

PHASE CHANGES IN IRON-CARBON ALLOYS IN SOLID STATE AT CONCENTRATED ENERGY FLOW TREATMENT

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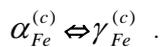
Abstract: The paper studies the mechanism, kinetics and morphology of phase changes primarily at heating by concentrated energy flows (CEF). The objects of study have been a medium carbon low-alloy steel 37Cr4 (DIN), a high-carbon tool steel X210Cr12 (DIN) and grey cast irons with flake and spheroidal graphite (GG 15, GG 30, GGG 50 - DIN) treated by plasma and electron beam heating.

It has been established that the mechanisms of phase changes at heating with CEF differ considerably from the familiar ones and can be classified as mechanisms of the following type: of migration by plastic deformation; of migration with a wave effect; of baric migration; of thermokinetic migration and of accelerated migration under the impact of electrodynamic fields and radiation. These mechanisms have been tested and proven by the fixed imbalance conditions of the structures obtained in the experiments.

Key words: CONCENTRATED ENERGY FLUX; SURFACE TREATMENT; PHASE CHANGES; SOLID STATE TRANSFORMATION

1. Introduction

According to the theory of phase changes, the transformations in the iron-carbon system take place in balance or imbalance conditions. The phase changes under thermokinetic conditions may be caused by either classical diffusion or other mechanisms called diffusionless. These assumptions refer to phase changes at different velocities. In this case both theories, the diffusion theory and the energy theory, determining the mechanism of transformation fix the single possible case of phase changes based on diffusion: the formation of crystallization centers and their expansion. The basic force of phase changes at heating, apart from the concentration differences, is the heat treatment under balanced (gradual) temperature elevation. The diffusion mobility of carbon is considered to be greater, i.e. the main reason for phase changes is the re-distribution of its atoms and at a final phase a polymorphic re-distribution of iron atoms takes place by the diagram



CEF treatment considerably differs from classical heat treatment in the following parameters [1-4]:

- it is not thermal in its pure form; it is accompanied by a number of phenomena taking place along with heat treatment – electron, photon, plasma, electromagnetic, acoustic and baric. On no account should it be considered that these components of energy treatment remain unchanged or can be ignored, theoretically at least;

- it is highly inhomogeneous in time, i.e. it is of pulse-dynamic or quasipulse character which by itself causes a wave effect of treatment. The latter, in turn, encompasses both heat treatment and the other types of energy treatment;

- CEF is highly inhomogeneous not only in time but in space. This causes a field effect in the distribution of energy parameters. Each point in the field, to be more precise – in the material – appears to be under the impact of energetics impacts of different magnitude and direction.

Taking into account all the above mentioned, the processes of phase changes, especially those at heating, should also be based on other mechanisms of atom migration, not only on purely diffusion ones [5-7]. The study of these changes and the mechanism of their accomplishment is the purpose of the paper.

2. Analysis

Kinetics and morphology of the changes in graphite and carbides

In the classical theory of heat treatment, when heating is accomplished at relatively low velocity (about up to 10² K/s at speed methods of heating such as bath, flame and induction heating) a mechanism and kinetics of phase changes in iron-carbon alloys have been accepted and proven and it is typical of them that they

are accomplished in compliance with the theory of balanced transformations. In this case it is considered that the transformations are complete, i.e. they take place until the total disappearance of phases, which are unstable at the elevated temperatures irrespective of that some inhomogeneity of their chemical composition is allowed. The mechanism of changes is diffusional caused by the differences in the concentration and the elevated temperature, being the same in all parts of the macro- and microvolumes. In this case the quantitative proportion between different phases is taken on the basis of the existing balance lines in the Fe-C (Fe₃C) diagram. As a consequence of the gradual heating and the time sufficient for re-crystallization, it is considered that, for example, ferrite turns into austenite from an initial balance condition from energetics point of view without the presence of deformation defects such as duplicates, increased dislocation accumulation (low angle boundaries), slippage planes of crystallographic plates.

Graphite is considered to be an absolutely stable phase, i.e. no likely changes in its phase condition or quantitative proportion with other phases are considered.

