

PHASE TRANSFORMATIONS AND DEFECTS IN ALLOYS

UDC 621.785.4

NEW CONCEPTS OF THE NATURE OF BAINITIC TRANSFORMATIONS IN STEELS

V. M. Schastlivtsev¹Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 7, pp. 24–29, July, 2005.

Special features of the $\gamma \rightarrow \alpha$ transformation occurring in a wide range of cooling rates (0.1 – 500,000 K/sec) in pure iron and in carbon and chromium steels are considered. It is shown that four stages of the $\gamma \rightarrow \alpha$ transformation are possible in the steels, the first of which has a diffusion or massive nature, and the other three can be characterized as displacement transformations. The genetic tie between the upper and lower bainite and transformations occurring through stages *II* and *III*, respectively, in pure iron is shown. The difference between the upper and lower bainite is determined by the difference in the mechanisms of motion of the phase boundary, which can be accompanied by redistribution of carbon atoms. Stage *IV* corresponds to athermal martensitic transformation.

Studies of the processes of transformation of austenite in cooling performed as early as in 1921 – 1923 showed that alloy steels had three temperature ranges where austenite decomposed the most intensely. For example, at relatively high temperatures (670 – 550°C) steels acquired a ferrite-pearlite structure, whereas at a temperature below 300°C austenite transformed into martensite. At intermediate transformation temperatures the structure formed in the steels had another nature often described as “secondary ferrite.” It did not attract the attention of researchers for a long time, because many of them presumed that this transformation was connected with nonuniform distribution of alloying elements.

In 1930 the work published by Davenport and Bain described the structural component formed at intermediate temperatures as an acicular dark-etching aggregate resembling neither pearlite nor martensite. Somewhat later the structure was called bainite in the USA, and the name was finally accepted by all specialists. However, as it is noted in [1], bainite had not been studied appropriately for a long time.

First of all, this is explainable by the fact that in the first two thirds of the XX century metal scientists and heat treatment specialists were concentrated primarily on the development of compositions for high-strength medium-carbon alloy steels and on conditions for their heat treatment. These steels

possessed high hardenability, and their hardening for martensite with subsequent annealing ensured a high yield strength $\sigma_{0.2}$ at satisfactory impact toughness in parts with large cross section. For example, in the case of hardening and low-temperature tempering the yield strength of such steels as 30KhGS, 30KhN3A, 38KhN3MF, 45KhN2MF, etc. attained 1500 – 2000 MPa at impact toughness exceeding 39 J/cm². After hardening and high-temperature tempering such steels exhibited $\sigma_{0.2} = 850 – 1200$ MPa at a higher impact toughness.

Numerous studies showed that the appearance of structural components other than martensite in the structure of hardened steels, for example, pearlite, bainite, or ferrite, lowered substantially the set of mechanical properties. For this reason, producers of critical parts strived to obtain a fully martensitic structure. This circumstance also explains the great attention to the nature and properties of martensite. The disadvantages of such steels were the susceptibility of some of them to temper brittleness and poor weldability.

It should also be noted that in the second half the XX century metallurgists created alloys with still higher strength, the high properties of which were based on the phenomenon of additional hardening of martensite by dispersed intermetallic particles segregated in aging. However, these steels known as maraging ones, were too expensive and contained scarce alloying elements, which explains their use only in aircraft and rocket engineering.

¹ Institute for Metals Physics of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.

In the last third of the last century the use of large welded structures required creation of new types of steel possessing good weldability in addition to high strength. The necessity for reducing the content of carbon in such steels to a minimum resulted in degradation of the strength properties, because the creation of martensitic structure in them was impossible. The strength properties of low-carbon steels can be raised in three ways. Firstly, they can be alloyed with strong carbide-forming elements so as to realize fully the effect of precipitation hardening by particles of second phase and to decrease the size of austenite grains. This way causes lowering of the ductility of the metal. Secondly, the hardening can be ensured by various modes of thermomechanical treatment. In this case the additional hardening can be lost in the welding process. Thirdly, the steel can be alloyed with chromium, nickel, and molybdenum in order to realize hardening due to bainitic transformation.

