

On the Processes that Occur in the Metal Particles with Their Use in Catalytic Decomposition of Hydrocarbons through the Carbide Cycle Mechanism

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Abstract

The part played by highly dispersed particles of metals of iron subgroup in catalytic decomposition of hydrocarbons through the carbide cycle mechanism has been considered. A crucial correlation between their crystallographic characteristics and the structure of formed graphite composites has been shown. The major factors have been determined that enable controlling the processes of formation of graphite filaments and fibres.

INTRODUCTION

Diversified composite materials, including the carbon ones, occupy the significant place in modern technical progress. Owing to unique properties of carbon materials, their assortment has been quickly expanding in recent years. Carbon nanofibers, which are produced in the course of catalytic decomposition of gas hydrocarbons over the disperse particles of metals of iron subgroup and their alloys with some other metals, fell within a sphere of peculiar interest.

Such nanofibers possess an ultrahigh strength, specific adsorption properties, heat-insulating, conducting, heat-resistant, and other properties [1].

Previously, we had deciphered the mechanism of formation and shaping of various morphological and crystallographic species of such graphite phases with nanosized characteristics [2–4]. The mechanism has received the name “carbide cycle mechanism” from its basic stage, namely, decomposition of hydrocarbons through the intermediate carbide-like compounds.

In general, the essence of such multiphase mechanism is as follows (Fig. 1, b). On a certain crystallographic surface (facet) of a microcrystal of the metal particle that we named “frontal”, adsorption and decomposition of hydrocarbons proceeds through an intermediate stage of formation of unstable carbide-like compounds. Precipitating carbon atoms dissolve in the metallic particle (“the head”), and by means of diffusive transfer through “the body” of the metal particle, they are born to its alternative facet named “back”. On this facet, carbon precipitates into a separate phase of graphite. The structure of this phase is formed epitaxially under the influence of the features of back facet. As is shown in [5], the process of growth of carbon filaments with diffusive transport of carbon through the bulk of metal particle is possible only in the definite range of sizes of such particles. These sizes depend on the diffusion coefficient of carbon through their body. For Ni and Co particles, the diffusion coefficients of carbon are practically identical [6]; therefore, their maximum admissible sizes lie within the same limits, $<1000 \text{ \AA}$. For Fe, the diffusion coefficient of carbon is two orders

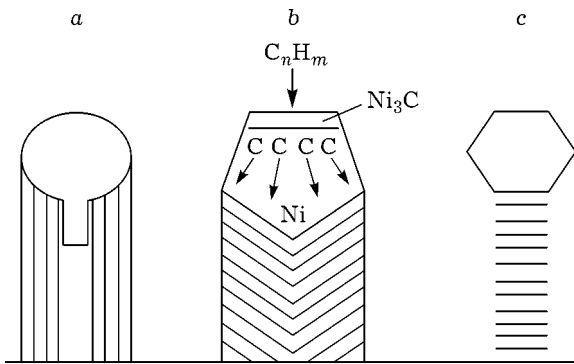


Fig. 1. Basic crystallographic structures of graphite filaments.

higher than for Ni and Co, and the maximum admissible particle sizes are in the range $<10\,000\text{ \AA}$. This mechanism has been previously described by us in detail in [7]. Within the limits of the present article, we will not pose the problem of considering a vast number of works devoted to the features and species of such nanofibers. However, it should be remarked that a variety of nanofibers depends not only on the nature of decomposed hydrocarbon, temperature, and diluent, but, first of all, on the peculiarities of the metal head that is the site for the entire process, on its composition, on its initial state, and the state during the growth of graphite phase. Strangely enough, this is an issue that is rather poorly studied and elucidated in the literature.

In the article presented, we mounted an attempt to discuss the regularities and features of the behaviour of disperse metal particles, which define the entire process of formation of carbon compositions through the carbide cycle mechanism. A series of our works accumulates the sufficient body of information, generalization and analysis of which now makes it possible to come to this question without additional experiments.

DISCUSSION AND ANALYSIS OF ACCUMULATED INFORMATION

The information accumulated until this moment contains, at first sight, some contradictions and at the same time offers the possibility for them to fit into a uniform consistent pattern.

