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ON THE MECHANISMS OF COPPER EFFECT ON STRUCTURE FORMATION IN CAST IRON

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The complex effect of copper on structure formation in cast iron is analyzed. It is shown that the action of copper can be not only graphitizing but also chilling. Theoretical and experimental methods are used for investigating the mechanisms of the different copper effects. Special features of structure formation in copper irons during their crystallization are studied with the use of designed sections of the Fe – C – Cu diagram. It is shown that the mechanisms of the pearlite-forming and anti-graphitizing actions of copper have a more kinetic nature than a thermodynamic one.

INTRODUCTION

Copper is one of the main alloying elements in iron and steel. It has substantial influence of the structure and properties of cast iron. However, the action of copper is diverse and ambiguous. Depending on the copper content, on the chemical composition of the iron with respect to other elements, and on the kinetic conditions of structure formation the action of copper can be graphitizing or chilling [1]; copper can change the intensity of pearlite formation and produce an ambiguous effect on the mechanical properties of irons [2]. The causes and mechanisms of this complex action of copper have not been studied exhaustively, though in the recent years the studies and applications of copper cast irons have been amplified.

The main and most often used manifestations of copper influence on the formation of structure in iron are the effects of pearlite formation in the structure, elevation of the susceptibility of the iron to graphitization, stabilization of austenite, and elevation of the hardenability. The mechanisms of some effects (for example, of stabilization of austenite and of elevation of the hardenability) are well known [2, 3] and do not require additional investigation. However, other manifestations of copper influence are sometimes called not only ambiguous but also anomalous and even puzzling [4].

The present work had an aim to study the special features and mechanisms of copper influence on the formation of structure in cast iron.

METHODS OF STUDY

We analyzed the mechanisms of various actions of copper on structure formation in iron using theoretical and experimental methods. The theoretical analysis was based on constructing some sections of the stable and metastable phase diagrams of alloys of the Fe – C – Cu system and estimating the possibility of phase and structural transformations on the basis of these sections. In order to check the results of such analysis and to determine the possible thermokinetic deviations from equilibrium structure formation we performed experimental studies with the use of methods of control of iron chilling and metallographic and local x-ray spectrum analyses.

Design and construction of the sections of the Fe – C – Cu phase diagrams were performed according to the method of [5], which has been tested repeatedly, described in detail, and used for analyzing the Fe – C – Mn system [6].

The tests were performed for specimens of gray iron with flaked graphite (GI) and of high-strength iron with globular graphite (HI) with variable content of copper (from 0.28 to 5.5 wt.% in the GI and from 0.12 to 8.0 wt.% in HI); the other elements in the compositions were as follows (in wt.%): 3.1 – 3.3 C, 2.1 – 2.3 Si, 0.5 – 0.7 Mn, 0.12 – 0.17 P, 0.03 – 0.05 S for GI and 3.2 – 3.4 C, 2.4 – 2.6 Si, 0.25 – 0.35 Mn, 0.05 – 0.07 P, 0.01 – 0.02 S, 0.03 – 0.04 Mg for HI.

Melting was performed under laboratory conditions in an IST-0.06 installation in a crucible with acid lining. Spheroidizing of graphite was ensured by modifying the iron

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in an open casting ladle by a “sandwich process” with the use of Fe – Si – Mg – Ca – REM additives.

The susceptibility to GI with faked graphite to chilling was checked on wedge samples cast into core-sand molds. The microstructure of copper irons with globular graphite and their susceptibility to chilling were studied by metallographic analysis with the help of a MIM-8M and Neophot-2 microscopes under magnifications of up to × 1500; local x-ray spectrum analysis was performed using a “Cameca” installation with linear probing of regions with different structural components.

RESULTS AND DISCUSSION

In what follows we present the results of separate studies of various manifestations of copper influence on structure formation in the metals and discuss the possible mechanisms of these structural effects.

