

THE STRUCTURE FORMATION FEATURES OF THE ALLOY $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ DURING THE CASTING IN THE METAL MOLD AND THE FOLLOWING HEATING AMORPHOUS INGOTS

ОСОБЕННОСТИ ФОРМИРОВАНИЯ СТРУКТУРЫ СПЛАВА $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ ПРИ ЛИТЬЕ В МЕТАЛЛИЧЕСКУЮ ИЗЛОЖНИЦУ И ПОСЛЕДУЮЩЕМ НАГРЕВЕ АМОРФНЫХ СЛИТКОВ

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Abstract: The structure formation features of the bulk glass alloy $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ under conditions of melt casting in a copper mold and subsequent heating of amorphous ingots, are studied. It is shown that for certain parameters of the model (the thickness of the ingot and its heating rate), the main contribution to the total crystallized volume fraction passes from frozen crystal growth processes to the processes of nucleation and growth of new crystals. Regardless of the dominant crystallization process during heating, amorphous ingots of the $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ alloy are crystallized to form a coarse crystalline structure.

Keywords: MELT CASTING INTO THE MOLD, SOLIDIFICATION, THERMAL CONDITION, CRYSTALLIZATION KINETICS, MICROSTRUCTURE PARAMETERS

1. Introduction

It is known that under conditions of quenching from the melt in the structure of amorphous metal alloys, it is possible to obtain nanoscale crystallization centers. The volume density of such crystals and their average sizes depend on the conditions for the preparation of such materials [1, 2] and determine their final properties, thermal stability and transformation features upon heating [3-5]. In this regard, in this work, the main purpose was to study the features of the formation $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ alloy structure during cooling under conditions of melt casting into a copper mold and during heating amorphous ingots.

2. Method of calculation

Studies were performed using computer simulation methods. In studies, a previously developed model of melts and glasses crystallization [6] was used.

According to the used model, two stages of structure formation were considered. The first stage takes place under conditions of melt cooling in a massive copper mold. At this stage, crystallized the volume fraction x_-^e (in studies chose the thickness of the ingots, which provide the formation x_-^e no more $5 \cdot 10^{-2}$) and in a unit of volume formed N_-^S crystallization centers with average sizes \bar{R}_- . At the second stage, the processes of crystallization that occur during the heating of amorphous ingots are modeled. It was considered that they are carried out both by the growth of already existing frozen-in crystals, and by homogeneous nucleation and further growth of new crystals. As a result of the frozen crystals growth formed a fraction of the transformed volume x_{-+}^e , which consists of N_-^S crystals with sizes \bar{R}_{-+}^e . Simultaneously with the growth of crystals formed as a result of cooling, the processes of nucleation and growth of new crystallization centers occur. The result of this process is the formation N_+^S crystals having a size \bar{R}_+ , which contribute to the total crystallized volume the part of x_+^e . The resulting volume fraction of the crystalline phase, formed at different stages of the process:

$$x_-^e + x_{-+}^e + x_+^e = 1. \quad (1)$$

Calculations x_-^e , x_{-+}^e и x_+^e carried out by the kinetic equations obtained in the approximation of the effective rates of nucleation and growth of crystals [7].

For spherical crystals formed by nucleation and further isotropic growth in a supercooled melt with effective rates, the fraction of the crystallized volume can be determined using the equation:

$$x_-(t_-) = \frac{4}{3} \pi \int_{t_-^m}^{t_-} (1 - x(t'_-)) I(t'_-) \left[R_c(t'_-) + \int_{t'_-}^{t_-} (1 - x(t''_-)) u(t''_-) dt''_- \right]^3 dt'_-, \quad (2)$$

where t_-^m – the melting point temperature T_m at melt cooling; R_c – the critical nucleus radius; t_- , t'_- , t''_- – current times, belonging to the time interval of crystallization $[t_-^m, t_-]$: $t_-^m \leq t'_- \leq t''_- \leq t_- \leq t_-^e$.

A similar kinetic equation was used for the formation of new crystals during the heating of metallic glass:

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

where $t_+^b \geq t_+^e$ – heating start time; t_+ , t'_+ , t''_+ – current time points corresponding to the heating stage: $t_+^b \leq t'_+ \leq t''_+ \leq t_+ \leq t_+^e$; t_+^e – time of crystallization completion during heating.

