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MODELLING OF MECHANISM OF STRUCTURE FORMATION BY NON-EQUILIBRIUM COOLING

МОДЕЛЮВАННЯ МЕХАНІЗМУ СТРУКТУРОУТВОРЕННЯ ПРИ НЕРІВНОВАЖНОМУ ОХОЛОДЖЕННІ

The article presents the result of computer modeling of structure formation nano- and microcrystalline states on non-equilibrium crystallization with cooling from 10^5 to 10^{12} K/s. The given computer modeling makes it possible to predict the formation of structures in metastable states.

***Keywords**: amorphous and X-ray amorphous states, supercooling, thermal stability, cooling rate.*

Сучасні функціональні нано- і мікрокристалічні матеріали отримують в умовах нерівноважної кристалізації зі швидкістю охолодження від 10^5 (splat — cooling) до 10^{12} К/с (гартування з пароподібного стану). Нерівноважна кристалізація призводить до формування низки метастабільних станів: сильно пересичених твердих розчинів проміжних фаз, аморфних і нанокристалічних структур. Природно, що за цих умов нерівноважного охолодження у структурному і фазовому складі відбуваються суттєві зміни, які обумовлюють надалі фізичні властивості зразків. Перш за все це стосується початкових стадій кристалізації, що супроводжується утворенням і густиною первинних зародків, які надалі формують остаточну структуру зразків. Тому визначення долі закристалізованого об'єму для різних швидкостей охолодження є актуальною науково-технічною задачею. Метою статті є дослідження впливу нерівноважних швидкостей кристалізації на визначення величини закристалізованого об'єму. У роботі із застосуванням теплофізичних параметрів кристалізації показано, що об'єм закристалізованої речовини змінюється як через нові кристали, так і через приріст об'єму "старих" кристалів. За отриманими розрахунками встановлено 3 типи кривих охолодження. Запропонована модель дозволяє відрізняти речовини, які при великих швидкостях охолодження кристалізуються в аморфному та рентгеноаморфному станах, а також особливості їх подальшої кристалізації. Показано, що у сплавах і чистих металах процес загартування проходить як за різними типами нерівноважної кристалізації, так і за різним процесом формуванням густини первинних зародків. Надалі доцільно дослідити вплив розмірів малих зразків на температуру плавлення та особливості їх швидкої кристалізації.

***Ключові слова**: аморфний і рентгеноаморфний стани, переохолодження, термічна стійкість, швидкість охолодження.*

Problem's Formulation

Rapid quenching (splat cooling) of alloys from the melt could form completely extended solid solutions, new metastable crystalline phases and amorphous solid phases [1]. These effects were attributable to the high cooling rates (>10^5 K/s). Crystallization under nonequilibrium conditions will obviously be accompanied by a change in the structural characteristics of the alloys, which, in turn, depend on the initial stages of crystallization, namely, on the number and size of the emerging primary crystals in the liquid matrix. During the crystallization of small volumes, when the size of the critical nucleus is close to the size of the sample, the temperature at the beginning of crystallization will coincide with the temperature of the first nucleus. In the case of significant supercooling, the process of transition of the liquid to the amorphous state takes place in the temperature range, and the temperature of amorphization is taken to be the temperature at which the coefficients of the properties characteristic of the substance in the liquid and amorphous state are equal. The temperature of the beginning of crystallization depends on the conditions of crystallization of the volume of the liquid sample and the physical properties of the substance. There is a critical cooling rate for each volume when crystal nucleation is no longer observed, and amorphization of the metal takes place. That is, with an increase in the cooling rate for liquid clusters of different volumes, the crystallization temperature decreases, supercooling increases, and the cooling rate has the greatest effect [1, 2].

Analysis of recent research and publication

In the scientific literature, much attention is paid to studies of the behavior and processes of changing the size of already crystallized particles during heat treatments of amorphous and nanocrystalline samples, without comparing them with the features of the initial nucleation of nuclei depending on the rate of nonequilibrium crystallization and the thermodynamic parameters of the elements [2—10].

Formulation of the study purpose

The research aimed to determine the fraction of the crystallized volume under specific conditions of the crystallization rate from several 10^5 to 10^{11} K/s, which will determine the features of the formation of the final structure. For this purpose, we will analyze from a thermo-kinetic point of view the processes during nonequilibrium crystallization.

