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Peculiarities of the eutectic transformation during decarbonization of the Fe-W-C system

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The course of multiphase transformations is possible with a diffusional change in the carbon concentration in alloys of the Fe-Me-C system. This becomes possible under the condition that there is a three-phase region bounded by the conode triangle on the isothermal section of the ternary state diagram. For example, carburization of ferritic iron alloys with carbide-forming α-stabilizers (W, Mo, Cr, V, Ti) causes a three-phase reaction α→γ+carbide [1-2]. As a result, a eutectoid structure is formed. It consists of austenite, or a product of its transformation, and a special carbide. These structures are not formed when the temperature changes, but when the carbon concentration changes. This distinguishes them from the classical eutectoid. It was established that the indicated reaction proceeds in the reverse direction by the peritectoid mechanism during decarburization [3]. Crystallization with the formation of austenite and carbide is possible during isothermal decarburization of a high-carbon melt of the Fe-C-carbide-forming element system. It is similar to the eutectic transformation. Crystallization by the eutectic mechanism was previously observed during the decarburization of the melt of the Fe-Mo-C system [4].

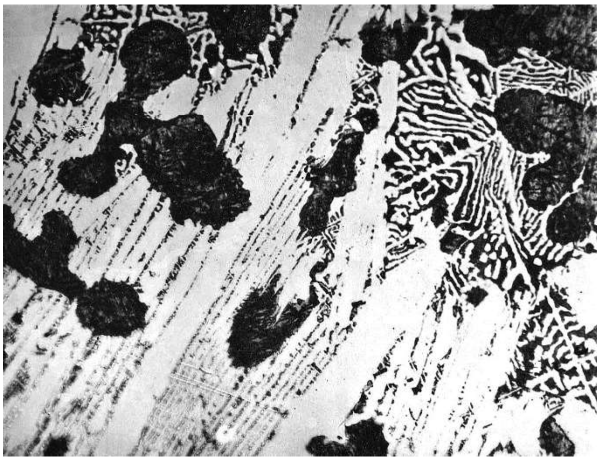
Keywords: diffusion changes, α-stabilizer, extrapolation of the lines, decarburization of the Fe-Mo-C melt system.

The goal of the work is to study the mechanisms of phase and structural transformations during the decarburization of the Fe-W-C melt.

The composition of the original alloy was determined based on the isothermal section of the Fe-W-C state diagram at the decarburization temperature (~1200 °C). As a result of the analysis, a synthetic experimental alloy with a carbon concentration close to eutectic - 12% W, 3.8%C, the last Fe was smelted on the basis of armco-iron in a resistance furnace in an inert atmosphere. Then the resulting ingot was cut into samples of the required sizes. The parameters of the samples (5×5×5 mm) were chosen in such a way that when processing the results, they could be imagined as a body of finite dimensions. Decarburization was carried out in a wet hydrogen environment in two stages. At the first stage, a refractory shell was created on the surface of the samples by decarburizing for 1 hour at a temperature below the eutectic melting point (1050 °C). At the second stage, the decarburization temperature was increased to 1190 °C. The core of the sample went into a single-phase liquid state at this temperature, and the decarburization process intensified. The samples were quenched in water from the decarburization temperature after finishing treatment. The directions of diffusion flows were studied by the method of geometric thermodynamics.

The structure of the alloy in its initial state is presented in Figure 1 a. Two types of eutectics are observed in it. The first type is austenite-carbide eutectic. It is based on cubic carbide M_6C, called "fish skeleton", which is typical for high-carbon alloys of the Fe-W-C system. The second type of eutectic is ledeburite. It partly consists of a coarse conglomerate of phases. In this work, special attention was paid to the processes occurring at the second stage of decarburization.