The volume fraction of the crystalline phase x_{-+} , which is formed due to the growth of frozen centers, was calculated as follows:

$$x_{-+}(t_+) = 4\pi N_-^S \int_{t_+^b}^{t_+} R_{-+}^{-2}(t'_+) [1 - x(t'_+)] u(t'_+) dt'_+. \quad (4)$$

Calculations of the crystallization kinetics under the conditions of melt cooling were performed by a consistent numerical solution of equation (2) with the Fourier heat conduction equations [8] for melt with a half-thickness l_1 and copper mold with wall thickness l_2 using the algorithm described in detail in the work [9]. The calculations were performed by the finite difference method in an implicit scheme [10].

The crystallization processes during heating were modeled, assuming that an amorphous ingot having an initial temperature T_+^b is heated by heat exchange with the working medium, the temperature of which rises linearly with a predetermined velocity v_+ . The part of crystallized volume $x(t_+)$, included in the integrands of the equations (3) and (4), calculated taking into account the relative contributions of all the transformation mechanisms analyzed in the model:

$$x(t_+) = x_-^e + x_{-+}(t_+) + x_+(t_+). \quad (5)$$

3. Results and analysis

Figure 1 shows the results of the calculated analysis of the crystallization kinetics of the alloy $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$, performed using equation (2) for castings with half-thickness ranging from 0,25 to 500 mm. For all values l_1 determined the cooling rate v_c at melting point T_m , the final value of the crystallized volume fraction x^e , nucleation rate I and growth rate u , as well as structural parameters N_-^s and \bar{R}^e , fixed at the end of the cooling process.

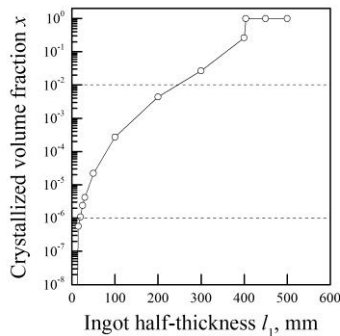


Figure 1 – The calculated dependence of the crystallized volume fraction, obtained during casting of the melt $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ in the copper mold, from the ingot half-thickness.

As the results of calculations show, with an increase in the half-thickness of the ingots under study, the proportion of the crystallized volume fraction during the entire cooling period increases from 10^{-21} ($l_1 \approx 0,25$ mm) to $\sim 0,99$ ($l_1 \geq 404$ mm). It should be noted that the general nature of dependencies $x^e(l_1)$, as well as critical cooling rate values ($v_c = 0,97$ K·c $^{-1}$) and critical half-thickness mold casting ($l_1 = 20$ mm), at which the volume fraction of the crystalline phase becomes 10^{-6} , correlates well with experimental data [11,12]. According to the calculated analysis, in the conditions of melt casting $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ in a copper mold it is possible to obtain a wide range of structural states, for which the density of nuclei of crystals can vary from $6 \cdot 10^5$ to $6,5 \cdot 10^{14}$ m $^{-3}$, and their average sizes are from $1,2 \cdot 10^{-9}$ to $6,9 \cdot 10^{-5}$ m.

Obtaining such a wide range of structural states with different volume density and sizes of crystallization makes it possible to analyze the influence of the thermal history of the alloy on the crystallization kinetics of castings during subsequent heating. For this purpose, different half-thickness castings (0,25 – 300 mm), according to equations (3) and (4), the volume fractions of the crystalline phase were calculated, one of which (x_-^e) formed by nucleation and growth of new crystals in an amorphous matrix, and the second (x_+^e) formed due to the growth of frozen crystals. Calculations were performed for heating rates 0,017, 0,03, 0,7 and 1,67 K·s $^{-1}$.

As an example, fig. 2 shows the calculated kinetic curves $x_-(t_+)$, $x_+(t_+)$, $x(t)$ for ingots with half-thickness 0,5 mm, 7 mm and 10 mm, heated at rate 0,7 K·s $^{-1}$. As can be seen, depending on the half-thickness of the ingots, the crystallization mechanisms considered in the model make different contributions to the total crystallized volume fraction x . So when heating ingot with a half-thickness 0,5 mm (fig.2a) crystallization is carried out due to the mechanism of formation of new crystals ($x_-^e \approx 0,97$, $x_+^e \approx 2,2 \cdot 10^{-2}$). However, with increasing casting thickness x_-^e and x_+^e changing to the opposite so when $l_1 = 10$ mm $x_+^e \approx 6,4 \cdot 10^{-2}$, and $x_-^e \approx 0,93$ (fig.2c). In ingots with a half-thickness $l_1 = 7$ mm there is an approximate equality of the volume fractions of the phases formed by different mechanisms: $x_+^e \approx 0,57$, $x_-^e \approx 0,42$ (fig.2b).

