Decomposition of Fe$_5$C$_2$ catalyst particles in carbon nanofibers during TEM observation

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Abstract

The effect of an electron beam on nanoparticles of two Fe carbide catalysts inside a carbon nanofiber was investigated in a transmission electron microscope. Electron beam exposure does not result in significant changes for cementite ($\theta$-Fe$_3$C). However, for Hägg carbide nanoparticles ($\chi$-Fe$_5$C$_2$), explosive decay is observed after exposure for 5–10 s. This produces small particles of cementite and $\gamma$-Fe, each covered with a multilayer carbon shell, and significantly modifies the carbon-fiber structure. It is considered that the decomposition of Hägg carbide is mostly due to the damage induced by high-energy electron collisions with the crystal lattice, accompanied by the heating of the particle and by mechanical stress provided by the carbon layers of the nanofiber.

Keywords: carbon nanofiber, HRTEM, iron carbide, electron beam

1. Introduction

Nanofibers and nanotubes are usually grown using a metal catalyst and therefore contain metal carbide nanoparticles. During the decomposition of carbon, only in few cases the catalyst retains its pure metal structure [1–3]. It is universally accepted that metastable Fe-carbides with high carbon content serve as precursors for growing carbon nanostructures. During the growth, the carbide may decay to form iron [4]. Different Fe-carbides have been obtained during the growth of carbon nanostructures using an iron catalyst [5–9]. Owing to their nanometer size, homogeneous composition and encapsulation in carbon shells, which ensures isolation from external influences, these carbides possess a number of unique properties. Because the parameters of the growth environment vary with time, whereas the thermodynamic conditions of the nucleation of certain Fe-carbides are very similar [10,11], sometimes catalyst particles containing the lattice of a certain carbide also include layers of another carbide [12].

Some properties of nanoparticles differ from those of macroscale specimens of the same substance. For example, the melting temperature of a nanoparticle is often about one-third lower than that of a bulk sample [13]. Because most carbides have metastable compositions, the peculiarities of carbide nanoparticles are of interest.

Several noteworthy transformations under electron-beam irradiation have been recently observed, such as a transformation from graphite to diamond [14] and the formation of nano-onions from nanodiamonds [15] and from amorphous or disordered graphite [16]. Interesting changes were also observed in oxidized iron particles [17]. Under electron-beam irradiation, they rapidly became particles with $\alpha$-Fe, $\gamma$-Fe or Fe$_3$C phases, covered with graphitic film.

In this article we report the effect of the electron beam of a transmission electron microscope (TEM) on nanoparticles of metastable iron carbides formed from a catalyst during the growth of metal-catalyzed carbon nanofibers. In particular, nanoparticles of the two types of iron carbide found in carbon...
nanofibers, $\chi$-Fe$_3$C$_2$ and $\theta$-Fe$_2$C, were subjected to direct electron-beam irradiation in the TEM column.

2. Experimental details

Carbon nanotubes and nanofibers were grown by chemical vapor deposition (CVD), as described in detail elsewhere [12]. The process was carried out in two stages in a silica tube with an inner diameter of 35 mm and a length of 650 mm. The gaseous products that resulted from polyethylene pyrolysis at 450 °C were transported from the first reactor stage to the second reactor stage by an Ar flow of 0.2 liter min$^{-1}$ along with a H$_2$ flow of 0.05 liter min$^{-1}$. Fe powder was placed at the second stage and was heated to a suitable temperature ranging from 500 to 1000 °C. The process duration was usually 30 min. Some of the obtained nanofibers were dissolved in alcohol, placed on a TEM grid and dried. The TEM studies were carried out using a JEM-2010 high-resolution TEM equipped with an energy-dispersive spectroscopy (EDS) detector. The acceleration voltage during the observation was 160 kV and the electron source in the microscope was a LaB$_6$ cathode.

3. Results and discussion

A typical carbon nanofiber containing a catalyst particle in the middle is shown in figure 1(a). Figure 1(b) shows a magnified image of the area of the fiber circled in figure 1(a). As seen from the figure, distorted carbon layers are oriented parallel with the lateral surface of the catalyst particle. Notably, the fiber, similarly to a nanotube, has an internal cavity, here tiled by parallel carbon flakes replicating the shape of the particle. Because the catalyst particle has a lens-like shape, the flakes are oriented in different directions. EDS analysis of the elemental content showed the presence of iron and carbon. Analysis of the microdiffraction patterns indicated that the particles consist of iron carbides: Hägg carbide ($\chi$-Fe$_3$C$_2$) or cementite ($\theta$-Fe$_2$C).

During the examination of the obtained carbon nanofibers in the TEM when the catalyst particles were exposed to electron-beam irradiation (with an electron current density of about 10–30 pA cm$^{-2}$), we observed the decay of some of the particles inside the fiber (figure 2).

