STRUCTURE FORMATION IN IRON ALLOYS. NONEQUILIBRIUM STRUCTURES

We present the fourth paper of a series devoted to analysis of processes of structure formation in iron alloys. The results of the analysis of the phase diagram of the Fe – C – Mn system made in the first three papers and of the performed eutectoid polyhedration of this diagram are used for discussing the processes of formation of nonequilibrium structures in manganese steels. Results of microstructural and microprobe observations of squeezing of manganese in steel 20G from ferrite into retained austenite are presented. It is shown that a special austenite-carbide component with pearlite-like structure is formed in steel 110G13L.

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ALLOYS OF THE Fe – C – Mn SYSTEM. PART 4. SPECIAL FEATURES OF STRUCTURE FORMATION IN MANGANESE AND HIGH-MANGANESE STEELS[1]

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A eutectoid polyhedration of the phase diagram of the Fe – C – Mn system is presented, which shows that the structure of manganese steels can contain eutectoids of two kinds that can be in a state of peritectoid equilibrium with austenite. A conode polyhedration of the diagram is performed as applied to the composition of steel 2G. The structural features ensuring precipitation hardening or composite hardening of steels 20G and 110G13L are considered.

INTRODUCTION

In the earlier published works [1 – 3] we presented computed and plotted isothermal and polythermal sections, projections of the phase diagram of the Fe – C – Mn system, and diagrams giving a general notion of the studied part of the system.

It is known that in low-carbon ferrite-pearlite steels manganese increases the strength substantially virtually without worsening the ductility and the impact toughness. The mechanism of such effect of manganese has not been studied, though in some of my works [4 – 6] I gave data on the possibility of heterogenization of ferrite and formation of a microcomposite structure. Analysis of the plotted part of the Fe – C – Mn diagram makes it possible to substantiate this mechanism of manganese influence and to outline ways for practical use of this effect.

In the present work we will consider a eutectoid polyhedration of the phase diagram of the Fe – C – Mn system and its conode polyhedration as applied to the composition of steel 20G and describe an experimental study of special features of structure formation in steels alloyed with manganese.

METHODS OF STUDY

We base our analysis of special features of structure formation in manganese steels on the use of eutectoid and conode polyhedration of the Fe – C – Mn phase diagram. We performed the eutectoid polyhedration of the diagram over the thalwegs of displacement of conode triangles of eutectoid equilibria $\gamma \leftrightarrow \alpha + Cem$ and $\gamma \leftrightarrow \alpha + \varepsilon$, where *Cem* is used

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The third paper appears in *Metalloved. Term. Obrab. Met.*, No. 9(603), pp. 3 – 7 (2005).

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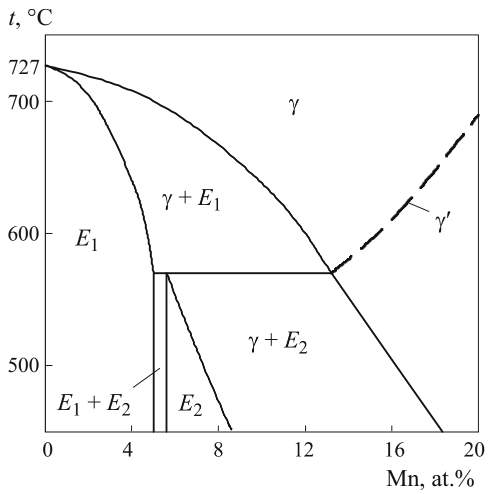

Fig. 1. Eutectoid polyhedration of the Fe – C – Mn diagram: E_1) $\alpha + Cem$ eutectoid; E_2) $\alpha + \varepsilon$ eutectoid; γ') austenite in the $Cem \leftrightarrow \alpha + \varepsilon$ eutectoid equilibrium.

for cementite, the ε-phase is represented by an M_7C_3 carbide, and the $\alpha + Cem$ (alloyed pearlite) and $\alpha + \varepsilon$ eutectoid mixtures in the polyhedration of the phase diagram are denoted E_1 and E_2, respectively. The section of the diagram representing its eutectoid polyhedration is presented in Fig. 1. The dashed line in the section characterizes the temperature dependence of the manganese content in eutectoid austenite γ' that belongs to the $Cem \leftrightarrow \alpha + \varepsilon$ domain of the three-phase equilibrium.