It has been demonstrated that crystallographic and morphological characteristics of graphite filaments, being formed in catalytic decomposition of hydrocarbons over the highly dispersed particles of metals of iron subgroup, depend on their properties, and different crystallographic facets of such particles play their specific part. The result is that at least three basic crystallographic species of graphite nanofibers (see Fig. 1) are likely to form, the combination of which can yield a set of secondary structures [5, 8, 9].

Hence, it was supposed that there are such crystallographic and morphological forms of highly dispersed metal particles that determine the features of carbide cycle mechanism and kinds of graphite structures formed. It is evident that the properties of such particles can be controlled by the procedure of their preparation and by admixtures of other metals [8].

However, the preceding apparently comes into conflict with another fact. In 1976, the phenomenon of crystallization of an amorphous carbon film by nickel particles with the size of $10^2\text{--}10^3\text{ \AA}$, at a temperature that was $680\text{ }^\circ\text{C}$ lower than the temperature of the known eutectic (1591 K), was observed *in situ* in the column of a microscope. Labile particles of nickel in the amorphous carbon film, 500 \AA thick, changed their form, moved towards amorphous carbon and a trace of graphite chips trailed behind them [10].

The phenomenon of a viscous-flow state of a metal particle at unusually low temperature has found its explanation in later studies of the carbide cycle mechanism of graphite structure formation during catalytic decomposition of hydrocarbons. Such a state arises under conditions of an intensive diffusive stream of carbon atoms from the frontal to the back side of metal particle and condensation of atomic carbon from the solution in metal into the graphite phase on the back facet. The contribution of these two factors has been evaluated by us in [5]. Simultaneously, it is worth noting that the carbide cycle mechanism has supplied a natural explanation for the nature of a huge gradient in the concentration of carbon between the frontal and the back sides of the metal particle. Indeed, owing to disintegration of com-

pounds of Ni_3C type, carbon concentration in the near-surface layer of the frontal side of nickel particle will be close to 25 %. Meanwhile the strength of carbon solution in metal on the back side will be close to an equilibrium one, *i.e.* <0.1 %. To put it otherwise, we deal here with the huge difference in the values of chemical potential pertaining to atomic carbon formed on the frontal side and that of the graphite phase on the back side of a metal particle. The velocity of the diffusion motion of carbon atoms through the bulk of, for example, nickel particles appeared to be 36600 \AA/s , and the time of carbon atoms passing between Ni ions inside a lattice appeared to be $1.9 \cdot 10^{-4} \text{ s}$.

Transition elements Fe, Co, and Ni have small atomic radii. So for Ni it is as great as 1.24 \AA . Therefore, carbon atoms with the radius of 0.77 \AA do not fit into the octahedral hollows of the closest face-centered cubic packing of Ni atoms. Owing to this, in the process of diffusion of carbon atoms through the bulk of nickel particle, a disruption of the structure of nickel crystal lattice occurs, which is accompanied by an oscillation of ions of metal at the instant that carbon atoms pass between them. The process is accompanied by a significant energy release when carbon condenses from the metal solution into an individual graphite phase on the back side of the metal particle. Hence, the particle of metal is brought into strongly non-equilibrium conditions, in an unusual dynamic state. A structure arises that is named the dissipation structure. The theory of dissipation structures assumes their spontaneous formation when the transition from disorder to the new ordered state takes place, the latter resulting from interaction between the system and the environment [11]. In the nonlinear process considered, a substantial role is played by the feedback phenomenon, in which hydrogen being evolved during the decomposition of hydrocarbons hydrogenates the intermediate unstable carbide-like compounds of Ni_3C type to form methane (methanation process). The depth of the methanation process is governed by thermodynamic equilibrium in this reaction. As a consequence, the second channel of the removal of carbide-like compounds from the near-surface layer of the frontal side of the metal particle opens. In such an event, the stationary

states may arise in the system, the stability of these states being determined by the uniformity in the streams of energy and matter. Each dissipation level is associated with the individual stable steady-state non-equilibrium structure with its specific properties. In our case, depending on a dissipation level, *i.e.* on an intensity of thermal and diffusive streams of carbon atoms, the system can pass through a number of states from a slow rearrangement of crystalline structure to the emergence of the viscous-flow (pseudo-fluid) state. Clearly, only partial relaxation of such a system occurs upon termination of the process of decomposition of hydrocarbons and upon termination of the diffusive stream of carbon.

