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FEATURES OF THE INFLUENCE OF GRAIN BOUNDARIES DURING δ-γ-TRANSFORMATION ON THE FORMATION OF WELD METAL STRUCTURE (REVIEW)

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ABSTRACT

A review of the literary research results is presented, on the basis of which it is seen that the algorithm of modeling the structural composition of the metal, prediction of its mechanical properties should contain a description of reactions on the formation and development of dendritic structure. The models built on the description of reactions of γ-α-transformation do not provide the possibility for evaluation of the process of the structure formation as an integral complex — from the beginning of dendrites nucleation to the final composition of the microstructure. The results of the studies, performed in recent decades describing the effect of refractory compounds, regarding inoculation to melts of low-alloyed steels and, in particular, welding pool, on the development of nucleation processes, growth and decay of dendrites during metal crystallization are presented. The probable influence of inoculants on the primary structure formation is shown in order to improve the properties of weld metal.

KEYWORDS: low-alloyed steel, welding pool, inoculation, dendrites, austenite, primary structure

INTRODUCTION

The widespread use of high-strength low-alloyed steels in manufacture of military equipment, infrastructure, power equipment and other structures of critical importance for Ukraine significantly increased the relevance of problems of providing high mechanical properties of welded joints. The complex of service properties of weld metal is determined by its structure. Therefore, a great attention in recent years has been paid to creating computer models for formation of weld microstructure and predicting its mechanical properties. The formation of microstructure of weld metal of low-alloy steels begins with the nucleation and growth of dendritic structure and processes of δ-γ-transformation [1, 2]. However, the main attention in these models is usually paid to the processes of γ-α-transformation [3, 4].

The processes of nucleation and decay of dendrites during cooling of the weld pool metal have a high activity at elevated temperatures, but until recently most experimental studies have been based on the observations of grain-boundary complexes at room temperature. The structure and features of the development of high-temperature complexes were more frequently studied by rapid cooling of a sample to room temperature. Moreover, in almost every case, the changes occurred in the structure and chemical composition of grains during cooling remained unknown. High-temperature S/TEM metallography, which has recently become available for studies, may turn out to be one of the best experimental methods for studying features of the dendritic structure development. The results of the experiments indicate that modern metallography allows observing the grain boundary complex under conditions of continuous cooling. Some observations of in situ reactions at elevated temperatures have become the basis for the creation of a numerical model of the dendritic structure formation [5], but this area of studies remains largely unexplored.

Studying the mechanisms of nucleation and growth of the new phase can potentially explain their spatial heterogeneity, as well as deepen understanding of methods for suppression of the coarse-grain structure formation that can be useful, for example, during thermostabilization of polycrystalline materials. The studies aimed at deepening understanding and control of processes on grain boundaries contribute to modeling interphase interactions and development of new materials with improved grain structure morphology and increased level of mechanical properties.

CHARACTERISTICS OF MAIN PROCESSES ON THE BOUNDARIES OF DENDRITIC STRUCTURE

The attempts to better understand the causes of microstructural formations with an increased tendency to brittle fractures of the metal motivated the development of process studies on the boundaries of structural grains. On the boundaries of dendrites, certain processes may proceed, associated with such properties as energy at the grain boundary, entropy, enthalpy and concentration of adsorbate. These processes may cause changes in such nonequilibrium properties of grain boundaries as mobility, cohesive strength and sliding resistance, which is a distinctive feature of in-