Carbides are also relatively stable. They do not change like the stoichiometric proportion between chemical elements. Only dissolution in austenite is allowed. The iron carbide is only in the form of Fe₃C.

As was already mentioned, the kinetics of the physical and chemical processes in time and space at CEF treatment make it possible to analyze phase change morphology in its basic aspects: high and ultra high velocities of heating, existence of mechanisms of atom migration different from the classical diffusion mechanisms, high heterogeneity of the conditions of transformation of each point of macro- and microvolumes in time and space.

The moment the cycle of heating terminates, high-velocity cooling commences. In this case the term “homogenization” is provoked by the temperature of overheating and the turbulent mixing of the liquid phase of melting. At this point, processes unfamiliar to the theory of phase transformations of iron-carbon alloys into solids may be observed: partial or complete dissolution of the graphite phase in the molten metal; washing away of the graphite in the molten metal and change in the locations of graphite inclusions; partial or complete evaporation of graphite; intensive migration of the carbon from the graphite inclusions in solid state; partial or complete dissolution of carbides in the solid phase and the molten metal.

As a consequence of these processes, at a follow-up crystallization both considerable change in the number and quantitative proportion between phases and increased homogenization in the macro- and microvolumes may be observed. In addition, the higher the velocity or the heating temperature, the higher the degree of the homogenization of the molten metal and the alloy after crystallization.

A tendency towards leveling the concentration in solid state is observed particularly with regard to the carbon content at the

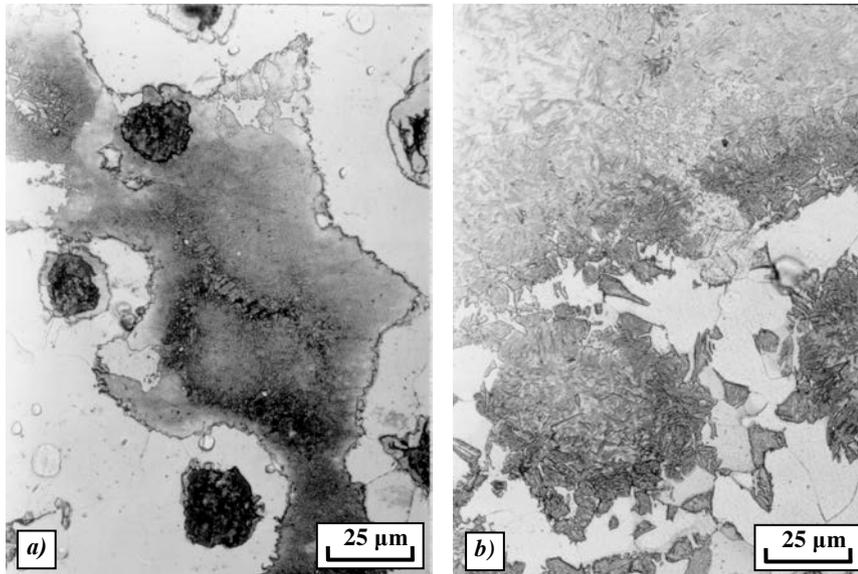


Fig.1 Particularly and fully dissolution of graphite in phase changing from solid state zone of GGG 50 after electron beam treatment by parameters: $N_s=3.6 \cdot 10^3 \text{ w/cm}^2$, $v=1.2 \text{ cm}$, $E_v=3.10^3 \text{ J/cm}^3$ – a) beginning and - b) end of zone.

“perlite-graphite” and “ferrite-graphite” boundaries at CEF heating. Of course, the migration of carbon towards ferrite is more obvious than towards perlite due to considerable concentration differences. Fig.1 shows the tendency of carbon to migrate from the graphite in the ferrite with the increase of temperature on the surface of treatment.

The migration path considerably increases around the graphite inclusions which are close to the surface and are undissolved in the molten metal (see fig.2). It is theoretically possible for the graphite inclusions, i.e. the carbon in the solid phase, to be completely dissolved. Undoubtedly, this process is also connected with the migration of iron atoms from the austenite in direction opposite to the movement of carbon atoms.

