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Nanofibre growth from cobalt carbide produced by mechanosynthesis

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Abstract

Mechanical alloying was used to prepare cobalt carbide. Microstructural characterization of samples was performed by x-ray diffraction, differential scanning calorimetry and transmission electron microscopy methods. In order to produce carbon nanotubes, the cobalt carbide was precipitated after heating at 800 and 1000 °C for 10 min. Nanofibres of about 10–50 nm in diameter, 0.04–0.1 μm in length and 20–200 nm in diameter and 0.6–1.2 μm in length were obtained after heating at 800 and 1000 °C, respectively, by means of this process.

1. Introduction

Interest in the applications of carbon nanotubes has been growing since the appearance of these macromolecules. It has been known for a long time [1] that carbon filaments are grown from carbon containing gases in the presence of metal particles as a consequence of a catalytic reaction. In the last decade, several researchers have searched for a method to produce large fractions of carbon nanofibres and to control their properties in order to use them, mainly in petroleum and electronic industries [1]. Most of the works in this area [2], have used several metals like Fe, Co, Ni and Mo to catalyse the growth of carbon nanofibres. They have concluded that the formation of nanofibres depends upon a nucleation and growth process from metal carbide. However, no mention has been made of the crystalline structure of metal carbides

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involved in the catalytic process. Another important conclusion [2] was that metal particles used in these experiments must be nanosized and have strong magnetic properties. Although the carbon is comparatively inert at room temperature, at higher temperatures it forms carbides with many elements, particularly with metals and metal-like elements. The purpose of the present work is to produce nanocrystalline cobalt carbide by a metallurgical method and to study the possibility of using such carbide for the production of carbon nanofibres.

1.1. Experimental details

The milling of elemental powders of cobalt and carbon soot was carried out in a high-energy mill Fritsch Pulverissette Analyssette Laborette (Type D6.102 No 1861) for 15 h under an argon atmosphere. The purity of powders was 99.99% with mean particle sizes 30–100 μm. The molar ratio of metal to carbon was 3:1. 1 wt% of methanol was used as a control agent. The milling container and balls were made of stainless steel. The weight ratio of balls–powder was 20:1. The milled powders were heat-treated at 400 °C for 10 min (in argon atmosphere), in order to homogenize the carbide. Then, some powders were treated at 800 °C and the others at 1000 °C for 10 min to grow the nanotubes in a similar manner to that reported in the catalysis [1–4]. The heating rate was 0.3 °C s^{-1} from room temperature to 800 or 1000 °C and the cooling rate was 0.03 °C s^{-1}. Thermal characterization of milled powders was carried out by a differential scanning calorimeter (DSC) in a DUPONT TA-9900. Powder samples obtained before and after heating were characterized by x-ray diffraction in a Siemens D-500 diffractometer using Co Kα ($\lambda = 0.179$ nm).

2. Results and discussion

2.1. X-ray diffraction patterns

The x-ray diffraction (XRD) patterns of elementary and mechanically alloyed powders are shown in figure 1. The starting powder of cobalt is a mixture of the fcc and hcp structure (figure 1(a)). Lattice parameters are $a_0 = 2.507$ Å and $c = 4.070$ Å for the hexagonal system and $a_0 = 3.544$ Å for the cubic. The structure of carbon is cubic $a_0 = 14.11$ Å and an amorphous region is also present (figure 1(b)). Figure 1(c) shows the XRD pattern of 15 h milled powders. In this pattern, an orthorhombic structure of cobalt carbide was formed with a stoichiometry Co_3C, and lattice parameters of $a = 4.444$ Å, $b = 4.993$ Å and $c = 6.707$ Å. Crystal sizes were determined to be about 5–20 nm using the Scherrer equation. Figures 1(d) and (e) show the XRD patterns of heat-treated samples. The diffraction peaks, corresponding to carbon and cobalt are separated from those of orthorhombic cobalt carbide. This fact could indicate the nucleation of metallic particles, as well as the formation of some carbonic structures. It is particularly important to notice that in the case of cubic carbon peaks, the diffraction peaks (220) and (422) appear at 800 and 1000 °C, but they are not present in figure 1(b) corresponding to carbon soot. Another important feature of the heat-treated samples at 800 °C (figure 1(d)) is that another type of carbide was detected: CoC_X. The crystalline structure of this carbide is cubic, and only the diffraction peak (200) was observed. The movements of carbon interstitial atoms to the surface of metal particles during heat treatment may form this kind of carbide.

