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# A new method synthesizing the encapsulated ZrC with graphitic layers

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## Abstract

A new method has been found to synthesize the filled carbon particles, which is different from other methods for synthesizing the encapsulated carbides. It involves high energy milling the carbon with ZrO<sub>2</sub> ball and succedent heat treatment in 1800°C. In addition, a particle with sunken surface is observed while surface of others are convex. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Since the first observation of encapsulated LaC<sub>2</sub> in 1993 [1,2], the study of encapsulation of materials inside carbon nanoparticles is driven by the potential applications, which lie in areas as diverse as magnetic recording and nuclear medicine. There are two ways preparing capsules; one is using the modification of the arc-evaporation technique for fullerene synthesis. The other is carrying out high-temperature heat treatments on microporous carbons which have been impregnated with a compound of the material to be encapsulated

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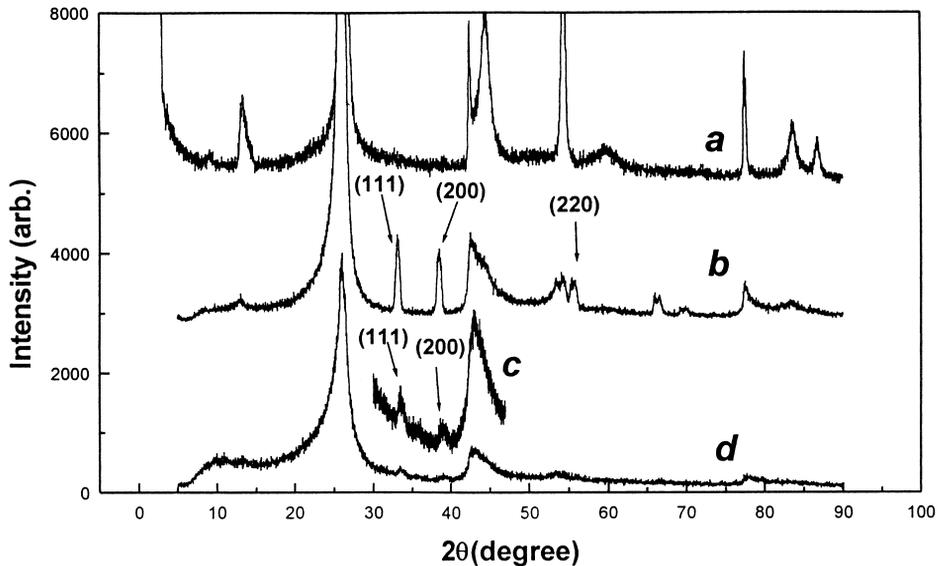


Fig. 1. (a) the primary graphite unmilled. (b) the heat-treated milled sample. (c) part of *d* is magnified by 5 times ( $30^\circ \leq 2\theta \leq 47^\circ$ ). (d) the just milled sample. (111), (200), (220) are three most intense peaks of ZrC (cubic structure).

[3]. In this report, we describe a new technique for preparing filled carbon particles whose size is several hundred nm.

## 2. Experimental

A planetary mill is used to grinding the natural graphite (produced in China). The vial is stainless steel, and the balls are  $ZrO_2$ . The milling time is 24 hours. The milled sample is then heat-treated at  $1800^\circ C$  in a vacuum furnace with protection of nitrogen gas. The pressure of the nitrogen gas is 100Pa. Transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) are conducted using a JEM-200CX, and field emission scanning electron microscopy (FESEM) using JEOL-6301F. The element analysis is carried out by the EDS (ISIS Link 300) attached on the JSM6301F. X-ray diffraction (powders) studies were carried out using a RIGAKU D/max II (Cu K  $\alpha$  radiation).

## 3. Results and discussion

Generally, the carbonaceous materials only react with  $ZrO_2$  at above  $1900^\circ C$  [4]. However, the abrasion of the  $ZrO_2$  balls causes some fine  $ZrO_2$  break off from the milling balls and mix with graphite power. Moreover, the long time milling with high energy is a mechanical alloying (MA) process, which cause the  $ZrO_2$  powers react with carbon at room temperature. Thus the ZrC is obtained at room temperature [Fig. 1]. In addition, the XRD

pattern shows that part of graphite has transferred from the crystal to the amorphous structure during long time milling. When the just milling graphite is exposed in the air, it self-combusts immediately. This means the milling carbon is more active, which facilitate the reaction of  $ZrO_2$  with carbon. The XRD pattern of the just milled samples shows that peaks of ZrC are very weak, which is caused by that the powers are too fine and crystallization is not perfect. The XRD pattern of the samples heat-treated at  $1800^\circ C$  shows sharp peaks of cubic form of ZrC (NaCl structure). The calculation by the Scherrer formula shows that the size of the ZrC is among several hundred nm. Although the milled graphite is also heat treated at high temperature, the amorphous structure is still kept. When the heat-treatment temperature is lower than  $1800^\circ C$ , the peaks of ZrC are still very weak.

