

**PRODUCTION AND CHARACTERIZATION OF FE-C_{GRAPHITE}
AND FE-C_{FULLERENE} COMPOSITES PRODUCED BY DIFFERENT
MECHANICAL ALLOYING TECHNIQUES**

**PROIZVODNJA I KARAKTERIZACIJA KOMPOZITNIH
MATERIJALA, FE-C_{GRAFITA} I FE-C_{FULERENA} PROIZVEDENIH
RAZLIČITIM TEHNIKAMA MEHANIČKOG LEGIRANJA**

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ABSTRACT

Metallic powders of iron (Fe) and two allotropic phases of carbon (graphite and fullerene) were mixed and mechanically alloyed using a ball milling. The powders were consolidated in form of pills by means of a spark plasma sintering technique (SPS). Powders obtained by mechanical milling (MM) as well as the consolidated pills were characterized using XRD, SEM and TEM. The results of characterization show that fullerene withstands milling and very high homogeneity of the composites with nanometric graphite and fullerene particles dispersed in the metallic matrix. Nonetheless, the morphology of the MM powders present phase is different in all systems. The SPS process allows the Fe-C_{Fullerene} system to reach relatively high densification joined by some growth of the phases. Nevertheless the temperature, time and pressure utilized during the consolidation of the composites are not severe enough permitting the particles to preserve their nanometric size. The characterization indicates that the sintered samples consist of a metallic matrix (Fe) with a fine dispersion of Fe₃C in the case of Fe-C_{graphite}. In the case of Fe-C_{fullerene}, Fe and fullerene are found without the presence of carbides. The microhardness measurements show that the system Fe-C_{graphite} presents lower values.

Key words: Mechanical milling Mechanical alloying Fullerene, Graphite Composite materials Spark plasma sintering, Nanostructured materials Electron microscopy

ABSTRAKT

Metalni prah železa i dve alotropske faze ugljenika (grafit i fuleren) su mešane i mehanički legirane koristeći mlin sa kuglama. Oba praha su konsolidovana u obliku pilula koristeći spark plasma tehniku sinterovanja (SPS). Prahovi dobijeni mehaničkim mlevenjem (MM) kao i konsolidovane pilule su metalografski ispitivane uz pomoć XRD, SEM i TEM uređaja.

Rezultati metalografske karakterizacije pokazuju da je fuleren otporan na mlevenje. Takođe je primećena visoka homogenost kompozita sa nanometarskim grafitom i fulerenskim česticama raspoređenim u metalnoj osnovi, dok je morfologija prisutnih faza prahova dobijenih mehaničkim mlevenjem različita u svim posmatranim sistemima.

SPS proces omogućava Fe-C_{Fuleren} sistemu da postigne relativno visoku gustinu pomoću rasta pojedinih faza. Parametri procesa očvršćavanja kompozita kao što su temperature, pritisak nisu ekstremni dopuštajući česticama da zadrže njihovu nano veličinu. Istraživanje je pokazalo da se ispitivani uzorci sinterovanog materijala sastoje od metalne osnove (Fe) i fino dispergovanih Fe₃C čestica kada je u pitanju Fe-C_{grafit}. U slučaju sistema Fe-C_{fuleren}, Fe i Fuleren su nađeni bez prisustva karbida. Sistem Fe-C_{grafit} ima znatno nižu tvrdoću.

Ključne reči: mehaničko mlevenje, mehaničko legiranje, grafit, fuleren kompozit materijal, Spark plasma tehnika sinterovanja, elektronski mikroskop

INTRODUCTION

Since the discovery of fullerene, C₆₀, by Kroto *et.al.* and the macroscopic processing of C₆₀, C₇₀ and other fullerene molecules by Krätschmer *et.al.*² and their prediction as well as the production of carbon nano-tubes by Iijima *et.al.*³, (Figure 1) a great attention has been given to their characterization due to their paramount potential in diverse applications. Fullerenes have supreme properties, such as light weight, nanometric size, hollow core, and exceptional mechanical properties¹⁻⁸. Barrera *et. al.*⁴⁻⁵ have found great applications for fullerenes as reinforcement particles in structural applications.

