SUPERCOOLING DURING CRYSTALIZATION OF FUSIBLE METAL PARTICLES IN MULTILAYER “CARBON-METAL-CARBON” FILMS

S.I. Petrushenko, S.V. Dukarov, V.N. Sukhov
V.N. Karazin Kharkov National University, Kharkov, Ukraine
E-mail: petrushenko@univer.kharkov.ua; tel. +38(057)707-55-89

The results of studies of phase melting-crystallization transitions in thin films of fusible metals between thicker layers of amorphous carbon are given. It has been found that, due to poor wetting in contact systems under study, thin layers of fusible metals decompose into separate islands while first heated. Such films are a model of the system “fusible particles in the refractory matrix”. Using two independent in situ techniques (electrical resistance measuring and electron-diffraction studies during heating and cooling) values of supercooling during crystallization of liquid phase nanoparticles in multilayer C-Bi-C, C-Pb-C, C-Sn-C films, equal to 115, 135, and 160 K, respectively have been obtained.

PACS 64.60.My, 64.70.D-

INTRODUCTION

Numerous researches in recent time have led to more practical use of materials based on various forms of carbon [1, 2], among which an important place is occupied by the composite structure, in which it is possible to achieve the combination of properties of various materials, including high resistance to radiation damage. Nanocomposite materials, the inclusions of which mostly not only change the properties of the bulky matrix significantly, but they themselves can be active elements of individual electronic devices such as switches, memory elements, strain sensors [3], etc. are of particular interest to researchers.

The properties of such materials are related to the phase state of inclusions and conditions of phase transitions, as many of the mechanical properties of crystalline materials strongly depend on the kinetics of crystallization, which is primarily determined by the reached magnitude of supercooling [4, 5].

In paper [6] it is shown that during heating and cooling of glass, alloyed by bismuth nanoparticles, and of multilayer films, in which thin layers of bismuth were alternated with the layers of Al₂O₃, at certain temperatures, a sharp change in the transmittance of the samples occurs. This phenomenon, according to the authors, is associated with melting and crystallization of bismuth embedded nanoparticles. Melting-crystallization hysteresis observed in [6], was about 200 K.

The prediction of vacuum condensates morphology is also often not possible without knowledge of the limits of the stability of the liquid phase. For example, in [7] it has been found that during various supercooling, the condensed films of bismuth consist of islands of different shapes.

Thus, studying the liquid phase stability limits is necessary for many practical applications. At the same time, the study of supercooling is difficult enough as the value of supercooling is influenced by a number of factors among which the key factors are mostly various kinds of impurities [8-10], which are potential centers of crystallization. To get rid of them there are various purification methods and multiple remelting of the substances under study that may be combined with the containerless methods under microgravity or electrostatic levitation [11].

The micro volumes method, consisting in splitting of the sample into a plurality of individual particles, which makes it possible to reduce the influence of impurities significantly, is rather easy to implement and at the same time it is important for the applied use prospects. To implement this method practically one can use vacuum condensates, which allow obtaining the required purity and dispersion of samples. In particular, the method of condensation mechanism change [10, 12] helped to obtain extremely large supercooling at which the crystallization of the cooled melt is almost homogeneous [10]. Nanocalorimetric [8, 13], optic [6, 14], and electron-diffraction techniques [7] can also be used to study supercooling and liquid phase behavior in multicomponent systems.

The results obtained by using the method of condensation mechanism change (e. g. [10, 12, 15, 16]) in the study of liquid phase stability limits for free particles, allowed to reveal that, in cases when the particles are obtained in sufficiently pure vacuum conditions, the key factor determining the value of supercooling is the nature of interaction of the melt with the substrate material, at which the condensation of substance is made.