Pearlite-forming action of copper. Copper promotes refinement and stabilization of pearlite [2, 7]. To a certain degree this is connected with the fact that copper increases the stability of austenite and shifts the pearlitic transformation to the range of lower temperatures. However, this factor does not explain the higher stability of pearlitic cementite in copper irons in the process of their low-temperature graphitizing annealing. One of the authors of the present work considered the thermodynamic mechanism of stabilization of pearlitic cementite due to the higher solubility of copper in this cementite in earlier works [1, 8]. However, more careful studies and thermodynamic computations performed recently have shown that the actual solubility of copper is low in all kinds of cementite; the higher content of copper in pearlitic cementite detectable by phase analysis is explainable by mechanical “contamination” of the cementite plates with copper. This has already been mentioned in [7] in the description of results of a phase analysis. Therefore, a purely thermodynamic explanation of the increase in the stability of eutectoid cementite is not exhaustive.

It has been shown in [7] that the stability of eutectoid cementite is a result of thermokinetic processes that accompany the phase transformations in iron and steel alloyed with copper. It has been mentioned that the special features of the properties of copper pearlite are explainable by its three-phase structure. Analysis of the mechanism of formation of three-phase copper pearlite shows that the cementite plates formed in the eutectoid transformation squeeze the copper earlier dissolved in these austenite volumes due to the very low solubility of copper. The ferrite layers formed in the process also emit a part of the dissolved copper and it accumulates on the boundaries between the cementite flakes and the ferrite layers enveloping the cementite plates. Thus, the pearlite formed in copper iron consists of cementite plates, a thin envelope of a copper ε-phase, and ferrite layers.

Thermokinetic analysis of formation of an envelope from the copper phase was performed with the use of the equations for the diffusivities of carbon and copper in austenite [9], i.e.,

$$D_{\mathrm{C}}^{\gamma(\mathrm{Cu})} = 0.0135 \exp\left(-\frac{140{,}000}{8.314\,T}\right), \ \mathrm{cm^2/sec};$$

$$D_{\mathrm{Cu}}^{\gamma} = 3.0 \exp\left(-\frac{252{,}000}{8.314\,T}\right), \ \mathrm{cm^2/sec}.$$

Here $D_{\mathrm{C}}^{\gamma(\mathrm{Cu})}$ is the diffusivity of carbon in the copper austenite and D_{Cu}^{γ} is the diffusivity of copper in the austenite.

At a temperature of 1000 K the diffusivities have the following values: $D_{\mathrm{C}}^{\gamma(\mathrm{Cu})} = 6 \times 10^{-10}$ cm^2/sec and $D_{\mathrm{Cu}}^{\gamma} = 2 \times 10^{-13}$ cm^2/sec.

The diffusion field of each element is proportional to $\sqrt{D}$. Therefore, the ratio of the diffusion fields of carbon and copper is

$$DF_{\mathrm{Cu}}/DF_{\mathrm{Ca}} = \sqrt{\frac{D_{\mathrm{C}}^{\gamma(\mathrm{Cu})}}{D_{\mathrm{Cu}}^{\gamma}}} = \sqrt{\frac{6\times10^{-10}}{2\times10^{-13}}} = \sqrt{3000} = \sim 55.$$

If we assume that the diffusion field of carbon in the time of formation of the pearlitic colony is equal to the distance d in between plates in pearlite, the diffusion field of copper in this time will be $DF_{\mathrm{Cu}} = d/55$, i.e., this field has very little thickness and cannot ensure formation of even a single-atom layer of a copper phase. It seems that the copper phase is formed on the base of the copper mechanically squeezed by the crystallization front of cementite and ferrite. We assume that (1) about 1/3 (in correspondence with the coefficient of copper distribution between austenite and ferrite, which is equal to about 1.5 [7]) of the copper contained in the eutectoid austenite is squeezed from the ferrite and virtually all copper is squeezed from the cementite, (2) the ratio of the volumes of ferrite to cementite in the pearlite is about 7, (3) the copper content is 0.72 at.% in the eutectoid austenite and about 90 at.% in the copper ε-phase, and (4) the distance between plates in the copper pearlite $d = 0.3$ μm [4]. We used these data to compute the thickness a_ε of the copper-phase envelope near cementite plates, i.e.,

$$a_\varepsilon = \frac{a_\alpha/3 + a_{Cem}}{a_\alpha + a_{Cem}} \times \frac{0.72d}{90} = \frac{10}{3\times 8} \times \frac{0.72\times 0.3}{90} = 0.001\ (\mu\mathrm{m}).$$

Here a_{Cem} and a_α are the thicknesses of cementite and ferrite plates, respectively.

