EFFECT OF INITIAL MOLD TEMPERATURE ON THE CRYSTALLIZATION KINETICS OF $Cu_{47}Ni_8Ti_{34}Zr_{11}$ ALLOY

ВЛИЯНИЕ НАЧАЛЬНОЙ ТЕМПЕРАТУРЫ ИЗЛОЖНИЦЫ НА КИНЕТИКУ КРИСТАЛЛИЗАЦИИ СПЛАВА $Cu_{47}Ni_8Ti_{34}Zr_{11}$

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Abstract: *Using the method of mathematical modeling, the effect of the initial temperature of the mold T_2^0 on the thermal conditions and kinetics of crystallization of chill castings of $Cu_{47}Ni_8Ti_{34}Zr_{11}$ alloy was investigated. According to the results, established that the value T_2^0 can have a significant effect on the final structure of the ingots. Depending on the value of T_2^0, it is possible to provide thermal conditions under which formation of amorphous, amorphous-crystalline and fully crystalline states is possible. It is shown that the changes in the initial temperature of the mold are reflected in the final parameters of the microstructure of the resulting ingots, the average crystal size can vary from tens of nanometers to several micrometers.*
KEYWORDS: *MELT CASTING INTO THE MOLD, THERMAL COOLING MODE, CRYSTALLIZATION KINETICS, MICROSTRUCTURE PARAMETERS*

1. Introduction

Advantages of materials with amorphous and nanocrystalline structures, in comparison with traditional crystalline analogs, today is not in doubt. Therefore, the study of the conditions for obtaining such materials is a priority of modern science. The success of development in this area is due to an understanding of the relationship between the chemical composition of alloys and technological parameters that allow controlling the nucleation and growth of crystals during cooling of a metallic melt. In the study of these relationships is most convenient to use methods of mathematical modeling. With their help, it is possible to study the joint development of thermal and kinetic processes under melt cooling conditions and, accordingly, to determine the influence of thermal regimes on the formation of the final structure of the casting.

In connection with the foregoing, the paper presents the results of a joint solution of the thermal and kinetic problems applied to the conditions of chill casting melt. The bulk amorphizing alloy $Cu_{47}Ni_8Ti_{34}Zr_{11}$ (Vit101) was selected as the test material, which was cooled in a copper mold with a wall thickness of 15 mm.

2. Method of calculation

The mathematical basis of the model was based on the one-dimensional Fourier thermal equation for melt (containing a source of latent heat release due to crystallization) and for a copper mold with boundary conditions that take into account the features of casting the melt into the mold [1]. And also on the kinetic equation, which describes the change in the crystallized volume fraction with time [2]:

$$x(t) = \frac{4}{3}\pi \int_{t_m}^{t_e} (1 - x(t'))I(t')\left[R_c(t') + \int_{t'}^{t_e} (1 - x(t''))u(t'') \right]^3 dt',$$

where I – frequency of formation of crystal nuclei with a critical radius R_c; u – crystal growth rate; t_m – the time to reach the melting temperature by the melt T_m; t, t', t'' – current times: $t_m \leq t' \leq t'' \leq t_e$, t_e – the time of ingot solidification processes end, or due to achieve them the glass transition temperature T_g, or due to complete crystallization processes ($x(t_e) \approx 9,9 \cdot 10^{-1}$).

The system of equations described above mathematical model was performed finite difference method using an implicit finite difference scheme [3]. A detailed mathematical model and algorithm for the solution are presented in the paper [4].

To study the effect of the initial mold temperature on the thermal regime and the crystallization kinetics of the investigated alloy, the primary results of the simulation were obtained in the form of the time dependences of the melt temperature $T_1(t)$ and the crystallized volume fraction $x(t)$. Besides calculating the temperature field and the kinetic depending developed computer program enabled to calculate the parameters of the alloy microstructure: the number of crystals per unit volume of N_S and the average radius of crystals $\bar{R}$.

The dependences $T_1(t)$ and $x(t)$ were plotted for the central melt zone. Calculations were performed for the half-thickness castings $l_1=550$ µm, which is critical for this alloy for casting into a mold at room temperature [5]. The initial temperature of the mold T_2^0 was varied from 293K to 793K. The values of heat transfer coefficient at the boundary of the melt-mold is determined from the relations presented in [6] to $l_1=550$ µm it was $3,2 \cdot 10^3$ W·m^{-2}·K^{-1}, and on the boundary of the mold-air environment, according to the [7], was assumed to be 5 W·m^{-2}·K^{-1}.