The industry and building sites demand millions of tons of such steels. For many reasons, economic ones including, the set of alloying elements used in the production of high-strength weldable steels turned out to be rather narrow. Today we can single out two types of high-strength weldable steels denoted HSLA (high strength low alloy) in foreign literature. Steels of type HSLA-80 (the figure indicates that the yield strength is equal to 80 kg/mm² or 800 MPa) can have a composition close to steel 05G2BT, for example, 0.03% C, 1.8% Mn, 0.05% Nb, 0.02% Ti. The high strength of such steels is primarily ensured by precipitation hardening. Steels of the second type have a more complex composition and a higher level of strength. For example, steels of type HSLA-100 ($\sigma_{0.2} \geq 1000$ MPa) have a composition close to that of domestic grade 05KhGN4DMF, for example, 0.04% C, 0.6% Cr, 0.9% Mn, 3.6% Ni, 1.6% Cu, 0.6% Mo. The high strength is ensured by bainitic hardening.

It is paradoxical that unambiguous description of structures observed in low-carbon alloy steels is still lacking. At least two standpoints exist on the mechanism of the bainitic transformation. One of them [2] is given in most domestic textbooks on metals science and is based on the morphological closeness of martensite and bainite crystals, the presence of texture on a polished surface in both transformations, the initiating effect of elastic stresses, etc. A similar approach prevails abroad, for example, in monograph [3] devoted to description of bainite. It is assumed that growth of crystals of bainitic ferrite is preceded by redistribution of carbon in austenite, which causes formation of depleted and enriched regions. Then follows martensitic transformation in the depleted austenite regions, segregation of carbides in the enriched regions, lowering of the concentration of carbon in them for this reason, etc. The majority of definitions of bainitic structure are based on description of the interrelation between ferrite and carbide phases. However, analysis of thermodynamic functions of austenite shows that spontaneous lamination of austenite is impossible, which makes us doubt the theories based on this assumption.

Review [4] presents examples of definitions of the structure of steels formed in the process of bainitic transformation. Even these definitions bear some eclecticism. For example, according to one of the definitions (Aaronson) based on morphological consideration of the structure bainite is divided into nodular, columnar, upper, lower, grain boundary allotrimorphic, and inverse varieties. The very names show that the morphological definitions (nodular, columnar) are mixed with definitions based on the kinetic diagram of decomposition of austenite (upper and lower bainite). The Bainite Committee of the Japan Institute for Steel has recommended the description of the main phase in low-carbon steels as polygonal, quasi-polygonal, Widmanstätten, and granular bainitic ferrite, and cubic martensite [4]. The number of definitions suggested for structural components that are less important in the structure of steels is even greater.

It becomes obvious that such an approach does not help in determining the mechanism of bainite formation. At the same time, the interest to phase transformations in low-carbon steels allows us to turn to works on pure iron and iron alloys specially chosen for studying the mechanism of bainitic transformation in steels. The decisive role in formulation and realization of such works belongs to Professor D. A. Mirzaev (YuzhUGU).

As an alternative, we should mention a series of works where bainite growth is described by analogy with growth of Widmanstätten ferrite, i.e., as diffusion growth of ferrite α -crystals in a two-phase region the boundaries of which are formed by continuation of lines GP and GS in the phase equilibrium diagram of the Fe–C system below the eutectoid horizontal (works of Zener, Cohen, Hillert, and Lyubov).

In order to appreciate this standpoint we should turn to the works of Academician V. D. Sadovskii [1]. Studying the kinetics of formation of bainite (then known as acicular troostite) in alloy steels he established that that with decrease in the concentration of carbon the maximum rate of formation of bainite increased, and the upper temperature boundary of bainite formation B_i increased simultaneously. He concluded that the temperature of bainite formation B_i in iron alloys where the content of carbon is reduced to zero should coincide with the martensite point of the carbonless matrix of the alloy, and the bainitic transformation should transform into a martensitic one. In principle, this equally refers to carbon steels too, but at that time nobody knew about the existence of the martensite point of iron. Later, it was shown experimentally in [5] that the martensitic transformation in iron and in its binary substitutional alloys has a stepped kinetics, and the structure formed can often be treated as bainitic ferrite.