The production of a composite metal-C_{Graphite} and metal-C_{Fullerene} by mechanical alloying (MA) has been the subject of some other investigations^{4-8, 11}. The main goal in all these researches has been to preserve the carbon after sintering and improve the mechanical properties of the sintered materials made from MM powders. The consolidation process usually leads to a transformation of a more stable phase such as graphite from the metastable fullerene that can occur during the milling process. In a similar manner, Tamari *et. al.*⁹ utilized the Spark plasma sintering (SPS) technique, which due to its processing conditions seems to be very promising in retaining nanocrystalline particles into the specimens. It is for this reason that this research was conducted using fullerene as a unique reinforcement to produce a composite with improved mechanical properties. Since the SPS technique offers a high densification of powders avoiding extreme conditions, the resultant composites can be post processed by thermomechanical treatments that can further produce hard particles such as diamond.

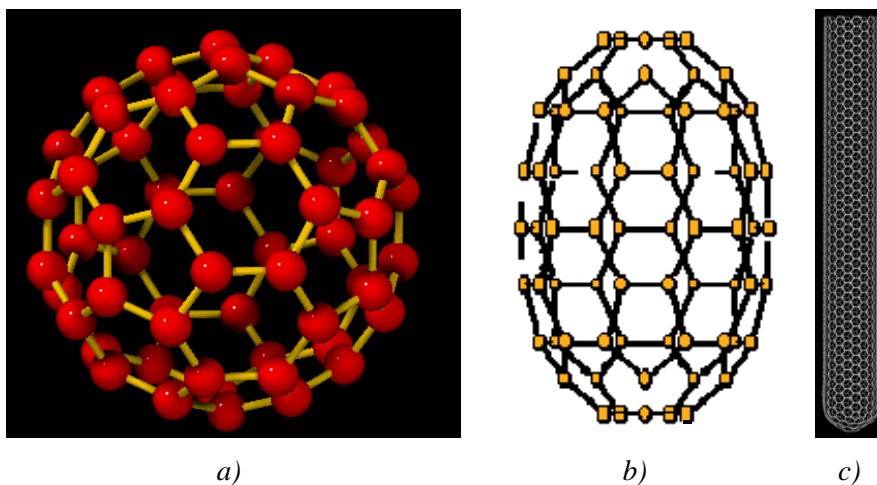


Figure 1 - Representative images of the characteristic molecules of fullerene¹⁻³
 a) C₆₀, b) C₇₀ and c) Bucky Tube

EXPERIMENTAL PROCEDURE

Powders of Iron (“Fe” 99.9% purity and a particle size <150 μ m), C (99.9% purity and a particle size <5 μ m) and (C₆₀ + C₇₀+ amorphous C) mixture were used for the mechanical alloying. The C₆₀ + C₇₀ + C mixture contains approximately 20% of fullerene (C₆₀+C₇₀). In this mixture there is ~77.5 at.%C₆₀ and ~22.5 at.%C₇₀. Mixtures for both composite systems were prepared using powders of graphite or fullerene (15at%C) and Fe powders.

The MM process was carried out in two different mills, one of low and one of high energy (horizontal and Spex respectively). Preliminary research indicates that similar microstructure characteristics (such as crystal size and dispersion of phases) can be achieved with either 2h of MM in Spex or 100h in horizontal mill¹¹. For that reason on this research MM were carried out using 2h on Spex or 100h in horizontal mill. A ball to powder weight ratio of 1:100 is used in all cases. Methanol is added in the Spex mill (as a control agent), while no control agent is added in the horizontal ball mill. The charge and discharge operations have been carried out under an inert atmosphere (argon). The resulting powders, from the horizontal mill, were sintered using an SPS apparatus at 773K, 100MPa of pressure for a period of 600s. The dimensions of the sintered samples are 13 mm in diameter by 2.5 mm in thickness. Figure 2 depicts a scheme of the SPS apparatus. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize all samples.