3. Results and analysis

Figure 1 shows examples of the obtained dependences $T_1(t)$ and $x(t)$. It can be seen that by changing the initial temperature of the mold it is possible to obtain three types of ingot cooling regimes. The first mode (at $T_2^0 = 273K$) characterized by a smoothly falling cooling curve (fig.1a), under such conditions, the processes of nucleation and growth of crystals are suppressed. The melt under this regime solidifies to form an insignificant amount of the crystalline component ($x \approx 4 \cdot 10^{-6}$), those an amorphous structure with "frozen" nuclei of the crystalline phase is formed, the average dimensions $\bar{R}$ of which are 17 nm, $N_S=2,4 \cdot 10^{17}$ m^{-3}. The realization of such a cooling regime is possible at $273K \leq T_2^0 \leq 643K$, the volume of the crystalline phase formed in this case is $4 \cdot 10^{-6} \leq x \leq 4 \cdot 10^{-4}$, and N_S and $\bar{R}$ with an increase in T_2^0 varies from $2,4 \cdot 10^{17}$ m^{-3} to $1,1 \cdot 10^{18}$ m^{-3} and from 17 nm to 44 nm, respectively.

In the second cooling mode (fig. 1b) the curve $T_1(t)$ is also characterized by reduction in temperature during the cooling process. However, the cooling of the melt is carried out in two stages. At the first stage at the initial moments of time, there is an intense decrease in temperature, and in the second stage, starting from a certain time t_{eq}, the slope of the cooling curve changes and a significant slowdown of the cooling process occurs. Such a course of the temperature curve can be explained by the fact that before the t_{eq} mold temperature is much lower than the temperature of the melt and the ingot cooling occurs due heat transfer to the metal mold. From the moment t_{eq}, in the region of deep supercoolings, the

temperature of the melt and molds are compared with each other, and cooling occurs due to heat exchange with the surrounding air environment. Such a cooling regime is observed at $643K < T_2^b < 723K$ with the formation of a volume fraction of the crystalline phase of $4 \cdot 10^{-4} < x < 9,9 \cdot 10^{-1}$. The crystalline component is formed by rapid nucleation ($I \sim 10^{18}$ m^{-3}·s^{-1}) at very low crystal growth rates ($u \sim 10^{-11}$ m·s^{-1}), i.e. increase a crystallized volume fraction is mainly due to increasing the volume density of crystals to values 10^{20} m^{-3}, and their average size in this case is increased to 132 nm.
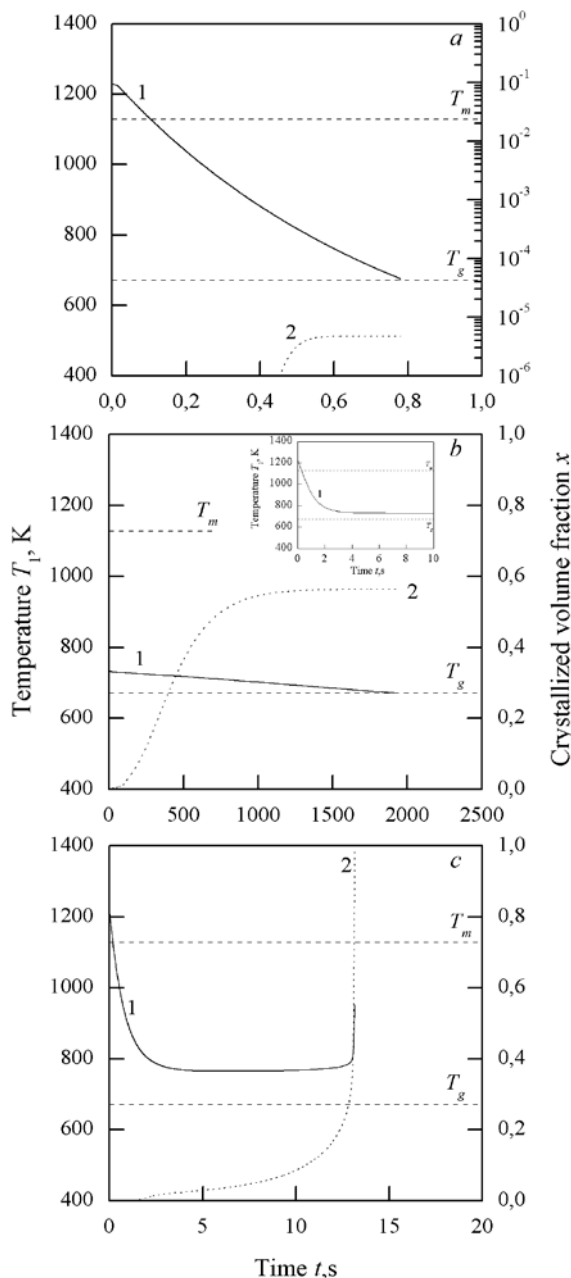

