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Nanostructures obtained from a mechanically alloyed and heat treated molybdenum carbide

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Abstract

Mechanical alloying was used to prepare molybdenum carbide. Microstructural characterization of samples was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. Molybdenum carbide was heated at 800 °C for 15 min in order to produce carbon nanotubes. Nanoparticles of about 50–140 nm in diameter and nanotubes with diameters of about 70–260 nm and 0.18–0.3 μm in length were obtained after heating at 800 °C, by means of this process.

Keywords: Mechanical alloying; Nanotubes; Nanoparticles; Carbides

1. Introduction

A new family of selective nanostructured catalysts is being developed through the entire world every day, to improve the efficiency of a variety of important chemical reactions. Many chemical reactions require extreme conditions, like high temperatures, pressures, etc., and catalysts must be highly selective in such conditions. The new catalysts must also operate at lower temperature and increase their efficiency during reactions without having an active participation in them other than being selective.

Transition metal carbides are well known by their stability at high temperatures and their hardness; they also have 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 large specific areas [1], though this problem can be solved when carbide is nanostructured.

New catalysts 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 those of the platinum metals group: large surface area, thermal stability, chemical purity and macroporosity without micropores. The improved performance could considerably reduce energy consumption and associated emissions of pollutants derived from chemical processes.

The principal problem is to produce them at both low cost and low temperature in a simple process with fewer chemical reactions [2,3]. A challenging part of the problem is to produce a carbide composite matrix reinforced with nanoparticles, nanofibers and nanotubes using simple metallurgical methods [4].

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 a simple technique to produce nanostructured materials; some carbides have been produced in the past by this method [5], including molybdenum carbide.

It was found in the literature that carbides are formed during the production of metal filled nanotubes, therefore, it was decided to study the possibility of employing nanostructured carbides to produce metal filled nanotubes, using successfully cobalt and titanium carbides heat treated in a range of

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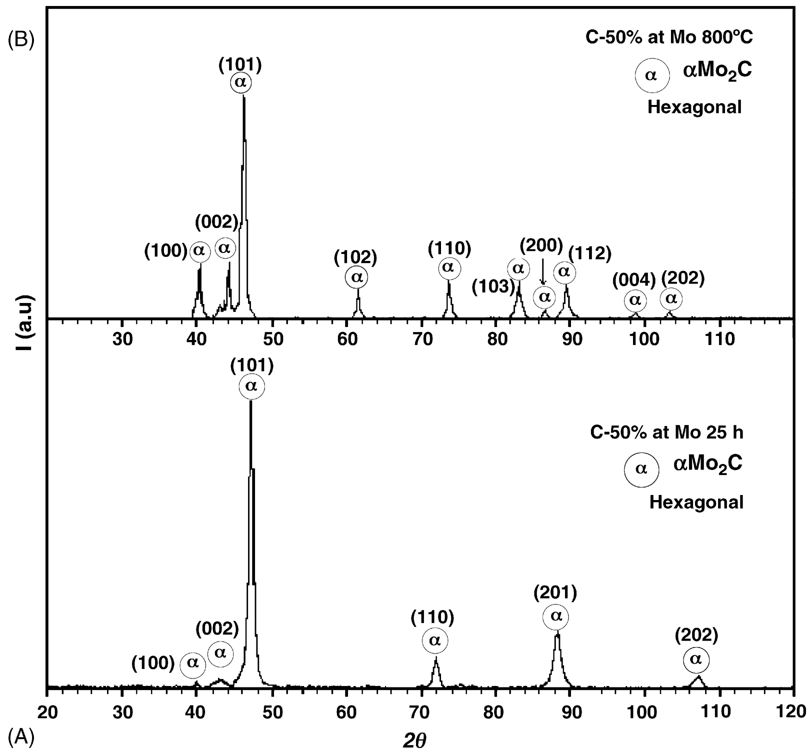

Fig. 1. X-ray diffraction patterns of: (A) milled and (B) heat treated powders. Molybdenum carbide was formed by this process and the phase is preserved even under heat treatment.

800–1000 °C in argon atmosphere, during short periods of time similar to those used in catalytic methods [4].

The purpose of the present work is to study the formation of nanostructures (nanotubes, nanofibers and nanoparticles) in molybdenum carbide produced by mechanosynthesis and heat treatment in short periods of time and to prove that this is a competent method to produce nanostructures from a solid solution.

2. Experimental procedure

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

Powder samples were characterized by X-ray diffraction (XRD) in a Siemens D-500 difractometer using Cu Kα (λ = 1.54 Å), then they were observed with two instruments, a scanning electron microscope (SEM)/FIB NOVA 200 with point resolution of 1.1 nm and a transmission electron microscope (TEM) Tecnai T20 with point resolution of 1.8 Å.