It can be seen that both eutectoids (E_1 and E_2) are in peritectoid equilibrium with austenite. Eutectoid E_1 can be replaced by eutectoid E_2 only at a temperature below 570°C at over 13 at.% Mn in austenite.[3] However, for this process to occur the kinetic conditions ensuring thermodynamic equilibrium should be obeyed too. At the same time, it is known that at a temperature below 600°C the diffusion of substitutional alloying elements (including manganese) and the self-diffusion of iron decelerate so much that this leads to the occurrence of diffusion-free processes and promotes preservation of a considerable amount of retained austenite in the structure of the alloy. Therefore, it is most probable that the eutectoid-peritectoid transformation does not occur under conventional conditions and that the austenite matrix is preserved in the structure of steels bearing about 13% Mn. This is confirmed by the practice of fabrication and use of castings from steel 110G13L, though some special components (carbides, double-phase mixtures, etc.) can appear in some regions of the structure of this steel; they are removable by accelerated cooling of the castings from a purely austenitic condition (commonly from a temperature of 1000 – 1050°C).

Maximum supersaturation of austenite occurs at elevated rates of crystallization (for example, in chill casting). Strongly supersaturated manganese austenite is very unstable and tends to decompose and form secondary carbide segregations. The high rate of formation of these segregations should ensure their flake or acicular shape.

RESULTS AND DISCUSSION

It can be expected that already in the process of cooling of a casting the structure of high-manganese alloys acquires a special component consisting of austenite and carbide flakes (or needles). Such a structure (in which austenite has partially undergone pearlitic transformation) has been detected in heat treated steel 110G13L (see Fig. 2) [7]. It has been shown that when the steel is cooled very slowly, "dense clusters of carbide flakes form in isolated regions, which resembles a pearlitic structure. Transition to thin-flake pearlite occurs on the boundaries of these regions contacting untrans-

[3] For steels the content of manganese expressed in atomic and mass percent has very close values.

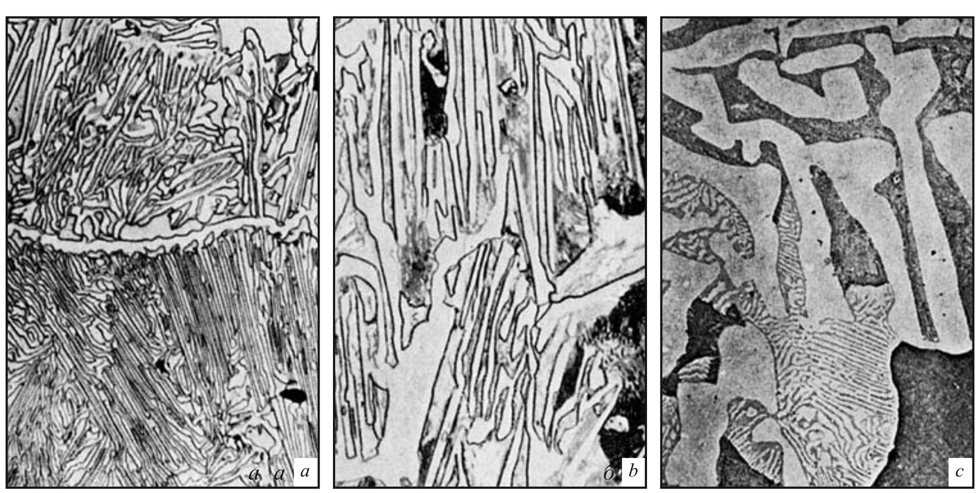

Fig. 2. Domains of microstructure in steel 110G13L with clusters of coarse carbide flakes and regions of austenite and pearlite lying between the flakes [7]: *a*) × 1000; *b*) × 1500; *c*) × 5000.

formed austenite. Dense clusters of coarse flakes are not pearlite, because between the flakes we observe thin-flake pearlite instead of ferrite." It should be noted that the spaces between the clusters of carbide flakes contain not only pearlite but also regions of austenite. This stricture is observable more clearly on an electron microscopic photograph (Fig. 2*c*).