At the same time, there are not mostly so much consistent and reliable data in the literature on the limits of stability for the liquid state of the particles embedded in a more refractory matrix now. Thus, a number of papers (e.g. [17, 18]) suggest that the size dependence of supercooling during the crystallization of the liquid phase in the matrix of the particle does not occur. On the other hand, the authors of [6] have established that reducing the amount of bismuth nano inclusions in the matrix of Al₂O₃ from 30 to 10 nm, the crystallization temperature is reduced by about 30 K. However, the observed increase of nearly 100 K of bismuth nanoparticles melting temperature in a refractory matrix complicates the interpretation of the results.

A significant supercooling value change during the crystallization of the liquid phase of a fusible component of multilayer films was observed in [19]. It has been found that if bismuth in the copper matrix is in the form of individual particles approximately 100 nm in size, its supercooling increases by more than 50 K, compared with the case when it forms a single system of inclusions in the copper matrix, the typical dimension of which is comparable with the size of the entire sample.

This phenomenon is due to the fact that in large samples, under random factors the probability of the crystal phase nucleus formation well before reaching the maximum supercooling temperature possible in the given contact pair is higher [19].

A similar phenomenon was also observed in [13], in which it has been found that the reproducibility of value of supercooling increases sharply during the transition from micro- to nanometer particles, what can be obviously explained by a decrease in the probability of the heterogeneous nucleus formation in the particles of nanometer size.

Different interpretations available in literature are probably related not only to the fact that the value of supercooling is affected by impurities and other random factors, but also it is limited by the applicability of the known methods of studying for the phase transitions to the systems of “nanoparticles in the matrix”. Thus, the combination of vacuum methods for producing with new in situ methods of determining the phase transition temperatures, which allow fixing melting and crystallization of a fusible component directly in the vacuum chamber is of particular interest.

Such methods are suggested in [19–21]. In these methods, it is suggested that multilayer vacuum condensates are used as a model of “a particle in the refractory matrix” system, and phase transformation temperatures determination is based on the fact that melting and crystallization of a fusible component in such systems may be accompanied by a sharp change in their electrical [19, 20] and mechanical [21] properties. As the results in [19, 20] have shown, the use of vacuum condensates, the morphology of which is determined by the conditions of the condensation, allows not only receiving the data about supercooling of substances while minimizing the impact of uncontrolled impurities, but in some cases, within certain limits, controlling the temperature of the liquid phase crystallization.

Furthermore, it is worth noting that such objects (heating and cooling of which are accompanied by a significant and abrupt change in their electrical, [19], mechanical [21] or optical [6] properties) can be used in modern technology. Thus they can be used as various kinds of temperature sensors and switches, RAM (random-access memory) and permanent memory.

**EXPERIMENTAL**

As the subject of our research we have chosen multilayer films in which originally continuous layers of fusible metal (Bi, Sn, Pb) were between thick amorphous carbon films. The mass thickness of metal layers was chosen to achieve the desired value of the electrical resistance of the sample and in different experiments it was 20-100 nm. These systems are characterized by the absence of chemical compounds and mutual dissolution, as well as the almost complete non-wetting of carbon by melts of the chosen metals [10, 22].

Carbon deposition was carried out by its evaporation from the voltaic arc, which allows to obtain the amorphous carbon film [23]. Condensation of metal films was carried out on the freshly-condensed carbon underlayer in vacuum 10^{-6} mm Hg by their evaporation from molybdenum (Bi, Pb) and tantalum (Sn) boats. The thickness of the deposited component was determined in the course of their preparation by means of the quartz resonator.

For the registration of phase transitions two independent **in situ** methods were applied. The jumps in electrical resistance of samples accompanying melting and crystallization of the fusible component were used in the first one [19, 20]. Melting and crystallization temperature were determined by electron diffraction while disappearing when heated (melting) and appearing while cooled (crystallization) of reflections from the fusible component crystal lattice in the second one.

For the implementation of the first technique the films were condensed on a glass substrate with copper electrical contacts connected to the automatic measurement system. This enables us to measure electrical resistance as in case of the samples condensation and during the process of cooling and heating them in a vacuum chamber directly without its depressurization. The substrate was suspended on thin contact wires, and the radiation of tungsten coil was used for heating it at a distance of 1...2 cm from the back side of the substrate. The substrate temperature was measured by means of a K-type thermocouple.