3. Results and discussion

3.1. X-ray diffraction patterns

Fig. 1 shows X-ray diffraction patterns of milled and heat treated powders where the following observations can be drawn:

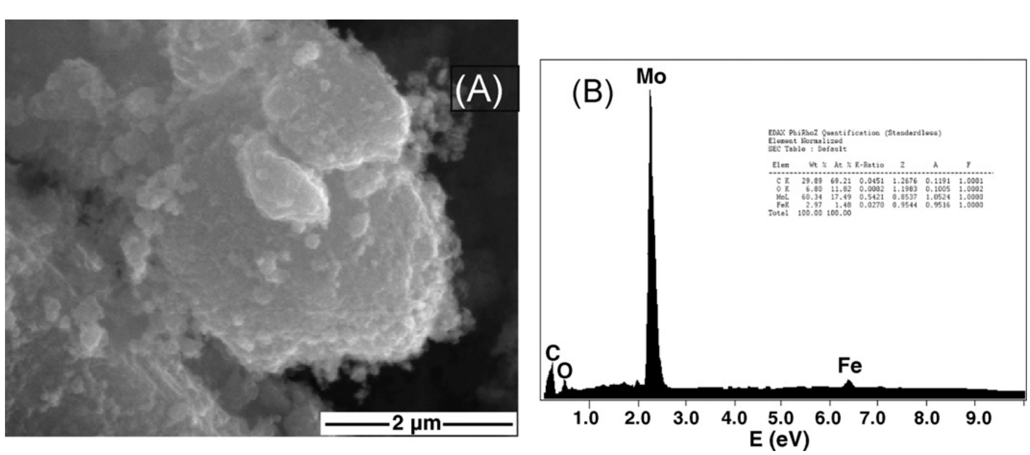

Fig. 2. (A) Scanning electron micrograph of as milled powders. The main part of particles presented have a flake-like form. (B) EDX analysis revealed the presence of both oxygen and iron in the sample, besides carbon and molybdenum.

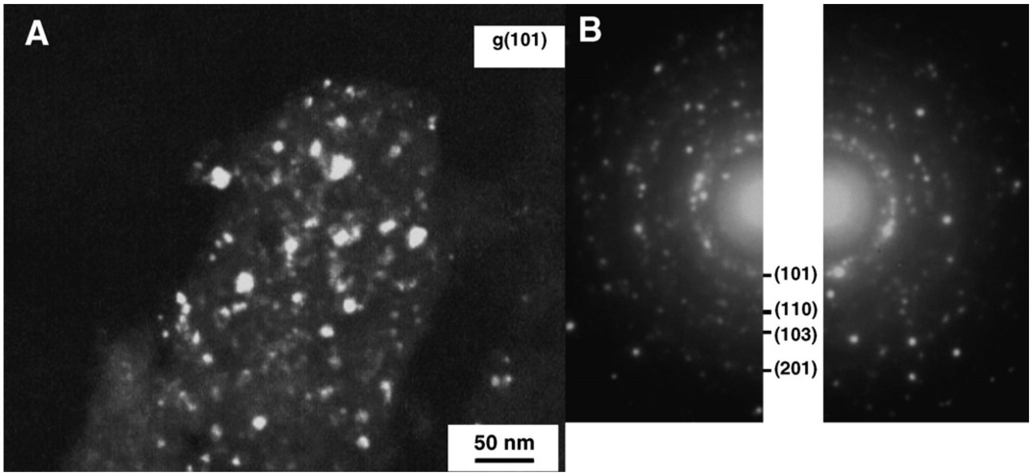

Fig. 3. (A) Molybdenum carbide: αMo_2C dark field image and (B) after 25 h this hexagonal polycrystalline phase was observed by electron diffraction.

(A) Only one phase was found after 25 h of milling, molybdenum carbide: αMo_2C having hexagonal structure and lattice parameters $a = 4.012$ Å and $c = 4.74$ Å.

(B) Carbide phase is preserved after heat treatment; however, several diffraction peaks previously observed in heat treated carbide were not present in the corresponding carbide pattern obtained by milling. The difference between the carbide diffraction patterns is 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. This fact is demonstrated by the increment in the broadening of X-ray diffraction peaks, as it can be appreciated in (1 0 1) and (2 0 2). This broadening has an inverse relationship to the crystallite size according to Scherrer equation [6].