At low content of manganese in the metal (up to 4 – 5%) only one kind of eutectoid may form in its structure (alloyed pearlite E_1). However, in this case too, manganese increases the probability of the presence of a considerable amount of retained austenite in the structure of the metal due to the noticeable decrease in the temperature of the eutectoid transformation. This is well known from the results of studies of heat treatable alloys bearing several percent of manganese. However, even in the case of only 1 – 1.5% Mn in low-carbon steels their structure formation is influenced by the austenitizing effect manganese.

We have proved the austenitizing effect in structure formation of steel of type 20G experimentally and mentioned it in some earlier works [5, 6]. In order to determine the mechanism and conditions of manifestation of this effect we analyzed structure formation in this kind of steel. For this purpose we used regions of some isothermal sections of the Fe – C – Mn diagram, which corresponded to the composition of the analyzed steel. These regions are shown enlarged in Fig. 3. The dashed lines reflect the metastable continuation of the boundaries of the α + γ double-phase region. It has been shown above that this metastable equilibrium is frequently realized in the process of structure formation, especially in accelerated cooling from the temperatures of austenite state. The light gray color in the sections marks three-phase regions of eutectoid equilibria α + γ + *Cem* and α + γ + ε and an intermediate double-phase α + ε region, which are usually not realized at 600 – 500°C due to the effect of kinetic factors. The process of eutectoid transformation in the temperature range of 700 – 600°C occurs only partially for the same reason. These factors make it possible to estimate structure formation in steel 20G in terms of the changes in the position of the *ab* (α – γ) conodes not only in the regions of stable equilibrium but also in metastable regions. The conodes in the metastable region are represented by the dash-and-dot lines. Point *M* on the conodes is a figurative point of steel 20G having a standard composition (0.2 wt.% or about 1 at.% carbon and 1 at.% manganese). The change in the position of conode *ab* upon a decrease in the temperature was used to perform conode polyhedration of the phase diagram as applied to steel 20G (Fig. 4).