For electron microscopy and electron diffraction studies we used a transmission electron microscope Selmi EMV 100BR, equipped with an attachment developed in the laboratory for **in situ** diffraction studies of samples during heating and cooling directly in the electron microscope column.

**RESULTS AND DISCUSSION**

It has been established that the resistance of carbon films that do not contain a fusible component has a semiconductor character and decreases monotonically with temperature increasing. The energy of activation of carbon film conductivity is about 0.28 eV, which is typical for the majority of semiconductors [24]. Thus, in contrast to Cu-Bi-Cu and Cu-Ph-Cu films [19], the resistance behaves reversibly in the first heating cycle and after the sample being cooled it is back to the value which is close to the original one. Possibly, this may be due to the fact that carbon is an extremely refractory material and its heating up to 300...400 °C does not result in appreciable activation of self-diffusion processes usually actively flowing in thin films [25, 26] and causing annealing of defects and irreversible reduction of resistance of the sample in the case of metal films [19].

There is only a diffuse halo in the electron-diffraction patterns corresponding carbon films, and annealing of the samples to 400 °C directly into an electron microscope column does not result in any change in the diffraction pattern.

When studying the films containing layers of fusible metal, it has been found that in the first heating cycle, at the temperature near its melting point, the resistance of samples increases sharply. The results of electron microscopy studies (Fig. 1) showed that it is due to the irreversible breakdown decomposition of the initially continuous film into an island one.
In the following heating cycles resistance decreases monotonically up to the melting temperature of the fusible component \( (T_s) \), near which there is a particular feature of a more rapid decrease in electrical resistance (Fig. 2). According to \([19, 20]\) it indicates melting of a fusible component. While cooling, the electrical resistance of the sample increases monotonically up to a certain temperature, at which a more rapid increase in electrical resistance starts. It is has a significant temperature range and it stops at a certain characteristic for each metal temperature \( T_g \). According to \([19, 20]\), the presence of such features on the cooling curves can be caused by crystallization of the supercooled melt. Thus, even if the fusible component is bismuth, which typically provides the most relative change of resistance in the phase transition \([19]\), the value of a sudden change of electrical resistance turns out to be small. In order to make these sudden changes more visible instead of three-layer films we formed the multilayer structures in which up to five-layers of the fusible component were alternated with layers of the refractory carbon matrix.

The average activation energy of conductivity in the obtained samples is lower than in the carbon films and it is 0.12...0.2 eV, which allows us to consider the studied films as promising subjects for manufacturing of visible and infrared radiation sensors, solar cells, etc.

More clearly the emergence of a new phase can be detected by a change in the angle of the tangent to the cooling curve. To do this, using numerical differentiation method of Savitzky-Golay the temperature dependences of the thermal resistance coefficient were obtained (Fig. 3), clearly showing the position and character of the phase transitions. It can be seen that the melting process in the investigated films is stretched in a significant temperature range, which is significantly higher than the one observed in \([27]\) for polycrystalline films of fusible metals on a carbon substrate. Apparently this is due to a significant spread according to size of the particles that constitute the studied films, as well as it is possible due to the fact that the process of the resistance decrease may be caused not only by the appearance of the liquid phase, but also by an avalanche increase in the activity of diffusion processes in the pre-melting area.

*Fig. 1. TEM image of the C-Pb-C film, after its heating to melting point of lead*

*Fig. 2. Electrical resistance of multilayer C-B-C (a), C-Pb-C (b) and C-Sn-C (c) films versus the temperature*

*In situ* electron diffraction studies (Fig. 4) have shown that in the electron diffraction patterns corresponding to the heating of the sample, the diffraction of a fusible metal occurs before its melting temperature \( T_s \). Diffraction reflections from metallic layers are no longer available in electron diffraction patterns obtained at above \( T_s \). During cooling, the reflexes don’t also occur up to a certain temperature corresponding to the beginning of a faster growth of electrical resistance on the cooling samples graphs (see Fig. 2).
Supercooling values determined by both methods agree with each other and are 115, 135, and 160 K for C-Bi-C, C-Pb-C, C-Sn-C films, respectively.