In order to understand the possible causes of such growth behavior of crystals of bainitic ferrite we should turn to the thermodynamic stimuli of motion of a phase boundary. For example, in [6] J. Cahn predicted theoretically the existence of at least two modes of motion of a phase boundary under the action of a thermodynamic force. Firstly, a phase bound-

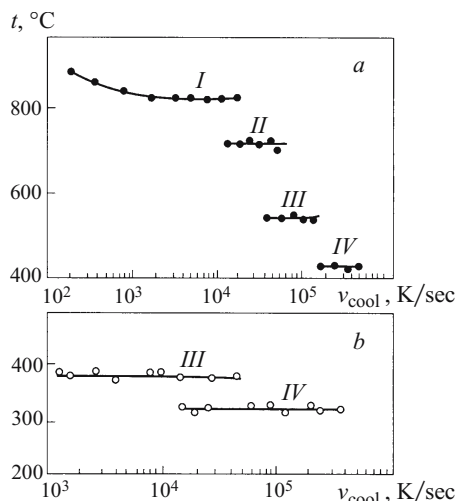


Fig. 1. Initial temperature of $\gamma \rightarrow \alpha$ transformation as a function of the cooling rate for Fe-C alloys: a) 0.005% C; b) 0.4% C.

dary can migrate slowly due to side displacement of jogs, which occurs at low values of the driving force. Secondly, a boundary can move over a normal at a high speed at high driving forces. These results have been amended in modern works, where boundaries are treated like systems of grain-boundary or interphase dislocations.

A relaxation theory of polymorphic transformations has been developed in [7], where the authors assume that the kinetics of the transformations and the structure of the new phase are determined primarily by the mechanisms of relaxation of phase stresses that appear close to the contact of two phases with imperfectly matched lattices. The highest elastic energy and the lowest surface energy are typical for unrelaxed crystals. Their formation should occur at a minimum transformation temperature. Triggering of different mechanisms of stress relaxation (twinning, slip over one or several systems, etc.) causes decrease in the elastic energy and growth in the surface energy of nucleation. The energy barrier of the nucleation decreases; therefore, formation of relaxed crystals can occur at a higher temperature. Triggering of all possible mechanisms of relaxation divides the total temperature range of the transformation into several temperature intervals. Each interval is characterized by its own relaxation mechanism, and each transformation is characterized by its own C-shape curve shifted over the time scale the longer the higher the temperature of the considered transformation stage. For the lowest stage, where the surface energy is low, the lattices of the two phases are coherent and the energy barrier is also low, and the transformation acquires an athermal nature, whereas for the stages occurring at higher temperatures it should be isothermal.

Let us pass to a more detailed description of experimental data. Determination of martensite points in pure iron and in its carbonless substitutional alloys is complicated by the high-temperature stage of the normal $\gamma \rightarrow \alpha$ transformation that leads to formation of polyhedral and virtually equiaxed

ferrite grains. The rate of the normal transformation increases markedly in iron cleaned from interstitial impurities. In order to cool austenite below the stage of normal transformation the cooling rate should exceed $(10 - 30) \times 10^3$ K/sec. Such and higher cooling rates (up to 500×10^3 K/sec) have been attained in [5]. Analysis of inflections on the cooling curves made it possible to determine the temperature of the $\gamma \rightarrow \alpha$ transformation and of the martensite points. Unexpectedly, it turned out that martensitic transformation in iron and in its binary substitutional alloys had a stepped kinetics. In fact, iron had as if three martensite points; with allowance for the normal transformation the $\gamma \rightarrow \alpha$ transformation occurred in four stages (Fig. 1a).

