"Avalanche" crystallization of amorphous metals

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It is shown that local initiation of the crystallization of amorphous bismuth and ytterbium films can lead to an avalanchelike propagation of the phase transition through the entire sample. The rate of motion of the avalanche-crystallization front reaches 10 m/sec for Yb and 20 m/sec for Bi. No crystallization is realized in the case of amorphous gallium films. It is found that the activation energy E of the transition from the amorphous to the crystalline state is less than the latent heat Q of the transition in the case of Bi and apparently also Yb. For Ga, on the contrary, $E > Q$. The prevailing viewpoint that the necessary condition for the development of a self-maintaining avalanche crystallization of amorphous substances is satisfaction of the inequality $\beta Q > E$ (where β is the thermal-energy dissipation factor) is confirmed.

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1. INTRODUCTION

It is known that amorphous metals and alloys usually crystallize when heated to a definite temperature T_{a-c}. The value of T_{a-c} is 13–23 K for amorphous films of pure metals of thickness $D > 200$ Å and can reach several hundred degrees for amorphous metallic alloys. Amorphous metals and alloys are crystallized by heating via formation of crystalline seeds in the amorphous matrix and their subsequent growth. It appears that a different crystallization mechanism takes place when the film reaches a critical thickness in the course of condensation (even at $T < 4$ K).[1] In this case the transition of the film from the amorphous to the crystalline state (the a–c transition) is faster, apparently because of avalanche-like release of the latent heat of the transition on the phase boundary. The rate of propagation of the crystallization front at such processes was first measured for amorphous Ge layers.[2] The crystallization of an amorphous Ge layer of thickness $D > 10$ μm was initiated by a localized energy pulse, after which the crystallization propagated over the entire sample with a front velocity $V = 0.25$–1.2 m/sec. Such a self-maintaining crystallization, which proceeds with high velocity and is characterized by avalanche-like energy transport, is called a "explosive" or "impact." It seems to us that the term "avalanche" crystallization is more suitable. The temperature of the avalanche-crystallization front of Ge is approximately 500° higher than the initial sampie temperature.[3]

Avalanche crystallization initiated by a pulse was observed in amorphous films of the alloy (InGa)Sb (Ref. 4). The velocity of the crystallization front was in this case 2–5 m/sec. It was found[4,5] that avalanche crystallization is initiated only in samples whose initial temperature exceeds a limiting (critical) temperature $T_{\lim}$. The value of $T_{\lim}$ depends on a method of producing the amorphous films, on its composition, thickness, and thermal history, as well as on the substrate material. In the case of amorphous Ge films[2] and the metallic amorphous alloy (InGa)Sb (Ref. 4), no $T_{\lim}$ lower than room temperature was observed. In some studies,[2,4] the existence of a limiting thickness $D_{\lim}$ was also noted. At $D < D_{\lim}$, other conditions being equal, no avalanche crystallization was realized in amorphous films. In contrast to the cited studies, where the avalanche process took place at $T \sim 300$ K or higher, crystallization in films of the amorphous alloy $Fe_{0.7}Ni_{0.3}$ (Ref. 6), with a linear velocity 10–20 m/sec, was observed at a temperature ~4.2 K. In this case, however, the time of action of the crystallization-initiating electron beam greatly exceeded the time of the a–c transition and, since the heat could be carried away only through the film, additional heating of the latter was inevitable. It is therefore difficult to agree with the authors of Ref. 6 that the crystallization of the amorphous alloy $Fe_{0.7}Ni_{0.3}$ under the conditions of their experiment was self-maintaining. It is more probable that in their case the crystallization mechanism was similar to that proposed for amorphous Ge films scanned by a laser beam at $T < T_{\lim}$ (Refs. 5, 7, 8).

The present paper is devoted to an investigation of the conditions for the initiation of avalanche crystallization of pure amorphous metals at temperatures $1.5\text{ K} < T < T_{a-c}$.