Partial and complete “assimilation” of carbides after CEF treatment in the zones of phase changes in solid and liquid state is typical of chrome and tungsten tool steels. As a result of the solid phase overheating and the follow-up melting, chrome, tungsten and combined carbides dissolve in the austenite or in the molten



Fig.2 Incompleteness due to partial evaporation of graphite inclusion at the bottom of the molten bath in GG 15 upon laser treatment with the following parameters: $N_s=1.9 \cdot 10^4 \text{ w/cm}^2$, $E_v=1.58 \cdot 10^4 \text{ J/cm}^3$.

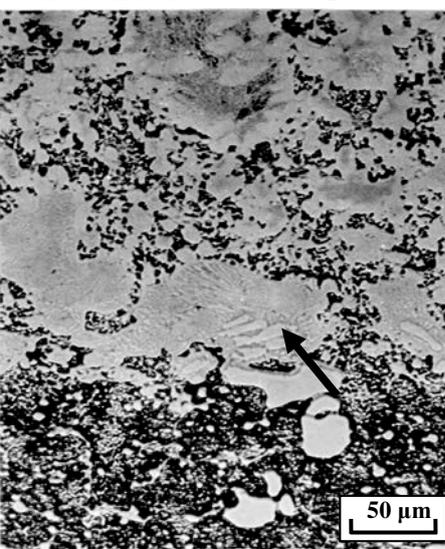


Fig.3 Partial and complete dissolution of carbides in X210Cr12 upon laser treatment with the following parameters: $N_s=2.6 \cdot 10^4 \text{ w/cm}^2$, $V=1.6 \text{ cm/s}$, $E_v=1.62 \cdot 10^4 \text{ J/cm}^3$.



Fig.4 Carbon migration from graphite and “halo” formation with increased carbon content B4500-2 upon electron beam treatment with $E_s=2 \cdot 10^3 \text{ J/cm}^2$.

metal which in itself is a typical process of homogenization (see fig.3)

A common feature of the migration of carbon from graphite and carbides is the direction of the prevailing migration flow opposite to the heat flow. This fact verifies our hypothesis about the field effect and the existence of thermokinetic migration. The considerable velocity of carbon movement from the graphite inclusions justifies the thesis about baric migration. In practice, the unlimited possibilities for migration in the molten metal facilitated by its mixing lead to the complete dissolution of carbides and carbon despite the limited time of treatment.

The migration flow at the graphite-ferrite, graphite-austenite and graphite-perlite boundaries is characterized by the formation of a “halo” around the graphite inclusion and by carbon content exceeding considerably or to a lower degree the content of the adjacent phases (see fig.4). This migration flow is intensified under the influence of the baric factor: the increased pressure in graphite, its lower thermal capacity and increased temperature in comparison with the adjacent phases and structural components. The pressure which graphite exerts on its surface leads to deformation in the zones subject to tensile stresses, i.e. in the adjacent phases and reactive congestion in the mass of the graphite inclusion. These stresses of second order are especially high at the graphite-metal base boundary. Depending on the intensity of treatment they may reach colossal values and may lead to changes in both the metal base and the graphite. Theoretically, a phase transition of the carbon from the graphite polymorphic modification into the metastable phase of diamond is possible. Such theoretical possibility is absolutely grounded in the cases of shock hardening (with power density of 10^{10} W/cm^2).

In the situations we studied, the quantity of carbon in the adjacent phases increases and can reach the concentration of the stoichiometric proportion of cementite 6.67% carbon at boundary surface. In this case a carbide encasing is observed around the graphite. It is possible that carbide is obtained under the specific heating conditions, with the temperature not having reached the critical melting temperature. We call this cementite synthesized. What is typical of it is that it appears around the graphite in the