Since the lattice parameter of the copper phase is about 0.36 nm, the envelope of this phase consists of only few atomic layers, i.e., the envelope is very thin. However, even at this small thickness the envelope is a serious hindrance for carbon diffusion, because it is known that carbon diffusion through the copper phase is virtually absent [2]. Therefore, the decomposition (graphitization) of the copper pearlite by way of only carbon diffusion is hindered and is in fact possible only due to preliminary diffusion of copper.

Thus, the main mechanism of the pearlite-forming action of copper has a more kinetic nature than a thermodynamic one and consists in squeezing of copper by the plates of crystallizing pearlitic cementite and formation of a thin film of a copper ε-phase on these plates, which is virtually impermeable for carbon and therefore markedly stabilizes the structure of the plate pearlite. Though the formation of the three-phase pearlite has a thermodynamic nature, which follows from the Fe – C – Cu phase diagram [2, 7], the stability of this structure is primarily determined by the geometrical arrangement of the phases and by their diffusion characteristics.

Graphitizing and chilling actions of copper. It is known that copper is a graphitizing element in cast iron. It is poorly soluble in cementite, especially in its high-temperature kinds (primary and eutectic). For this reason it promotes removal of ledeburite chilling and refinement of the eutectic structure in eutectic crystallization. According to the intensity of the graphitizing action copper is inferior to silicon (commonly by a factor of 2 – 3) but in some cases the use of copper as a graphitizing element is more preferable than the use of silicon [2].

The graphitizing action of copper is not invariable and depends on its content in iron and on the chemical composition of the metal with respect to other elements. Specifically, an opposite (chilling) effect of copper present in a considerable amount in iron with flaked and globular graphite has been established in [1] as early as 30 years ago in the process of iron crystallization. Since high-copper irons have not yet found application, this effect has not been studied in other works. However, the tendency of lowering of the intensity of the graphitizing effect of copper has been reported in some works where the susceptibility of copper irons to chilling was studied [2, 10], though the transfer from the graphitizing action of copper to a chilling one has not been stated in these works.

For this reason we had to evaluate the intensity of the graphitizing action of copper as a function of the copper content in iron and to determine the concentration boundary of the transfer from the graphitizing action of copper to a chilling one. The results of an experiment on chilling of copper irons with flaked graphite are presented in Fig. 1 (curve *1*) in comparison with known data [2] (curve *2*).

It can be seen that both curves behave similarly and reflect the highest graphitizing action of copper when it is contained in the metal in an amount of up to 2%. In the range of 2 – 3% copper concentrations the intensity of the copper effect is much lower, and at 3 – 4% its graphitizing action remains virtually constant (i.e., the intensity remains invariable). At about 4% copper both curves have an inflection that indicates a change in the nature of the copper effect, i.e., this content can be treated as a concentration boundary where the graphitizing action of copper is replaced by chilling action.

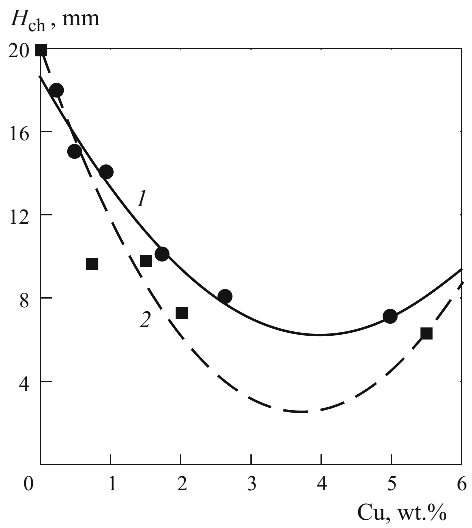

Fig. 1. Effect of the copper content on the susceptibility of gray iron with flaked graphite to chilling (H_{ch} is the chilling depth): *1*) data of the present study; *2*) data of [2].

The more intense effect of copper in the initial part of curve *2* (as compared to curve *1*) seems to be a result of different conditions of the experiments.