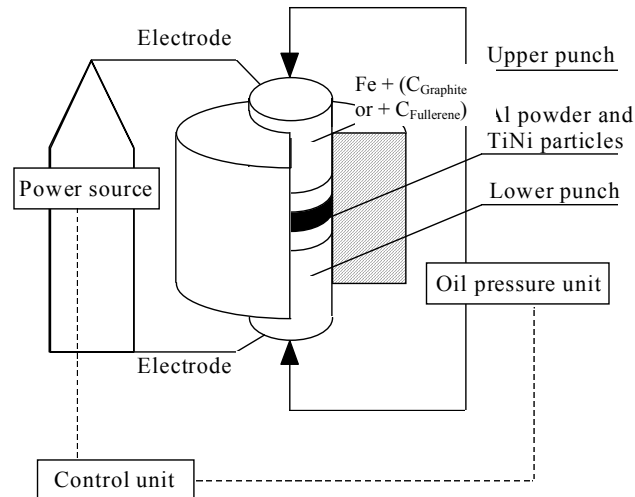


Figure 2 - Diagram of the SPS apparatus

RESULTS

Mechanically Alloyed Powders

Figure 3a and 3b depicts XRD patterns of pure fullerene before and after MM in Spex at different times. The XRD pattern of the fullerene before mechanical milling shows clearly all the peaks that correspond to such phase; however after 2h of milling the peaks start broadening. This indicates that some microstructural changes, such as refinement of the crystalline structure, are taking place. Nevertheless the FCC crystalline structure of the fullerene remains unchanged since the position of the peaks remains unaffected. Figure 3c shows a TEM dark field (DF) image with its corresponding diffraction pattern (DP) of as-milled fullerene. The comparison of the reflections of fullerene before and after MM does not indicate major changes in crystalline structure.

In contrast, pure graphite after 2h of MM in Spex shows an almost amorphous phase (Figure 4), and the reflections of this phase become weaker in intensity but broader.

SEM micrographs of the as-milled powders of three composites $\text{Fe-C}_{\text{graphite}}$ and $\text{Fe-C}_{\text{fullerene}}$ MM in different mills are depicted in Figure 5. The powders after MM of the three systems show significant differences in size and morphology, but their chemical composition, as measured by EDX, is highly homogeneous. The powders of the $\text{Fe-C}_{\text{Graphite}}$ system after MM in either mill are integrated by small particles ($\text{Diam.} < 10\mu\text{m}$) and large particles ($\text{Diam.} > 100\mu\text{m}$). However, their morphology is different; the “big” particles

from Spex have an irregular shape, and the ones obtained from the horizontal mill have a thin foil like shape. This difference is probably due to the control agent used in Spex, which promotes agglomeration. In the Fe-C_{Fullerene} system all particles are of similar size (<5µm), although some times they form clusters, which in some cases reach sizes between 40 and 50µm.

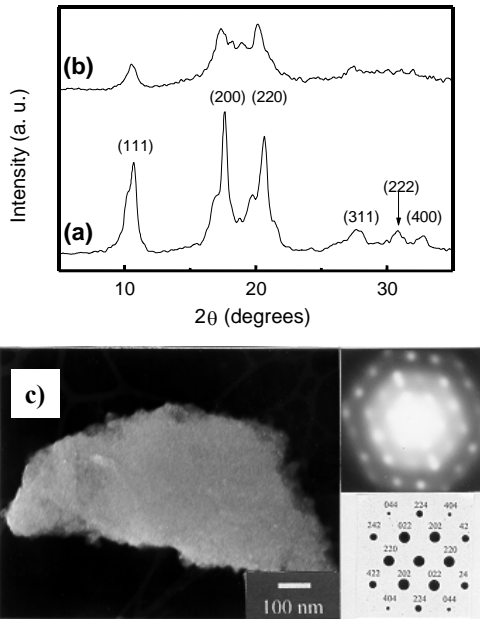


Figure 3- Characterization of pure fullerene using XRD a) before and b) after 2h of MM on Spex. c) TEM DF and DP of a fullerene particle after 2h of MM

