THERMAL REGIMES AND CRYSTALLIZATION KINETICS DURING CASTING LIGHT VITRIFY GLASS MELTS INTO A METAL MOLD

ТЕРМИЧЕСКИЕ РЕЖИМЫ И КИНЕТИКА КРИСТАЛЛИЗАЦИИ ПРИ ЛИТЬЕ ЛЕГКО СТЕКЛУЮЩИХСЯ РАСПЛАВОВ В МЕТАЛЛИЧЕСКУЮ ИЗЛОЖНИЦУ

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Abstract: *Using an original mathematical model the calculate analysis of the relationship of thermal modes of castings production with crystallization kinetics and microstructure parameters of the alloy $Cu_{47}Ni_8Ti_{34}Zr_{11}$ is made. It is shown, that at cold mold casting in castings of different thickness are fixed three types of microstructure: amorphous with inclusions of so-called "quenching nucleus", amorphous-crystalline and polycrystalline with microscale size of the crystals. For castings with a completely crystallized nanocrystalline structure proposed method of isothermal quenching melts, which is realized by casting the melt into the preheated mold. Determined values of the initial mold temperature interval provides for the formation of castings having a grain size of 100 nm for justifiable from an economic point of view intervals.*

***KEYWORDS**: METAL MOLD CASTING, ISOTHERMAL QUENCHING OF MELT, CRYSTALLIZATION KINETICS, MICROSTRUCTURE PARAMETERS*

1. Introduction

Creation of metal materials with amorphous and nanocrystalline structures concerns priority directions of a science and modern technologies. Progress in this area require deep understanding of interrelations of a chemical composition of alloys and technology factors with the physical parameters which control a kinetics of crystals nucleation and growth processes. The important role in studying of noted interrelations is played a method of mathematical modeling. Results of modeling researches create theoretical preconditions for working out of new production technologies of precision alloys which provide controllability with processes of structure formation and reception of materials with predicted microstructures and properties.

One of ways of amorphous alloys production is casting in metal mold. This way apply to the class of so-called bulk metal glasses [1] developed in last years which solidify without crystallisation in sections more than 1 mm, i.e. at melt cooling rates less than 10^3 K/s. In the present work calculated analysis of structure formation processes at solidification of easily amorphization alloy $Cu_{47}Ni_8Ti_{34}Zr_{11}$ (Vit 101) in copper mold with thickness of working walls of 15 mm, are presented. The first block of calculations carried out in the assumption, that before melt casting the mold is at a room temperature (such technological version of process we will name casting in cold mold). In calculations of the second block initial temperature of mold set from relation $T_2^0 = T_g + (5–43)$ K, where T_g=671 K – glass transition temperature an investigated alloy [2] (casting in hot mold [3, 4]). In the latter case analyzed possibility of creation of an isothermal mode of crystallisation, assume, that with its help can be received completely crystallized casting with the sizes of structural components to 150 nm.

2. Method of calculations.

Calculated researches carried out a method of the coordinated numerical decision of thermal and kinetic problems. Thermal problem represented system of one-dimensional differential Fourier equations for melt, which contain of latent transformation heat source, and copper mold with boundary conditions, which formalize physical assumptions used in model relative to initial temperatures of melt and mold, and also heat exchange conditions on borders a melt-mold-working environment.

Solidification kinetics of casts modeled in assumptions, that process occurs by spontaneous nucleation and the subsequent normal growth of spherical crystals. Delay of transformation at the expense of collisions of the adjacent crystals considered by means of approach of effective nucleation and growth rates [5], according to which increments of number of the crystallization centers and the crystals sizes for an elementary time interval are proportional to a volume fraction of a parent phase. Within the limits of this approach the kinetic equation describing change in due course of a crystallized volume fraction, received in the form of:

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

where I, R_c – properly, formation frequency and critical radius of crystal nucleus; u – growth rate of crystals; t_m – time of achievement by melt a fusion temperature T_m; t, t', t'' – present situations times: $t_m \le t' \le t'' \le t \le t_e$, t_e – time of the crystallization ending ($x(t_e) \approx 0{,}99$).