Sometimes this decay was very rapid and it appeared as if the particle had exploded accompanied by the marked deterioration and destruction of the surrounding nanofiber structure. In other cases, the particle and fiber deteriorated gradually, enabling the decay to be controlled by varying the electron-beam intensity (decreasing the beam current by a factor of approximately 5–10 was usually sufficient to delay the further destruction of the particle and nanofiber). The transient process of the particle decay, the dislocation of the particle fragments and the simultaneous fiber destruction lasted from 5 s to approximately 1 min (estimated from the start of electron-beam irradiation until the stabilization of the changes in particle and nanofiber). It is pertinent to note the following important features and stages of this process: At the initial stage of the electron-beam exposure, the particle starts to change its shape and volume. If the destruction process is sufficiently slow, the changes are first observed at the sharp edges of the particle (figure 2(a)), then the particle disintegration begins by it splitting in two parts along the fiber cross section. This particle appears to be Fe$_3$C$_2$. According to figure 2(d), the particle is twinned in the (100) plane [12]. A trace of the twinning plane is shown in figure 2(a) by the arrow. Upon further irradiation, the two fragments of the catalyst particle start moving along the fiber in opposite directions, deforming the fiber and changing its structure (figure 2(b)). During this motion, the front edges of the fragments hardly change their shape. Some of the catalyst remains in the center of the fiber and the remainder spreads along the fiber in the form of a number of small particles, each covered with a carbon shell, or in the form of a shapeless mass. The transformation of the particle from the state shown in figure 2(a) to the state shown in figure 2(b) took about 10 s. Approximately the same time passed between the stages shown in figures 2(b) and (c).

It is worth noting that whereas the external surface of the fiber retains its initial shape, the internal fiber structure changes markedly. If we proceed with continuous electron-beam irradiation, after a certain time (from approximately 5 s to 1 min) the structures of the particle and fiber eventually stop changing. At this stage, the large
fragments of the initial catalyst particle, which were moving along the fiber, are usually surrounded by a carbon shell. The part of the fiber where the motion of the particle fragments took place contains small inclusions (figure 2(c)) of the catalyst material (as a rule, these inclusions are also surrounded by a carbon shell) and dense curved carbon plates with complex shapes, usually consisting of from one to several tens of graphite atomic layers (figure 3).

Usually, the smaller the particle size, the faster it decays. However, in our study we did not observe any decay of particles of less than approximately 50 nm or more than approximately 400 nm.

If, during the process of particle decay and fiber destruction, we widen the electron beam, Thus decreasing the intensity by a factor of approximately 5–10 from the initial value of ~10–30 pA cm⁻², the structures of the particle and fiber cease to deteriorate, and the fragments of the catalyst particle stop moving. By subsequently increasing the beam intensity to its former value, one can restart the deterioration process and the motion of the fragments. It appears that for a given particle there exists a certain threshold value of irradiation intensity, such that the exposure to a more intense electron beam triggers the decay. The decay time appears to depend more on the properties of the catalyst particle and the fiber than on the electron-beam intensity.

Analysis of the chemical and phase composition of the initial particle and the final decay products indicated that the initial particle was composed of Hägg carbide (Fe₅C₂), and the final decay products were either cementite (Fe₃C) or γ-Fe, that is, the decay followed the reaction:

$$\text{Fe}_5\text{C}_2 \rightarrow \text{Fe}_3\text{C} + \gamma-\text{Fe}.$$  

To explain this result, we try to answer the following questions: What is the reason for the decay of the catalyst particles? What changes are induced in the particle structure and how do they develop? Why do the catalyst particle fragments move along the carbon fiber and how does this motion affect the fiber itself?

Possible reasons for the Fe₅C₂ particle breakdown may be the effect of the electron-beam irradiation and the heating effect. High-energy (160 keV) electrons passing through the sample collide with and damage the crystal lattice and displace the atoms of the catalyst particle and the nanofiber, generating point defects [18, 19]. Moreover, these high-energy electrons generate low-energy secondary electrons, which may also play a role in the decay of the catalyst particle [20, 21].

Damage due to electron collisions can transform the Hägg carbide into cementite. In [12], it was shown that the rearrangement of some of the carbon atoms within the atomic cell of cementite transforms it into the cell of Hägg carbide. Such restructuring can be represented as a twinning defect in the initial crystal lattice. Carbon has a smaller atomic mass than iron, and the energy threshold of its displacement due to collisions is considerably smaller [22]. Therefore, the transformation of Fe₅C₂ to Fe₃C might be due to the displacement of some of carbon atoms in the Fe₅C₂ particle under the electron-beam irradiation (particularly when the fact that the Fe₃C crystal lattice is more stable structure and has a lower carbon concentration than that of Fe₅C₂ is taken into account).