The content of carbon in the tested iron specimen was only 0.005%, which was substantially lower than the solubility limit in the α -phase. The same picture was observed for other iron specimens, where the concentration of carbon was lower than its solubility limit in the α -phase. In pure iron the temperatures of the martensite points turned out to be 720, 540, and 420°C. With allowance for the upper stage of the normal or massive $\gamma \rightarrow \alpha$ transformation the corresponding stages were denoted I, II, III, and IV. For each of the three martensitic stages the initial point of the transformation was independent of the cooling rate in a quite wide range of cooling rates and then jumped downward to the temperature of the next stage [5]. It should be noted that in the purest iron specimens, where the carbon content was only $10^{-8} - 10^{-7}\%$, a cooling rate exceeding 500,000 K/sec turned out to be insufficient for reaching the fourth stage.

Growth in the content of carbon in the alloy changes considerably the picture observed. For example, the temperature of the first stage of the transformation (formation of equiaxed ferrite) depends on the cooling rate. Carbon additives decelerate the transformation in this stage, which is manifested in decrease in the critical cooling rate and lowering of the transformation temperature at the same cooling rate. The initial temperatures of stages II, III, and IV also fall with growth in the carbon concentration in the alloys. The temperature of the transformation in stage II falls the most markedly; at carbon content exceeding 0.03% it becomes lower than the transformation temperature in stage III. Therefore, medium-carbon iron alloys have only two transformation stages (III and IV) in addition to the normal transformation (Fig. 1b). In fact, this means that at a high cooling rate two martensite points can be observed in such alloys. The concentration dependence of the transformation temperatures of stages II, III, and IV on the content of carbon is presented in Fig. 2.

Such dependences of the initial temperatures of $\gamma \rightarrow \alpha$ transformation on the cooling rate have also been obtained for a series of alloyed iron alloys including those bearing such widely used alloying elements as nickel, chromium, and manganese. Specifically, a series of alloys bearing 4, 6, and 9% Cr and carbon varied in a range of 0.004 - 0.40% has been studied in [8, 9]. As an example, we present the results

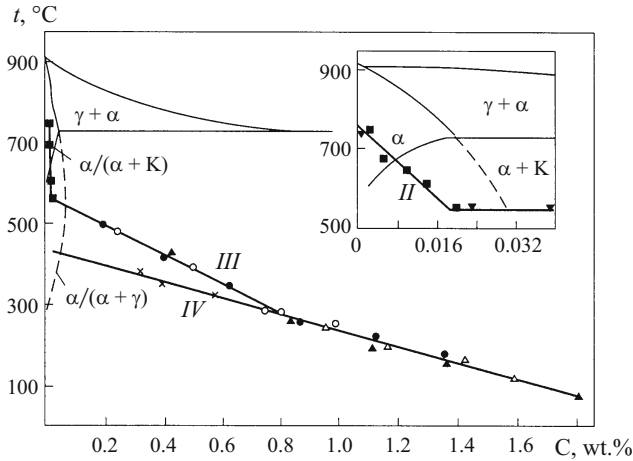


Fig. 2. Concentration dependence of the temperatures of stages II–IV of $\gamma \rightarrow \alpha$ transformation in Fe–C alloys as compared with lines of the phase equilibrium diagram of the Fe–C system (different symbols are used for data of different authors).

obtained for low-carbon alloy Fe – 4% Cr – 0.004% C (Fig. 3a) and for chromium steel 11Kh6 (Fig. 3b). These results also reflect the existence of four temperature plateaus and hence the existence of four kinetic mechanisms of $\gamma \rightarrow \alpha$ transformation. The resulting curves describing the dependence of transformation temperature in chromium steels on the carbon content are presented in Fig. 4. It also depicts the upper boundaries of bainite formation according to our data and published results.