The experimental alloy is in a single-phase liquid (l) state (point 1 on the state diagram, Fig. 2) at the initial moment of the second stage of processing (temperature 1190 °C). The composition of the melt reaches point 2 on the *ac* line in the decarburization process. A two-phase equilibrium of liquid with austenite is observed in this case. Further carbon depletion contributes to the initiation of crystallization with the formation of austenite. The concentration of tungsten in austenite at the interface with the liquid $X_W^{\gamma/l}$ is lower than in the original liquid according to the slope of the cone *2-3*. The composition of austenite at the boundary with the liquid phase is determined by item *3* according to the Fe-W-C state diagram. The difference in borderline concentrations of tungsten depends on the slope of cone 2-3. Thus, a tungsten concentration gradient occurs during austenite crystallization. This is accompanied by its redistribution between solid and liquid phases. The concentration of tungsten in the liquid phase constantly increases as the diffusion layer grows.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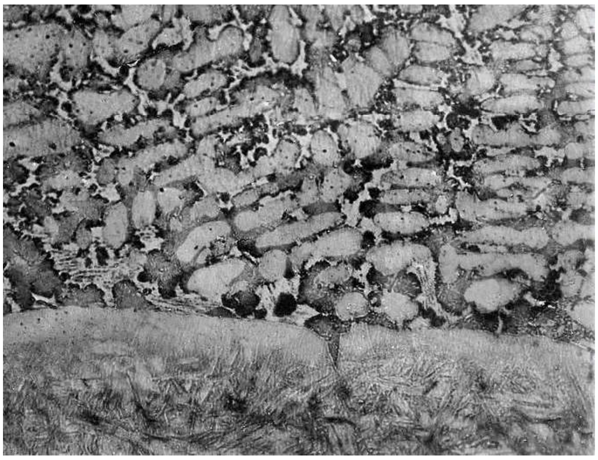
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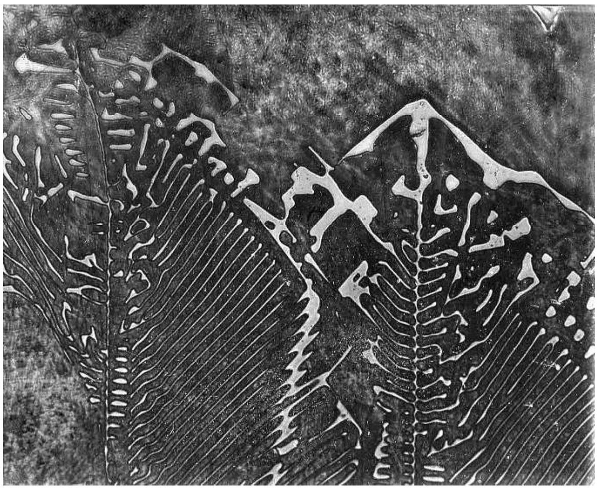
d

Figure 1 – Microstructure of the experimental alloy of the Fe-W-C system: a – initial state, b, c – crystallization front, d – crystallized structure after decarburization; a, b, d – ×500, c – ×200

The rate of advance of the crystallization front is determined by carbon diffusion in the solid phase. Diffusion in the liquid and convection mixing removes tungsten from the crystallization front at a rate several orders of magnitude higher than in the solid state. For this reason, a quasi-stationary process does not occur when the concentration of tungsten in the solid phase is equal to its concentration in the original melt. Given the small size of the samples, the concentration of tungsten in the austenite and liquid increases, respectively, with the lines *ac* and *bd* in the diagram (Fig. 2).

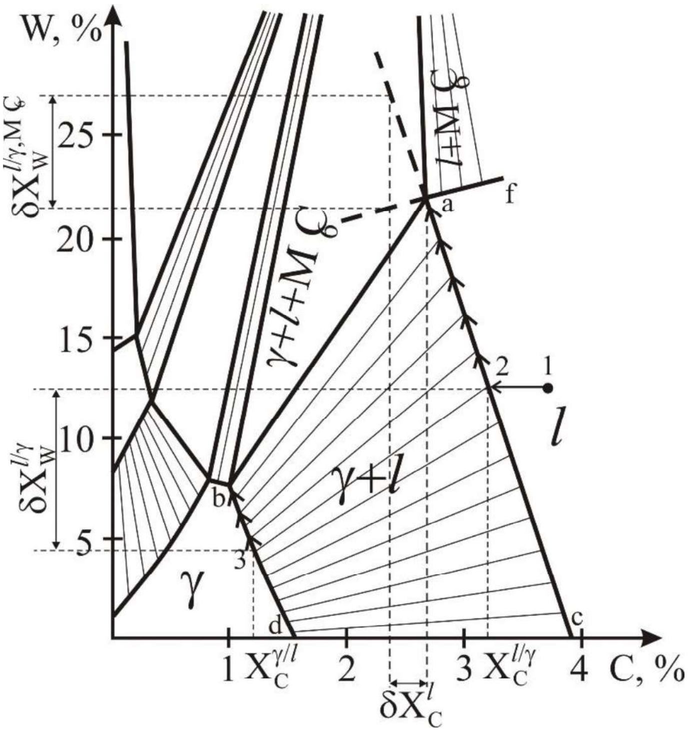

Figure 2 – Scheme of the isothermal section of the Fe-W-C state diagram at a temperature of 1190 ºC

It should be noted that the phases are separated by a relatively flat interphase surface at the initial stage of crystallization (Fig. 1 b). The flat crystallization front becomes unstable with increasing tungsten concentration at the crystallization front. Protrusions appear at the front (Fig. 1 c), which are then transformed into dendrites. The stability of the flat front can be estimated using as a basis the method proposed by Mullins and Sekerka [5]. A tangential flow of tungsten appears in the liquid when a sinusoidal disturbance with infinitesimally small amplitude is applied to the crystallization front. As a result, an increase in the amplitude of the disturbance becomes possible.