Figure 1 – The curves of the changes with time of the melt temperature (1) and the crystallized volume fraction (2) for the Vit 101 alloy castings by the half-thickness l_1=550 µm, obtained by casting in a copper mold at different initial temperatures of the mold T_2^b: $a - T_2^b$=293K; $b - T_2^b$=710K; $c - T_2^b$=743K.

Finally, the third cooling mode (fig.1c) ensures the formation of completely crystalline structures ($x \approx 9,9 \cdot 10^{-1}$), and the recalescence areas appear on the $T_1(t)$ dependences. Such cooling mode is observed for melt casting in a mold with initial temperature $T_2^b \geq 723K$. In these temperature conditions, an increase in the contribution of the crystallization processes of crystal growth processes is observed, crystal growth rate is increased by 3 orders of

magnitude ($u \sim 10^{-9}$ m·s^{-1}) at maintaining a high nucleation rate ($I \sim 10^{18}$ m^{-3}·s^{-1}). As a result in castings, complete completion of the crystallfizion processes and relative coarsening of the final microstructure, with an average crystal size of 0,2–2,3 µm and a volume density of crystals $2 \cdot 10^{19}$–$2 \cdot 10^{16}$ m^{-3} is observed at $T_2^b = 743 - 793$ K.

In a generalized form, the obtained modeling results, for the entire range of values of T_2^b, are shown in figure 2 as a function of the basic kinetic characteristic x vs. the initial temperature of the mold T_2^b. As can be seen in the range of values of T_2^b from 293K to 693K, a smooth increase in x from $4 \cdot 10^{-6}$ to $2,5 \cdot 10^{-3}$ is observed.
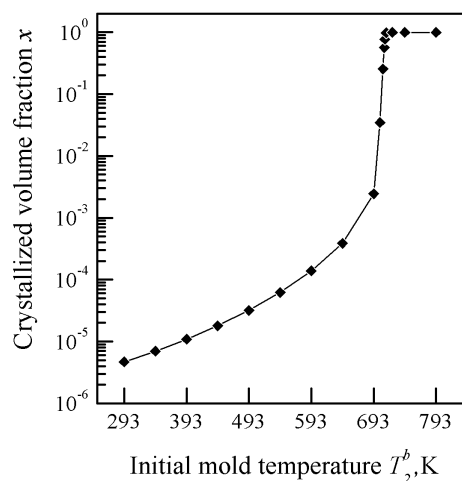

Figure 2 – Dependence of the crystallized volume fraction vs. the initial temperature of the ingot mold for castings with a half-thickness of 550 µm.

With a further increase in T_2^b, the rate of increase in the crystallized volume fraction increases sharply in a relatively narrow interval of values of T_2^b (692–723K) and a transition from an amorphous-crystal structure to a completely crystalline structure is observed. Thus, using mathematical modeling, it is shown that by setting the initial temperature of the mold, it is possible to affect on the final structure of the resulting castings of a given thickness.

4. Conclusions

1. Using the methods of mathematical modeling, thermal regimes and crystallization kinetics of Cu$_{47}$Ni$_8$Ti$_{34}$Zr$_{11}$ alloy under conditions of melt casting in a preheated copper mold have been studied.

2. It is shown, that depending on the initial temperature of the mold, ingots can be obtained in different structural states: amorphous, amorphous-crystalline and completely crystalline.

3. It is established that, by initial heating of the mold, it is possible to control the final parameters of the ingot microstructure. Depending on the value of $T_2^b = (293 - 793)K$, the average crystal sizes can vary from 14 nm to 2.3 µm.

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