TEM (Fig. 2.a) shows that the ZrC particle heat-treated is encapsulated with graphitic layers. It is noted that there is one recess in the surface, while other reported encapsulated nanoparticles are convex. Two zones are selected used for SAD. As shown in Fig. 2.b, the diffraction patterns shows that the interface at the position 1 between the ZrC particle and the carbon layers was identified as (111)ZrC/(002) graphite. However, at position 2, the spots line from (111) ZrC and the spots line from (002) graphite are not in the same direction (Fig. 2.b). The ZrC particle is so thick that other spots of ZrC except (111) plane can't be observed. However, the spots line (111) ZrC and that of (110) graphite in the same direction. From the morphology of the encapsulated ZrC, its crystallization is well, moreover both SAD patterns in position 1 and 2 show that the orientation of the (111) plane in the same direction. Therefore, the encapsulated ZrC is a single crystal.

The calculated angle between the (111) plane and (200) plane of ZrC (cubic structure) is  $54.7^\circ$ , and the measured angle between surface of ZrC at position 2 and surface of ZrC at position 1 is  $55^\circ$ . It is known that the surface of ZrC at position 1 is (111) plane of the ZrC, thus the surface at position 2 is (200) plane. The calculation also shows that the angle between (002) plane and (110) plane of graphite (hexagonal structure) is  $53.7^\circ$ . Therefore, the (112) planes of the graphitic layers in position 2 are parallel to (111) planes of ZrC. The (002) and (110) diffraction peaks are often observed in XRD and TEM for graphite, so does the (111) and (200) for ZrC. It is not sure that whether this relation is coincidental or requested by crystallography. It is reported that there is interspace existing between the carbides and the graphitic layers, which means that graphitic layers don't coat the carbides along the periphery of the carbides simply, but they arrange themselves in their own styles [2].

The HREM (Fig. 2.d) shows that the graphitic layers are very order, on the contrary the milled graphite near to the encapsulated ZrC is still disorder. Before heat-treatment, high energy milling causes the fine particles of  $ZrO_2$  gradually become ZrC particles which are near to the perfect crystal. These ZrC particles are very fine and aggregate with each other. Because the impact force of the milling balls is great, the peripheries of these fine particles are coated with the amorphous carbon (Fig. 3 a). After heat-treatment, these fine particles close to each other will connect and grow into one particle, thus the carbon atoms in the gap among these ZrC will be precipitated to the periphery of the coalescent ZrC particles to form the graphitic layers. In addition that supersaturated carbon dissolved in the ZrC structure will also precipitate togetherly. On the one hand, the graphitic layers connecting the ZrC become the order structure. On the other hand, the whole filled articles were coated a piece of thick

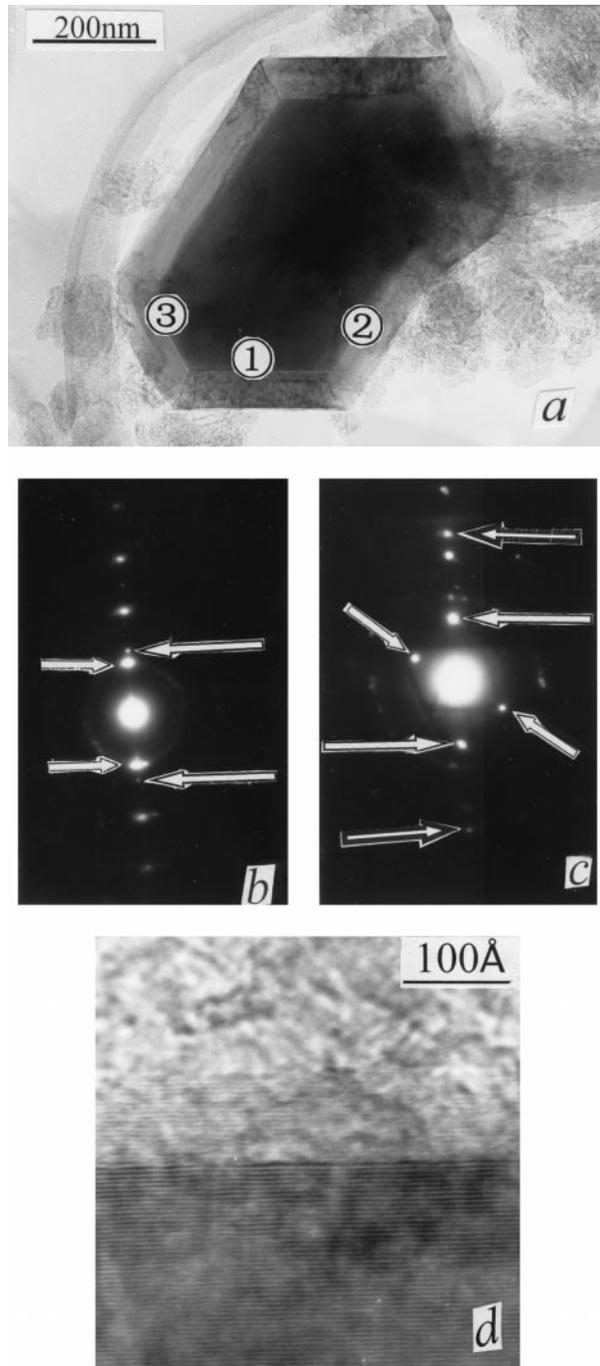


Fig. 2. The TEM micrograph of an encapsulated ZrC with graphitic layers. (a) The bright field image of the nanoparticle, (b) the pattern of SAD in position 1 in a. (c) The pattern of SAD in position 2 in a. (d) HREM micrograph of position 3 in a. The dots shown by large arrows refer to the  $\{111\}$  plane of the ZrC, and the dots shown by small arrows refer to the  $\{002\}$  plane of the graphite, while the dots shown by black arrows refer to the  $\{110\}$  plane of the graphite.

