

THE EXPLOSIVE CRYSTALLIZATION OF AMORPHOUS MICROWIRE

ВЗРЫВНОЙ ПЕРЕХОД В АМОРФНОМ МИКРОПРОВОДЕ

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Abstract: Amorphous microwire in a glass shell has low thermal inertia and can be rapidly heated to the crystallization temperature. We observed the transition process of the microwire from amorphous to microcrystalline state during its heating by pulse current of different amplitudes and durations. The crystallization of amorphous state proceeded in two ways depending on a pulse parameters: "slow" and explosive. In the second case electromagnetic waves emission (light flash) and burst of resistance were observed. The propagation velocity of the crystallization front in our experiments was 1 m/s.

KEYWORDS: AMORPHOUS MICROWIRE, EXPLOSIVE CRYSTALLIZATION.

The phenomenon of explosive crystallization (EC) of amorphous materials gains much attention of researchers in chemistry, physics, materials science and other disciplines. Amorphous materials are non-equilibrium "frozen" metastable states. As temperature increases, energy barrier separating this state from the equilibrium microcrystalline state, can be surmounted, and a possibility appears of transition into equilibrium nanocrystalline state. A distinctive feature of this transition is a possibility of existence, in parallel with slow processes, the fast ones associated with phase decomposition and with the crystallization front driving due to its substantial self-heating [1].

The growth rate of the crystalline phase in the initial regime associated with surmounting of the potential barrier is described by its Arrhenius dependence

$$U = U_0 \exp(-E/kT) \quad (1),$$

where U_0 is a constant, E is activation energy, k is Boltzmann constant, and T is absolute temperature. According to this equation, the crystallization temperature is not strictly specified. The growth process goes with rather high rate in some temperature range. Since the reaction of transition from amorphous to microcrystalline material is exothermal, it is characterized by some specific heat release Q . The scale of this heat release plays a significant role in specifying of the transition character. If heat release during the transition is lower than heat emission of a sample into atmosphere, the transition goes "uniformly" in a sample volume with gradual decrease in non-equilibrium of amorphous material (the process is similar to isothermal). In the opposite case (explosive crystallization) emission of latent heat of the phase transition brings to local heating of a sample, acceleration of the transition process, decomposition of a phase, and generation of interphase boundaries. Heat emission is focused on the interface, crystallization front is self-heated and moves to amorphous material, transforming it into microcrystalline state. At that, the crystallization front propagation velocity can reach 32 m/s in the self-sustained regime [2, 3].

The EC was observed in amorphous film structures: semiconductors [4-6], metals [7, 8], dielectrics [9]. A significant role in these cases played a substrate, through which the heat emitted during self-heating was prevalently removed. The samples shaped amorphous films are convenient for studies, since they make it possible to monitor the transition process using different microscopes [5, 10, 11]. Dimensional scales in them are quite macroscopic (millimeters, centimeters). But we have studied the phase transition process in amorphous microwire.

The amorphous microwire obtained by Ulitovskii-Taylor method [] is rather important highly technological material as regards applications. Especially this concerns its magnetic and microwave properties. In the postwar years the technology developed by Ulitovskii provided substantial improvement in quality of galvanometers, which were the main devices for studies of electric and magnetic properties of materials at that time.

In this work we studied the Fe15Co60B10Si15 wire. Some pieces of this wire remained after our work [12] with colleagues from National University of Science and Technology MISiS. Diameter of the metal conductor was 16 micron, diameter of the glass shield (shell) was 26 micron. To heat the microwire we used a pulse current source (rectangular pulse of duration from 20 to 500 ms). A piece of the microwire 6-100 mm in length was mounted in indium-gallium alloy drop (which is liquid at room temperature) being contacts on electric layout made on foiled textolite. During the measurements on an oscilloscope the following characteristics were controlled: a change in voltage drop on a sample (a bridge scheme was used), current through the sample, and the output voltage of a source (a pulse generator).