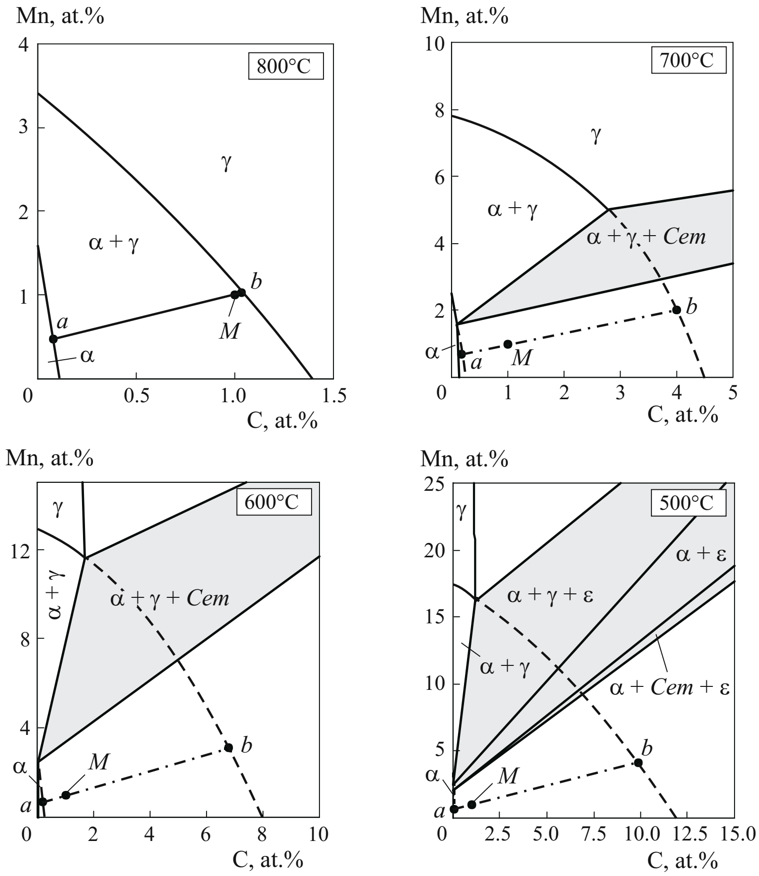

Fig. 3. Position of α – γ conodes at a temperature ranging from 800 to 500°C as applied to an alloy with 1 at.% C and 1 at.% Mn; at 700 – 500°C the conodes are drawn in regions belonging to supercooled alloys: *M*) the figurative point of the alloy; *a* and *b*) the nodes of α and γ phases, respectively.

In Fig. 4 the conode polyhedration of the Fe – C – Mn diagram is compared with the position of the α + γ double-phase region in the Fe – Mn system. It can be seem that in both cases the content of manganese in the equilibrium phases varies similarly. It should be noted that the solubility of manganese in ferrite is limited substantially. This especially concerns steel 20G. The maximum solubility of manganese in the ferrite of this steel amounts to 0.6 – 0.7%,

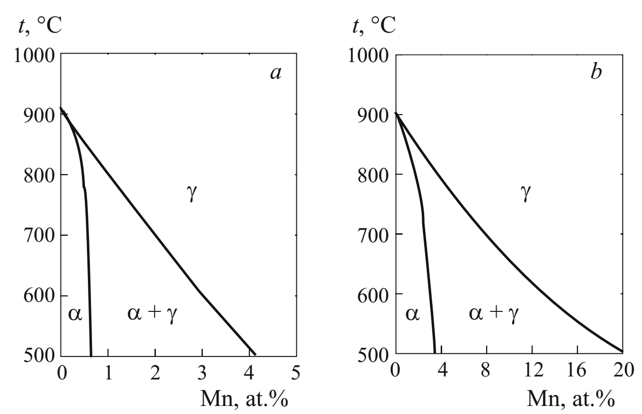

Fig. 4. Conode polyhedration in the α + γ double-phase region of the Fe – C – Mn diagram as applied to an alloy with 1 at.% C and 1 at.% Mn (*a*) as compared to the same region in the Fe – Mn system (*b*).

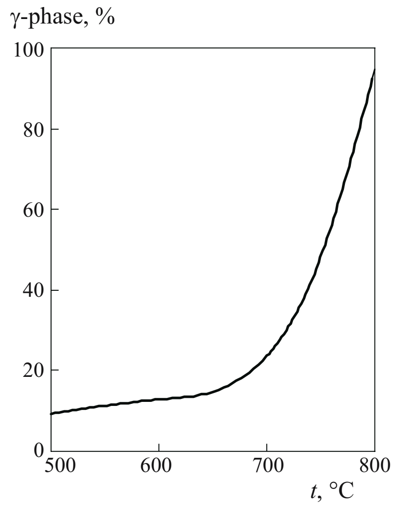

Fig. 5. Dependence of the amount of austenite in double-phase $\alpha + \gamma$ alloy with 1 at.% C and 1 at.% Mn on the temperature of isothermal hold (after cooling from the austenite range).

which is noticeably lower than the mean content of manganese in steel 20G.

The presented values of manganese solubility concern the ferrite-austenite metastable region. If the steel undergoes eutectoid transformation, the content of manganese in ferrite is still lower. This means that if the diffusion redistribution of manganese in ferrite, austenite, and cementite in steel 20G is hindered (which usually occurs under nonequilibrium conditions of structure formation), the crystallization of ferrite should be accompanied by mechanical squeezing of manganese atoms by its front and formation of austenite zones enriched with manganese.