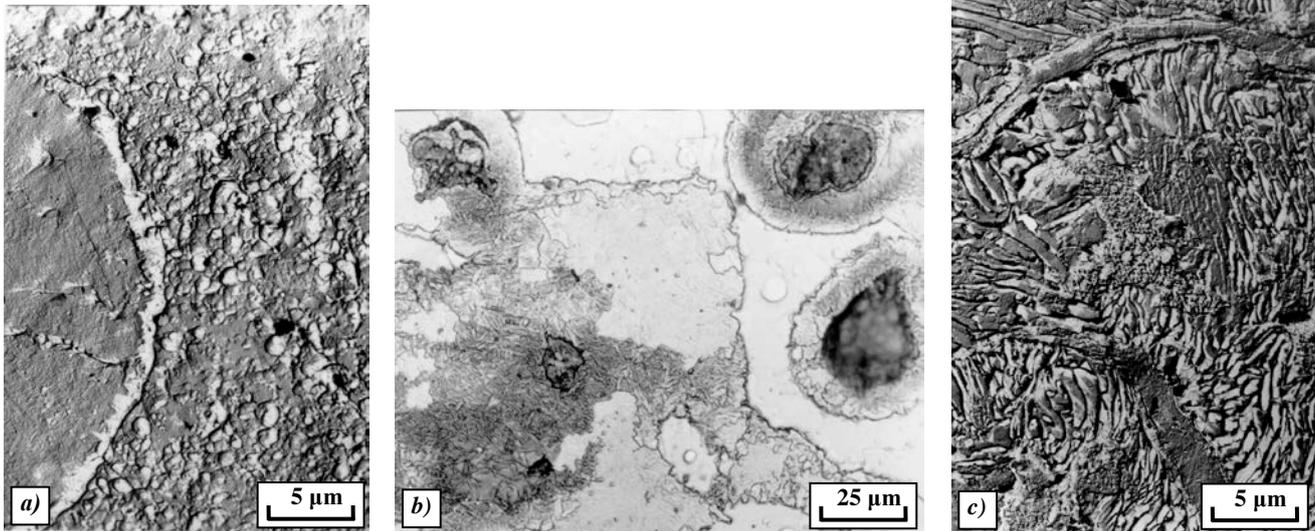


Fig.5 Synthesized carbide at grain boundaries to the graphite in iron by spheroidal – a), b) and wrought graphite – c) after arc-plasma ($N_s=9.2 \cdot 10^3 \text{ w/cm}^2$ - a) and b)) and electron beam ($N_s=7.2 \cdot 10^3 \text{ w/cm}^2$ - c)) treatment.

phase change zones in solid state, fig.5. The observation of the synthesized cementite in the zones around the graphite inclusions verifies the possibility of obtaining metastable conditions also in the process of heating. Due to the imbalance and dynamic character of the synthesis, it is likely for the carbide obtained to be provisionally called cementite as its stoichiometric formula may be different from M_3C . For example, it may be of carbide M_2C type, without excluding $M_{23}C_6$, M_7C_3 , M_6C or MC . In the situation of real alloys, carbides may also be of a mixed type between iron and other alloying elements. Obtaining metastable carbides under the conditions of very high velocities of heating is equally possible as the synthesis of Fe_3C carbide is.

It should be emphasized that the obtaining of synthesized carbide is connected with relatively minimum time of treatment (approximately 10^{-1} sec.). This means that the energy of treatment is also insignificant, i.e. heating and cooling are accomplished at high velocities, the resulting melting on the surface being at a very small depth. In this case the isolation of the graphite inclusions by means of the synthesized carbide may be favorable for enhancing the mechanical and corrosion-resistant properties of the cast iron in the surface layer.

The mechanism, kinetics and morphology of the changes in ferrite

Unlike the theory of classical phase transformations of ferrite-austenite, in our case we have grounds to consider that at the initial stage of transformation ferrite is in imbalance energy state. As a result of the dynamics of the thermal processes connected with

high velocities of heating and considerable temperature gradients within the microvolumes it is absolutely possible to observe microplastic deformations of the ferrite by the well-known patterns of movement of dislocations, slippage of crystallographic plates and duplication. Low angle boundaries are likely to form, without the real chance of reversion and re-crystallization due to the insignificant time of treatment. This microplastic deformation will be most clearly expressed at close order of phase location with a coefficient of expansion, heat capacity, density and heat conduction capacity different from those of the ferrite. Carbides and graphite are typical examples of such phases. With this regard, the perlite ferrite will tend to be most burdened with microdefects of microplastic deformation character. The perlite ferrite will have a relatively high level of Gibbs' free energy, and a high gradient of distribution in its volume respectively, and ultimately a great difference in the chemical potentials in the elementary microvolumes [8-10].

