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SYNTHESIS OF CARBON NANOSTRUCTURES BY THERMO-MECHANICAL MEANS

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ABSTRACT

Different C phases have been developed by mechanical milling, conventional heat treatments and Spark Plasma Sintering of C soot and transition metals (Fe or Ni). Transition metals are known to catalyze the development of different C phases. The energy input involved in such a processing method has been used to develop composite and ceramic materials made of transition metals and fullerenes and C soot. The as milled samples as well as the sintered composites show various dispersions of diamonds, fullerenes, carbon nanotubes, graphitic carbon, graphenes, among other nanostructures. Thus milling, heat treatment or sintering of quasi-amorphous carbon nanostructures with different transition metals under various conditions can be a simple route to synthesize the above mentioned phases in solid state. Results of electron (scanning and transmission) microscopy, Raman spectroscopy, XRD and nanohardness are presented and discussed accordingly.

INTRODUCTION

Discovered by Harry Kroto and Richard Smalley in 1985 by vaporizing graphite with a laser [1], the Fullerene containing 60 C atoms structured in a circular fashion has changed the idea of strengthening materials. Mechanical properties of fullerene and other carbon nanostructures (e.g. nanotubes) are up to three orders of magnitude higher than those observed in conventional materials. This is one of the centers of attention for materials scientist to develop the next generation of advanced materials (Harris, 1999). The synthesis of carbon nanostructures is usually conducted by evaporating carbon having a good control of their nucleation and growth [2]. This work looks into the idea of using soot and transforming it into other forms of carbon using a solid state approach by means of mechanical milling and sintering.

Cost effectiveness of the transformation was an important piece to this work. Mechanical milling was used to transform the purchased material into other carbon structures and even going further this worked looked at the as milled material after heat treatments were applied to some samples and other samples that were sintered. The in situ synthesized carbon structures include: multiwall carbon nanotubes, fullerene, diamonds and nano-onions [3-5]. Traces of Fe and Ni were used as a catalyst to synthesize the carbon nanostructures. The sintering as conducted by Spark plasma sintering that was reported previously to be efficient to promote phase changes [6]. Material characterization was performed using Raman spectroscopy, x-ray diffraction (XRD), and electron microscopy (scanning (SEM) and transmission (TEM) including high resolution (HRTEM)).

METHODS

Samples for the milling were prepared using commercially available Fullerene Soot purchased from SERES. Samples of 1 g of carbon and 1-50 wt% of Iron (Fe) or Nickel (Ni) were mixed and milled in a SPEX 8000 M mill using a 20:1ratio milling media to sample. The samples were milled from 0.5 to 50 h. The milled samples were heat treated in a conventional furnace in a protective atmosphere (He) or spark plasma sintering method (SPS). Raman was conducted on a Horiba/Xplora spectrometer equipped with a 638nm laser and 0.5μm spot size. XRD was carried on a Siemens D5000 apparatus operated at 30 kV and 40A, using *Cu-Kα* radiation with a wavelength (λ) of 0.15418 nm. The HRTEM was conducted on the TEAM-05 microscope with a resolution of 0.05nm. Additionally, a transmission electron microscope (TEM) with a resolution of 0.2nm was also used. Prior to TEM/HRTEM the samples were acid washed to remove metals.

RESULTS AND DISCUSSION

Raman spectroscopy shows the synthesis of graphene-like and graphitic carbon structures. Figure 1 shows the change taking place with the movement of the D band toward peaks in the area of 1335 cm^{-1} and toward 1580 cm^{-1} for the G band [7]. The Raman spectra (Fig. 1b) shows a well resolved D (1318 cm^{-1}), G (1578 cm^{-1}) and 2D (2660 cm^{-1}) bands that are characteristic of carbon structures such as graphitic (sp2) carbon (2D band). The D band peak shifts with increased milling time from 1318 cm^{-1} to 1326 cm^{-1} and to 1334 cm^{-1}. The red shift in the D band indicates the presence of sp3 bonds.

Figure 1a demonstrates that SPS and XRD has had an effect on the material with well defined D, G, and 2D peaks.

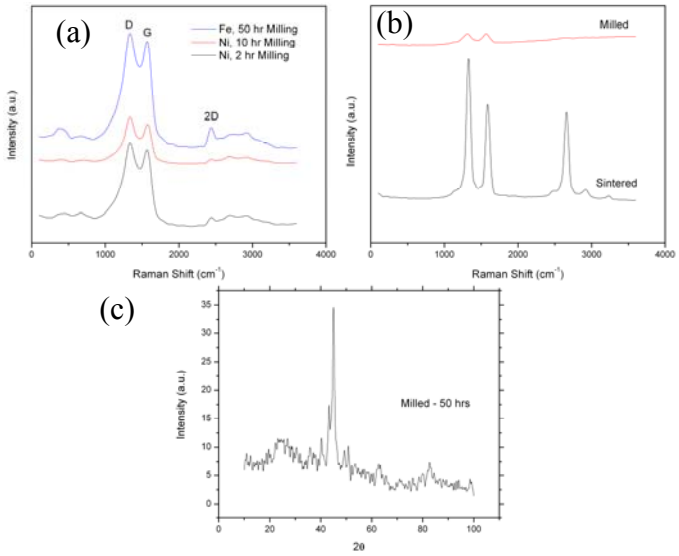

Figure 1 – Sample showing Raman before and after sintering (a) milled samples (b) Raman and (c) XRD.