It can be seen from Figs. 3 and 4 that the formation of ferrite in steel 20G begins at about 800°C. In eutectoid austenite (at about 715°C) the content of manganese amounts to about 2%, whereas in austenite supercooled to 500°C it attains 4.0 – 4.5%. Regions of austenite enriched with manganese to this extent cannot undergo full polymorphic transformation in further cooling. For this reason the structure of steel 20G should preserve microzones of retained austenite in addition to ferrite. These microzones should be located inside ferrite grains in the form of fine inclusions or a continuous thin branched skeleton ensuring composition hardening. The hardening should be especially considerable in the case of martensitic transformation of the austenite.

The amount of austenite preserved in the structure of the steel at 800 – 500°C has been calculated with the use of the rule of segments, and its temperature dependence is presented in Fig. 5. It can be seen that the amount of retained austenite exceeds 10%. This austenite can be preserved in the structure after normalization of the steel and have the form of microzones in ferrite grains.

The effect of heterogenization of ferrite was studied experimentally for steels of grades 20GL, 20GTL, 20GFL, and 20GFTL used widely for fabrication of critical car castings. As a rule, the microstructure of normalized steel 20GL is interpreted as a ferrite-pearlite one. However, some of its properties and their variation under the effect of alloying cannot be explained by the known mechanisms of hardening of steels with such microstructure (grain-boundary, pearlitic, and solid-solution ones) [5, 6]. The special features of the hardening mechanism of the steel have been determined by metallographic, phase, and thermokinetic analyses.

The microstructure of steel 20GL (see Fig. 6) was studied after cooling from temperatures of the austenitic range at different rates (from 0.03 to 210 K/sec) by methods of metallographic (light and electron microscopes) and x-ray spectral (Cameca and Camebax devices) analysis.

The microstructure of annealed and normalized steel 20GL ($v_{cool} = 0.05 – 0.08$ K/sec) contained ferrite grains of two kinds, i.e., "smooth" (light) and "rough" or textured (dark) ones (Fig. 6*a*), under low magnification (× 100 – 300). The inhomogeneous structure of the latter was determined at high magnification (× 800 and more). At 1.2 – 1.3% Mn and 0.37 – 0.45% Si in all the studied steels (20GL, 20GTL, 20GFL, and 20GFTL) we detected grains of inhomogeneous heterogenized ferrite. Inside and over the boundaries of such grains we observed (in about the same amount) fine inclusions with elevated hardness (Fig. 6*b*). In some cases these inclusions merged, forming a continuous fine border over boundaries of ferrite grains (Fig. 6*c*).

X-ray spectrum analysis with point probing performed with the help of a Camebax installation showed that the ferrite grains with a high degree of heterogenization contained more manganese (1.25 – 1.38%) than the "smooth" ferrite (0.95 – 1.08%). This meant that manganese segregated in inclusions, which allows us to interpret these inclusions and borders near the ferrite grains as retained austenite.

Linear probing of regions of heterogenized ferrite with penetration into boundary zones (borders of ferrite grains) was performed using a Cameca installation. The results of probing to determine the content of manganese and silicon are presented in Fig. 7. It can be seen that inside the ferrite grains the distribution of elements is very nonuniform. Some zones bear a very high content of silicon (up to 0.5 – 0.6%) and very low content of manganese (0.2 – 0.3%). In metallographic analysis in the Camebax installation these zones have a lighter color (Fig. 6*f*) and can be interpreted as pure ferrite. On the contrary, the fine dark regions are enriched with manganese and depleted of silicon. These regions can be treated as zones of retained austenite that has undergone partial martensitic transformation during the cold treatment of the steel, because the metallographic specimens were tested for bending strength at – 60°C.