This means that the transformation of ferrite into austenite is absolutely likely to start not on the surface along the boundary of the grains where the concentration gradients are most significant and the concentration of submicrodefects as per classical theory – greatest. In other words, the classical theory of ferrite transformation into austenite envisaging the obtaining of crystallization nodes and their development under some time-energy circumstances tends to be inapplicable.

All considerations mentioned above provide for the opportunity to formulate the hypothesis of diffusionless

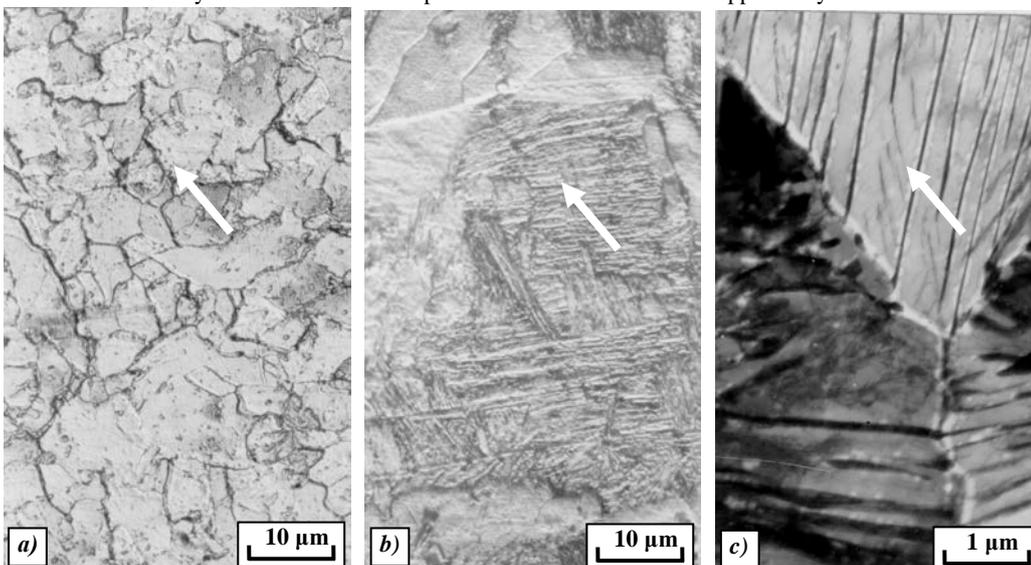


Fig. 6 Microstructure of Armco iron upon hardening: a) - Armco iron surface layer; b) - perlite of 37Cr4 steel; c) - upon laser treatment ($N_s=1.6 \cdot 10^4 \text{ w/cm}^2$).

polymorphic transformation of ferrite into austenite under CEF treatment conditions. What is more, this austenite apart from having the hereditary properties of the deformed ferrite, it has an additional phase peening resulting from the ferrite-austenite transformation. When, at the follow-up cooling taking place in a millisecond period of time, the highly unstable austenite appears to be in the conditions of martensite transformation it undoubtedly will turn into low-carbon martensite.

When heating the ferrite at high velocities under the conditions of superheating, the metastable transformation is only possible