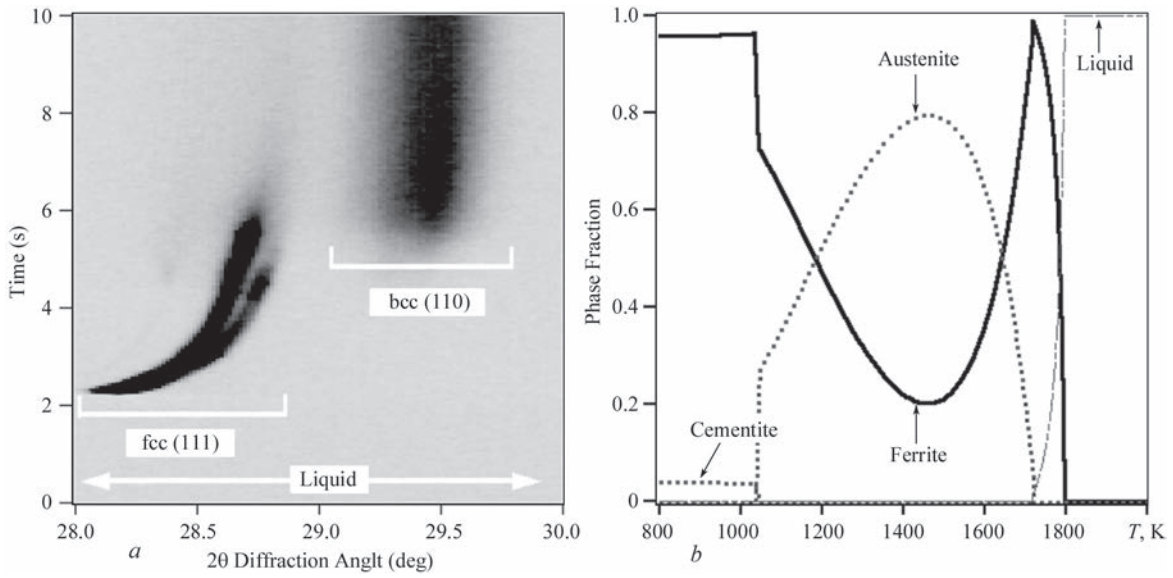

Figure 1. X-ray diffraction with resolution on cooling time of steel melt (*a*) and predicted equilibrium fraction of phase as a temperature function (*b*) [3]

tergranular interaction. Thermodynamics and kinetics of formation and decay of dendritic structure play a large role in the formation of microstructure and mechanical properties of welded joint metal.

In the peritectic systems, which include Fe–C alloys, at the stage of the dendritic structure formation, the high-temperature phase will easily overcool in the region of coexistence of high- and low-temperature phases, and the boundary between a high-temperature δ-phase and a liquid phase is the most probable place for nucleation of a low-temperature γ-phase (Figure 1).

The work of adhesion W_{ad} of the grain boundary is equal to the reverse work required for the transformation of the grain boundary into two free surfaces. For brittle fracture, such a dependence can be described by the ratio

$$W_{ad} = 2\gamma_S - \gamma_{GB},$$

where γ_S and γ_{GB} is the surface and grain boundary energy, respectively. Reduction in the energy of grain boundaries is associated with disordered transitions on grain boundaries, which involves an increase in the adhesion work and, therefore, grain boundary strength. However, in many systems studied experimentally, such transitions are associated with embrittlement of grain boundaries [6, 7]. Local features of the process can outweigh conventional thermodynamic considerations in such cases. For example, high-enthalpy bonds formed between adjacent structural lattices can significantly help to reduce marginal energy when interacting with low-enthalpy bonds in the interface, which can cause brittleness. This mechanism proposed by Luo et al. [7], allows explaining the brittleness in alloys. Alternatively, the energy on the grain boundary may be reduced by increasing entropy. An increase in entropy can be the result, for example, of an increase in a free volume of boundary or an increase in the concentration of liquants, which can also reduce the strength of the boundaries. The effect of a total work of adhesion on the strength and impact toughness of the metal is difficult to model in general on the basis of the abovementioned equation because the energy of two resulting surfaces is equally difficult to predict.