We used ferromagnetic resonance (FMR) as a method of characterization of the microwire state. For this we observed FMR in the microwire in amorphous or microcrystalline state. In amorphous state FMR is easily detected in some segments of the microwire of 2-3-mm length (with their regular position in the resonator) [12]. In the microcrystalline state FMR is not detected in similar segments during measurements on our ESR-spectrometer.

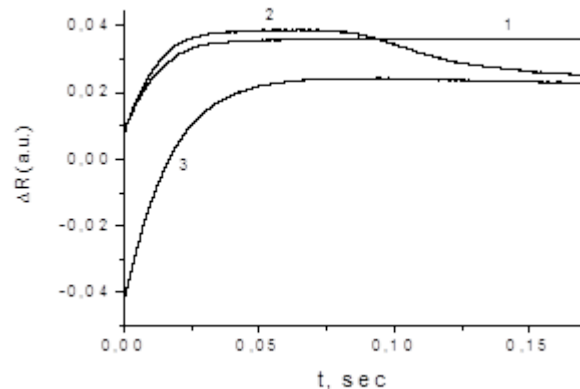


Fig. 1. Examples of recording of the dependence of a change in resistance on time from the beginning of the current pulse.

Fig. 1 shows dependencies of a resistance change value on time counted from the beginning of a current pulse. The curves 1 and 2 response to a current pulse amplitude increment curves 2 and 3 are registered at the same output pulse of the generator. After the process described by curve 1, the sample remains in amorphous state (FMR after this treatment is observed). After passing curve 2 the sample transits into new state (absence of FMR). Curve 3 corresponds to impact of a current pulse on the sample in new state. After pulse switching the microwire begins to heat to the temperature defined by amplitude of the current in the pulse. The heating time of the sample was about 20 ms, thus for 50 ms the sample almost reached the equilibrium temperature corresponding to the current amplitude in the pulse. This is well seen in the

curves, where no radical changes are observed (curves 1 and 3). Curve 2 is noticeably different from the abovementioned curves. It has a break, after which resistance begins to decrease with time. The break in the curve lasts for about 40 ms, after which equilibrium is established in the new system (exponential decrease in temperature with respect to new resistance value). Multiple repetitions of such experiments has shown that as far as we observe the time dependence of type 2 (break) under action of a current pulse, the sample changes its properties. In these measurements it was noticed that at the moment of the abovementioned break during heating, the microwire, if observed within 100 ms from the pulse beginning, shortly (during time far shorter than the current pulse duration) emits light. Surely, the flash duration we estimated already after the respective measurements.

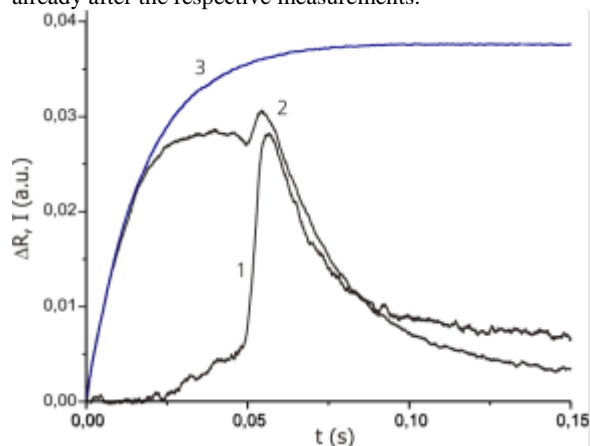


Fig. 2. A change in: (1) brightness of glow, (2) resistance, (3) resistance of the sample earlier undergone the structural transition depending on time from the beginning of the current pulse.