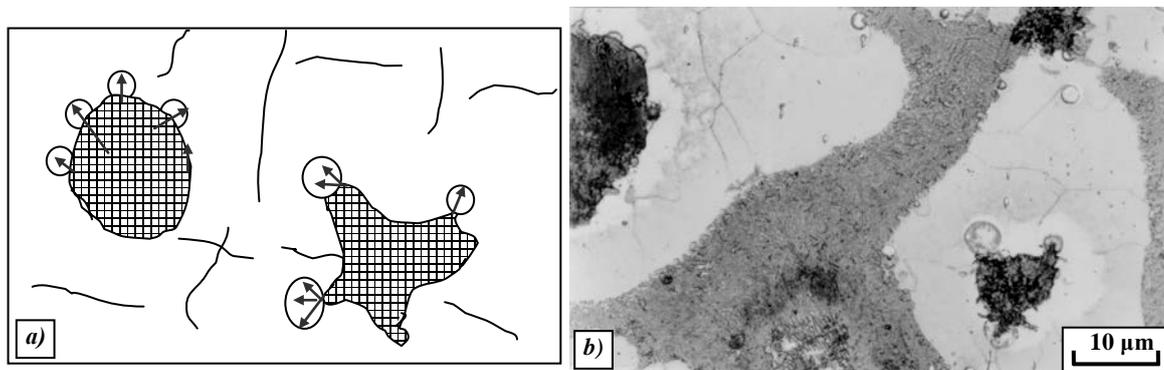


Fig.7 Diagram (a) and photography (b) of the initial stage of carbon migration in the ferrite of GGG 50 upon electron beam treatment with the following parameters: $N_s=3.6 \cdot 10^3 \text{ w/cm}^2$, $v=1.2 \text{ cm/s}$, $E_v=3 \cdot 10^3 \text{ J/cm}^2$.

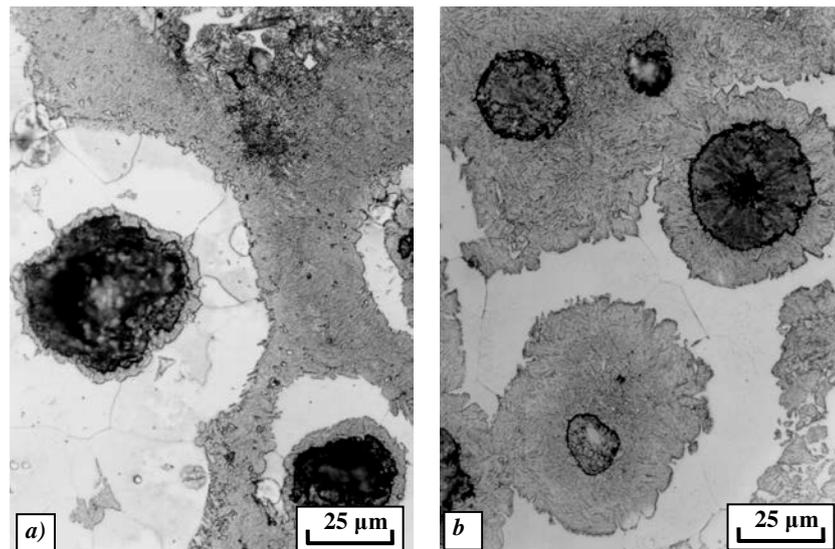


Fig.8 Interim stage (a) and final stage (b) of carbon migration in the ferrite of GGG 50 upon electron beam treatment with the following parameters: $N_s=3.6 \cdot 10^3 \text{ w/cm}^2$, $v=1.2 \text{ cm/s}$, $E_v=3 \cdot 10^3 \text{ J/cm}^2$.

thermodynamically. The austenite differing in composition from the balanced one is unstable and its existence may be explained from thermokinetic point of view. Of course, in imbalance heating conditions, there are circumstances determined by concentration fluctuations which define the existence of stable austenite as well. If fluctuation genesis of austenite with carbon concentration different from the balanced one is assumed, then this austenite will tend to obtain a stable condition very rapidly. Such a tendency may be eliminated by constant introduction of new quantities of energy in the system and by maintaining a great difference in the free energies of the final ferrite phase and the emerging austenite phase even in the conditions of rapidly growing migration activity of the atoms caused by the fast heating. At heating, at each moment of new austenite crystal emerging they may appear to be unstable due to the lack of carbon. With the further increase in temperature, more favorable conditions for carbon re-distribution are created which may not take place and part of the ferrite may not turn into austenite despite the high degree of overheating.