Simultaneous crystallization of austenite and M_6C carbide becomes thermodynamically possible when the liquid composition reaches point a on the state diagram (Fig. 2) in the decarburization process. This is accompanied by redistribution of components between phases. Extrapolation of the lines that separate the liquid and two-phase *l+γ* and *l+M₆C* regions on the diagram to the amount of liquid carbon depletion δX_C^l determines the difference in tungsten concentrations in the liquid at the interphase boundaries with austenite and M_6C carbide ($\delta X_W^{l/\gamma,M_6C}$). The specified concentration gradient ensures redistribution of tungsten between austenite and carbide, which grow cooperatively. The mechanism of joint growth is similar to classical eutectic crystallization, which occurs during cooling. The structure after co-crystallization of austenite and carbide is shown in Figure 1 d. As can be seen, the morphology of eutectic $\gamma+M_6C$ crystallized in isothermal conditions during decarburization is similar to the structure obtained during crystallization of cooling of the Fe-W-C system melt. It is a eutectic of the "fish skeleton" type. The difference in the differentiation of structural components is explained by the different speed of advance of the $l\rightarrow\gamma+M_6C$ cooperative transformation front.

Conclusions. It was established that the melt of the Fe-W-C system crystallizes in the process of isothermal decarburization. This is accompanied by redistribution of tungsten between solid and liquid phases. It is shown that the composition of the liquid ahead the crystallization front changes continuously during the diffusional change of the composition in samples of finite dimensions according to the isothermal section of the state diagram. The nonvariant $l\rightarrow\gamma+M_6C$ transformation becomes possible when the melt concentration of the "liquid" top of the $l+\gamma+M_6C$ conode triangle is reached. It is similar to eutectic, which occurs during cooling. The morphology of the two-phase structure $\gamma+M_6C$ obtained as a result of decarburization is similar to the eutectic crystallized upon cooling.

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FeW - C жүйесінің декарбонизациясындағы эвтектикалық түрленудің ерекшеліктері

Көп фазалы түрлендірулердің жүруі Fe-Me-C жүйесінің қорытпаларындағы көміртегі концентрациясының диффузиялық өзгеруімен мүмкін болады, бұл үштік күй диаграммасының изотермиялық учаскесінде конод үшбұрышымен шектелген үш фазалы аймақ болған жағдайда мүмкін болады. Мысалы, феррит темір қорытпаларын Карбид түзетін α-тұрақтандырғыштармен (W, Mo, Cr, V, Ti) көміртектендіру α→γ+карбидтің үш фазалы реакциясын тудырады [1-2]. Нәтижесінде эвтектоидты құрылым пайда болады. Ол аустениттен немесе оны түрлендіру өнімінен және арнайы карбидтен тұрады. Бұл құрылымдар температура өзгерген кезде емес, көміртегі концентрациясы өзгерген кезде пайда болады. Бұл оларды классикалық эвтектоидтардан ерекшелендіреді. Аталған реакция декарбонизация кезінде перитектоидтық механизм бойынша кері бағытта жүретіні анықталды [3]. Аустенит пен Карбид түзу үшін кристалдану FE-C-Карбид түзуші элемент жүйесінің жоғары көміртекті балқымасын изотермиялық декарбонизациялау кезінде мүмкін болады. Бұл эвтектикалық түрлендіруге ұқсас. Эвтектикалық механизм бойынша кристалдану бұрын Fe-Mo-C жүйесінің балқымасын декарбонизациялау кезінде байқалған [4].

Түйін сөздер: диффузиялық өзгерістер, α-тұрақтандырғыш, сызықтарды экстраполяциялау, Fe-Mo-C жүйесінің балқымасын декарбонизациялау.

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Особенности эвтектического превращения при декарбонизации системы FeW-C

Протекание многофазных превращений возможно при диффузионном изменении концентрации углерода в сплавах системы Fe-Me-C. Это становится возможным при условии, что на изотермическом участке диаграммы тройного состояния имеется трехфазная область, ограниченная треугольником конода. Например, науглероживание сплавов ферритного железа карбидообразующими α-стабилизаторами (W, Mo, Cr, V, Ti) вызывает трехфазную реакцию α→γ+карбид [1-2]. В результате образуется эвтектоидная структура. Она состоит из аустенита или продукта его превращения и специального карбида. Эти структуры образуются не при изменении температуры, а при изменении концентрации углерода. Это отличает их от классической эвтектоидной. Установлено, что указанная реакция протекает в обратном направлении по перитектоидному механизму при обезуглероживании [3]. Кристаллизация с образованием аустенита и карбида возможна при изотермическом обезуглероживании высокоуглеродистого расплава системы Fe-C-карбидообразующий элемент. Это аналогично эвтектическому превращению. Кристаллизация по эвтектическому механизму ранее наблюдалась при обезуглероживании расплава системы Fe-Mo-C [4].

Ключевые слова: диффузионные изменения, α-стабилизатор, экстраполяция линий, обезуглероживания расплава системы Fe-Mo-C.

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