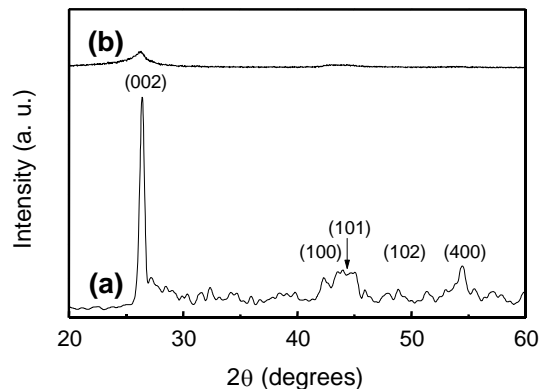


Figure 4 - XRD pattern of pure graphite a) before and b) after 2h of MM on Spex

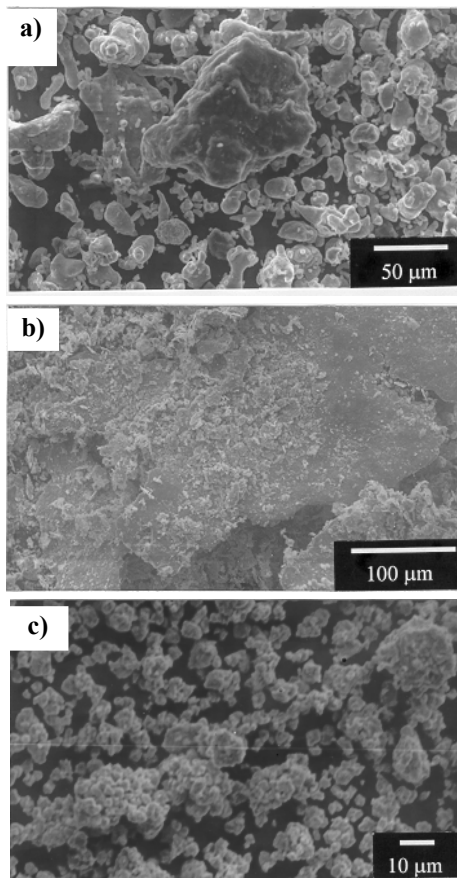


Figure 5 - SEM Micrographs at different magnifications of the MM systems after 2h in Spex of the a) Fe-C_{Graphite}, and 100h in in horizontal mill of the b) Fe-C_{Graphite} and c) Fe-C_{Fullerene} systems

The XRD patterns before and after MM of the Fe-C_{Graphite} system shown on Figure 6 depict that graphite becomes amorphous after 50h of milling. In the Fe-C_{Graphite} XRD pattern of the powders before milling the (002) plane of graphite and (110) and (211) of Fe can be identified. After 50h of MM (Figure 6b) the number of reflections for iron increased, but the graphite reflection disappeared.

The analysis of the TEM/DP confirms the presence of Fe, amorphous graphite, and fullerene. Figure 7 presents DF, DP, and indexation parameters for all the powders. In all cases the bright particles on the DF correspond to nanometric graphite or fullerene dispersed in the Fe matrix. The DF shows clearly the existence of nanometric grains as well as the presence of pure C_{Graphite}, C_{Fullerene}, and Fe.

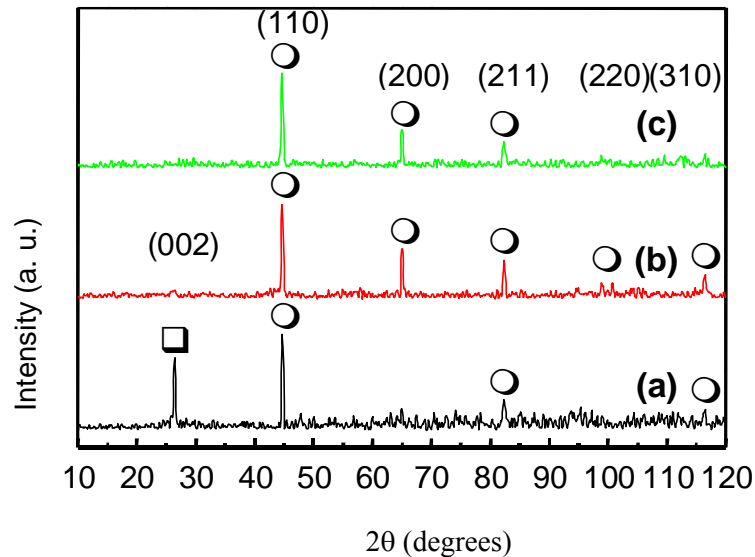
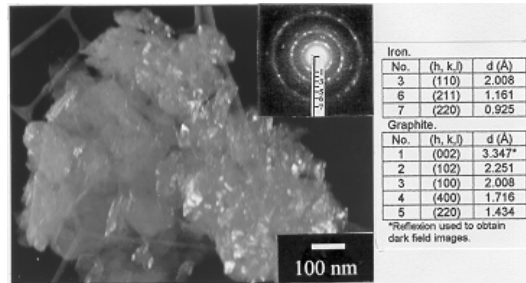


Figure 6 - XRD patterns of the Fe-C_{Graphite} MM in the horizontal mill
a) 0h, b) 50h and c) 100h

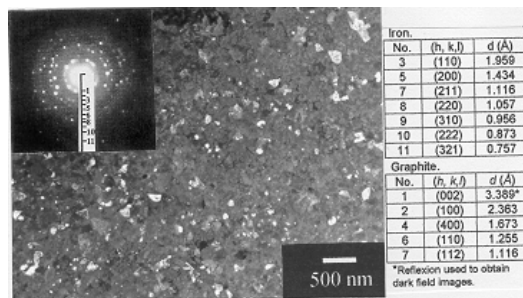
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CHARACTERIZATION OF THE SINTERED COMPOSITES USING THE SPS TECHNIQUE