In this respect, the time factor is of vital importance and ferrite transformation into austenite is considered to be diffusionless with a mechanism of migration corresponding to slippage of crystallographic plates with a certain peculiarity such as incomplete transformation (see fig. 6a and b). The resulting austenite features a number of slippage planes situated in the most favorably oriented crystallographic plates partially inherited from the ferrite.

When the mode of cooling commences the austenite turns into ferrite by a similar diffusionless scheme. In this case we could call the newly formed metastable phase cubic martensite, i.e. a phase formed under the conditions of low-carbon imbalance austenite with close-packed martensite morphology. To be more

precise, this is a kind of mosaic modified ferrite with block orientation of the mosaic formations (fig.6b). Unlike cubic martensite obtained at voluminous heating (fig.6a), the dimensions of the ferrite grains and of the mosaic blocks are with less dispersity

and with less clearly outlined grain boundaries.

The possible increase of carbon content in austenite, martensite respectively, may be facilitated by the avalanche (wave) migration caused by the thermal shock of CEF treatment in the interval from the beginning of ferrite-austenite transformation to the beginning of martensite transformation.

The hypothesis of diffusionless moment of the transformation of ferrite into austenite was absolutely verified by our experiments (fig.6). The ferrite in the space among the cementite plates turns into austenite and after that into close-packed low-carbon martensite. The untransformed ferrite in the form of separate continuous or broken areas of thickness less than 0.2

boundaries with the cementite. The martensite inherits the defective structure with the clearly visible slippage planes from the microplastic deformation (fig.6c).

A feature typical of this transformation is the characteristic heredity of the structures with certain subdefects, phase peening and preservation of the cementite armature, i.e. the ferrite phase takes part in the reinforcement effect, the cementite retaining its specific morphology and properties. At the same time, the close-packed low-carbon martensite features the defectiveness inherited from the ferrite, the phase peening obtained and finally, the high-strength properties preserving relatively plastic ferrite transition zone at the boundary with the cementite.

The issues considered above allowed for an objective explanation of the enhanced strength properties and heat resistance of the structures obtained in low-carbon steels after CEF treatment in comparison with those after traditional hardening.

Of course, the ferrite phase transformation mechanism described does not exclude the possibility for changes in the variations well-known by the classical theory of heat treatment, as well as in the combined mechanism which includes the diffusionless period as an initial or attending phase of ferrite transformation. There are actual thermodynamic and concentration conditions for these.

The mechanism of the transformation of ferrite into austenite in the grains at a distance from the phase boundaries with cementite and graphite is similar to the classical one with some conventions. They concern mainly the migration paths of carbon atoms movement from adjacent phases abundant in such atoms or structure compounds (graphite, cementite and perlite).

The mechanism, kinetics and morphology in the area of ferrite-graphite phase boundary

The migration of carbon atoms from the compact graphite inclusions to ferrite forms the character of the phase changes at CEF treatment. The picture of interaction can be divided into three stages: initial, interim and final. The initial stage coincides practically with the temperature at the beginning and with the transformation of perlite into austenite. It is mainly characterized by

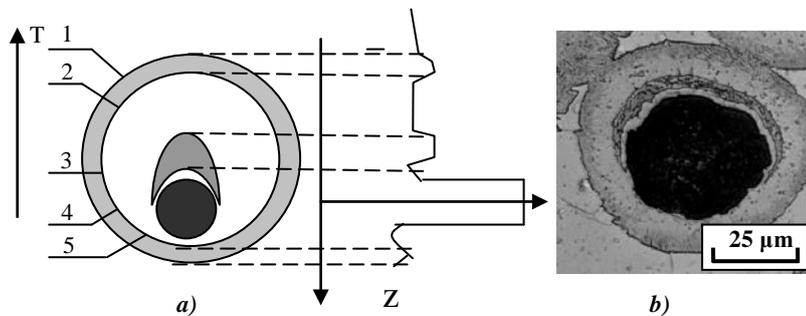


Fig. 9 Field and wave character of the migration flow of the carbon in ferrite: (a) diagram, (b) photograph of GG 30 structure upon electron beam treatment with $E_s=1.6 \cdot 10^3$ w/cm² with structure upon cooling: 1 – high carbon martensite; 2 and 4 – low carbon martensite; 3 – quazi-ledeburite; 5 – graphite.

the appearance of migration nodes at the graphite-ferrite boundary. These nodes are located at the side of higher temperature, i.e. closer to the surface of treatment (fig.7) or around the peaks at the non-spherical form of graphite.