The multi-stage mechanism of the $\gamma \rightarrow \alpha$ transformation can be explained quite simply, if we assume that the rate of growth of the α -phase in different transformation stages is connected with a change in the growth mechanism. In stage I two growth mechanisms are possible, i.e., diffusion and massive ones. In the former case for alloys bearing carbon or alloying elements the growth of ferrite at high temperatures and low cooling rates is limited by the volume diffusion of carbon or the alloying elements. In the latter case we can presume the presence of a narrow peak of carbon concentration close to the interphase. The interphase can be incoherent or partially coherent. The stresses caused by the transformation are removed due to the motion of vacancies.

In our opinion, the appearance of stages II, III, and IV in iron is explainable by the existence of two mechanisms of motion of interphase dislocations described by Cahn, Roitburd, and Hillert. The first mechanism has the form of thermally activated motion developed due to migration of kinks on boundaries of ferrite plates and due to climb of mismatch dislocations. This mechanism is realized in stage II. The process is limited by the diffusion of vacancies through the interphase, and the growth occurs rather slowly. If the transformation occurs in the double-phase region, carbon on the γ/α boundary can be redistributed. Hillert has shown [10] that in this case the force of joint braking exceeds the driving force. Therefore, local equilibrium is established on the

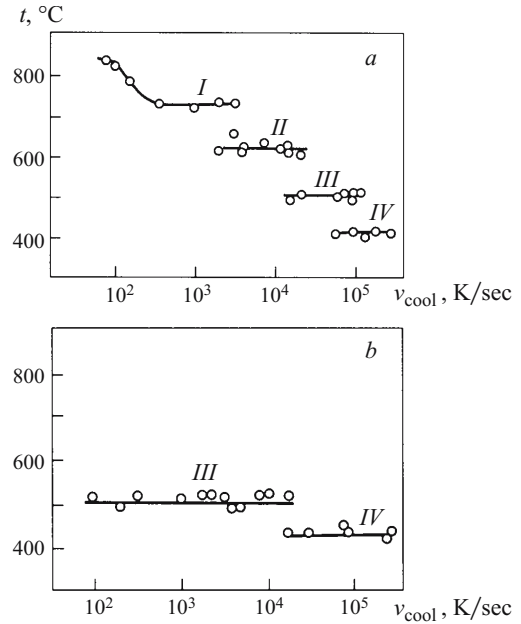


Fig. 3. Effect of the cooling rate on the temperature of $\gamma \rightarrow \alpha$ transformation in alloys Fe–4% Cr–0.004% C (a) and Fe–6% Cr–0.11% C (b).

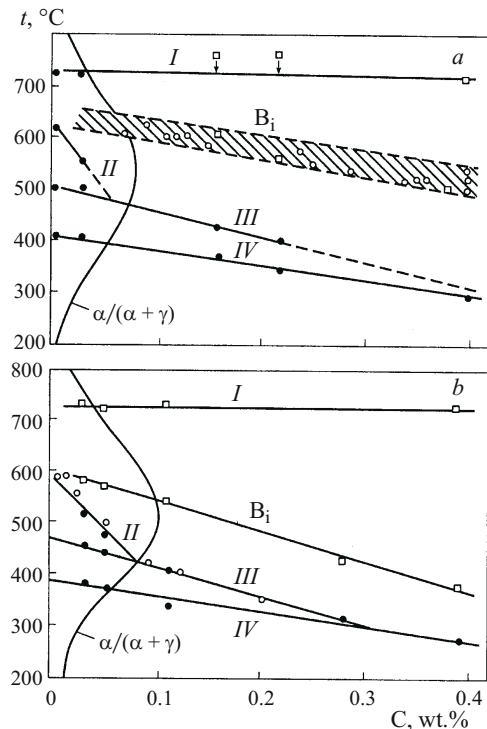


Fig. 4. Dependences of the temperature of $\gamma \rightarrow \alpha$ transformation on carbon concentration in steels bearing 4.3% Cr (a) and 6.5% Cr (b) (different symbols are used for data of different authors).

interphase, and diffusion growth occurs. Diffusion-free transformation requires supercooling to the single-phase region, which explains the location of plateau II on the tempe-