The structure of the borders over boundaries of ferrite grains can be estimated using the curves of distribution of manganese and silicon in them (Fig. 7*b*). The content of manganese in the borders increases to 4 – 6% and the amount of silicon decreases by a factor of 1.5 – 2 as compared to ferrite. The austenitic nature of the borders is also

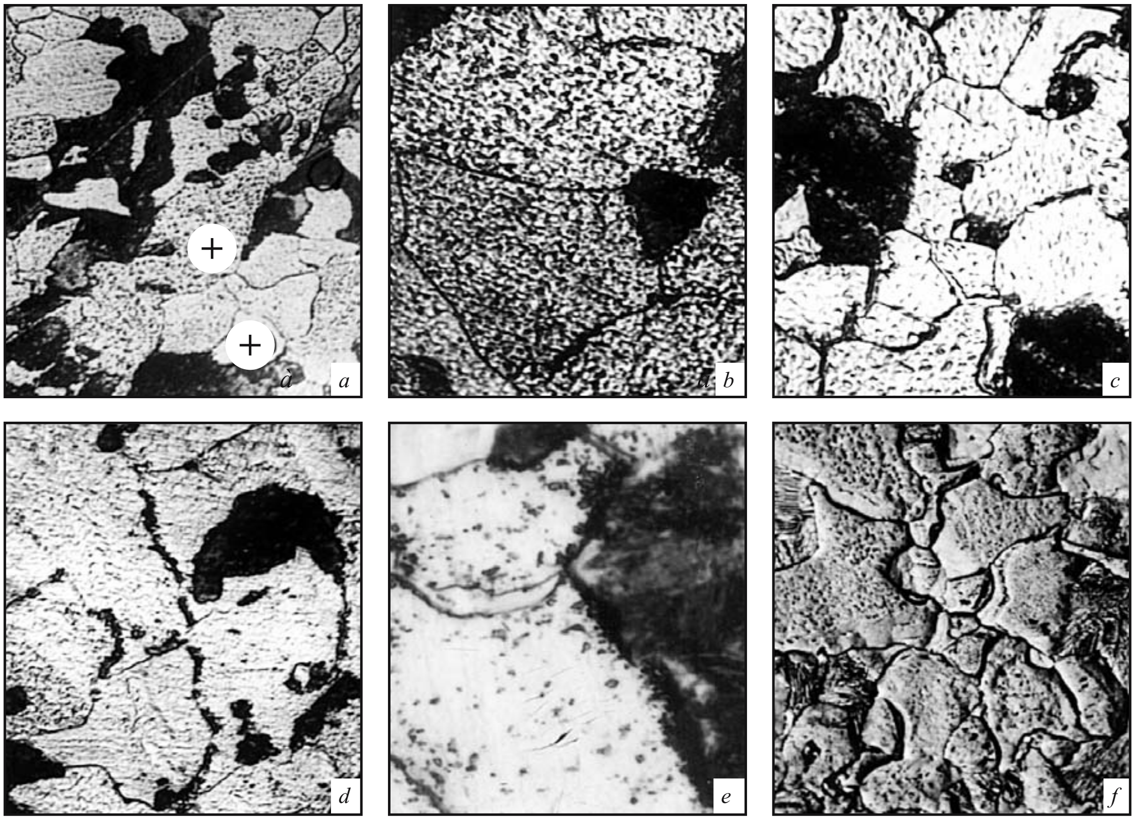

Fig. 6. Microstructure of steel 20GL with heterogenized ferrite: *a*) × 300 (the places of point probing are encircled); *b*, *c*) × 900; *d*) × 1350; *e*) × 2000; *f*) × 800.

confirmed by their pearlitic or intermediate decomposition in the process of cooling of the metal (Fig. 6*d*) or martensitic transformation in cold treatment of the metal (Fig. 6*e*).

The structure of alloy steels (manganese, nickel, etc.) consisting of ferrite and regions of untransformed or partially decomposed austenite has been studied in several works (for example, in [7]). Such a structure is called granular bainite. Most frequently it forms in low-carbon steels cooled continuously in the temperature range of the upper part of the bainite range. In the process of growth the hypoeutectoid ferrite progressively surrounds austenite regions enriched with carbon and other austenization promoters that sometimes decompose later into conventional ferrite and thin-flake pearlite.