However, not all the carbide particles studied in the TEM were decomposed by the electron beam under the same conditions. We did not observe the decay of single particles (without a fiber). Furthermore, particles smaller than ~50 nm or larger than ~400 nm that were located inside nanofibers did not undergo any changes during electron-beam irradiation. Apparently, the effect of the beam was insufficient to cause the decay of the carbide in this study.

The heating effect of the electron beam, although it should not be significant in our experiment [19], may play
an important role in the decomposition of Fe$_2$C$_2$, considering that the decomposition time of the particle clearly depends on its size. This may be related to the time required to increase the temperature of the particle to a certain critical value (that varies for each particle). Furthermore, heating lowers the energy threshold of damage due to electron collisions with crystal lattice and promotes bond breaking. However, we consider (for the same reasons as we discussed for the damage due to the electron collisions) that the heating alone cannot be entirely responsible for the observed effects.

The mechanical action of the fiber may also promote the breakdown of the catalyst particles. The high pressure inside carbon nanostructures consisting of closed shells is well known. Calculations performed in [23] show that the internal pressure in a multiwall nanotube can be as high as 100 MPa. Blank and Kulnitskiy [24] estimated the pressure inside a nanofiber to be not less than 1–2 GPa. The reason for such a high pressure is the surface tension of the carbon shell caused by the strong in-plane interactions of carbon atoms. The faceting of the catalyst particles (which typically takes place during the growth of nanotubes and nanofibers [24]) also originates from the forces caused by the surface tension. Thus, these forces are able to maintain the stress in a Fe$_2$C$_2$ catalyst particle inside a nanofiber. Such a supposition is confirmed by the experimental observation of twin defects in some of the particles that exploded; for nanocrystals of such a size, the deformation is realized predominantly through the twinning process; thus, deformation can result in the generation of deformation twins [25]. In our case, the twinning may be the result of the relaxation of the internal stress of the particle. Note that some particles containing a few layers of cementite demonstrated a low probability of exploding, and no explosion occurred if the particle was composed of several layers of Hägg carbide enclosed in cementite. The explosive decay was most frequently observed in twinned Hägg carbide particles.

Considering all the points discussed above, we cannot precisely specify the reason for the observed phenomena, but we outline the following issues, which are considered to be the most probable causes of Fe$_2$C$_2$ decomposition.

During the electron-beam irradiation, some carbon atoms of the Fe$_2$C$_2$ lattice become removed from their initial position. The displacement of the carbon atoms in a certain direction leads to the formation of a Fe$_2$C fraction [12]. Cementite probably does not change once it is formed as it is more stable than the Hägg carbide.

In addition, the catalyst particle is compressed by the nanofiber. This compression may promote the transformation of Fe$_2$C$_2$ into Fe$_2$C. The absence of compression may also explain why the nonencapsulated particles were unaffected by irradiation. The pressure inside the nanofiber is thought to depend on its structure. Consequently, particles inside different nanofibers, or even inside the same inhomogeneous nanofiber, were subjected to different pressures. This might explain the observed variation of sensitivity to electron exposure between particles.

The reasons why sufficiently small and sufficiently large particles were unaffected by irradiation are still unclear. Obviously, large particles require higher total energies and thus take a much longer time to explode. However, the resistance of small particles is puzzling and might be related to their different crystalline structure.

Regarding the presence of γ-Fe particles, which are known to be stable only at high temperatures and pressures, such particles, as shown in figure 3, are surrounded by multilayer carbon shells. This observation indicates that the high elastic modulus of carbon layers on the surface prevents the γ-Fe particle from expanding and being transformed to α-Fe.

4. Conclusions

We have studied the explosive decay of Hägg carbide nanoparticles (χ-Fe$_2$C$_2$) located in carbon nanofibers grown by CVD. The decay was caused by electron-beam irradiation during TEM observation, and the final product of the decay was either cementite (Fe$_2$C) or γ-Fe. The structure of the nanofiber containing the particle was changed markedly after the decay. We consider that the damage induced by electron collisions with crystal lattice, accompanied by the heating of the particle and the mechanical stress provided by the carbon layers of the nanofiber, is responsible for the decay. The damage to the nanofibers and the motion of the catalyst particle fragments along the nanofiber may originate from the diffusion of carbon through these fragments.

The controlled decomposition of catalyst in carbon nanotubes reported here may have important applications in the preparation of nanotube-based nanostructures. For example, spintronic devices can be fabricated using a combination of a ferromagnetic catalyst and nanotubes [26]. Such fabrication requires a specific arrangement of the catalyst, which can be achieved through the selective decomposition of unwanted fragments in an electron microscope, as outlined in this paper.

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