

Influence of the rate of cooling on the formation of non-equilibrium eutectics in pre-eutectic alloys of the AL-SI system

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Abstract: Computer experiments were carried out with a simulation model of alloy crystallization in this work. The model was preliminarily calibrated for alloys of the Al-Si system. The presence of a non-equilibrium eutectic in pre-eutectic alloys with a silicon content of 1.0% - 1.6% has been detected. The minimum cooling rates at which the formation of an eutectic in these alloys is possible have been determined.

KEYWORDS: CRYSTALLIZATION, EUTECTIC, NONEQUILIBRIUM EUTECTIC, COMPUTER MODEL OF CRYSTALLIZATION

1. Introduction

One of the ways to improve the competitiveness of foundry products is to develop new technological processes and improve existing ones. The solution of this problem can be significantly facilitated by simulating of the process of the metal's primary structure formation during crystallization, as the primary structure significantly affects the final properties of the alloy. Nowadays methods of simulation are widely used for the construction of models of crystallization. They allow both to create computer models to study the peculiarities of structure formation in castings during crystallization, and to approach consciously the improvement of casting technologies [1, 2].

The methodology of thermodynamics is usually used for theoretical research and for creating models of crystallization. In theoretical physics, thermodynamics is divided into three subsections, depending on the internal state of the physical system, namely: equilibrium thermodynamics, linear non-equilibrium thermodynamics and nonlinear non-equilibrium thermodynamics [3, 4]. The last two subsections aroused and have been developing since about the middle of the twentieth century. However, they have not yet found wide application in applied sciences. There are several reasons for this. First, there is the so-called "the inertia of thinking", which makes us to act with the usual, generally accepted methods, abstracting from a thorough analysis of the conditions for their application, even in science. Secondly, there is a certain gap between theoretical, fundamental research and the application of their results in solving specific, applied problems. This gap is a consequence of the shortage of time and of the material resources both among "theorists" to deal with "uninteresting" problems of the applied level, and among "practitioners" to master new achievements of theory. Thirdly, there are still no clear criteria for determining which subsection to refer to in each specific case. Therefore, this situation requires creative development with the involvement of modern knowledge and theories. Therefore, it seems expedient to find out previously which system one has to deal with in each specific case, and, consequently, which physical concepts and theories can be used. To do this, it is necessary to establish the criteria for "equilibrium" or "non-equilibrium" of the process or system. Having such an objective, physically substantiated criterion, it is possible to choose both the method of describing of a specific system, and the corresponding mathematical apparatus with sufficient reliability. To substantiate the choice of such a criterion, first of all, it is necessary to analyze the characteristic features of "equilibrium", "weakly non-equilibrium" and "strongly non-equilibrium" systems.

2. Preconditions and means for resolving the problem

The study of the behavior of equilibrium systems is the most developed branch of thermodynamics, and historically it is its first stage. Therefore, the theory of the most of the available technological processes is based precisely on its principles. In equilibrium, changes of flows, forces and entropy are equal to zero. Despite the fact that real technological processes occur over a finite period of time (with a finite speed), during which in most cases the system does not have time to come to a state of equilibrium, the use

of the equilibrium theory remains decisive (including in metallurgy). Within the framework of this theory, thermodynamic potentials are determined for typical thermodynamic systems, the extrema of which set states - attractors, to which the system with certain boundary conditions tends. For an isolated system, such a potential is the entropy S , for a closed system under isothermal conditions - free energy F . Linear thermodynamics reflects the stable predictable behavior of systems which are tending to the minimum level of activity, that is typical for most metallurgical processes [4].

In weakly non-equilibrium systems (the area of applicability of linear non-equilibrium thermodynamics), the driving forces of changes (gradients of thermodynamic potentials, which, in turn, can be determined by gradients of concentrations, temperatures, etc.) are small and the flows depend on the magnitude of the driving force linearly. Onsager's reciprocity relations are satisfied. For the field of linear thermodynamics, the theorem on the minimum production of entropy was proved [4], from which it follows that such a system always tends to a stationary state in which the increase of entropy is equal to zero.