2. TECHNIQUE

The technique of obtaining amorphous metallic films was described in detail earlier.[1] The metals were evaporated with resistive evaporators made of purified tungsten wire. The pressure of the residual gases (mainly H_2 and He) in the working ampoule prior to the start of the evaporation was ~10^{-12} Torr. We investigated amorphous films of ytterbium, bismuth, and gallium condensed on a polished glass surface cooled to $T = 4.2$ K. The thicknesses of the investigated films were 300–800 Å for Yb, 240–450 Å for Bi, and 1000–1200 Å for Ga. The shape of the film was determined by the opening in a stainless-steel mask placed on the substrate (Fig. 1). Platinum contacts (1 and 2 for the currents, 3 and 4 for the potential) were sealed into the substrate. The film length (between contacts 1 and 2) was 12–13 mm, and the width 0.7–0.8 mm. The a–c transition was initiated in the sample by passing through the film section between contacts 5 and 6 a single rectangular current pulse of duration 10–100 μsec from a G5-54 generator. The pulse amplitude was chosen such that the power released in this section of the film was sufficient to heat its temperature T_{a-c}. A current density

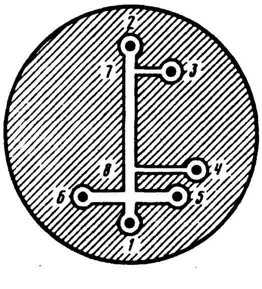

FIG. 1. Mask that determines the shape of the film: 1–6 platinum contacts for electric measurements, 7–8 film section monitored by an S8-1 oscilloscope.

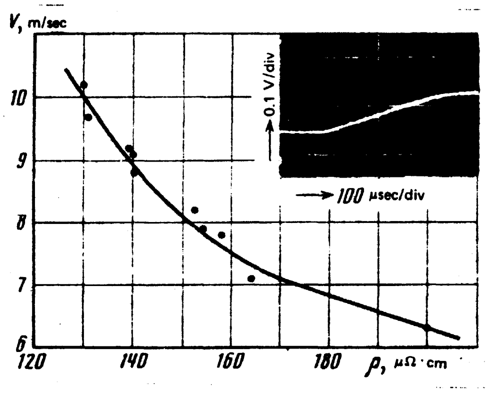

FIG. 2. Dependence of the avalanche-crystallization front velocity on the purity (determined by the value of ρ) of amorphous Yb films. Inset—typical oscillogram of avalanche crystallization of Yb film.

sufficient for complete crystallization of section 5–6 (during the time of the pulse) is ~3×10^5 A/cm^2 for Yb and Bi, and ~10^6 A/cm^2 for Ge. If the current pulse initiated avalanche crystallization of the remainder of the film, the crystallization wave propagated from section 5–6 along section 1–2. Since the resistivities ρ of the investigated metals in the amorphous and crystalline states differ by approximately one order, the potential difference on the film section 7–8 also changes during the time of the a–c transition by approximately one order. The potential difference and its variation were registered by a potentiometer R363-3 connected in parallel in the film circuit and by a storage oscilloscope S8-1. The oscilloscope, operating in the slaved regime, was triggered by a synchronizing pulse shifted relative to the main pulse of the G5-54 generator by 10–100 μsec. The oscilloscope determined the time of passage of the crystallization front along the film section 8–7, from which the front velocity V was calculated. If the crystallization wave does not propagate in the film section 1–2, the instruments show no change in the potential difference. The a–c transition of the film section 5–6 (under the influence of the current pulse) was revealed by the change of its resistance. The "slope ratio" method[9,10] was used to determine the activation energy of the a–c transitions of all the investigated metals.

3. EXPERIMENTAL RESULTS

A. Velocity of crystallization front

The most thoroughly investigated were the Yb films. It turned out that no avalanche crystallization is initiated in amorphous Yb films of thickness less than the limiting value $D_{\rm lim}$. In this case the current pulse flowing through the film section 5–6 (see Fig. 1) produces a complete a–c transition, but no crystallization wave propagates along section 1–2.

The limiting thickness of the amorphous Yb films, determined for a substrate temperature 4.2 K, is 350–450 Å, with the lower values corresponding to purer samples. In Yb films with $D>D_{\rm lim}$ the current pulse initiates avalanche crystallization of the entire film, and the crystallization-front velocity is 6–10 m/sec. It was found that within the limits of experimental error (10%) V is independent of the initial film temperature (in the range 1.5–11 K) and of its thickness (in the interval 450–800 Å). It turned out, however, that the velocity of the film in the course of the avalanche crystallization depends strongly on the purity of the films. It follows from Fig. 2, which shows a plot of V against the resistivity (which can serve as a measure of the purity of the metal) that the purer the film the larger V. In practically all cases of avalanche crystallization of Yb, the front velocity is constant. This is evidenced by the linearity of the sloping section, which characterizes the a–c transition on the oscillogram (see inset of Fig. 2).

