300 ° C. The carbides formed in Fe-Cr-C mixtures segregate at grain boundaries limiting their magnification during heat treatment. The addition of carbon helps maintain the nanostructured state of the sintered material. The crystallite size is thus limited to 60 nm in the 2% carbon mixture sintered at 1300 ° C.

R E F E R E N C E S

[1]. *Huang B, Ishihara K. N, and Shingu P. H*, Metastable phases of Al–Fe system by mechanical alloying, *Mater Sci Eng A* **231** (1997) 72-79.

[2]. *Hoang-Viet Nguyen, Ji-Soon Kim, Young-Soon Kwon, and Jin-Chun Kim*, Amorphous Ti–Cu–Ni–Al alloys prepared by mechanical alloying, *J. Mater Sci* 44 (2009), 2700-2704.

[3]. *Suryanarayana C, and Al-Aqeeli Nasser*, Mechanically Alloyed nanocomposites, *Prog Mat Sci* **58** (2013) 383-502.

[4]. *Suryanarayana C.* Mechanical Alloying and Milling. Marcel Dekker, New York, NY 2004.

[5]. *D.L Zhang*, Processing of advanced materials using high-energy mechanical milling, Prog *Mat Sci* **49** (2004) 537-560.

[6].*Arami H, and Simchi A*, Reactive milling synthesis of nanocrystalline Al/Cu/Al_2O_3 nanocomposite, Mater Sci Eng A **464** (2007) 225-232.

[7]. *Nasser Al-Aqeeli, Kachalla Abdullahi, C. Suryanarayana, Tahar Laoui, and Saheb Nouari*, Structure of Mechanically Milled CNT-Reinforced Al-Alloy Nanocomposites, Materials and Manufacturing Processes **28** (2013) 984–990

[8]. *T. Mousavi, F. Karimzadeh and M. H. Abbasi*, Mechanochemical assisted synthesis of NiTi intermetallic based nanocomposite reinforced by Al_2O_3, J. Alloys Compd. **467** (2007) 173-178.

[9]. *Chul-Jin Choi,* Preparation of ultrafine TiC–Ni cermet powders by mechanical alloying, Journal of Materials Processing Technology **104** (2000) 127-132

[10]. *H. Gleiter*, Nanostructured materials: basic concept and microstructure, Acta. Mater., Vol. **48** (1) (2000) 1-29

[11]. *Oladotun P. Bolade, Akan B. Williams, Nsikak U. Benson*, Green synthesis of iron-based nanomaterials for environmental remediation: A review, Environmental Nanotechnology, Monitoring and Management (2019) 1-67

[12]. *Williamson GK, Hall WH*, X-ray line broadening from filed aluminium and wolfram, Acta Metall., **1** (1953) 22–31.

[13]. *Snyder R.L., Fiala J., Bunge H.J.*, Defect and microstructure analysis by diffraction, IUCr Monographs on Crystallography 10, Oxford Science Publications, 1999.

[14]. *E. Gaffet, G. Le Caër*, In Encyclopedia of nanoscience and nanotechnology Vol. 5, No. 129, (2004) 91-129

[15]. *F.Z. Bentayeb, S. Alleg, B. Bouzabata, J.M. Grenèche*, Study of alloying mechanisms of ball milled Fe–Cr and Fe–Cr–Co powders; Journal of Magnetism and Magnetic Materials, Vol. **288**, (2005) 282-296

[16]. *Paolo Matteazz, Gerard Le Caer*, Room-Temperature Mechanosynthesis of Carbides by Grinding of Elemental Powders, Journal of the American Ceramic Society - Vol. **74**, No. 6, 1382-1390 (1991)

[17]. *E. Ivanov, G. Golubkova*, Mechanical alloying of Cr-C mixtures and low temperature synthesis of chromium carbides, J. Alloys Compd. **190** (1992) L25–L26.

[18]. *H. Huang, P.G. McCormick*, Effect of milling conditions on the synthesis of chromium carbides by mechanical alloying, J. Alloys Compd. **256** (1997) 258–262.