That is, such a system exchanges energy with the environment, tends to "forget" the initial conditions and eliminates local fluctuations. The only hint of the area of its existence is the linear dependence of flows on the magnitudes of the driving forces.

Strongly non-equilibrium systems are described by the laws of non-equilibrium, nonlinear thermodynamics. The stay of the system in such a non-equilibrium state is a necessary, albeit insufficient, condition for self-organization (that is, for the formation of dissipative structures). The stationary state in this case is uniquely determined using the properly chosen potential. It is namely this state that must be identified, first of all, using the criterion of non-equilibrium. In other words, it is necessary to determine the presence of a state in which fluctuations can lead to a new regime. Conventionally speaking, the criterion should allow to draw a boundary (threshold) when it becomes possible to enter an unstable state (bifurcation), in which two equally probable results are possible: either the system can remain on the thermodynamic branch, or it will pass into a new structural and energy state which is necessary for maintaining this dynamic structure. When crossing a threshold (bifurcation point), the role of fluctuations and of element of randomness increases sharply, while before this threshold, elements of determinism and predictability prevail [5].

For chemical systems in a strongly non-equilibrium state, there is no universal law from which one could draw a conclusion about the behavior of all systems without any exceptions [6]. However, in the theory, a relation was obtained that makes it possible to relate the conditions of chemical instability with kinetic and thermodynamic parameters [5]:

$$\delta_x P(\lambda_c) = 0 \quad \text{for } t > t_0, \quad (1)$$

where: $\delta_x P$ - can be interpreted as an increase of production of entropy by the active part of the system; λ_c - is a measure of distance from equilibrium.

Determining the conditions under which the loss of thermodynamic stability can occur is reduced to determining the sign of the quantity $\delta_x P$, and ultimately, of the quantity [5]:

$$\delta_x P = \delta w \frac{\delta A}{T}, \quad (2)$$

where: w - the reaction rate; A - chemical affinity; T - the temperature.

You can go the other way and develop a criterion for the non-equilibrium of the system by analyzing experimental data. Obviously, the possible variants of the criterion, which determines the degree of non-equilibrium of the system, include the rate of the process, its homogeneity [7, 8], and the desired level of coincidence between theoretical results and experiment. It's clear that such a criterion will not have an exclusively physical and mathematical foundation and will not claim to be universally applicable to all physical laws.

State diagrams can be considered as peculiar models of alloy crystallization. However, they are constructed in the approximation of equilibrium conditions. At the same time, it is known that with an increase of the cooling rate, the lines of the diagrams shift, and phases appear that should not exist at such compositions and temperatures [8; 9], the structure of the alloys changes. Thus, it means that the conditions of crystallization in this case cease to be equilibrium. Therefore, one of the possible criteria for non-equilibrium during crystallization can be the cooling rate at which non-equilibrium phases appear.

The aim of this work is to study the effect of the cooling rate on the formation of a non-equilibrium eutectic in alloys of the Al-Si system.

The studies were carried out within the framework of a computer experiment using a simulation model of alloy crystallization [1], which allows registering the formation of a non-equilibrium eutectic.

3. Solution of the problem under consideration

The method of preparing of a simulation model for research is based on the selection of model's parameters in order to maximize the coincidence of the simulated cooling curves and structural elements of the macro-grain with those ones obtained in a real experiment [10]. The model was calibrated on the Al + 8.2% Si alloy (by weight).