Avalanche crystallization is also easily initiated in amorphous Bi films whose thickness exceeds $D_{\rm lim}$ (250–350 Å). An oscillogram of the a–c transition obtained for avalanche crystallization of a wedge-shaped Bi film with a thickness decreasing smoothly from ~450 Å shows that the crystallization wave "attenuates" in the thickness region $D\approx D_{\rm lim}$. For certain amorphous Bi films, whose thickness is somewhat larger than $D_{\rm lim}$, a variable velocity of the crystallization front was observed (from 5 to 13 m/sec). The maximum front velocity observed in the case of pure Bi films of thickness ~450 Å is ~20 m/sec. For all the Bi films the avalanche crystallization was initiated at temperatures 6.5–7 K (above the superconducting-transition temperature).

Attempts to initiate avalanche crystallization in pure amorphous Ga films 1000–1200 Å thick at temperatures 9–14 K were unsuccessful. The current pulse produced complete crystallization of the film section 5–6, but no crystallization wave propagated in the rest of the film. It is interesting that in this case (just as for Yb and Bi films with thickness $<D_{\rm lim}$) the crystallization of the film section 5–6 (Fig. 1) has no influence whatever on the kinetics of the a–c transition of the remainder of the film when it is subsequently heated to $T=T_{\rm a-c}$.

B. Activation energy of a–c transitions

As shown in Ref. 10, the change of the resistivity of amorphous metals by annealing can be described by a kinetic equation of the form

$$d\rho/dt=\nu_0F(\rho)e^{-E/kT}. \qquad (1)$$

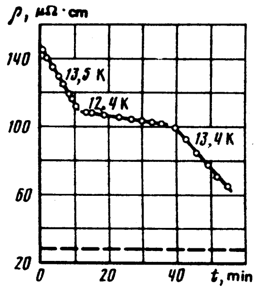

FIG. 3. Isothermal sections of the variation of the resistivity with time for an amorphous Yb film in the course of its heating. The film thickness is 700 Å. The dashed straight line shows the value of ρ for a completely crystallized film.

Here t is the time, ν_0 is a frequency factor, $F(\rho)$ is a certain continuous function of the resistivity, E is the activation energy, and k is Boltzmann's constant.

According to the "slope ratio" method[9] the activation energy is determined from the isothermal $\rho(t)$ plots at different temperatures in the course of annealing of one sample.

It follows from (1) that

$$\frac{E}{k}=-\left(\ln\frac{S_1}{S_2}\right)\bigg/\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \tag{2}$$

where S_1 and S_2 are the values of $d\rho/dt$ at temperatures T_1 and T_2 (directly before and immediately after the change of the temperature from T_1 to T_2).

For all the metals investigated in the present study, the isothermal sections of $d\rho/dt$ were linear. By way of example, Fig. 3 shows the change of the resistivity with time at different temperatures for one of the Yb films. The activation energy determined from similar plots by means of Eq. (2) are listed in Table I.

The activation energy for amorphous Bi films agrees with the values obtained from the heat release in the a–c transition process.[11] The last column of the table gives the crystallization heats obtained in Ref. 11 for Bi and Ga.

It should be noted that within the limits of experimental error the activation energy was found to be independent of the film thickness (in the investigated thickness interval). A small number of random impurities, which determine the range of the resistivities of the amorphous Yb films shown in Fig. 2, likewise does not influence (within the limits of error) the value of E.

4. DISCUSSION OF RESULTS

According to the present paper (as well as Refs. 2–4) the process of avalanche crystallization of amorphous substances is self-maintaining. There is no doubt that the principal role is played in this case by the heat Q released in the course of the a–c transition. The internal stresses are apparently immaterial.[2]

TABLE I. Activation energies of a–c transitions and crystallization heats of amorphous Yb, Bi, and Ga.

Metal	E, kcal/g · atom	Q, kcal/g · atom
Yb	0.8±0.1	–
Bi	0.8±0.1	1.45
Ga	0.9±0.15	0.29

As assumed by most workers,[1,2,4,12,13] the necessary condition for the development of avalanche crystallization is the inequality

$$\beta Q>E, \tag{3}$$

where $\beta<1$ is the thermal-energy dissipation factor. The value of β is closer to unity the more the rate of release of the crystallization heat exceeds the rate of heat transfer to the substrate.