Besides calculations of the basic kinetic dependence x (t), approach [6] allows to make the additional analysis of the crystals nucleating and crystals growth kinetic processes, which results give the valuable information on features of a microstructure rapid quenched materials [6, 7].

The coordinated decision of the equations of heat conductivity with the kinetic equation (1) carried out a method of final differences with implicit difference scheme [8]. All details of mathematical basis of model, computing algorithm and calculations temperature dependent parameters I, R_c, u for alloy Vit 101 are presented in works [9, 10].

3. Results and analysis

For studying of influence of mold temperature on a thermal mode and crystallization kinetics of casts Vit 101 counted dependences on time of temperatures of melt T_1 (t) and mold T_2 (t), and also crystallized volume fraction x(t). Calculations carried out for casts in the half-thickness $l_1 = 0{,}7 \cdot 10^{-3}$ m, derived by casting under pressure in Cu-mold with thickness of working walls $l_2 = 15 \cdot 10^{-3}$ m. Initial temperature of mold T_2^0 changed in limits from 333 to 714 K, initial temperature of melt, and also values of heat-transfer coefficient on borders the melt-mold-air environment accepted the equal: $T_1^0 = T_m + 100$ K; $\alpha_1 = 2{,}67 \cdot 10^3$ W·m^{-2}·K^{-1}, α_1=5 W·m^{-2}·K^{-1}.

As follows from fig. 1, at casting of melt Vit 101 in the cold (T_2^0 =293 K) mold the temperature of melt with time $T_1(t)$ continuously decreases to values, less T_g, keeping during all period of process t_e higher values in comparison with temperature of mold. The amorphous structure is as a result fixed with is negligibly small (~$2{,}3 \cdot 10^{-5}$) a volume fraction so-called „frozen nucleus”, having the

average sizes $\overline{R}$ ≈23 nm. Qualitatively similar structure is predicted by the modeling calculations executed in the assumption $T_2^0 \le T_g$.

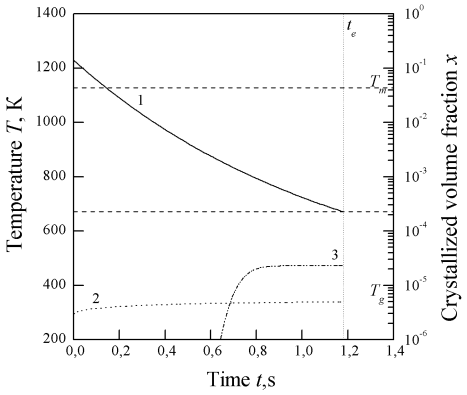

Figure 1 – Plots of changes in due course temperatures of melt (1), mold (2) and crystallized volume fraction (3) for casts from alloy Vit 101 with half-thickness l_1=0,7·10^{-3} m, received by casting in copper mold with initial temperature T_2^0 =293 K.

At heating of mold to temperatures $T_2^0 > T_g$ character of dependences $T_1(t)$, $T_2(t)$ and $x(t)$ essentially changes. The analysis of the calculation data presented on fig. 2 ($T_2^0 = T_g$+20 K), show, that during rather short time interval t_{iso}≈56 s curves $T_1(t)$ and $T_2(t)$ approach and the further stages of transformation occur in isothermal conditions ($T_1 \approx T_2 = T_{iso}$) at deep supercoolings of melt $\Delta T_r^{iso} = (T_m - T_{iso})/T_m$. For a considered example the temperature of an isothermal stage makes T_{iso}=719 K, and the reduced supercooling ΔT_r^{iso} =0,36. In similar conditions crystallization is carried out by rapid nucleation (I_{iso}=3·10^{17} m^{-3}·s^{-1}) and the subsequent growth of crystals with very low rates (u_{so}=1,4·10^{-10} m·s^{-1}). At such combination of parameters I and u increasing of crystallized volume fraction occurs preferentially at the formation of new crystallization centers which by the moment of the termination of transmutation t_e=1,3·10^3 s reach sizes $\overline{R}$ =94 nm.