First, in a natural experiment, the cooling curve was recorded and a thin section was made to study the structure of the alloy. Then, the thermo-physical characteristics of the alloy were introduced into the model: density, specific heat, specific heat of crystallization, and coefficient of thermal conductivity. The simulation model was calibrated in three stages. At the first stage, the cooling rate during the solidification of the melt was set by selecting the heat transfer coefficients in such a way that the initial sections of the experimental and calculated cooling curves coincide. At the second stage, the coincidence of the experimental and calculated cooling



Fig. 1. Comparison of the real cooling curve of the Al-8.2% Si alloy (1) with the cooling curve (2), modeled using a simulation model

curves was achieved by adjusting the value of the adaptation coefficient. At the third stage of setting up the model by selecting its parameters, we sought out a match between the modeled alloy structure with that one, which was obtained in a real experiment.

The real and modeled cooling curves of the Al + 8.2% Si alloy are shown in fig. 1 [11]. The initial sections of the cooling curves practically coincide. Small discrepancies are observed only upon cooling after the end of crystallization. This is due to the fact that in a real experiment, after solidification, the volume of solid metal decreases due to shrinkage, and its contact with the mold wall worsens. As a result, the real heat transfer coefficient decreases and the temperature decreases more slowly.

In the areas corresponding to the formation of a solid solution of the Al + 8.2% Si alloy, there are also some differences between the real and simulated curves. These differences are explained by the constant change of the content of the second component in the liquid. As a result, the value of the latent heat of crystallization changes, which was not taken into account in the mathematical formulation of the heat conduction problem for this model.

A small deviation in the value of the eutectic temperature (5 - 7 °C) is due to the presence of impurities that always exist in a real alloy. If they are present, complex eutectics ((α + Si) + FeAl₃ and (α + Si) + Al_xFe_ySi_z [12]) can be formed, the formation temperature of which is slightly lower than the temperature (α + Si) of the eutectic.

4. Results and discussion

The presence of a non-equilibrium eutectic is fixed on the dependence of the rate of formation of solid phase centers $\frac{dN}{dt}$ on

time t . Figure 2 shows: the cooling curve, the number of formed centers of the solid phase and the rate of their appearance during the crystallization of the Al-4.4% Si alloy. An alloy of this composition

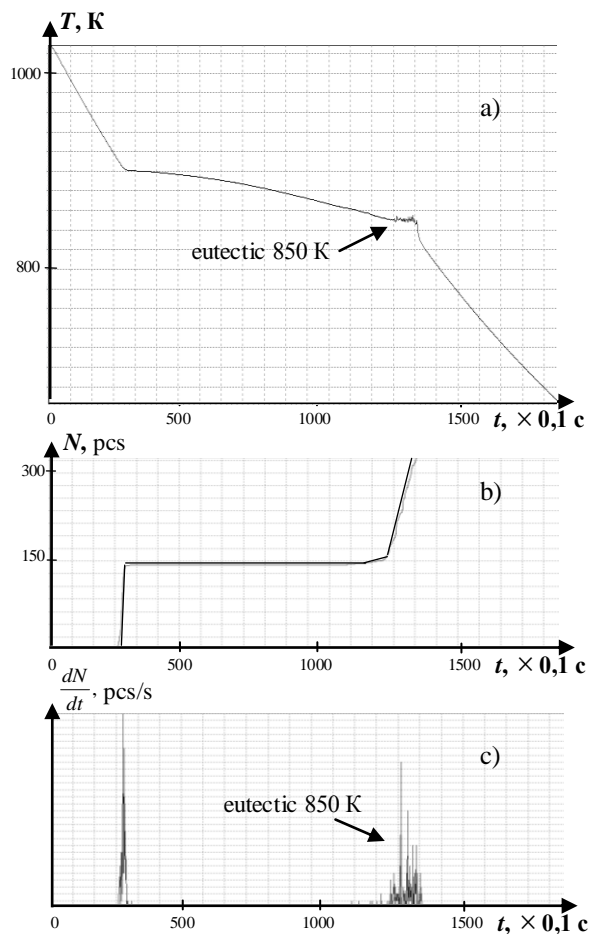


Fig. 2. Cooling curve (a), the number of centers of the solid phase (b) and the rate of their formation (c) during the crystallization of the alloy Al-4.4%Si