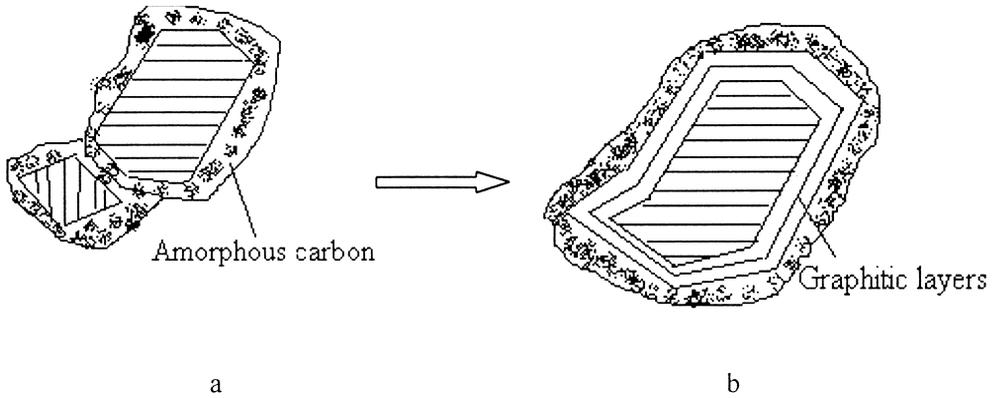


Fig. 3. The schematic diagram of evolution of the encapsulated nanoparticles, the shadowed section refers to the ZrC crystal. (a) The just milled sample, (b) the heat-treated sample.

amorphous carbon, which blocks these fine ZrC particles coalesce with others continuously. Then the fine ZrC encapsulated with graphitic layers are formed. Because the final ZrC are made of much finer ZrC particles, there exist the recess in the surface possibly. The evolution process can be described by Fig. 3. The SEM micrograph (Fig. 4) imaged by the back-scattered electrons but not second electrons shows that these encapsulated particles heat-treated dispersed in one particle. The element analysis is carried out by EDS shows that these particles contain Zr and Carbon. The size of these particles is also can be seen, which close to 1  $\mu\text{m}$ . This is consistent with the result of the TEM and XRD. In addition, there is no ZrC in some particles.

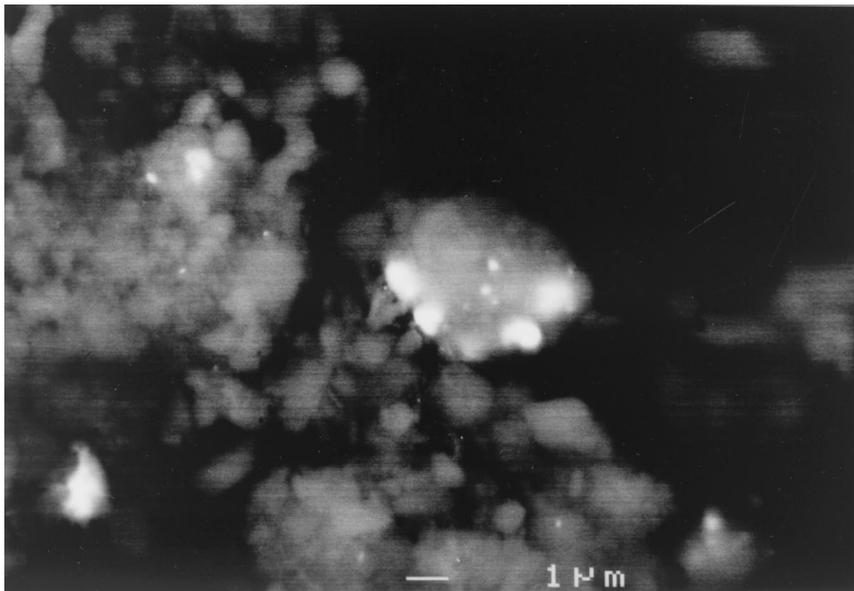


Fig. 4. The SEM micrograph imaged by the back-scattered electrons shows the distribution of ZrC. The bright zone contains ZrC.

Therefore, if we want to prepare the encapsulated carbides particles with graphitic layers, we can firstly milled the metal or metal oxides with excess carbon materials greatly, then heat-treated the milled mixture to certain temperature to synthesis these encapsulated particles. In addition, if we want the nano-scaled particles, the materials should be milled to the smaller size, then the nanoparticles can be achieved.

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