SYNTHESIS OF NANOSTRUCTURES FROM CARBIDE SHEETS

L. Diaz Barriga Arceo*, V. M. Lopez Hirata *, V. Garibay Febles**, E. Orozco***, E. Palacios Gonzalez**
L. Bucio G.***, C. Reza Sn. German* and F. Leyte Guerrero**

* ESIQIE UPALM IPN, Apdo. Postal 118-395 C. P. 07051 D. F. México email: A luchell@yahoo.com ,

** Programa de 2Ingeniería Molecular, I. M. P, Lázaro Cárdenas 152, C. P. 07730 D .F . México, vgaribay@imp.mx,

*** Instituto de Física UNAM, Apdo. Postal 20-364 C.P. 01000 D.F. México

ABSTRACT

Mechanical Alloying was used to prepare both monometallic carbide and bimetallic carbides by milling of pure elemental powders of cobalt, molybdenum, titanium and carbon, and mixtures of Ni-Mo, with carbon, in a high-energy rotatory mill under an Ar atmosphere. The nanocrystalline carbides were used to produce metal filled nanotubes and nanoparticles, by means of precipitation after 15 minutes heating at 800°C. Microstructural characterization of the as-milled and heat-treated powders was performed using both Scanning (SEM) and Transmission Electron Microscopy (TEM) techniques. Milled powders presented flake-like shapes. In heat treated powders, filled, decorated and intercalated nanotubes, carbide nanorods and nanoparticles were observed. Nanotubes appeared mainly in bimetallic samples and nanorods in monometallic carbides.

Keywords: Nanotubes, nanoparticles, nanostructures, nanorods, mechanical alloying

1 INTRODUCTION

Conventional transition metal carbides are well known by their stability at high temperatures; their hardness; they have a low chemical reactivity and maintain corrosion resistance at high temperatures. However, transition metal carbides produced by conventional methods usually do not have high catalytic activity since they do not have high surface specific areas, but this problem can be solved when carbide is nanostructured **[1]**.

New catalysts and advanced materials comprised of carbides, oxycarbides of molybdenum and other transition metal or metal oxide formed by (or reinforced with) nanoparticles, nanotubes or nanorods, are expected to have catalytic properties analogous to platinum group metals, i.e.: high surface area, thermal stability, chemical purity, and macroporosity without micropores; like ceramics, this group of materials have unique physical properties such as good thermal and electrical conductivities and ultra-hardness. The improved performance could reduce considerably energy consumption and associated emissions of pollutants from chemical processes.

Molybdenum based carbides are representative of transition metals carbides with those attractive chemical and physical properties. α-Mo_2C, is a good example of these advanced materials having stable crystalline orthorhombic structure (also reported as a slightly distorted hexagonal closest packed structure) and their good chemical performance. The main goal is to produce carbides and oxicarbides at low cost in a simple process, at low temperatures, with fewer chemical reactions **[2]**. A challenging part of this process is to produce a carbide composite matrix **[1]** reinforced with nanoparticles, nanofibers and nanotubes using a simple metallurgical method instead of conventional ones **[3].**

In recent years, mechanical alloying has proved to be a very reliable method to produce nanostructured supersaturated solid solutions using the combination of several chemical elements. This is an easy way to produce nanostructured material, and some carbides have been produced before by this method **[4]**.

It was also found that carbides are formed during the catalytic production of metal filled nanotubes, so in this work, the possibility of using nanostructured carbides to produce metal filled nanotubes and other nanostructures is presented. In previous works we could successfully produce nanoparticles nanofibers and nanotubes **[5]** in heat treated cobalt carbide in a range of 800°C to 1000°C in argon atmosphere, during periods of time similar to those used in catalytic methods.

The purpose of the present work is to illustrate the formation of nanotubes, nanofibers and nanoparticles and intercalation compounds in carbide sheets produced by mechanosynthesis and heat treatment in short periods of time .

2 EXPERIMENTAL PROCEDURE

Milling of C and metal (Co, Ni, Mo Ti) elemental powders was carried out in a Fritsch Pulverissette Analyssette Laborette (Type D.6102 No.1861) high energy mill for 25 hours under argon atmosphere. Two balls sizes were used during milling, half of them having 1/4 inch diameters, and the rest 1/8 inch diameter. The balls/ powder weight ratio was 20:1. Both the balls and milling container were made of stainless steel. The milled powders were heat treated in argon atmosphere at 800°C for 15 minutes After this, the sample was cooled down at a rate of 0.03°C $-s^{-1}$.