The influence of copper on the structure and on the susceptibility of high-strength irons with globular graphite to chilling was studied with the help of metallographic analysis. The microstructure of cast irons with different contents of copper is presented in Fig. 2. It can be seen that as the content of copper grows, the structure becomes more pearlitic. At 4 – 4.5% Cu inclusions of secondary and eutectic cementite start to appear, at about 6% Cu we observe individual regions of ledeburite, and at 8% Cu the metal crystallizes with prevalence of the structure of ledeburite. Thus, the concentration boundary of the beginning of the chilling action of copper is at about 4% Cu for cast iron with globular graphite too.

In order to estimate the special features of structure formation in copper cast irons during their crystallization we used the constructed sections of the Fe – C – Cu phase diagrams. Figure 3 presents superimposed eutectic polyhedral representations of the phase diagrams of stable (the solid lines) and metastable (the dashed lines) systems. These systems are characterized by stratification of the melt into iron – carbon (phase L_1) and copper (phase L_2) strata. Both systems are also characterized by a $L_1 \rightarrow L_2 + \gamma$ monotectic reaction (where γ is austenite); the stable system possesses nonvariant peritectic equilibrium $L_1 + L_2 \rightarrow \gamma + G$ at about 1170°C (with formation of an austenite-graphite eutectic) and the metastable system possesses a four-phase eutectic equilibrium $L_1 \rightarrow L_2 + \gamma + Cem$ at about 1130°C (with formation of an austenite-cementite eutectic, i.e., ledeburite). However, the phases of both eutectics are accompanied by a monotectic melt (phase L_2). The amount of this phase is low (only several percent), but it crystallizes the last and there-

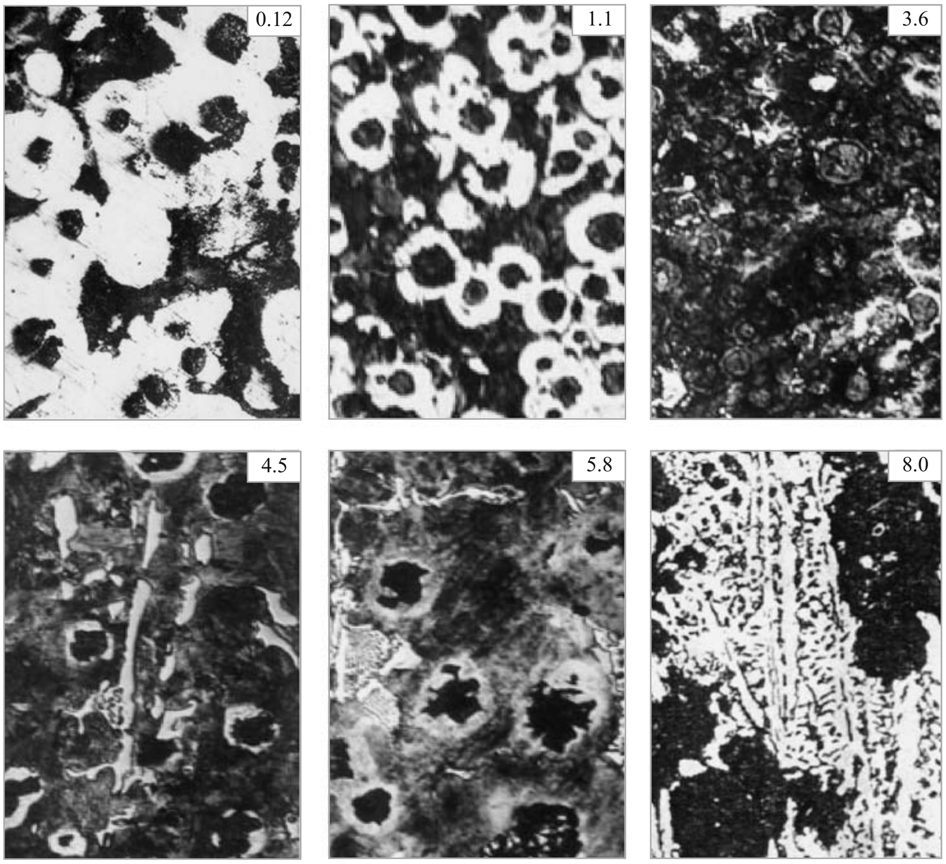

Fig. 2. Microstructure of high-strength irons with different contents of copper (indicated on the photographs in %). × 300.