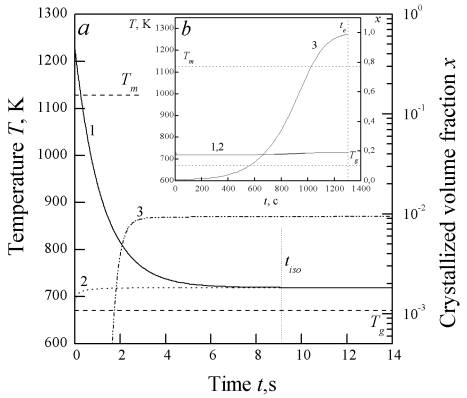

Figure 2 – Calculated dependences $T_1(t)$ (1), $T_2(t)$ (2), $x(t)$ (3) for the thin (0,7·10^{-3} m) casts from an alloy Vit 101, obtained by casting in the hot (T_2^0 =691 K) copper mold: *a* – initial stage of process; *b* – isothermal stage.

As can be seen from fig. 3, at a mold heating to temperature 714 K, which on 43 K exceeds temperature of a glass transition of alloy Vit 101, the isothermal condition of crystallisation is maintained only on the limited temporary segment. At the final stage of process the balance escaped at crystallisation and outputed in mold thermal streams is broken, that induce increasing of crystallising casting temperature from 742 to 796 K and caused by a change of a temperature condition deceleration of nucleation processes and acceleration of crystals growth. Consequence of similar modifications of parametres I and u is essential roughening microstructures of casts, which medial sizes of grains make 137 nm.

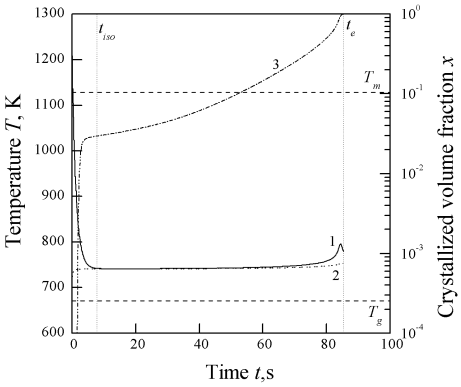

Figure 3 – Results of the calculated analysis of a thermal condition and crystallisation kinetics of casts with half-thickness 0,7·10^{-3} m, obtained by casting of melt Vit 101 in copper mold, heated to temperature T_2^0 =714 K: 1 – $T_1(t)$; 2 – $T_2(t)$; 3 – $x(t)$.

The analysis of all set of the obtained calculation datas shows, that with increase of a preliminary superheat of mold concerning temperature of a glass transition from 5 to 43 K number of the crystallization centers formed in unity of volume during all continuance of a solidification, decrease approximately on one order of magnitude (10^{20}-10^{19}) m^{-3}, and mean sizes of crystals are incremented from 68 nanometers to 137 nm. Thus common duration of process is reduced from ~9,0·10^5 s (~250 hours) to 85,4 s.

Thus, results of the performed modelling explorations argue to the basic possibility of realisation of the method of isothermal quenching of melts which allows to obtain nanoscale structures in thin casts of alloy Vit 101 immediately in the course of their solidification.

4. Conclusions

1. On an example of alloy Vit 101 features of structure formation are explored at moulding in hot casting-form. Determined the interval of casting-form temperature values T_2^0 =(676–714)K, which providing an establishment of an isothermal mode of a solidification castings, at temperatures on (5–71)K exceeding a glass transition point.
2. It is shown, that at an isothermal stage of process crystallisation is carried out with close to maximum ~(10^{15}–10^{18}) m^{-3}·s^{-1} nucleation rates and very low ~(10^{-13}–10^{-9}) m·s^{-1} rates of crystals growth, owing to what it is fixed completely crystallized structures with in the average crystal sizes from 67,6 до 137 nm.

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