Presenting the main material

Consider a drop with a volume of V_{cryst} which cools at a rate of υ_{cool}. In the temperature interval $(T_i - T_l)$, where T_l is the temperature at the beginning of crystallization, and the entire volume of the drop is occupied by the melt. And after some time Δt after the melt reaches the temperature T_l, a part of its volume (V_l) crystallizes. At the first moment, the growth of the solid phase takes place due to the appearance of new crystals, and then — due to the growth of previously formed crystals and the appearance of new ones in the residual volume of the liquid: $V_i = V - V_i$. Over time Δt the radius of the spherical crystal (R) increases: $u(T_i)\Delta t$, where $u(T_i)$ is the growth rate of the crystal at temperature T_i. Change in the volume of the solid phase due to the crystallized T_i portion of the melt over time Δt consists of:

$$\Delta V = V_i - V_{i-1} = \frac{4}{3}\pi(R_{i-1} + u(T_i\Delta t))^3 - \frac{4}{3}\pi R_{i-1}{}^3;$$

at $\Delta t \to 0$

$$\Delta V = 4\pi R^2{}_{i-1}u(T_i)\Delta t.$$

That is, the volume of the drop increases due to its surface points, the number of which is proportional to the surface area. It can be assumed that the surface of the solid phase is formed by the surfaces of all existing crystals at that time. However, as a result of their collisions, the growth of several points will be blocked. Thus the number of surface points that are capable of growth is proportional to the part of the melt $(1-X)$. Then the increase of the crystalline phase over time Δt in parts of the volume of the drop will be:

$$\Delta X(T_i) = S(T_i)u(T_i)\Delta t$$

and the radius of the crystal and its surface, which are formed at different crystallization temperatures, can be found according to the following formulas:

$$\sum_{i=1}^{n}(R(T_i) + \sum_{j=1}^{n}u(T_j)\Delta t);$$

$$4\pi[(R(T_i) + \sum_{j=1}^{n}u(T_j)\Delta t]^2.$$

The number of crystals that are formed at a temperature T_i per time Δt is:

$$\Delta N(T_i) = I(T_i)(V - V_i)\Delta t \Rightarrow \Delta N(T_i) = I(T_i)V(1-X))\Delta t.$$

Then the total surface area of the crystals at the temperature T_n will be equal to:

$$S = 4\pi\sum_{i=1}^{n}I(T_i)(1-X(T_i))\Delta t[(R(T_i) + \sum_{j=1}^{n}(T_j)\Delta t)]^2$$

and volume growth over time Δt is:

$$\Delta V_n = [V\sum_{i=1}^{n}I(T_i)(1-X(T_i))\Delta t(R(T_i) + \sum_{j=i}^{n}u(T_j)\Delta t)^2][1-X(T_n)]u(T_n)\Delta t +$$

$$+\frac{4}{3}\pi VI(T_n)\cdot[1-X(T_{n-1})]\Delta tR^3(T_n)$$

$$\Delta X(T_n) = [\sum_{i=1}^{n}I(T_i)(1-X(T_{i-1}))\Delta t(R(T_i) + \sum_{j=i}^{n}u(T_j)\Delta t)^2]u(T_n)[1-X(T_{n-1})]\Delta t +$$

$$+\frac{4}{3}\pi I(T_n)(1-X(T_{n-1})]\Delta tR^3(T_n)$$

$$X(T_n) = X(T_{n-1}) + \Delta X(T_n).$$

The temperature change of the drop due to the crystallization of part of the substance ΔX is calculated according to the formula:

$$\frac{dT}{dt}=\frac{q\dfrac{dX}{dt}-c_P{}^s\vartheta_{cryst}}{-c_P{}^lX+c_P{}^s(1-X)},$$

where: *dX/dt* is the crystallization rate; *dT/dt* is the change rate of temperature liquid state; $c_p{}^l$, $c_p{}^s$ are atomic heat capacity of liquid and solid states, respectively.

At the temperature of the beginning of crystallization (T_1), the part of the volume that crystallized is determined by the volume of the formed crystals:

$$X(T_1)=\frac{4}{3}\pi I(T_1)R(T_1)^3\,\Delta t\,.$$

The temperature change of the drop is:

$$\Delta T_i=\frac{\vartheta_{cool}c_P{}^l\Delta t-q(X(T_1)-0)}{c_P{}^sX(T_1)+c_P{}^l(1-X(T_1))}$$

temperature T_2 is defined as: $T_2 = T_1 - \Delta T_1$.

At this temperature, the total surface area of "old" embryos (S_{old}) is equal to:

$$S_{old}=4\pi I(T_1)V\Delta t(R(T_1)+u(T_1)\Delta t)^2\,.$$

Over time, Δt the volume of the crystallized substance changes due to new crystals and an increase in the volume of "old" ones by the amount:

$$\Delta X(T_2)=I(T_1)(1-0)\Delta t(R(T_1)+u(T_1)\Delta t)^2u(T_2)(1-X(T_1))\Delta t+\frac{4}{3}\pi I(T_2)(1-X(T_1))\Delta tR^3(T_2)\,.$$

As a result of crystallization $\Delta X(T_2)$ of the substance, the temperature of the drop will be:

$$T_3=T_2-\Delta T_2=T_2-\frac{\vartheta_{cool}c_P{}^c\Delta t-q\Delta X(T_2)}{c_P{}^sX(T_2)+c_P{}^l(1-X(T_2))}\,.$$

The process continues either until the complete end of crystallization (X=1) or when the glass transition temperature is reached T_g.