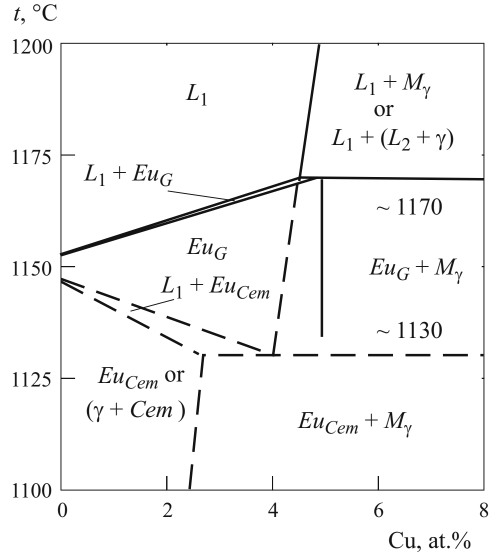

Fig. 3. Superimposed eutectic polyhedral representation of the phase diagrams of stable (the solid lines) and metastable (the dashed lines) Fe – C – Cu systems.

fore lies between regions of the earlier crystallized phases and envelops the latter. Crystallization of the copper melt finishes at a temperature below 1094°C by a peritectic reaction $L_2 + \gamma \rightarrow \varepsilon + G$; this melt is replaced by a solid copper ε-phase, which can be seen in the lower (with respect to the content of copper) part of the isothermal section of the diagram at 1094°C and in the full diagram of this section (Fig. 4). Thus, the crystallizing ε-phase can lie over boundaries of grains of other solid phases or their aggregates.

It can also be seen from the section presented in Fig. 4*a* that all process and equilibria with segregation of ε-phase are typical only for the alloys bearing over 4 at.% copper (or 4.5 wt.%). At a lower copper content the metal crystallizes without formation of ε-phase, but this phase can segregate from the copper austenite in cooling of the metal. Therefore a structure with inclusions of ε-phase of different geometry (from globular one to film one) can form at a lower content of copper in the metal too.

Our analysis of the diagrams and the results of metallographic studies show that film segregations of a copper ε-phase begin to appear in the structure of iron when the copper content in it exceeds 4% (Fig. 5), which matches the results of experiments on iron chilling. By enveloping the graphite inclusions, especially in the early stages of their formation, the copper phase prevents their further growth, which causes supercooling of the retained melt and formation of a chilled structure. This is especially typical for

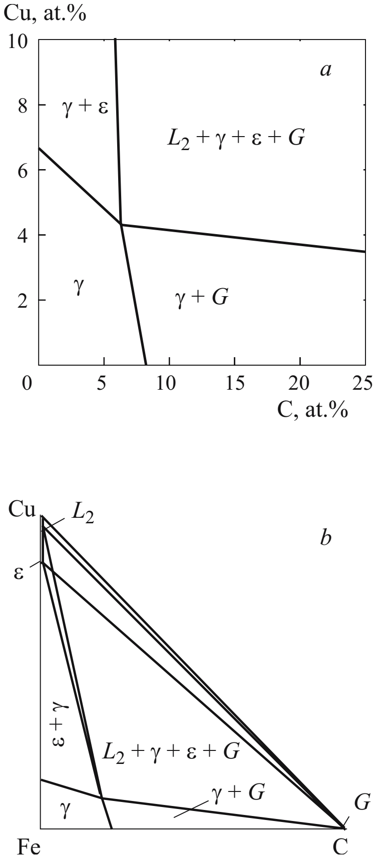

Fig. 4. A part of an isothermal section of the Fe – C – Cu diagram at 1094°C (*a*) and complete diagram of this section (*b*).

high-strength iron with globular graphite, which is susceptible to chilling as it is. The mechanism of this structural effect is close to the kinetic mechanism of stabilization of copper pearlite described above.