Initiation of avalanche crystallization is always accompanied by an external energy pulse sufficient to overcome the activation barrier E of some volume of amorphous metal. Crystallization of this volume is accompanied by a release of the heat of crystallization Q. If the inequality (3) is satisfied, the thermal energy βQ is sufficient to heat a film section next to the crystallized one to $T>T_{\text{a–c}}$. The latter undergoes an a–c transition, heat Q is again released. and so on, i.e., an avalanche-like reaction develops.

It is seen from Table I that condition (3) will be satisfied for Bi but is certainly not satisfied for Ga (for which $Q<E$). It is from this that it follows that avalanche crystallization of amorphous Ga is impossible.

It is known[14] that the thermal relaxation (cooling) of the metallic film on a dielectric substrate is described by the equation

$$\frac{d(\Delta T)}{dt}=\frac{1}{CD}\frac{dQ'}{dt}. \tag{4}$$

Here $\Delta T=T_1-T_2$ is the difference between the temperatures of the film and of the substrate, C is the heat capacity of the film per unit volume, dQ'/dt is the heat flux through the film–substrate interface.

It follows from (4) that the thinner the film the faster it cools. This can lead to a decrease of β in equality (3). Obviously, at $D=D_{\text{lim}}$ the thermal energy Q becomes less than E, so that development of avalanche crystallization becomes impossible.

The heat of the a–c transition was not determined for amorphous Yb films. It is known, however, that as a rule the heat of crystallization of amorphous metals and alloys is approximately half their melting heat (see the review[1]). The melting heat of ytterbium is 1.83 kcal/g · atom.[15] It can be assumed that $Q\sim 1$ kcal/g · atom for amorphous Yb. This does not contradict the inequality (3) in the case of amorphous Yb films.

Thus, our results confirm the need for satisfying the condition (3) if avalanche crystallization is to develop.

There is as yet no quantitative theory of avalanche crystallization of amorphous substances. Nonetheless, a simplified theoretical model based on the use of the equation of one-dimensional thermal conductivity,[16] explains qualitatively the principal aspects of avalanche crystallization. In addition to the a–c transition in the solid state, this model suggests the possibility of melting of the amorphous substance immediately prior to its crystallization. In other words, the front of the avalanche crystallization can be a narrow ($\sim 10^{-1}$ D) zone of molten substance. Consideration of a liquid zone may be justified, in the opinion of the authors of the model, only in the case of substances whose having different structures in the amorphous and liquid states. Germanium, in particular, is one such substance.

The structure of amorphous metals is as a rule analogous to the structure of the corresponding melts,[17] so that the "liquid zone" model can hardly be realized for them. Our preliminary experiments have shown that the temperature of the front of avalanche crystallization of amorphous Yb and Bi films is at any rate less than 200 K. This result excludes the existence of a molten zone in avalanche crystallization of the investigated metals. The theoretical model[16] yields for the avalanche-crystallization front velocity (without formation of a liquid zone) the expression

$$V\sim\varkappa^{1/2},$$

where $\varkappa$ is the thermal diffusivity of the substance. Since the thermal conductivity of metallic films at low temperatures is due mainly to electrons[18] and $\varkappa\sim l$ (Ref. 19) (where l is the mean free path of the electrons), one should expect

$$V\sim l^{1/2}\sim(1/\rho)^{1/2}.$$

The $V(\rho)$ plot shown in Fig. 2 agrees satisfactorily with this relation (especially if it is recognized that ρ is determined accurate to 10–15%). It can apparently be stated that the results agree qualitatively with the simplest theoretical notions.[16] It must only be assumed that an increase in the amount of impurities in the amorphous Yb decreases the electron mean free path, in accordance with the relation $l\sim 1/\rho$.

Generalizing the results of the present paper, we note the following:

1. Avalanche crystallization of amorphous films of pure metals can be initiated even at $T\sim 1.5$ K, if the inequality $\beta Q > E$ is satisfied.

2. The avalanche-crystallization front velocity V is as a rule constant for each sample.

3. The value of V for the purest amorphous Yb and Bi films is ~10 and ~20 m/sec, respectively.

4. At least for Yb, the velocity of the avalanche-crystallization front does not depend on the film thickness (in the interval $D_{\lim} < D < 800$ Å) and of the substrate temperature (in the interval 1.5–11 K).

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