2.2. DSC curve

The DSC curve of orthorhombic Co_3C is shown in figure 2. One exothermal event is evident, an abrupt change at 422 °C. This behaviour has usually been associated with decomposition,

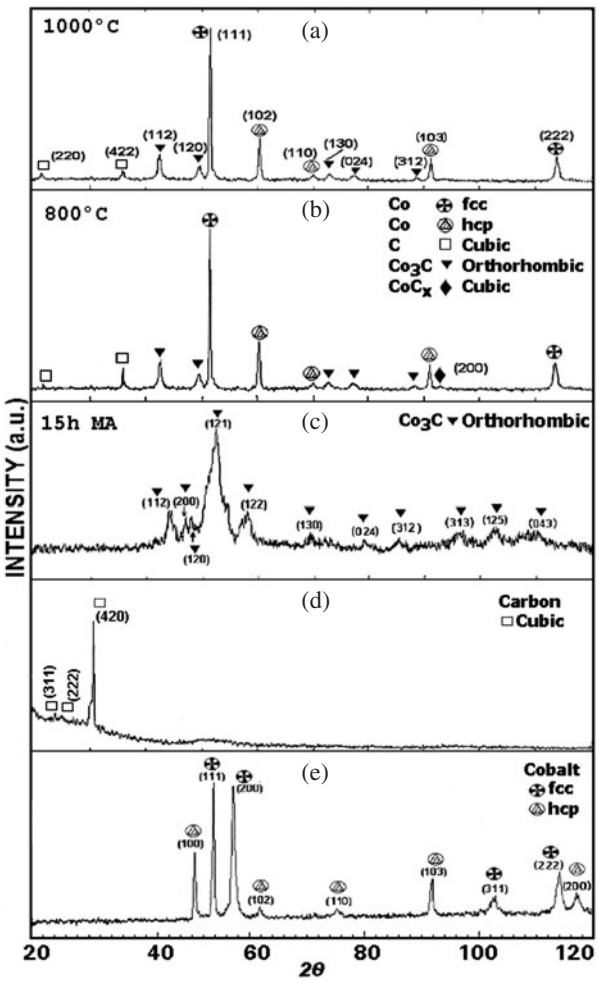

Figure 1. (XRD) patterns of elementary and mechanically alloyed powders. (a) The fcc and hcp structure of cobalt. (b) The carbon soot presenting a cubic structure and an amorphous region. (c) XRD pattern of as-milled powders for 15 h. An orthorhombic structure is present, and a cobalt carbide is formed with a stoichiometry Co_3C. XRD patterns of heat-treated samples at 800 °C (d) and 1000 °C (e), where carbon soot and cobalt are separated.

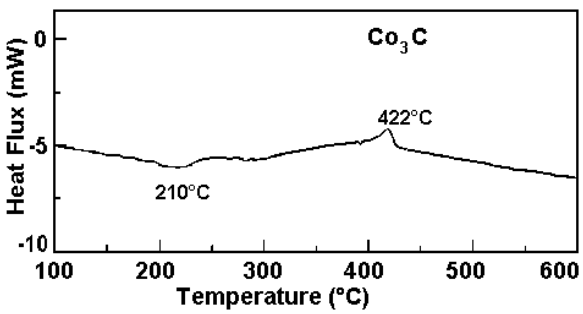

Figure 2. DSC curve of orthorhombic Co_3C.

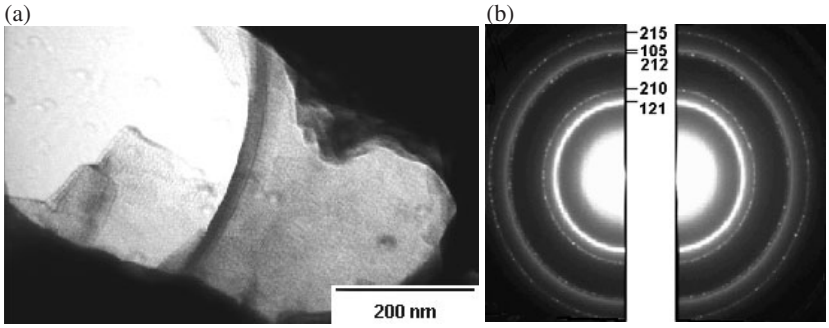

Figure 3. (a) Bright field electron transmission micrograph of cobalt carbide produced by MA and (b) the corresponding electron diffraction pattern.