The coefficient of grain boundary self-diffusion D_{GB} can be described by a method similar to the volumetric self-diffusion coefficient using the frequency rate of jumps of atoms ν, the parameter of the lattice a_0, free energy of vacancies formation $\Delta G_{f,b}$, energy barrier of activation of migration atoms ΔG_m, geometric value g in the follwing way [8]:

$$D_{GB} = g\nu a_0^2 \exp\left(\frac{-\Delta G_{f,b}}{RT}\right)\exp\left(\frac{-\Delta G_{m,b}}{RT}\right).$$

The energy of grain boundaries is greatly affected by diffusion processes. Borysov et al. [9] for the first time suggested that a free energy of activation of grain boundary diffusion $\Delta G_b (=\Delta G_{f,b} + \Delta G_{m,b})$ is proportional to the corresponding free energy of diffusion activation in lattices ΔG_l minus free energy γ. Although, this rule is empirical, it gives a reasonable predictability in alloys. An energy decrease on the grain boundary, in which enthalpy prevails should increase the activation energy and reduce diffusion on the grain boundaries. However, when energy decreases, an increase in entropy prevails, which should lead to an increase in diffusion.

The processes of dendrites decay are associated with a decrease in the energy of grain boundaries. Thus, the measurement of energy of grain boundaries can be used to characterize transformations. For today, there are procedures that allow measuring changes in

the relative energy of the grain boundaries, but it is much more difficult to measure their absolute energy [10]. As a result, relative energy is usually measured. Relative energy of the grain boundary χ_{GB} along the adjacent surface of the grain χ_S can be expressed as a function of the diadric angle θ_S in the groove according to the equation [8]

$$\frac{\gamma_{GB}}{\gamma_S} = 2\cos\frac{\theta_S}{2}.$$

Using the analysis of Mullins [11], it is possible to determine the relative interphase energy of the grain boundary. However, this method includes a number of approximations and assumptions. For example, it is assumed that two surface energies are equal to each other, the grain boundary is normally located to the surface, the anisotropy of the interface energy is small. Although these assumptions are unfair for any boundary of one grain, it was found that for a large database on measuring dihedral angles of grain boundaries, the average value and the width of the distribution are reproduceable and significant values [12]. In recent years, the methods of X-ray in-situ diffraction, which have become widespread, have simplified these measurements. As a result, a special procedure was created for reliable measurement of the energy of grain boundaries [13].

Changes in the boundary energy of dendritic grains have an indirect effect on the distribution of γ-ferite grains in the metal. Comparative studies of anisotropy of distribution of grain size and anisotropy of grain boundary energy have shown that there is a reverse relationship between these two values in polycrystals, which involves the existence of relatively larger amount of grains with low boundary energy than high-energy grain boundaries [10, 14]. Thus, a change in the type of intergranular layer in the sample, which leads to changes in the energy of the grain boundaries, also affects changes in the size of grains in the process of transformation.

EFFECT OF WETTING PROCESSES ON DENDRITE DEVELOPMENT

On the boundaries of dendrites, a layer is formed, enriched with liquation elements, and also elements formed as a result of the interaction of dendrites with nonmetallic inclusions. The presence of these elements in the boundary layer determines the peculiarities of wetting the surface of dendrites, affects the kinetics of its development and the structural morphology. Dendrite wetting and development reactions have been the subject of study for the last several decades, as a result of which during the wetting process, a preliminary wetting stage was singled out [15, 16]. Preliminary wetting is the type of variation in the boundary structure, that occurs when the layer of material of a fixed equilibrium thickness is formed at the boundary interface in the thermodynamic vicinity of the wetting transition, i.e., near the temperature or composition, at which the wetting transition will occur. This term refers to the adsorption transition of the first kind, in which the film of the material separating two phases is broken both by adsorption composition as well as over the thickness.

In the process of growth, a dendrite moves in a metal melt. In this case, the boundaries of a dendrite are partially wettened with a liquid with a certain edge angle, when $\gamma_{lv} + \gamma_{sl} > \gamma_{sv}$ where γ_{lv} and γ_{sv} are the surface energy of the liquid and solid phase, and γ_{sl} is the surface energy of the boundary interface liquid/solid body. After the liquid completely wettens the surface and is distributed over it to form a continuous film, whose thickness depends on a number of liquation elements in the layer and has a surface energy $\gamma_{sv} \equiv \gamma_{lv} + \gamma_{sl}$ as is determined by thermodynamics. Preliminary wetting refers to the transition between partial and complete wetting, in which a thin layer of material is formed, which covers the surface, but has an equilibrium thickness, which is controlled by thermodynamic variables of the state (e.g., temperature, pressure) and does not depend on the amount of available liquid.