Powder samples were characterized by X-Ray diffraction in a Siemens D-500 difractometer using Cu Kα

(λ=1.54 Å). The samples were observed with two instruments, a Scanning Electron Microscope (SEM) SEM /FIB NOVA 200 with point resolution of 1.7 Å and a High Resolution Transmission Electron Microscope (JEOL JEM 2200) with point resolution of 1.8 Å

3 RESULTS AND DISCUSSION

Molybdenum Carbide

Figure 1 shows X-Ray Diffraction patterns (XRD) of milled and heat treated powders where:

A) A single phase was found after 25 hours of milling, molybdenum carbide: αMo_2C with hexagonal structure and lattice parameters a = 4.012 Å and c= 4.74 Å. **B)** After heat treatment, the carbide phase is preserved; however, several diffraction peaks observed in heat treated carbide were not present in the corresponding carbide pattern obtained by milling. The difference between the carbide diffraction patterns can be attributed to nanostructure alteration during heating; because after heat treatment, crystal sizes are larger than those of milled sample so it is possible to improve the resolution of this technique **[6].**

This carbide is also reported as an orthorhombic structure because the (0001) surface in the hexagonal system is equivalent to the (001) surface in the orthorhombic system. A discussion about the similarity of both structures could be found in reference **[1].**

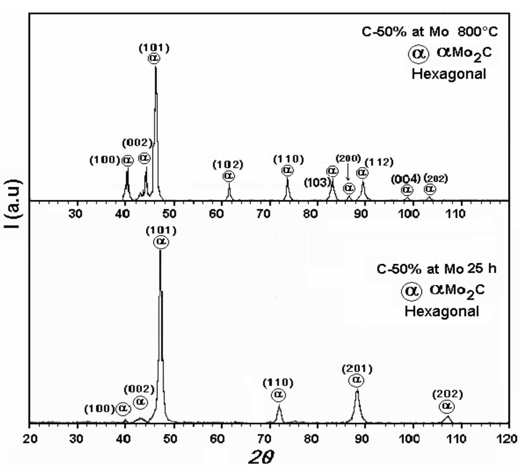
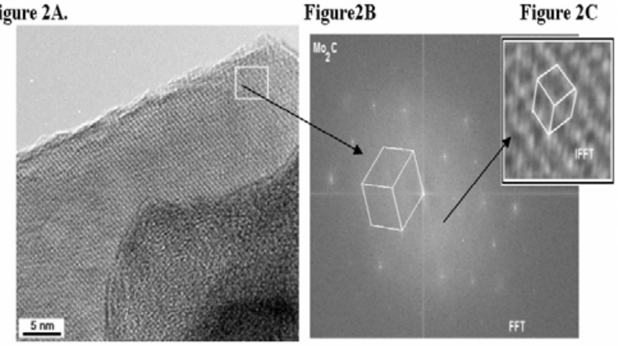


Figure 1 Mo_2C

Molybdenum carbide milled powders observed in bright field HRTEM are presented in micrograph of **Figure 2A**. Here, carbide stacked foils are presented. In **Figure 2B** the corresponding electron diffraction pattern, simulated by Fast Fourier Transform (FFT) using the Digital Micrograph Program, shows a slightly distorted hexagonal structure in reciprocal space corresponding to (0001) αMo2C carbide **[1]**. Lattice parameters measured, are a = 3.982 Å and c= 4.73 Å, in good agreement with X-Ray diffraction results. Inverse FFT is observed in **Figure 2C** showing the equivalent orthorhombic unit cell in real space.

Figure 2 Mo_2C sheets

Figure 2A. Figure2B Figure 2C



The bright field micrograph of heat treated powders is shown in **Figure 3**; here, it is possible to observe that several agglomerated nanoparticles with close to spherical shape along with other irregular shapes were formed. Nanoparticles radii are in a range of 10 to 70 nanometers. Some hexagonal nanocrystals are present too. In **Figure 3A** a carbide nanoparticle is shown with 25 nm in diameter. The geometric figure drawn in the nanoparticle has an equivalent size of four carbide cells.