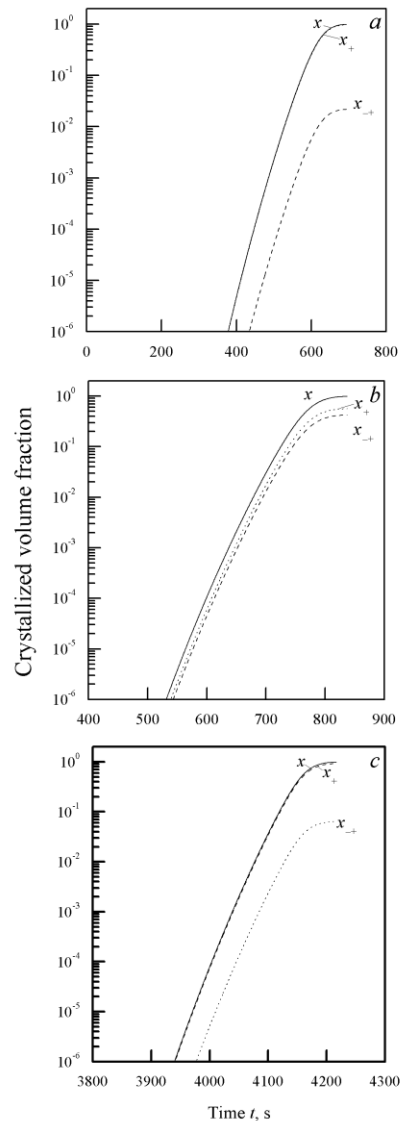


Figure 2 – Dependence of the volume fraction of the crystalline phase on the heating time for amorphous castings $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ with half-thickness (mm): 0,5 (a), 7 (b), 10 (c), appropriate heating rate $v_+ = 0,7$ K·s $^{-1}$.

With a decrease in the heating rate, the growth processes of quenched nuclei dominate in wider intervals of ingot half-thicknesses l_1 , the half-thicknesses, in which both mechanisms make equal contributions to the total fraction of the crystallized volume, are shifted towards smaller thicknesses (fig. 3).

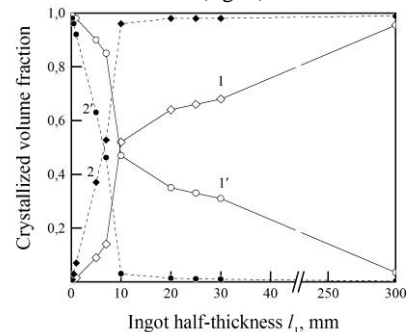


Figure 3 – Calculated dependencies of contributions to the crystallized volume fraction of two competing crystallization mechanisms on the half-thickness of amorphous castings $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$, corresponding to the heating rates 0,017 K·s $^{-1}$ (light symbols) and 1,67 K·s $^{-1}$ (dark characters): 1, 2 – x_- ; 1', 2' – x_+ .

According to the calculated data, crystallization processes occur during supercooling 100–200 K relative to the melting point. Under these conditions, nucleation processes occur at a rates of 0–10 7

$\text{m}^{-3}\cdot\text{s}^{-1}$, and the crystal growth rate varies within $\sim 10^{-7}\text{--}10^{-9}\text{ m}\cdot\text{s}^{-1}$. But, despite such low values I and u , due to very long crystallization time intervals ($10^2\text{--}10^5\text{s}$), during the heating time in a unit of volume crystallize $\sim 10^{11}\text{--}10^{14}\text{ m}^{-3}$ new crystals, the final size of which ($\bar{R}_t^e \sim 10^{-5}\text{ m}$) not inferior to the size of crystals growing from frozen-in crystallization centers. This result of computational analysis confirms the need to take into account the two mechanisms of crystallization of metal glasses.

4. Conclusions

1. Through modeling studies alloy $\text{Zr}_{41,2}\text{Ti}_{13,8}\text{Cu}_{12,5}\text{Ni}_{10}\text{Be}_{22,5}$ It was found that, with an increase in the half-thickness of amorphous ingots and a decrease in the heating rate, the main contribution to the total fraction of the crystallized volume is made by the growth of frozen-in crystallization centers.
2. It has been established that the equal contribution of the growth processes of frozen crystals and the processes of nucleation of new crystallization centers during heating in the range of $\nu_t=0,017\text{--}1,67\text{ K}\cdot\text{s}^{-1}$ observed in castings with a half-thickness from 10 to 6,5 mm.
3. It is shown that upon heating the amorphous alloy ingot $\text{Zr}_{41,2}\text{Ti}_{13,8}\text{Cu}_{12,5}\text{Ni}_{10}\text{Be}_{22,5}$ possible to obtain structures with mean crystal size of 10 μm .

5. References

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