Wetting transitions can also occur at interfaces of solid bodies such as grain boundaries and phase boundaries. In addition, grain boundaries can be wettened either with a liquid or solid phase with a composition different from the main part, and in the first case, such wetting is associated not with a liquid metal and causes the embrittlement phenomenon [17, 18].

The process of crystallization of metal structure in welds of low-alloy steel, which begins with the epitaxial growth of delta-ferrite from the grains of a parent metal on the fusion surface because of high temperature gradients associated with the arc process, promotes the formation of a dendritic structure of a cell type with the grains of δ-ferrite, which have anisotropic columnar structure with main axes oriented in the direction of the maximum heat flow. At a further cooling of metal on the boundaries of cells δ/δ, allotriomphs of γ-phase are nucleated, which anisotropically grow along these boundaries, which leads to the formation of columnar grains of primary austenite. The kinetics of austenite formation and the size of its grains depends on the level of surface energy at the boundaries of δ/δ grains. The lower the surface energy on the dendrite boundaries, the higher the kinetics of austenite nucleation and the smaller the size of its grains [19].

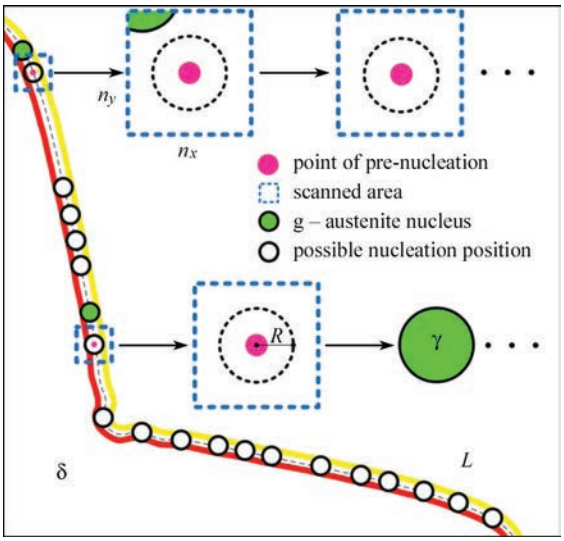

Figure 2. Schematic diagram of the austenitic phase formation [20]

EFFECT OF INOCULANTS ON KINETICS OF δ-γ-TRANSFORMATION

The process of metal crystallization in the conditions of peritectic reaction occurs in two separate stages. Initially, at the point of contact of three phases (liquid + δ-ferrite + γ-austenite) a bit lower than the peritectic temperature, a peritectic reaction ($L + \delta \rightarrow \gamma$) occurs, which leads to the formation of dendrites in the form of δ-ferrite with centers of γ-austenite nuclei at the interface boundary δ/*L*. In the future, the peritectic transformation begins with thickening of the γ-austenite layer on the surface of dendrites both due to δ-ferrite as well as liquid phases. The kinetics of this complex peritectic phase transition in the process of crystallization of steel depends on the composition of liquid layer on the surface of dendrites and the rate of melt cooling. The process of nucleation of γ-austenite represents a complex thermodynamic phenomenon in a nanoscale and is difficult for experimental observation, so for its research computer modeling methods are used.