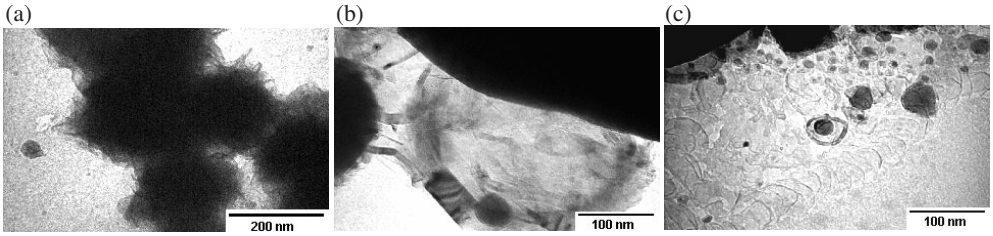

Figure 4. (a) The heat-treated carbide at 800 °C. A small amount of nanosized carbon fibres with cobalt nanoparticles. (b) Cobalt particles connected by nanofibres. (c) Cobalt nanoparticles and a carbon soot ring structure.

but this decomposition was found at 524 °C for a hexagonal Co_3C [5–7]. Also a small change in the curve slope was observed at around 210 °C.

2.3. TEM results

Figures 3(a) and (b) illustrate a bright field electron transmission micrograph of the mechanically alloyed (MA) cobalt carbide and the corresponding electron diffraction pattern, respectively. The ring pattern corresponds to a polycrystalline orthorhombic structure, like that observed in XRD patterns. TEM micrographs of the carbide heat treated at 800 °C are shown in figure 4. In this sample (figure 4(a)) only a small amount of nanosized carbon fibres was present. The geometry of such nanofibres is in agreement with that found by catalysis when soot is used and swollen amorphous-like nanofibres were formed [8, 9]. The diameter of such nanofibres was about 10 nm and the lengths were about 0.04–0.10 μm. However, these nanofibres are smaller than those found in catalysis. This fact could be attributed to the composition of carbide, and because during this process the system was not enriched with carbon as in catalysis, and there was no control over cooling rate and cobalt particles increased their diameter, avoiding the growth of fibres. Some fibres are perpendicular to the surface of cobalt nanoparticles (figure 4(b)) or contain the cobalt nanoparticles within them; the former happens when the radius of nanoparticles is of the order of the radius of fibres. By the way, these nanoparticles seem to be formed when cobalt drops (during heating) go into fibres by capillary action and solidify during cooling. An important result of this work was that a large amount of cobalt nanoparticles covered by graphite with sizes between 2 and 80 nm could be obtained by this method, (figure 4(c)), surrounded in some cases by curved nanofibres.

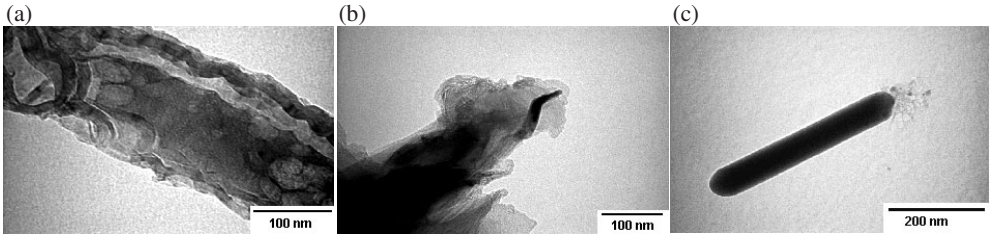

Figure 5. Micrographs of the heat treated sample at 1000 °C. (a) Carbide nanofibres, (b) cobalt passing through carbon soot at 1000 °C, (c) cobalt nanorod formed at 1000 °C.

Micrographs of a heat treated sample, at 1000 °C, are shown in figure 5. Larger curved fibres are observed, but they are carbide fibres (figure 5(a)). Cobalt and carbon soot separation from the carbide was more complete at 1000 °C. The dark areas correspond to metallic nanocrystals and graphite is surrounding them. Graphite is almost transparent to the electron beam. How cobalt flowing through graphite at this temperature can be observed in figure 5(b) and in this way, some cobalt nanorods are also formed (figure 5(c)).

3. Conclusions

Metastable and nanocrystalline Co_3C was prepared by mechanical alloying of cobalt and soot powders. The structure of this carbide was orthorhombic. The decomposition of this carbide occurred at 422 °C. During heat treatments of milled powders a small fraction of nanofibres grew, but their morphology was similar to that obtained from amorphous carbonic samples using catalytic methods. It was observed that the length of nanofibres could increase when applying temperature. In the literature, it is suggested that the length of the fibres can be greater if the following parameters are also controlled: enrichment of sample with carbon, cooling rate, and the use of some substrate like alumina. By this method, it is also possible to obtain large amounts of cobalt nanoparticles embedded in carbon, and also by increasing temperature to form nanorods.

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