As a result of the carbon migration in the ferrite the temperature of ferrite-austenite transformation and austenization in the zone around the graphite inclusions is lowered. In the follow-up cooling the austenite turns into martensite which forms a dense hard shell around the graphite. Due to the increase in the temperature of the graphite and the pressure exerted on it and as a result of the increase in the volume at the austenite-martensite transformation, the graphite becomes denser and the volume of its node decreases until it disappears (see fig.7).

The volume occupied by the martensite expands continuously. As a result of the increased carbon content it changes from close-packed into fine-grained (fig.8).

When increasing the treatment power density accompanied by an increase in velocity, i.e. by a decrease in energy density, a considerable concentration of the isotherms around the CEF axis is observed (see fig.9). This inevitably causes an increase in the temperature gradient, a formation and a clear expression of the wave and field character of the migration processes.

The wave and field character of the migration flows of carbon and other components cause the formation of a specific structure with variable contents and properties in line with the field and the wave formed. They are clearly expressed in laser, arc-plasma and electron beam sources having highly heterogeneous temperature fields obtained in the cases of pulse or pulse-intermittent treatment, as well as at the high power density of CEF [11-14].

3. Conclusions

Taking into account the issues discussed above, one should bear in mind that phase change processes at heating should be based not only on pure diffusion mechanisms of atom migration but also on a variety of other mechanisms which are as follows:

- the mechanisms of migration by plastic deformation. This mechanism depends on both the baric treatment of an energy pulse and on the temperature fields highly inhomogeneous in terms of time and space. At certain parameters of the treatment it may turn out that there are considerable differences in the temperature of phase boundaries or in a particular phase. This inevitably causes atom migration by the mechanism of slippage or an avalanche movement of dislocations and results in a phase transformation, e.g. "ferrite-austenite" without a preliminary diffusion process of re-distribution of carbon to have taken place. In any case, this process will be accompanied by phase peening and by an increase in the degree of the energetics imbalance of the new phase.

- the mechanism of migration of wave character of component distribution in macro and micro aspect. In this respect, the tendency towards balancing the concentration in the pure diffusion process may be deformed to a great extent. This means that at certain parameters of treatment there may not be a tendency towards balancing the concentration; just the other way round, there may be a reverse effect, i.e. there may be areas with highly

increased or decreased content of a particular component, e.g. carbon or another alloying element.

- the mechanism of baric migration, i.e. atom movement from microvolumes with a higher pressure to ones with a lower pressure and density. This mechanism would be particularly appropriate for surface layers where CEF treatment causes pulse pressure increase. It could also be accomplished in separate microvolumes, for example at the phase boundary graphite-metal base. Graphite dramatically increases its volume at elevated temperature. Moreover, it heats to a higher temperature due to its greater heat conduction and lower heat absorption differing in order from those, say of ferrite or austenite. With regard to this, the elevated temperature in the area of graphite inclusions may lead to the emission of graphite vapors at a certain moment of time which in turn would lead to an upsurge in pressure.

- the mechanism of thermokinetic migration or in other words, atom migration from volumes with lower temperature towards volumes with higher temperature. This mechanism is similar to that of a heat pump, well-known from the theory of fluid movement. At CEF treatment the epicenter of the heat field, i.e. the area with the highest temperature, is in the point of intersection of the source axis and the material surface in the spot of treatment. It is expected that with this mechanism, the more mobile carbon atoms would flow towards this center and a concentric field similar to the thermal one would be formed.

- the mechanism of accelerated migration under the influence of electrodynamic fields and radiation – electron, ion or neutron and photon. This mechanism has prevailing significance in the so called zones of energy transformation straight under the treatment surface. Hence, imbalance phases and compounds could be expected to form in this case.

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