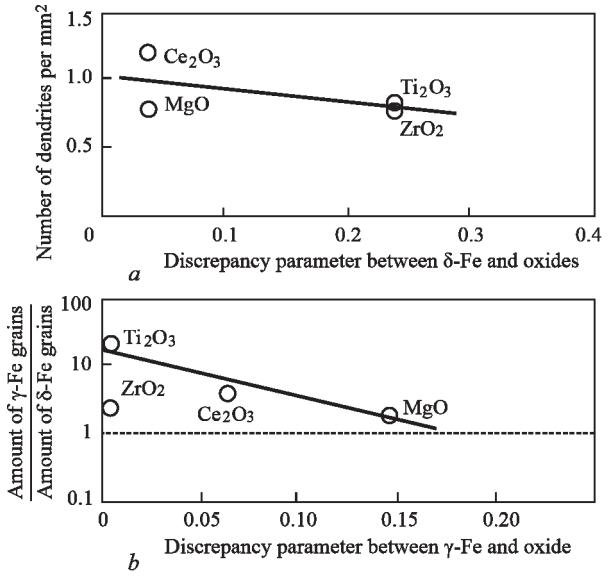

Figure 3. Effect of parameters of discrepancy of a crystal lattice of oxides to lattice parameters; *a* — δ-Fe; *b* — γ-Fe on the kinetics of crystallization [21]

The results of modeling, given in [20] showed (Figure 2) that the stages of γ-phase formation differ in the kinetics of the process. At the first stage, which corresponds to the preliminary wetting, on the dendrite surface, a limited number of nuclei of the new phase is formed. The formation of the main array of γ-phase occurs at the second stage.

Such a nature of the formation of nuclei is explained by the density of liquation elements in the liquid layer on the surface of dendrites. With a decrease in the melt temperature, the content of liquation elements in this layer increases, which affects the increased probability of the nucleation of a new phase.

At inoculation of refractory compounds to liquid metal, dendrites in the process of growth encounter nonmetallic inclusions and this may contribute to the change in the surface energy at the boundary interface *L*/δ.

The results of experiments on introduction of refractory oxides to metal metls, which are shown in Figure 3, *b*, demonstrate the ratio of an amount of γ-grains to δ-grains per unit area, applied to the diagram depending on the parameter of discrepancy of the lattice between γ-Fe and refractory oxide. The fact that this ratio increases with a decrease in the discrepancy parameter indicates that the rate of nucleation increases with an increase in the potential of this process. In other words, more than one nucleation event per one δ-grain occurs at the boundary interface δ/*L*.

The results shown in Figure 3, related to the effect of the discrepancy parameter on the size of the contact angle between the three phases — oxide, Fe(δ) and Fe(γ):

$$\cos\theta = (\gamma_{MO/Fe(\delta)} - \gamma_{MO/Fe(\gamma)})/\gamma_{Fe(\delta)/Fe(\gamma)}.$$

The mentioned results indicate that for a high rate of the γ-phase nucleation on the boundary interface δ/*L* (i.e. high value of cosθ), not only a low value of $\gamma_{MO/Fe(\gamma)}$ is required, which corresponds to the parameter of the discrepancy of lattice parameters between the oxide and γ-Fe, but also a high value of $\gamma_{MO/Fe(\delta)}$. On the upper diagram it is seen that this ratio does not increase with an increase in a number of particles per unit area N_A, indicating that the rate of nucleation of the γ-phase depends not only on a number of nucleation centers on the surface of dendrites. The value of a contact angle at the boundary of three phases has a much greater effect on the formation of a new phase.

Based on the mentioned results of the studies, it is seen that the algorithm of modeling the structural

composition of the metal, the prediction of its mechanical properties should contain a description of reactions on the formation and development of dendritic structure. The models that are built on the description of γ-α-transformation reactions do not allow evaluating the process of formation of structure as an integrated complex — from the beginning of the nucleation of dendrites to the final composition of the microstructure.

The recently published results of studies on the effect of inoculation of refractory compounds on melts of low-alloy steels, in particular, on weld pool metal [22], testify about the significant influence of physicochemical processes that occur at the stage of formation and development of dendrites, on the formation of a final structure of metal and confirm the need to take into account this stage of crystallization of welds when predicting their structural composition and the level of mechanical properties.

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