Figure 3 Figure 3A

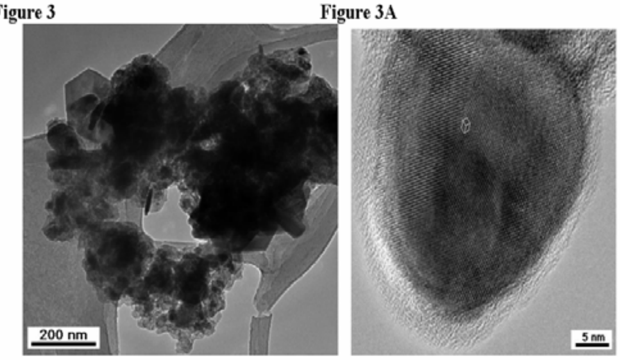
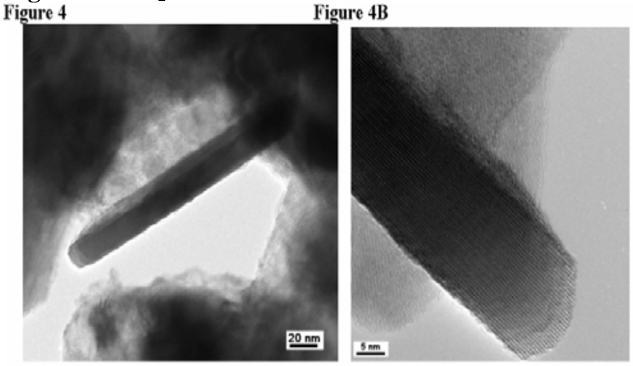


Figure 4 shows a bright field electron micrograph of a thin wall metal-filled nanotube opened at the top. **Figure 4B** shows another nanotube of this kind in more detail. Because the regularity of its surface it is assumed that nanotube is not broken and consists of several scrolled sheets.

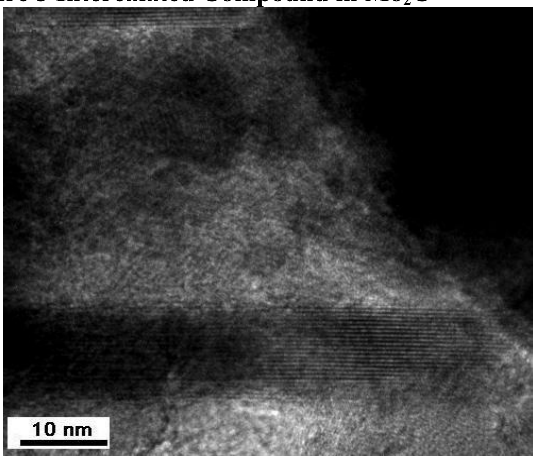
Figure 4. Mo_2C Nanotubes

Figure 4 Figure 4B



Several nanorods are formed with diameters of 50 nm and 0.3 μm of diameter and length respectively. An intercalation compound (**Figure 5**) is also formed in the sample.

Figure 5 Intercalated Compound in Mo_2C

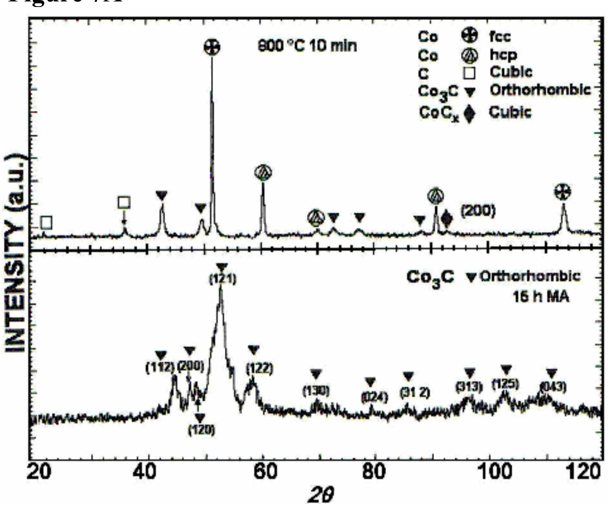


In previous results, we observed that by heating and freezing of milled α Mo_2C it is possible to obtain one-dimensional nanostructures. We believe this behavior could be similar to that one of eutectics production **[7-8]**. Previous works have reported that lamellar eutectic is not the only structure produced by this kind of solidification but rod-like structures are present too.