We added fourth channel of measurements, measurements of light intensity. For this purpose at a distance 3-4 mm from the microwire we placed a BURR-BROWN photodiode OPT-211, put the measuring scheme into a closed box, and detected emission from the microwire during action of a current pulse. Fig. 2 shows an example of light emission recording (curve 1) and a change in resistance of the sample (curve 2) under impact of the current pulse. From the beginning of the current pulse the microwire is heated from Joule heat. At that, its resistance increases. In Fig. 2 the dependence of a change in voltage drop of the same sample (its resistance) is shown as a supporting curve (gray curve) at higher temperature of heating, when structural reconstruction are finished (curve 3). The scale of curve 3 is changed to obtain superposition of the initial parts of curves 2 and 3. During heating to a certain temperature a change in the sample resistance is retarded with respect to the supporting curve and even begins to decline. Structural changes take place in the sample, which brings to drop in its resistance. Then a light flash glows, resistance at this moment also shows a burst, and then decreases with time. The flaming time is about 5 ms. Really weaker background glowing begins earlier and remains after the flash extinguishing. This is, probably, an ordinary heat emission corresponding to the temperature of the microwire at approach to the explosive transition of the material into microcrystalline state (~4000 C), which is sensed by a photodiode.

Here it should be noted difficulties, which are encountered during performing these measurements. Though the process of a sample heating by pulse current is rather flexible, the current can be changed quite accurately and gradually, the transition from amorphous state to microcrystalline is irreversible, i.e. on each sample it can be observed only once. Due to the existing spread of the microwire parameters (first of all of the cross section area), it is difficult to establish the desired current value necessary for controlled influence. On the one hand, we need often remount samples, which is by itself rather thorough task, on the other hand, at the initial moment, we do not know the critical current value, at which a sample is heated to or above the temperature of the

explosive transition into crystalline state. The value of this current for pieces of the microwire from different parts changed from 50 to 60 mA (density of the critical current was about $2 \cdot 10^4$ A/cm²). After we exceeded the transition temperature, we have got necessary information, an interest to a sample vanishes, and we need to mount a new one. If a sample could not be transitioned in the new state by the first pulse, then, as is seen from Fig. 2, there are some structural changes in it, and a fraction of amorphous phase in it decreases.

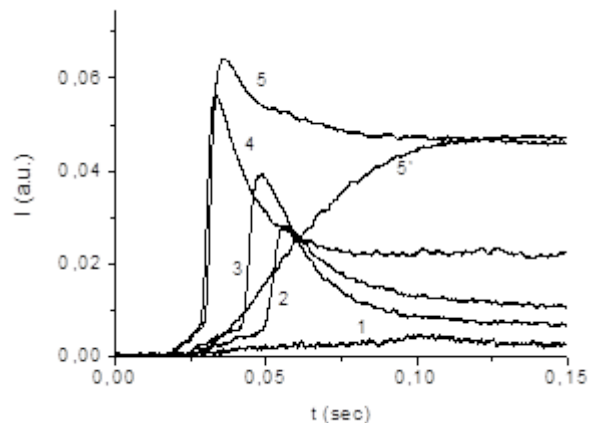


Fig. 3. Examples of changes in brightness of glow during action of the current pulse of over-critical amplitude.

Fig. 3. shows a set of curves detecting signals of surges in glow observed in five samples of the microwire, in which the transition is detected at the first current pulse application. It is seen here that a flash intensity decreases in proportion to time from a pulse beginning, however, time characteristics remain similar (flaming as well as extinguishing). Glow is flared to maximum amplitude for 5 ms, and extinguishes for the time of thermal inertia of a sample. A change in intensity of the background glow for different experiments (a signal amplitude in the right part of the figure) points to a difference between the final temperatures in each measurement. If the break in resistance is in time interval after 100 ms from the beginning of a pulse, there no noticeable light flash is observed (curve 1).