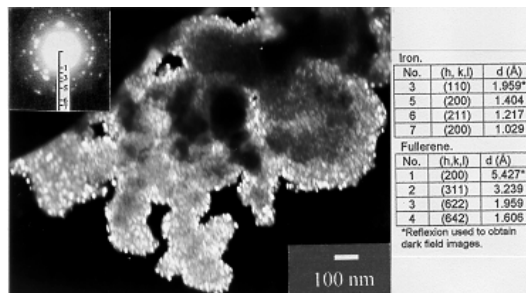
The sintering process was performed only for the MM systems using the horizontal mill. Figure 8 shows the respective XRD patterns after sintering of the Fe-C_{Graphite} (Figure 8a) and Fe-C_{Fullerene} (Figure 8b) systems. In Figure 8a, the reflections of Fe can be clearly observed, but not the ones for graphite. In contrast, the Fe-C_{Fullerene} system presents the (111) reflection of fullerene that, due to the sintering process, recrystallized. Furthermore, in both cases phases such as carbides, formed under SPS conditions, were identified.



a)



b)



c)

Figure 7 - TEM Micrographs of the MM systems after 2h in Spex
 a) Fe-C_{Graphite}, 100h in horizontal mill b) Fe-C_{Graphite} c) Fe-C_{Fullerene}

Table 1 - Vickers hardness of sintered samples

System	Vickers Microhardness, (μH_{100})
Fe- C _{Graphite}	722
Fe-C _{Fullerene}	690
Pure Fe	100

TEM micrographs (DF and bright field (BF)) and DP of the Fe-C_{Graphite} and Fe-C_{Fullerene} composites are presented in Figure 9. Contrary to the XRD results, TEM/DP of the Fe-C_{Graphite} system showed amorphous graphite, Fe₃C (Figures

9a and 9b) and pure Fe. The characterization of the Fe-C_{Fullerene} using TEM confirms the XRD results (identification of pure Fe and fullerene). Table 1 presents the results of microhardness of both composites. It can be observed that Fe-C_{Fullerene} composite is slightly harder (~4%) than the Fe-C_{Graphite} composite and both are ~7 times harder than pure Fe.

DISCUSSION

Milling of the fullerene does not produce alterations of its crystalline structure. The corresponding XRD (Figure 1) show some peak broadening that can be associated with a refinement of the grain size during milling. Because the fullerene phase stands the MM, the production of the composites Fe-C_{Fullerene} is possible by using this method. In agreement with this observation, the fullerene phase has been detected after milling. TEM observation shows that such powders have a nanometric grain size and two stable phases, Fe and fullerene. On the other hand, graphite cannot be detected by XRD (confirming the results shown on Figure 4). Nonetheless, TEM results present dispersed graphite, partially amorphous, in the FE metal matrix. Thus the combination of results from TEM and X-ray diffraction suggests that graphite is affected by mechanical alloying, making the production of Fe-C_{Graphite} composites more difficult. The absence of graphite peaks in the Fe base powders can also be due to fluorescence effects since Cu radiation was used for the X-ray diffraction experiments.

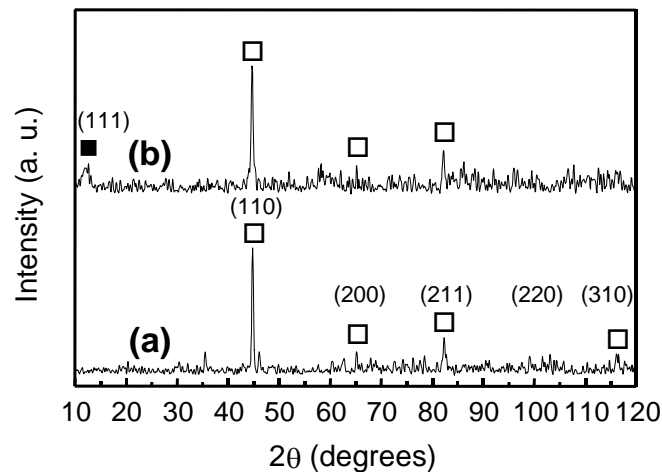
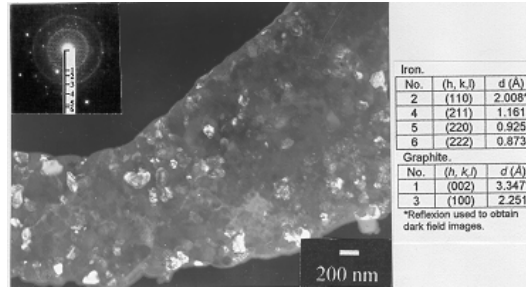
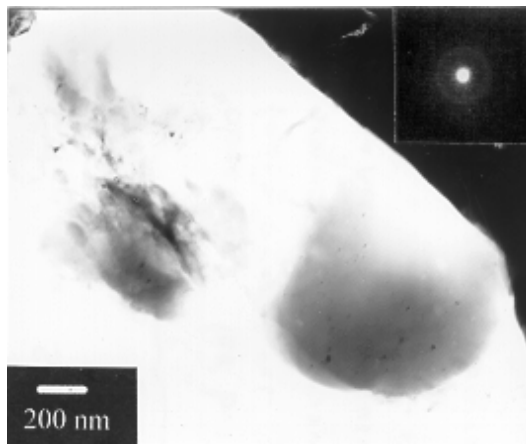