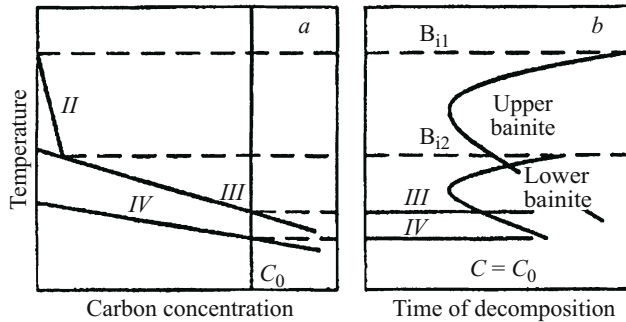


Fig. 5. Diagram of bainitic transformation in steels: *a*) temperatures of $\gamma \rightarrow \alpha$ transformation as a function of carbon content; *b*) diagram of isothermal decomposition of austenite in steel with carbon concentration equal to C_0 .

perature scale. The mechanism for stage *III* is different. This is conservative forced slip, in which the interphase should cause formation of a dislocation system. The evolution of stresses necessary for the slip corresponds to thermodynamic stimuli (driving forces) of 1250 J/mole. Growth of the α -phase can occur at a high speed. Therefore, diffusion-free reaction will occur in the double-phase region of the phase diagram. Martensitic stages *III* and *IV* can also occur in steels (see Figs. 2 and 4). This is manifested in a double-stage dependence of the martensite point on the cooling rate. The transition from the upper stage to the lower one, i.e., an abrupt decrease in the martensite point, occurs at a specific critical cooling rate of about 50×10^3 K/sec. However, the value of this rate decreases with growth in the carbon content and especially with growth in the content of the carbide-forming alloying elements.

Note that in medium-carbon steels subjected to rapid cooling the structure of the products of transformation in these stages is represented by lath martensite. The only difference is that in transformation of stage *III* the structure contains retained austenite in the form of thin layers over lath boundaries. After transformation of stage *IV* retained austenite is absent in the structure, and numerous twinned plates can be observed against the background of lath packs. All these facts indicate impurity braking of the interphase by carbon atoms in stage *III*.

With growth in the carbon content the temperature of stage *II* decreases abruptly almost in parallel with the $\alpha/(\gamma + \alpha)$ interphase in the Fe-C phase diagram or in the Fe-Cr-C diagram (see Figs. 2 and 4). Therefore, in steels bearing over 0.03% C the transformation occurs only through stages *III* and *IV* (two martensite points). The same behavior of plateau *II* is typical for carbonless Fe-Ni, Fe-Mn, Fe-Ru, Fe-Cu, and other alloys [11]. It can be seen that plateau *II* in iron alloys occurs only in the single-phase region of the phase diagram. The microstructure of the transformation in stage *II* consists of wide ferrite laths with numerous jogs over their boundaries.

Let us consider the correspondence between the upper temperature boundary of bainite formation B_i and the temperatures of the diffusion-free stages. If the values of B_i presented in Fig. 4 are extrapolated to the zero concentration of carbon, we will see that the resulting temperature is very close to the temperature of stage *II* of the carbonless alloy. It seems that the upper bainite has inherited likeness to the transformation products of stage *II*. However, bainitic transformation in steels occurs in the double-phase region, and therefore the crystals of upper bainite grow very slowly due to the limitation of the growth rate by carbon removal. In other words, the formation of upper bainite can be treated as realization of stage *II* under conditions of diffusion-controlled growth.

The range of existence of stage *II* of the transformation is limited with respect to the temperature and with respect to carbon concentration. For alloys of the Fe-Cr-C system at a temperature below 450–480°C, when stages *II* and *III* intersect, the bainitic reaction can be realized on the basis of martensitic stage *III*. This is illustrated by the diagram of Fig. 5, where the temperature boundaries of formation of upper bainite are approximately equal to the temperatures of stage *II* for the carbonless alloy, and the upper boundary of lower bainite corresponds to temperature of stage *III* of the carbonless alloy, i.e., to its martensite point determined at conventional cooling rates. In this case the curve of isothermal decomposition of austenite should have two maxima of the rate of bainite formation, which is indeed observed for some alloy steels and for carbon steel [12].