Cobalt carbide

Carbon and cobalt were milled together for 20 hours, to produce a nanostructured carbide with orthorombic structure found by XRD (**Figure 7 A)** and it can be observed in **Figure 8A** by HRTEM. It was found that its chemical composition was **Co_3C.** Lattice parameters were **a= 4.064 Å b= 4.993 Å and c= 6.707 Å**.

Figure 7A



After heat treatment some multiwalled nanotubes and nanorods were observed. Measured nanotubes diameters have values between 60 and 600 nm, and their lengths between 0.4 and 0.7 μm.

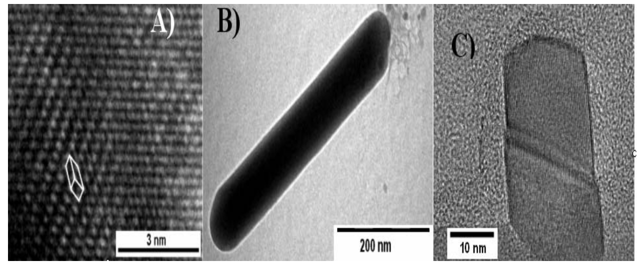
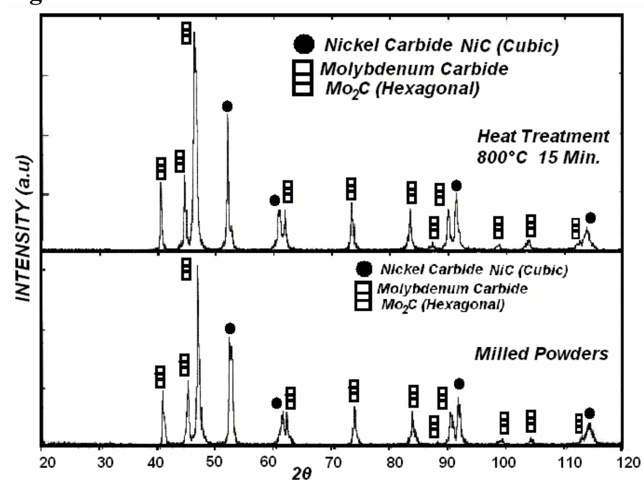


Figure 8. A) Orthorhombic Co_3C. B) Cobalt filled nanorod C) Coaxial Nanotube Growth

Nickel-Molybdenum-Titanium Carbide

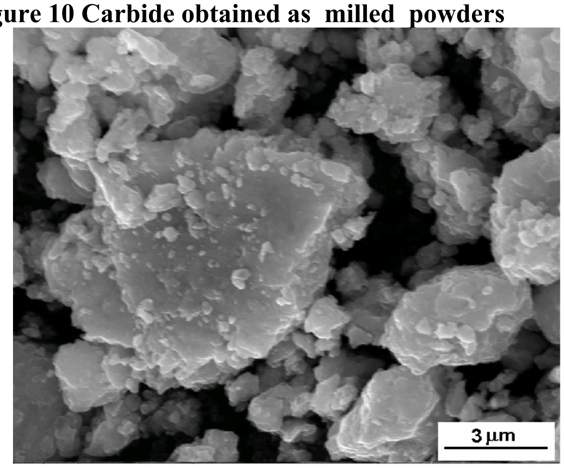
Figure 9 shows X-ray diffaction results of C-22%at Ni-25 %atMo-3%at Ti. We found two phases in the bimetallic carbide: a cubic NiC carbide and an hexagonal Mo_2C, however we did not observe Ti, even after heat treatment at 800°C, possibly because of Ti atomic percent.