Analysis of mathematical modeling of droplet crystallization shows that the "temperature-time" cooling curves can be divided into 3 groups (Fig. 1—4).

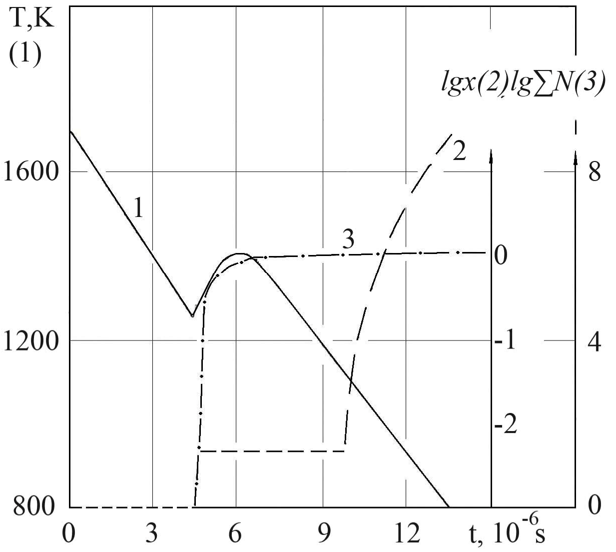

Fig. 1. Crystallization of drops according to the 1st type (model): 1 — cooling rate; 2 — the fraction of crystallized volume; 3 — the number of crystals

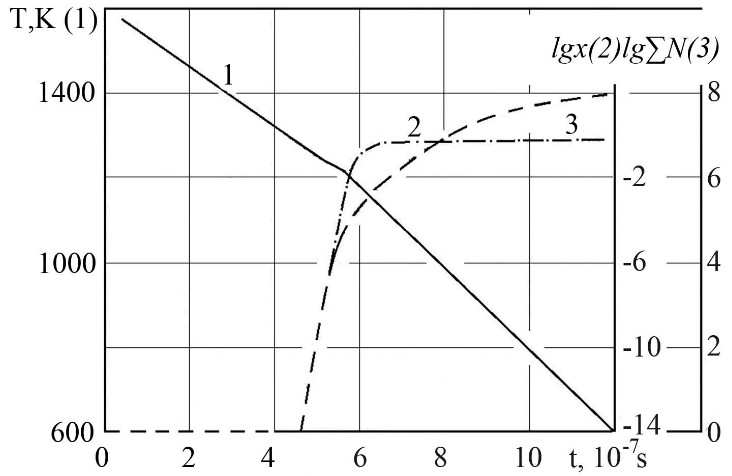

Fig. 2. Crystallization of drops to 2nd type (model): 1 — cooling rate; 2 — the fraction of crystallized volume; 3 — the number of crystals

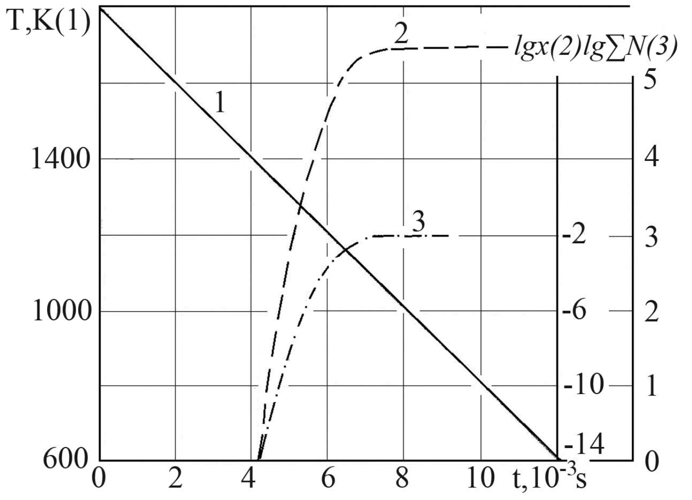

Fig. 3. Crystallization of drops according to 3rd type (model) 1 — cooling rate; 2 — the fraction of crystallized volume; 3 — the number of crystals