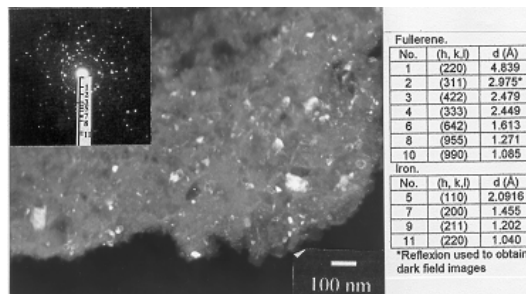
Figure 8 - XRD patterns of the composites after MM and sintering with the SPS for 600s at 773K and 100MPa. a) Fe-C_{Graphite} b) Fe-C_{Fullerene}



a)



b)



c)

Figure 9 - TEM/DF (a and c) and TEM/BF (b) micrographs with their respective DP of the Fe-C_{Graphite} (a and b) and Fe-C_{Fullerene} (c), systems.

The bright spots in micrographs a and c correspond to a) Fe
c) fullerene, figure b) BF of amorphous graphite

SEM micrographs of both Fe-C_{Graphite} and Fe-C_{Fullerene} systems milled in horizontal or Spex mills, follow the behaviour of ductile or malleable metallic materials in horizontal milling reported by Guerrero-Paz *at. al.*¹². This is a further indication that low and high energy milling media create similar results

but at different times. Also, the creation of highly homogeneous micrometric and nanometric particles after MM is possible. Thus densification (Sintering) using SPS technique further allows the production of substantially dense (~82% for the Fe-C_{Fullerene} system) materials, even at temperature, pressure and a short time.

The results of a previous research indicate that using similar MM and sintering techniques on Al-C_{Fullerene} and Al-C_{Graphite} systems creates Al₄C₃ in both systems. In this case it is important to notice that Al₄C₃ has a relatively low free energy of formation (-12.7 kcal at 298 K¹¹), which means that under the SPS conditions the formation of this phase is relatively easy. In contrast to the results presented in this research, the Al-C_{Fullerene} composite after sintering has a significantly higher hardness compared to the Al-C_{Graphite}¹¹.

The characteristics of the Fe base composites can also be explained on the basis of the distribution and nature of the added C phase and the influence of milling. In the case of Fe-C_{Graphite}, the solid composite has three phases, graphite, Fe and Fe₃C. Some of this graphite reacts with Fe to form the stable carbide. On the other hand, only the fullerene and Fe phases are identified in the final sintered sample in the system Fe-C_{Fullerene}, as shown in Figures 8 and 9. This result indicates a low reactivity between Fe and fullerene.

The previously discussed results show that the conditions selected for the SPS sintering of the composites produce promising results for post processing materials. Apparently, the selected temperature has been appropriate for the production of the Fe-C_{Fullerene} composite allowing the fullerene to recrystallize without reacting with Fe. Furthermore, the nanometric grain size obtained after MM is preserved after the sintering process, thus SPS technique prevents excessive grain growth.

CONCLUSIONS

1. Fullerene is stable upon mechanical milling for 2 hours in the high energy SPEX mill.
2. The as-milled powders show only the original components finely mixed. A nanocrystalline grain structure is formed in the powders during milling.
3. The sintered Fe-C_{Graphite} composite produce the Fe₃C phase.
4. A composite Fe-C_{Fullerene} can be produced.

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