Thus, the basic seeming inconsistency of the known experimental data is as follows. The numerous electron-microscopic patterns of the graphite filaments obtained through the carbide cycle mechanism show the perfectly faceted metal chips, which were the site for the entire process. Based on this evidence, an inference has been made that the entire process of growth of a filament may take place on these very crystals (with the distinct facets). However, the existence of viscous-flow (pseudo-fluid) state of such particles testifies that a perfectly organized crystalline structure of the graphite filament can form on the metal particle even in the viscous-flow state, wherein the particle may have no facets at all.

In our works, we have found an explanation for this inconsistency. It is as follows [5]. An emergence of the nucleus of an independent graphite phase is essential to precipitate carbon from its solution in the metal particle into this phase. This requires overcoming the high potential energy barrier. So it measures $\sim 170 \text{ kJ/mol}$ for Ni, and $220\text{--}300 \text{ kJ/mol}$ for Fe [7]. Therefore, at an early stage of hydrocarbon decomposition, just dissolving of carbon occurs until the limiting supersaturation of the solution is reached [12], at the level of which the potential energy barrier can be overcome and a nucleus of the graphite phase arises. During this period, the metal particle is in the solid state and preserves its faceting, as the reasons of its transformation, specifically, the diffusive stream and condensation of carbon atoms on the back facet, are not involved. When

a critical supersaturation is reached, the condensation of carbon atoms proceeds at those sites (facets) of the metal particle, which show the best epitaxial correlation with the structure of graphite. So, for example, the structure of nickel face (111) almost ideally matches (002) graphite plane. The analogous sites exactly become the back sides of the particle. A program of the structure of graphite filaments, including the location order in basal planes of graphite, appears to be involved into the structure of such crystallization sites.

Later on, even in the event that the metal particle transforms to the viscous-flow state, the carbon filaments keep "the epitaxial memory" and continue their preprogrammed growth. Moreover, upon termination of the process, the metal particle crystallizes from the viscous-flow state largely under the same program, which is passed on to it by the epitaxial feedback through the structure of the graphite filament. Certainly, such a feedback can only partially be realized, being a function of the crystallization time and of a stabilization of the structure, of temperature, and some other factors.

Hence, the depth and intensity of evolutionary processes in the metal head of a carbon filament mostly depend on the intensity of the diffusive stream of carbon and on temperature. The diffusive stream of carbon is in tangible relation with the diffusion coefficient of the metal of choice (Fe, Co, Ni, and their alloys with some other metals) and with the rate of formation of carbon atoms. One of two possible limiting stages can show up in the carbide cycle mechanism: either diffusive transfer of carbon, or the rate of formation of carbon atoms, *i.e.* the rate of hydrocarbon decomposition. The last-mentioned depends on thermodynamic stability of hydrocarbon. So, more stable hydrocarbons, specifically, methane, propane, are less effective in this respect than, for example, butadiene, and benzene. All of this gives an opportunity to control the process and to affect the state of the metal particle [13]. Under the slow process, a slow rearrangement of the crystalline structure of metal particle occurs. It is possible to observe the disappearance of certain facets and growth of the others. When the intensive process takes place, the faceting disappears at all.

In conclusion we will point out that an emergence of viscous flow in the metal particle results in an increase of its reactivity in the catalytic act of hydrocarbon decomposition due to weakening of bonds in the initial crystalline structure.

CONCLUSION

The features of structural evolution of highly dispersed particles of metals of iron subgroup at the different stages in development of the process of catalytic decomposition of hydrocarbons and growth of graphite composites through the carbide cycle mechanism are considered.

The potentialities and the ways to control the processes of formation and shaping of graphite filaments and fibres are analysed.

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