Amorphous state of the material is metastable. Its existence at normal temperatures is determined by presence of quite high energy barrier separating the amorphous state from microcrystalline. As temperature increases, surmounting over the barrier starts in activation way, and the material locally undergoes changes approaching to microcrystalline state. The transition is exothermal and is accompanied by heat emission, which can stimulate propagation of the transition to the adjusted part of a sample. At a certain ratio between heat emission and heat dissipation into atmosphere, self-propagation of the growth front of microcrystalline state begins, and the material transits spontaneously into this state. In literature this phenomenon is called explosive transition. At that, a sample is heated, and additional thermal radiation can arise above the background radiation associated with high starting temperature of the sample. Slightly below this critical condition the transition goes almost isothermally without typical for the explosive transition features. Atoms are driven to their equilibrium positions independently (not avalanche-likely), and the material is crystallized at "slower" rate. Transition from one regime to another can take place at increase in volume crystallization rate (Eq. 1), when heat dissipation cannot absorb emitted heat. AS it can be seen from Fig. 3, background radiation reaches some level before the light flash start. A characteristic of background radiation in our case is response of a photodiode to heat emission of heated microwire, i.e. to its temperature. The explosive transition process in our case begins at some temperature reached by the microwire.

Based on these considerations, most results obtained in this work can be understood. If at the first measurement we set current below the critical value, then there is slow transition to the critical state. Since the temperature of the sample is still near the critical value,

the process goes rather fast, and at the end of the pulse there can be small amount of the amorphous phase. The next pulse will bring to weakened explosive transition or to its slowing-down, to complete absence. Therefore, there are interesting data, when the explosive transition goes at the first applied current pulse. However, in this case also just a part of a sample has time to transit to crystalline state during the time from the beginning of the pulse to the moment of the beginning of the explosive transition. It is well seen from Fig. 2, where resistance begins to decrease actively, despite of temperature rise. This explains the dependence of the light flash on time from the beginning of a pulse, and the reason for the flash not to be seen after 100 ms since the pulse start.

Two observed effects, in our opinion, can be interesting for clarification of the crystallization front structure, this is burst of the sample glow and simultaneous increase in resistance. It is known from observations of the explosive crystallization in amorphous films that the crystallization front looks like a line, its width is far less than its length (in developed state). At that, brightness of its glow is far higher than background glow of the rest of the film (before, as well as after the front propagation). The case of amorphous microwire obtained by Ulitovskii-Taylor method is of a special interest since it is a quasi-one-dimensional object (in our case length is 5-10 mm, diameter is 0.016 mm). The crystallization front in the main stage of development propagates along the microwire axis, the front plane is perpendicular to the axis. This is confirmed by the made measurements. We studied more than ten samples, and most of them showed the same type of behavior (as in Fig. 2). Only in few cases the light flash was double or spread, probably, in these samples there were two or more nucleation centers of the crystalline phase. The problem of heat transfer in the case of the microwire is also simplified, it is reduced to heat exchange between the glass shell and surrounding gas.

Signal of the light flash (more precisely, the photodiode output voltage) first increases with time about 5 ms almost linearly, and then decreases with time of thermal inertia. We believe that this respects to heat accumulation in a sample as the crystallization front propagates, and is followed by the sample cooling after the end of the process. Between the explosive transition process (latent heat emission) and detection signal at the photodiode there are many complicated transformations. But if the crystallization front was responsible for signal from the photodiode, the output voltage would be close to a constant value. It is seen that the character of all observed transitions for different samples at the stage of rise and drop of the signal are similar (Fig. 2). This corresponds for our quasi-one-dimensional samples to the simplest picture of the process. The transition is nucleated somewhere in the middle point of an open wire and is propagated from there to both sides up to entry of the wire into indium-gallium solder. What happens inside the solder is difficult to imagine, since the thermal conditions there differ from the outside. With this regard, we may return to the data in Fig. 1, where smooth transition process without light flash is shown. It is seen that during the transition resistance of the sample decreases below the previous recording, where there was no transition. It seems that Joule heat has become far less than it is necessary for the transition to go on, however, the transition continues going at the same rate. Based on this, it can be assumed that the transition front can also propagate in the microwire being inside the solder. This causes difficulties in estimation of changes in electric resistance of the samples. On the whole, this character of the transition implies that the origin of the light flash (the signal detected by the photodiode) is heating of a sample by heat emitted upon the crystallization front propagation, but not by radiation from the front itself.