In [7], formation of granular bainite in the structure of steel 20G was observed after cooling the specimens in air or in an air flow (v_{cool} = 0.5 – 1 K/sec). However, as has been shown above, still finer differentiated granular ferrite can form in the structure of steel 20GL at lower cooling rates too (starting with 0.04 – 0.05 K/sec).

The presence of retained austenite can have a double effect on the properties of the steel. When forming inclusions or even a continuous branched skeleton inside ferrite grains, retained austenite promotes hardening of the metal (by a precipitation or composition mechanism). This effect is especially noticeable after martensitic transformation of retained austenite. This hardening is not accompanied by substantial decrease in the ductility and impact toughness of the metal.

If the retained austenite has the form of a border over boundaries of ferrite grains, this can lead to considerable embrittlement of the metal, especially at a low temperature. In some cases the borders can decompose by a pearlitic or intermediate mechanism (Fig. 6*d*). The presence of a consider-

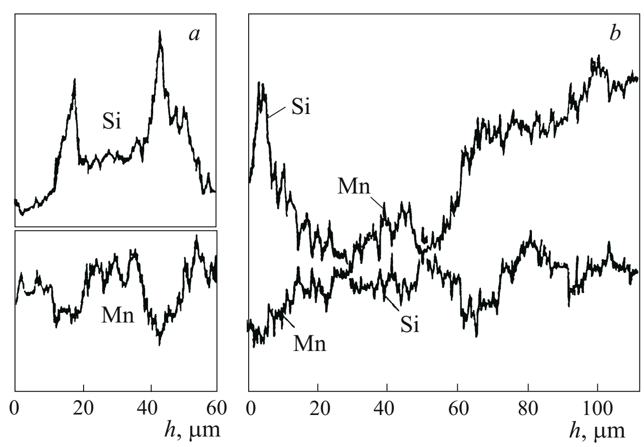

Fig. 7. Distribution of elements over ferrite grains (*a*) and in intragrain borders (*b*).

able number of such regions in the structure of the steel causes decrease in the impact toughness.

In steels of type 20GL bearing up to 1.4 wt.% Mn such regions are encountered episodically and do not influence considerably the properties of the metal. However, in massive and complex-geometry castings with considerable segregational heterogeneity with respect to manganese, dangerous zones with embrittled structure can appear. In the case of 2 – 2.5 wt.% Mn in the steel the number of austenite borders increases, which leads to marked embrittlement of the metal upon their intermediate or martensitic transformation.

CONCLUSIONS

1. The performed eutectoid polyhedration of the diagram and its analysis have shown that the structure of manganese steels can have two kinds of eutectoid ($\alpha + Cem$ and $\alpha + \varepsilon$) that are in peritectoid equilibrium with austenite. In steels bearing up to 5% manganese only one kind of eutectoid (alloyed pearlite) may appear. Substitution of pearlite by $\alpha + \varepsilon$ eutectoid can occur only at a temperature below 570°C at over 13% Mn in the austenite. However, due to the effect of kinetic factors the eutectoid-peritectoid transformation does not occur under conventional conditions of structure formation; steels bearing about 13% Mn preserve the austenite matrix.

2. Analysis of the conode polyhedration of the diagram in the range of the temperatures of polymorphic $\gamma \to \alpha$ transformation as applied to compositions of type 20G has shown that the structure of this steel can preserve microzones of retained austenite in an amount of 10 – 15% in addition to ferrite; these microzones occur inside ferrite grains and ensure precipitation hardening or composition hardening of the metal. The hardening can be especially considerable in the case of martensitic transformation of austenite. Heterogenization of ferrite in manganese steels has been confirmed and studied experimentally. It has been shown that at optimum chemical composition of steel 20G the hardening effect is not accompanied by decrease in the ductility and impact toughness of the metal. However, at an excess content of manganese intergrain austenitic borders can form and undergo intermediate and martensitic transformations accompanied by considerable embrittlement.

3. A special double-phase austenite-carbide component with a pearlite-like structure can form in high-manganese austenitic steels, for example, in steel 110G13L.

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