It can be seen from the sections of the diagrams that both eutectics (the stable and metastable ones) in iron bearing over 4% copper have a three-phase structure (Fig. 5*a*), i.e., in addition to the typical phases they also contain a copper ε-phase. The graphite and the ε-phase not only crystallize simultaneously but also tend to form a single component. The graphite inclusions can be fully enveloped by a copper phase if its content is sufficient for this; when its content is insufficient, the film only partially isolates the graphite inclusion and the latter continues to form in various distorted shapes (Fig. 5*b*).

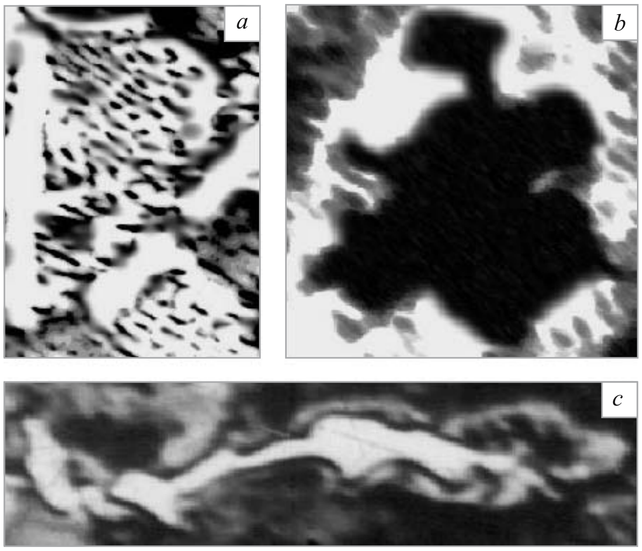

Fig. 5. Microstructure of typical regions of high-strength cast iron bearing 5.8 wt.% Cu. × 1000 (× 2): *a*) three-phase ledeburite; *b*) graphite inclusion enveloped into a film of a copper phase; *c*) region of cementite in an envelope of a copper phase and graphite.

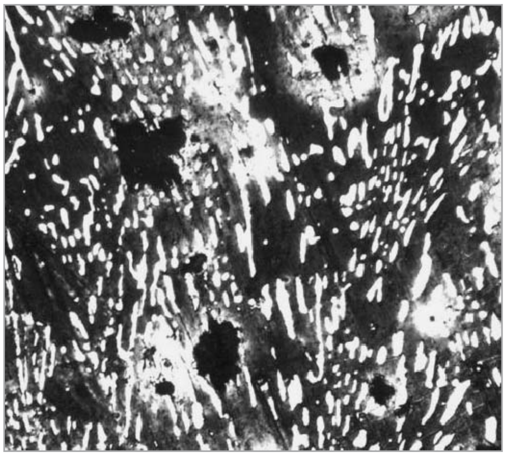

Fig. 6. Composite structure of mottle with 4.5 wt.% Cu. × 200.

The chilling action of copper does not always have negative consequences but can be used on purpose for fabricating mottles with special properties [11]. In such irons inclusions of copper phases ensures considerable transformation and refinement of the structure hindering the growth of graphite and cementite inclusions and removing the ledeburitic nature of the chilling. Under the effect of the copper phase cementite inclusions in mottles grow in the form of comparatively fine plates isolated from each other and ensure a composite structure pattern. One of the causes of this is the fact that the copper dissolving in the cementite segregates in front of its crystallization front (Fig. 5*c*). When the copper content in front of this front becomes high enough, the crystallization of cementite stops, and some time later graphite crystallization starts in this zone under the action of copper. This mechanism makes the cementite crystals separate from one another and grow in the form of short isolated plates, i.e., a composite structure arises (Fig. 6).

Precipitation hardening by the copper phase. In alloys of the Fe – Cu and Fe – C – Cu systems the ferrite (the α-phase) undergoes considerable precipitation hardening. This is connected with the fact that the α-phase is usually supersaturated with copper due to the low rate of copper diffu-