Now we shall come to discussion of the results on measuring of electric resistance. Here it will be relevant to present wider data on these measurements. The microwire produced using Ulitovskii-Taylor technique is of some presentation interest for demonstration of temperature change in resistance. The point is that it is coated with a glass shell, which is decomposed at the temperatures above the melting point of the wire material. In Fig. 1 there was no compensation of resistance of the sample at room temperature for

recording of curves 2 and 3. It is seen from Fig. 1 that resistance of the sample in microcrystalline state is far lower than the resistance in amorphous state. At the same time, dR/dT (where R is resistance of the microwire and T is temperature) in amorphous state is lower than in crystalline state. A difference in resistance values at room temperature is about 20% from the total resistance of a sample. If, for example, resistance of a sample in amorphous state is 40 Ohm, in microcrystalline state it is 32-34 Ohm. These are typical values.

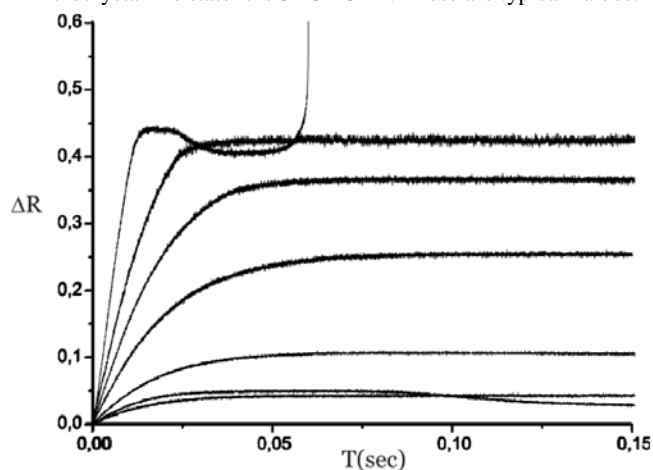


Fig. 4. A change in resistance (in relative units) during applying of current pulses with different amplitudes.

Using these estimations and the circumstance that we did not provide compensation of our measuring bridge scheme for the dependencies shown in Fig. 1, all typical values of changes in resistance can be presented. Fig. 4 presents the results of resistance measurements (in relative units) during applying of current pulses with different amplitudes. The first three curves correspond to the data in Fig. 1, but for another sample. Next curves correspond to increase in current amplitude. In the last figure but one the material is being melted, resistance is the maximum, which does not change (as well as temperature). In the last curve the material is melted (constant resistance range), in liquid state resistance of the sample decreases as temperature increases [13], then the glass shell is decomposed, the liquid material of the wire pours out, breaking continuity of the wire, and resistance rises abruptly. It was possible to get convinced in decomposition of continuity of the sample after the end of the experiment. If now the resistance measurements are used as a thermometer, assuming that resistance of strongly disordered alloy changes linearly with temperature [13], and to suppose roughly that the transition from amorphous to microcrystalline state is at 400°C, and the melting point for the material of the microwire is 1000°C, then from surge of the resistance amplitude at the transition, average heating of the sample can be estimated (about 100°C).

Therefore, observation of the effects of light flash rising and surge of resistance can be simply explained by heating, which does not give us information on structure of the explosive crystallization. The point is that in the first measurements we observed the light flash with a naked eye. The flash was bright white, not red, as it would have been at these temperatures. Unfortunately, we are not ready for these measurements, are not equipped with tool set and devices.

We observed the explosive transition from amorphous to microcrystalline state in the Fe₁₅Co₆₀B₁₀Si₁₅ microwire produced by Ulitovskii-Taylor method at applying current pulse. The explosive character of the transition appears at achievement of a certain temperature by a sample and is accompanied by light flash and short-time increase in electric resistance. The observed features of the transition are: behavior of the average resistance of the sample and radiation detected by the photodiode can be explained by thermal effects associated with exothermal character of the process and the rate of Joule heating of a sample. The propagation velocity of the front in our experiments is about 1 m/s (length 5 mm, time 5 ms). Despite some ambiguity in parameters of the microwire, it is possible to transit quite smoothly from isothermal

regime to the explosive, which provides additional possibilities in studies of the essence of the process.

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