Crystallography of α-, γ-, and ε-iron phases and iron carbides, formed inside carbon nanotubes. HRTEM studies.

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Carbon nanotube [1] can serve not only as a reaction chamber, but also as a container to store and preserve the structures unstable under normal conditions. In this study, by means of the catalytic growth in high isostatic pressure apparatus with varying the gas mixture composition, pressure and temperature, we obtained the carbon nanotubes inside of which we could identify some particles containing the α-, γ-, and ε -iron phases, as well as three different iron carbides: Fe_3C, Fe_5C_2, and Fe_7C_3. JEM-2010 high-resolution transmission electron microscope with the EDS and EELS techniques and JSM-7600F scanning electron microscope have been used.

The present study aims to investigate the following questions: orientation relationships between α-, γ- and ε -phases of iron and iron carbides, peculiarities of carbide formation inside carbon nanotubes, distinguishing characteristics of mutual transformations of carbides, reasons for formation of different carbon nanoconstructions.

The formation of high temperature γ-phase of iron and high pressure ε-phase of iron indicates the presence of high pressure and high temperature conditions during the nanotube growth. The closed graphene shells of the nanotube represent themselves a nanochamber which prevents γ -- and ε- iron particles inside it from transformation to α-iron after pressure unload and cooling. Different ways of iron – cementite (Fe_3C) transformation were considered earlier [2-3]. Authors based their conclusions on parallelism of (001) cementite plane and (112) ε-carbide plane. As we know, there were no experimental evidences of orientation relationships between ε -Fe and cementite up to now. We have found the parallelism of (001) of cementite and (100) of Hagg' s carbide (Fe_5C_2). Thus, (100) of Hagg' s carbide is parallel to (112) of α-iron. Also it is important to remark that (100) of Fe_5C_2 and (112) in bcc (α) iron are twinning planes, and the distribution of Fe atoms in these planes is favourable for the phase transformations. It was found that several atomic layers of cementite (Fe_3C) are located inside the layers of Fe_5C_2. Planes (001) of cementite and (200) of Fe_5C_2 appear to be parallel. Always parallelism of corresponding planes of Fe_5C_2 and cementite is observed whether there is a cementite between Fe_5C_2 or otherwise. So, we can present following orientation relationships between all phases, found in our study:

$$(131)\gamma \parallel (2\text{-}12)\varepsilon \parallel (112)\alpha \parallel (001)Fe_3C \parallel (100)\ Fe_5C_2$$

It is known that during the nanotube growth carbon atoms are catalytically decomposed on the catalysts surface thus building the nanotube walls, and along with this resulting in the incorporation of carbon atoms into the catalysts and formation of carbides. Often transformation of carbides to one another takes place in these cases. At high temperatures cementite decomposes into carbon and iron. It was shown by TEM analysis, that the twinning plane is (100) Fe_5C_2. This plane corresponds to {211} in bcc-lattice of α-Fe, and this means, that in a process of saturation of α-Fe with carbon and formation of carbides the twinning plane is inherited in all the new originated carbides. Cementite develops through the intermediate phase of ε-iron (α-Fe→ε-Fe→Fe_3C). Consequently, one can suppose, that twinning occurs in particle with hexagonal lattice before it turns into cementite, either twinning occurs in cementite before it turns into Hagg' s carbide.

Both carbides appear in a process of nanofiber growth in the same temperature range. Hägg carbide (Fe_5C_2) is formed on the cementite surface, but both carbides decomposed during metal dusting. The Gibbs energy of formation Δ G for Fe_5C_2 was determined at 500°C. This result combined with thermodynamic properties at other temperatures taken from literature strongly supports the existence of the equilibrium of three phases: α -Fe+Fe_3C+Fe_5C_2 at about 350°C in the binary Fe-C system. By analogy with mechanical twinning, which is the result of the mechanical stress, the new term " chemical twinning" was introduced. Processes, taking place in the catalyst particle in our work can be explained also by the " chemical twinning" , i.e., slight deviations from stehiometry, which can be achieved by the formation of thin layers.

We believe, that the twinning is the result of deformation of metal particle and is caused by the action of surrounding graphene shell. The deformation leads to the twinning of not only metal catalyst particles, but also to the twinning of carbides, which mechanical characteristics are exceeding corresponding characteristics of metal. It is known, that elastic modulus of carbon nanotube walls may achieve value of 1 TPa. Strength of nanotube layers and its capability of maintaining big loads can explain existence of observed particles of ε -iron. As it is known, γ-iron transforms into α-iron after cooling. This transformation is accompanied by the volume change of 9%. Thanks to high elastic modulus (1 TPa) of carbon nanotube, particles of γ-iron, being in close contact with nanotube walls, do not transform into α-iron.

The mechanism of twinning is connected with deformation of elementary crystal cell, leading to the change of orientation of part of the crystal relatively to the acting forces. Reoriented part of crystal suffers twin shift relatively to the other part of crystal. Value of this shift is determined by the symmetry of crystal lattice. Under real conditions, development of deformation occurs by the way of nucleation and propagation of interstitials of twinned component in original crystal. It was shown that for nanocrystals of small size (of the order of 10 nm) the deformation is realized through the twinning, whereas for crystals of bigger size key role belongs to the motion of dislocations.

Carbon nanotubes, obtained on iron catalyst have been studied by the HRTEM methods. It has been established, that in growth process the lattice of catalyst particle of bcc-iron transforms into γ- or ε - phases or into the following carbides: Fe_3C, Fe_5C_2 or Fe_7C_3. It has been shown that the inner parts of nanotubes suffer great pressure. Owing to the big values of internal pressure, nanotube can be considered as a nanoscale high pressure chamber. This is confirmed by the deformation twins in bcc-iron and in Hagg' s carbide, and also by the presence of fcc- and hcp-iron particles, closed in nanotube, which can exist only at high values of pressure and temperature.

References

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