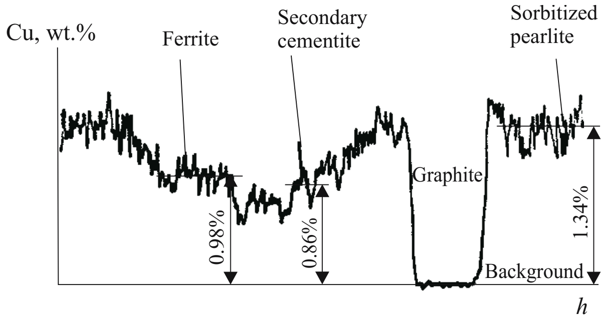

Fig. 7. Diagram of copper distribution in iron with globular graphite (1.1% Cu) (*h* is the distance along the line of probing).

sion and is susceptible to intense aging, especially artificial one. It is shown in [2] that this effect manifests itself in alloys of the Fe – C – Cu system not only in the structurally free ferrite but also in the pearlitic ferrite. This leads to substantial growth in the hardness and strength of the copper-alloyed pearlite both due to its refinement and under the action of solid-solution and precipitation hardening of the pearlitic ferrite.

A local x-ray spectrum analysis of various regions in the structure of iron with globular graphite alloyed with 1.1% Cu (Fig. 7) has shown that both the ferrite and the pearlite are substantially supersaturated with copper as compared to the equilibrium chemical composition. It follows from the Fe – C – Cu phase diagram [7] that at the temperature of nonvariant eutectoid equilibrium (near 715°C) the pearlite should contain 1.1% Cu and the ferrite should contain about 0.7% Cu. When the temperature decreases to 500 – 400°C, the equilibrium solubility of copper in these components decreases considerably (to 0.2% and lower). However, we have established that the actual content of copper in ferrite and pearlite is substantially higher and even exceeds the solubility at 715°C by 0.2 – 0.3%. Therefore, in the case of sufficient thermal activation (for example, in a hold at 400 – 500°C) ferrite in copper irons can age with considerable precipitation hardening. Indeed, it is shown in [4] that the aging effect at 500°C appears after a comparatively short hold and ensures substantial growth in the microhardness of the structural components.

CONCLUSIONS

1. High enough alloying of cast iron with copper produces several structural effects, the main of which are the pearlite-forming, graphitizing, anti-graphitizing, austenite-stabilizing, and aging ones. Some of the effects have a primarily thermodynamic nature (graphitizing and austenite-stabilizing; the latter causes growth in the hardenability). The mechanisms of the pearlite-forming and anti-graphitizing actions of copper are much more complex and have more kinetic nature than a thermodynamic one.

2. The main mechanism of the pearlite-forming action of copper consists in squeezing of copper by the surfaces of plates of crystallizing pearlitic cementite; this produces a thin film of a copper ε-phase on these plates, which is virtually impermeable for carbon and therefore markedly stabilizes of the structure of the plate pearlite. Though the formation of the three-phase pearlite has a thermodynamic nature, the stability of this phase is primarily determined by the geometry of the arrangement of the phases and by their diffusion characteristics.

3. The graphitizing action of copper is not constant and depends on its content in the metal and on the chemical composition of the metal with respect to other elements. When the copper content exceeds 4%, irons with flaked and globular graphite experience an inverse (chilling) action of copper in the process of their crystallization.

4. Crystallization of irons with an elevated copper content is accompanied by formation of film segregations of a copper ε-phase. Enveloping the graphite inclusions, especially in the first stages of their formation, the copper phase prevents their further growth; this causes supercooling of the retained melt and formation of a chilled structure. This is especially typical for high-strength iron with globular graphite, which is susceptible to supercooling on its own. The mechanism of this structural effect resembles the kinetic mechanism of stabilization of copper pearlite.

5. In high-copper irons both eutectics (the stable and the metastable ones) have a three-phase structure, because they also contain a copper ε-phase. The graphite and the ε-phase not only crystallize simultaneously but also tend to form a single component. The graphite inclusions can be fully enveloped by the copper phase if it is present in a sufficient amount; in the case of deficit of the copper phase the film can only partially isolate a graphite inclusion and then it can form in various distorted shapes, which may be one of the causes of the deglobularizing action of copper in irons with globular graphite.

6. In actual structures of copper irons ferrite and pearlite are substantially supersaturated with copper as compared to the equilibrium chemical composition. Therefore an appropriate thermal activation (for example, a hold at 400 – 500°C) of copper iron can cause aging of ferrite and considerable precipitation hardening.

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