Such diagrams can be used for explaining the difference between the structures of upper and lower bainite. The structural difference appears due to the fact that upper bainite nucleates in the form of low-carbon ferrite inheriting a low content of carbon in the products of stage *II* of the transformation for the given isotherm. If the mean content of carbon in the alloy exceeds its concentration in the α -phase formed in stage *II*, carbon diffuses into austenite. The carbon-enriched austenite may undergo a eutectoid $\gamma \rightarrow (\alpha + \text{carbide})$ transformation yielding nonlamellar products; therefore the carbide segregations in the structure of upper bainite are arranged over boundaries of ferrite plates. The crystals of lower bainite inherit the carbon concentration of stage *III* for the given isotherm. Therefore, the spontaneous tempering accompanying the transformation yields carbides distributed over the volume of the α -phase and regularly oriented with respect to its crystal lattice.

CONCLUSIONS

The suggested mechanism of multistage transformation of austenite in cooling describes well the intricate nature of bainite transformation in carbon and carbonless iron alloys without associating it explicitly with the presence or absence of carbon or carbide phase in the steel. We can state that hypothesis of V. D. Sadovskii [1] on connection between

bainitic transformation in steels and martensitic transformation in their carbonless matrix has been proved experimentally.

REFERENCES

1. V. D. Sadovskii, "Structural transformations in hardening and tempering of structural steels," in: *Proc. of the Inst. Metallofiz. and Metallurg., Issue 3* [in Russian], UF Akad. Nauk SSSR, Sverdlovsk (1945).
2. R. I. Éntin, *Transformations of Austenite in Steels* [in Russian], Metallurgizdat, Moscow (1960).
3. H. K. D. H. Bhadeshia, *Bainite in Steels*, The Inst. of Mater., London (1992).
4. G. Krauss and S. W. Thompson, "Ferritic microstructures in continuously cooled low- and ultralow-carbon steels," *ISIJ Int.*, **35**(8), 937 – 945 (1995).
5. D. A. Mirzaev, M. M. Shteinberg, T. N. Ponomareva, and V. M. Schastlivtsev, "Effect of the cooling rate on location of martensite points. Carbon steels," *Fiz. Met. Metalloved.*, **47**, Issue 1, 125 – 135 (1979).
6. K. Cahn, "The theory of crystal growth and the motion of interphase in crystalline materials," *Usp. Fiz. Nauk*, **91**, Issue 4, 677 – 689 (1967).
7. A. L. Roitburd and G. V. Kurdjumov, "The nature of martensitic transformation," *Mat. Sci. Eng.*, **39**, 141 – 167 (1979).
8. D. A. Mirzaev, S. E. Karzunov, V. M. Schastlivtsev, et al., "Gamma \rightarrow alpha transformation in low-carbon Fe – Cr alloys," *Fiz. Met. Metalloved.*, **61**, Issue 2, 331 – 338 (1986).
9. D. A. Mirzaev, S. E. Karzunov, V. M. Schastlivtsev, et al., "Special features of martensitic and bainitic transformation in chromium steels," *Fiz. Met. Metalloved.*, **62**, Issue 2, 318 – 327 (1968).
10. M. Hillert, "Diffusion and interface control of reaction in alloys," *Metal. Trans.*, **6A**(1), 5 – 19 (1975).
11. D. A. Mirzaev, M. M. Shteinberg, T. N. Ponomareva, et al., "Phase $\gamma \rightarrow \alpha$ transformation in binary iron alloys with copper, cobalt, ruthenium, and platinum," *Fiz. Met. Metalloved.*, **51**, Issue 2, 364 – 375 (1981).
12. O. P. Morozov, V. M. Schastlivtsev, and I. L. Yakovleva, "Upper and lower bainite in carbon eutectoid steel," *Fiz. Met. Metalloved.*, No. 2, 150 – 159 (1990).