Figure 2 shows HRTEM images of (a) graphene like particles, (b) diamond, (c) graphitic carbon, and (d) a carbon nanotube. All these particles were synthesized during milling (graphene-like and diamond), heat treatment (graphitic carbon) or spark plasma sintering (nanotube). These particles were synthesized from quasi-amorphous carbon by mechanical milling (Figs. A and b). After mechanical milling the milled powders were heat treated (Fig. 2c) in a conventional resistance furnace or treated by means of spark plasma sintering (Fig. 2d). The graphene-like particles can be clearly identified by the double-triple layer structure. A typical characteristic of diamond, under HRTEM, is the dumbbells that are clearly observed in Fig. 2b (arrow). The lattice parameter measured in the graphitic carbon is comparable to that of graphene and the higher magnification image clearly reveals the typical multi-layered structure.

CONCLUSION

This project showed that by using mechanical milling, carbon soot can be used to synthesize graphene, and diamond at room temperatures and graphitic carbon and carbon nanotubes at elevated temperature. Increasing milling time has showed to be an effective method to produce nanostructured diamond. The highly deformed graphene-like and graphitic carbon present in milled material can be transformed into more complex graphitic particles or carbon nanotubes depending of the heating method. The XRD, Raman and HRTEM results are in agreement and demonstrate the presence of the above-mentioned particles.

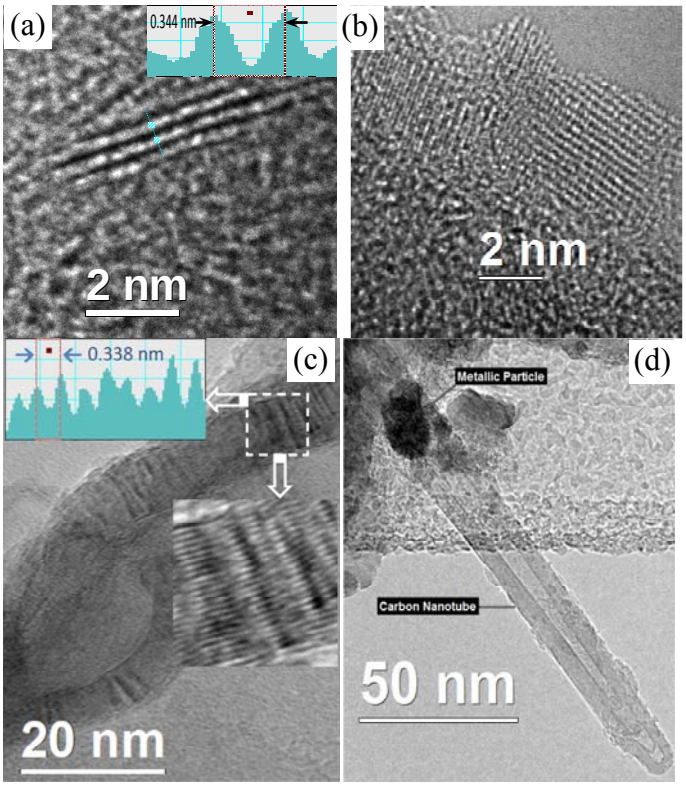

Figure 2 – mechanically milled samples (a-d) showing graphene-like particles (a), nanostructured diamond (b), graphitic carbon (c) and (d) nanotubes. (a-b) were milled and treated in resistance furnace (c) or SPS respectively.

REFERENCES

[1] P.J.F. Harris, Carbon nanotubes and related structures : new materials for the twenty-first century, New York : Cambridge University Press, Cambridge, UK ;, 1999.

[2] H. Kroto, H. Terrones, Interdiscipl Sci Rev, 25 (2000) 78-80.

[3] V. Garibay-Febles, H.A. Calderon, F.C. Robles-Hernadez, M. Umemoto, K. Masuyama, J.G. Cabanas-Moreno, Mater Manuf Process, 15 (2000) 547-567.

[4] I. Santana-García, F. Hernandez-Robles, V. Garibay-Febles, H. Calderon, Microsc Microanal, 10 (2010) 2.

[5] R.H.F.C. Santana I.I., Garibay Febles V. and Calderon H.A. , Solid State Phenom, 172-174 (2011) 727-732.

[6] J. Shen, F.M. Zhang, J.F. Sun, Y.Q. Sun, D.G. McCartney, Nanotechnology, 17 (2006) 2187-2191.

[7] E.F. Antunes, A.O. Lobo, E.J. Corat, V.J. Trava-Airoldi, A.A. Martin, C. Verissimo, Carbon, 44 (2006) 2202-2211.

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