Figure 9



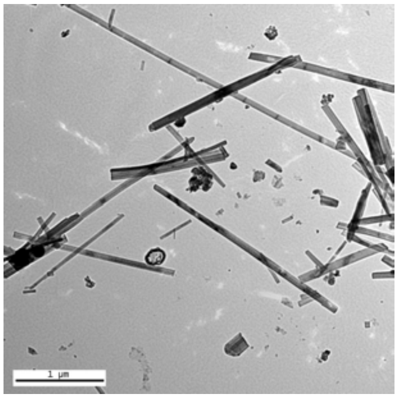
In **Figure 10** C-22%at Ni-25%atMo-3%at Ti milled powders are observed by SEM. They presented laminar structure and diameters in a range of 0.5 to 10 μm.

Figure 10 Carbide obtained as milled powders



Several metal filled nanotubes were observed in HRTEM bright field mode **(Figure 11)** in a Tecnai microscope. The diameters of such nanostructures vary from 20 to 60 nm and the lengths from 700nm to more than 2.5 µm.

Figure 10 Nanotubes from bimetallic carbide



In **Figure 10** it is easy to observe the nanotubes, some filled, others not completely filled, and others are broken, a ring structure and nanoparticles appeared too. Mappings obtained from one tube in **Figures 11a, 11b** and **11c** show that titanium and oxygen were present in several parts of the tube, mainly at the center and between the walls of nanotubes.

Figure 11a

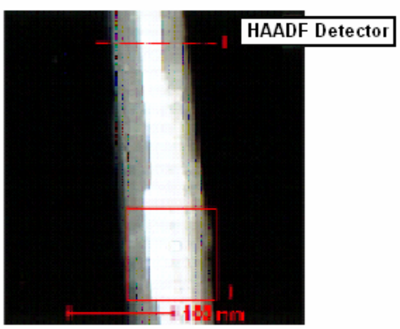


Figure 11b

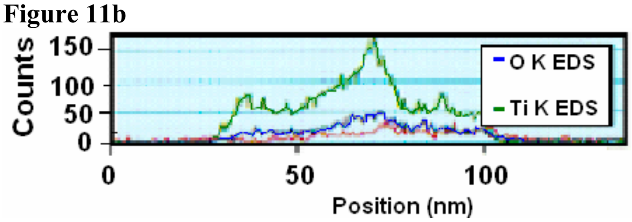
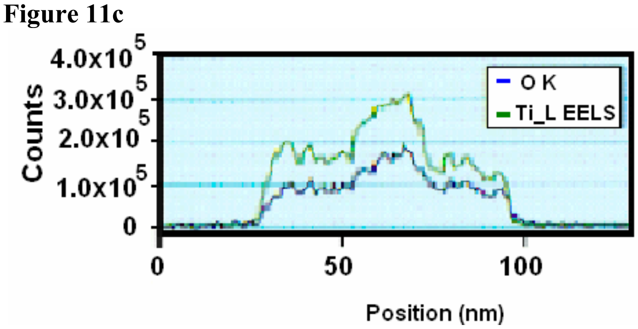


Figure 11c



The presence of such elements indicates that nanotubes are filled with TiO2. Titanium oxidation could appear because the chemical activity of nanostructures increase when crystal size decrease.

We present a summary of results in Table 1, which includes some of the main characteristics of nanotubes obtained by our method.

Table 1

Sample	Structure	Nanotube diameter (nm)	Length (µm)	Temperature / Time
Co_3C	Ortho rhombic	60 - 500	0.4 - 0.7	800°C / 15 min
Ti in C-NiMo	Cubic and Hexagonal	40 - 70	0.5 - 5	800°C / 15 min

From this table it is easy to conclude that in bimetallic carbides larger nanotubes were formed, possibly because they have larger diameter sheets. Impurities in bimetallic carbides tend to fill nanotubes cavities.

CONCLUSIONS

Metastable and nanocrystalline carbides were prepared by mechanical alloying with mixtures of C and Mo, Ni-Mo and Ti powders, after milling, in all cases, the powders presented single-phase lamellar structures.

During heat treatments of milled powders a small fraction of filled nanotubes, nanorods and carbide-opened nanotubes grew, their morphology was straight and similar to that obtained by catalytic methods. Nanoparticles, nanocrystals and intercalated metal-carbon sheets were obtained in all the carbides.

Carbide nanotubes are not transparent to electron beam so it was possible to observe nanotubes formed by several scrolled sheets, and coaxial nanotube growth.

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