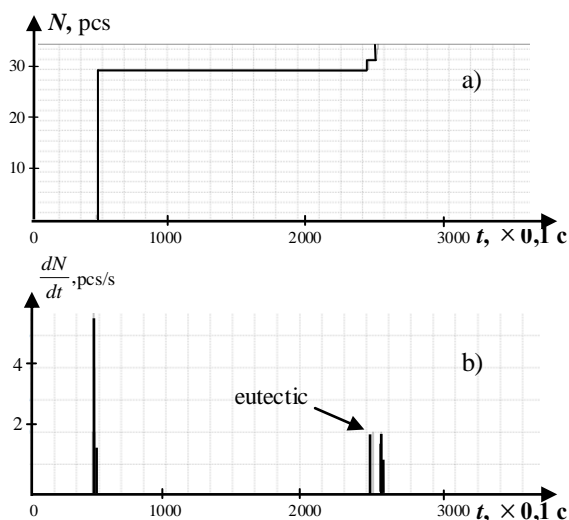


Fig. 3. The number of centers of the solid phase (a) and the rate of their formation (b) during the crystallization of the alloy Al-1.2%Si

forms a solid solution and an eutectic (at 850 K), which is recorded on the cooling curve. At that, the centers of the solid phase appear in two stages (Fig. 2 b). The first stage corresponds to the onset of crystallization and of the formation of a solid solution. The second stage is connected with the beginning of the formation of the eutectic. These stages are more clearly manifested by the dependence of the rate of formation of solid phase centers on time (Fig. 2 c). Thus, using this crystallization model, it is possible to record the presence of a non-equilibrium eutectic during the crystallization of pre-eutectic alloys.

Computer experiments were carried out for alloys of the Al-Si system with a silicon content of 1.0%; 1.2%; 1.4% and 1.6%. All these alloys are pre-eutectic ones and do not form an eutectic under equilibrium conditions. In the experiments, the rate of cooling of the sample (size 0.025m×0.025 m), at which a non-equilibrium eutectic began to form, was recorded. Figure 3 shows the fixation of a non-equilibrium eutectic on the dependence of the rate of formation of centers of the solid phase during crystallization of the Al-1.4% Si alloy. A small amount of eutectic is recorded at the temperature of 850 K and the cooling rate of 0.37 deg/s. The results for the investigated alloys are shown in Table 1.

The presence of a non-equilibrium eutectic in these alloys can be explained by the formation of local regions of the melt with an increased silicon content at certain values of the growth rate of the

Table 1 - Dependence of the cooling rate on the silicon content with the appearance of a nonequilibrium eutectic in Al-Si alloys

Content Si,%	1,0	1,2	1,4	1,6
Cooling rate, °C/s	3,80	2,00	0,37	0,12

solid phase.

To test the possibility of the formation of a non-equilibrium eutectic, which was established in the computer experiment, a full-scale natural experiment was carried out with an alloy of the Al-Si system. The temperature of the melt was recorded during its cooling at a rate of 0.5 - 0.7 deg/s. The mass of the alloy under study was 20 - 22 g, the diameter of the crucible, in which the melt was located, was 21 mm. With a silicon content from 0.1% to 0.3%, the melt crystallized as a solid solution. A non-equilibrium eutectic appeared at a silicon content of 0.3% and higher. It was reliably fixed both on the derivative of the cooling curve and in the structure of the alloy.

5. Conclusions

1. Non-equilibrium eutectic in alloys of the Al-Si system is formed even at low cooling rates, which is connected with the formation of local areas with an increased silicon content, which are formed due to incomplete equalization of the liquid composition after separation diffusion at the "liquid - solid" interface.

2. In a full-scale experiment, a non-equilibrium eutectic appears starting at a silicon content of 0.3% and above.

6. References

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