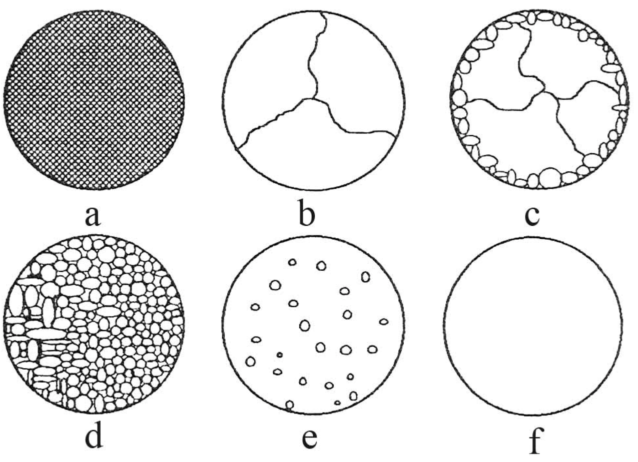

Fig. 4. The dependence of structural formation in alloys under conditions of high cooling: a — monocrystalline; b — coarse crystalline; c — coarse-crystalline in a polycrystalline border; d — fine crystalline; e — X-ray amorphous; f — amorphous

The first group is curves with recalescence (Fig. 1), which are observed in the process of crystallization of a nickel drop with a diameter of 2 μm at a cooling rate ~10^8 K/s: in the initial period of crystallization at 1225 K, the temperature stops at $3{\cdot}10^{-5}$s, after which the rate of crystallization increases sharply. The amount of released heat exceeds that which can be removed at a given temperature, so the temperature of the drop increases to a maximum temperature of 1680 K. Under such conditions, new crystals are unable to form: that is, the nucleation frequency at small supercoolings is very low, and the process of formation of a solid phase takes place due to the growth of a previously formed crystal in the form of a single crystal structure.

Crystallization of a drop with a diameter of ~100 μm at cooling 10^8K/s begins at 1290 K (Fig. 1), when the proportion of the crystalline phase (X) increases not only due to the growth of the formed first crystal, but also due to the formation of new crystals (Fig. 2). In the temperature range of 1290—1262 K, crystals form to $10^{1,5}$ and the rate of release of the heat of crystallization will exceed the rate of heat removal, as a result of which the temperature of the drops rises sharply to 1450 K. During the period of recalescence, no new crystals are formed, and the fraction of the crystallized substance $X=f(t)$ increases only due to previously formed crystals. About ~$8{\cdot}10^{-8}$ s after the start of crystallization, when the fraction of the crystallized substance already equals ~80 %, the rate of crystallization decreases sharply, as a result of which the temperature of the drop begins to decrease, and upon reaching 1262 K, new crystals begin to form, which do not have time to reach the sizes of the first crystals: as a result, large crystals are surrounded by small crystals.

The second type of crystallization takes place with a continuous decrease in temperature under conditions of increased cooling rates. Thus, in Ni-drops with a diameter of ~100 μm (cooling 10^9 K/s) on the "temperature-time" curve, instead of recalescence, a small bend is observed (Fig. 2). Crystals are formed in the range of 1260—920 K, their number reaches 10^6, and the proportion of the crystallized substance — 10^{-2}. At cooling 10^9 K/s for drops with a diameter of 10 µm, recalescence is still observed, as a result of which the hardened drop has a completely crystalline structure: the number of crystals is 10^3, and their radius is 10^{-6} m. The determined radius of the crystals that formed at the end of crystallization does not exceed 10^{-10}m. Increasing cooling rarely decreases the number of crystals and their radius, therefore the proportion of the crystalline phase also decreases (3rd type of crystallization). When the proportion of the crystalline phase becomes smaller than 10^{-6}, then such a structure is tentatively classified as X-ray amorphous. Indeed, an amorphous structure in a drop is formed only at a temperature that exceeds the critical one.

The established regularity of the cooling curves for Ni drops is also characteristic of several of other metals and alloys, however, the physical properties of the substance significantly affect the dependence of the structure change on the cooling rates. So, for a eutectic alloy $Au_{78}Ge_{13}Si_9$ at ~5 K/s the fraction of the crystalline phase in the amorphous matrix is ~10^{-3}, and in the alloy $Fe_{40}Ni_{40}B_{20}$ at cooling rate 10^{11} K/s is 10^{-12}.

Conclusion

In other words, the proposed model makes it possible to distinguish between substances that crystallize in crystalline, amorphous, or X-ray amorphous states, depending on the temperature and rate conditions of the initial stages of crystallization. The former includes a eutectic alloy $Au_{78}Ge_{13}Si_9$ in which the crystallization temperature of the amorphous state is higher than the glass transition temperature. In X-ray amorphous materials such as $Fe_{40}Ni_{40}B_{20}$ and pure Ni, crystal nuclei already exist in the amorphous matrix, so the crystallization process begins at temperatures lower than the glass transition temperature. The above modeling allows for more targeted control of crystallization processes to form the required structure in metals and several alloys. Cooling conditions affect the formation of an amorphous state with varying degrees of temperature stability.

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