3.2. SEM results

The uniform shape of powders, observed with this technique evidenced the formation of a single phase (Fig. 2(A)), also most particles are in a flake-like form. EDX spectrum presented in Fig. 2(B) revealed the presence of both oxygen and iron in the sample besides carbon and molybdenum. It is possible

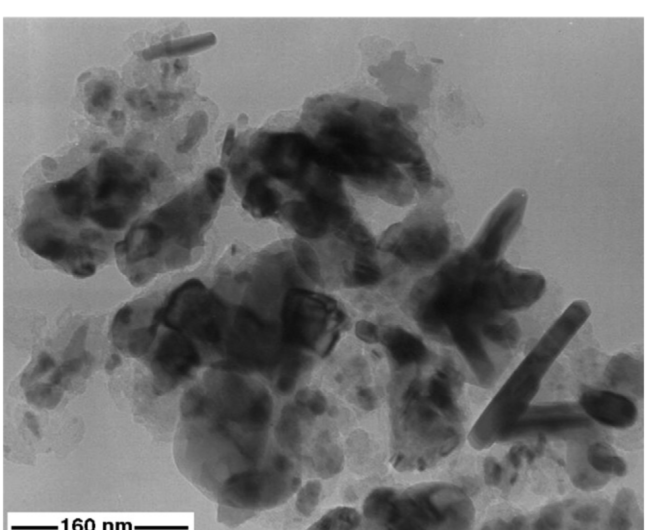

Fig. 4. The bright field micrograph of heat treated powders. Nanoparticles and nanotubes were formed.

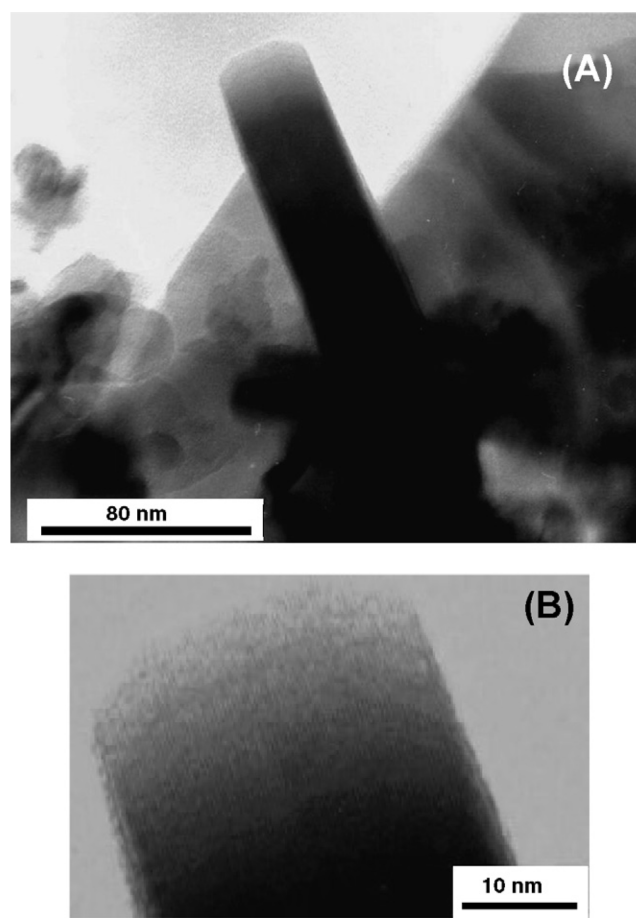

Fig. 5. (A) Quiral multiwall nanotube (B) opened at the top.

that a small amount of iron carbide, and some oxicarbide were formed during the mechanosynthesis, but these phases were not observed by XRD, possibly because only a very small amount was formed.

3.3. TEM results

Molybdenum carbide milled powders observed in dark field TEM are presented in the micrograph of Fig. 3(A); here, a particle containing nanocrystals is presented. Fig. 3(B) shows the corresponding electron diffraction pattern, where rings spacing indicates a polycrystalline hexagonal structure corresponding to αMo_2C carbide, which is in good agreement with X-ray diffraction results.

The bright field micrograph of heat treated powders is shown in Fig. 4, where it is possible to observe that several nanoparticles with close to spherical shape were formed. Nanoparticles radii are in a range of 25–70 nm. Some nanotubes having diameters between 70 and 260 nm and lengths between 0.18 and 0.3 μm are also present.

Fig. 5 shows a bright field electron micrograph of a thin walled metal filled nanotube opened at the tip, formed from the quiral rolling of carbide foils as is observed in Fig. 5(B).

4. Conclusions

Metastable and nanocrystalline Mo_2C was prepared by mechanical alloying with a mixture of C and Mo powder in a composition of C-50% at Mo. The structure of this carbide was determined as hexagonal.

A small fraction of filled nanotubes and nanofibers grew straight-shaped during heat treatment of milled powders similarly to those obtained by catalytic methods [2], but in this case, instead of using a vapor deposition method, nucleation and growth of such structures was carried out from a solid phase, therefore, it is possible to obtain nanoparticles by using this method.

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