

**THE CRYSTALLOGRAPHY OF IRON CARBIDES FORMATION IN THE  
PROCESS OF CATALYTIC GROWTH OF CARBON NANOSTRUCTURES:  
HRTEM STUDIES.**

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It is known that in the process of carbon nanostructures formation a catalyst particle is often transforms into one of iron carbides. The growth process is determined by the dissolution of carbon in the quasi-liquid catalyst particle, its diffusion through the particle and its segregation in the form of graphene layers in the case of supersaturation. Carbon nanofibers were grown in the present study by CVD process. TEM analysis has been carried out by JEM-2010 high resolution transmission electron microscope, equipped with EDS-detector.

Catalytic particles, found inside nanofibers, revealed the structure of  $\alpha$ -iron as well as structures of  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_5\text{C}_2$  and  $\text{Fe}_7\text{C}_3$  carbides. Crystallographic peculiarities: the orientation of the catalyst particle in the fiber, orientation relationships between lattices of  $\alpha$ -iron and carbides have been studied. Twins were identified in  $\text{Fe}_5\text{C}_2$ . It was found, that (100) is the twin plane in the monoclinic  $\text{Fe}_5\text{C}_2$  lattice, which is corresponds to {112} twinning plane of  $\alpha\text{-Fe}^1$ . The orientation of  $\text{Fe}_5\text{C}_2$  catalyst coincides with [100]-direction, which is corresponds to [112] direction of  $\alpha\text{-Fe}$  bcc lattice. It is known that the catalyst with bcc lattice is oriented mainly along [100], not along [112] direction. This disagreement may be explained in the following way. It is assumed that  $\text{Fe}_5\text{C}_2$  is formed from  $\alpha\text{-Fe}$  through  $\text{Fe}_3\text{C}$ -phase. It was shown, that the orientation of  $\text{Fe}_3\text{C}$  – catalyst  $[\overline{391}]$  with accuracy of  $3^\circ$  coincides with [100]  $\alpha\text{-Fe}$ . It can be shown, that  $[\overline{391}]$  direction in  $\text{Fe}_3\text{C}$ -lattice with the same accuracy coincides with  $[\overline{121}]$  of  $\alpha\text{-Fe}$ . The alteration of the crystallographic orientation occurs probably as the result of the twinning in  $\epsilon\text{-Fe}$  lattice. Further saturation of  $\text{Fe}_3\text{C}$  lattice by carbon resulted in the formation of  $\text{Fe}_5\text{C}_2$  lattice.

It was found that catalytic particles of  $\text{Fe}_7\text{C}_3$  structures take the octahedron shape, whereas the  $\text{Fe}_5\text{C}_2$  catalyst particles are characterized by flattened shape, coincident with the lens shape. Carbon nanofibers, containing  $\text{Fe}_5\text{C}_2$  catalyst, have unordinary form. Fibers are consisted of graphene layers, which cover the lens surface. At the same time direct parallel lines crossing fiber from the catalyst surface up to fiber's boundary, can be distinctly seen. It was found by HRTEM analysis that these lines contain ruptures of graphene layers. The possible mechanism of such structure formation is explained by the deformation, arising in the nanofiber growth process.

[1]. V.D.Blank, Yu.L.Alshevskiy, A.I. Zaitsev, N.V.Kazennov, I.A.Perezhogin, B.A.Kulnitskiy, Structure and phase composition of a catalyst for carbon nanofiber formation, Scripta Materialia, 55, 2006, 1035-1038.