It should be noted that according to [19], thanks to the good wetting, which prevents the formation of island film [28], bismuth in Cu-Bi-Cu films when condensed on the substrate at room temperature, i.e. vapour-crystal mechanism forms a single system of inclusions in the matrix. Such a system crystallizes almost immediately on the entire sample. In the carbon-based films under study an array of isolated fusible metal particles is formed due to the almost complete non-wetting soon after the first heating cycle, even if condensed in vapour-crystal mechanism (see Fig. 1).

Such particles are crystallized independently at random factors temperature, and the crystallization of the entire sample is stretched to a considerable range of temperatures. Furthermore, unlike the particles of fusible metals between the layers of copper, for which the resistance change direction in the phase transition coincides with the direction of the resistivity change of a fusible component when melting and crystallizing [19], in the case of a carbon matrix such a dependence is not observed, and the resistance decreases during melting and increases during crystallization for all investigated contact pairs.

Accordingly, the model of three parallel conductors, proposed in [19] to explain the causes of sudden changes of electrical resistance during phase transitions, and qualitatively describing the change in the electrical resistance in Cu-Bi-Cu and Cu-Pb-Cu films during melting and crystallization of a fusible component is completely inapplicable to metal particles between carbon layers.

The observed changes of electrical resistance can be explained as follows. The resistivity of the carbon film is much higher than that of metal. Unrelated metal particles bypass the individual sections of the carbon film to which they relate, reducing its total resistance. In this configuration of the sample, interface resistance between the liquid metal and the carbon film, which is free from stresses from the liquid metal side and to some extent can be considered ideal, becomes significant. At the same time, during crystallization due to various causes, such as a sudden volume change, mismatch of lattices, the difference in thermal expansion coefficients et al., the occurrence of stresses increasing its resistance is inevitable on the interface.

In such a model it is simple to explain the fact that for bismuth the quantity of resistivity changes in phase transitions is significantly higher than for those of tin and lead. As it is seen in Fig. 2 at the phase transition for C-Bi-C films relative increase in resistance is about 0.3, while for C-Pb-C and C-Sn-C samples the same magnitude is one order smaller and approximately equal to 0.04. One has to take into account the change in the electrical resistance of the metal itself at its melting (crystallization). Bismuth resistance decreases during melting and this effect is added to decreasing the resistance of the interface. At the same time, tin and lead resistance increases during melting, this partially compensates improving of interface conductivity. Therefore,
resistance changes of films with Sn and Pb particles during phase transitions turn out to be much less.

The contribution of each of these mechanisms can be estimated by comparing the relative change in resistance in the films in which an embedded metal has a positive and a negative change of resistance during melting (0.04 and 0.3). The evaluation on the basis of these values suggests that the contribution of the interface resistance change is about 60%, and change of resistance of the particle itself constitutes 40%.

As it can be seen, these processes are almost equal, what probably makes it possible to change the morphological structure of the embedded particles (for example, by adding small amounts of a third component, which will affect the wetting) to vary the magnitude of the effect, and even change its sign.

CONCLUSIONS

Using two independent in situ techniques, values of Bi, Sn, and Pb particles supercooling between the solid carbon films have been determined.

It has been found that in the multilayer carbon-based films all the investigated metals after melting form the structure consisting of isolated individual particles regardless of the conditions of condensation.

It has been shown that for nanoparticles of fusible metals located between the layers of amorphous carbon changes in films resistance at phase transitions take place both due to the change in resistivity of a fusible component, and due to the change in the quality of the contact at the metal-carbon interface.

REFERENCES


ПЕРЕОХЛАЖДЕНИЕ ПРИ КРИСТАЛЛИЗАЦИИ ЧАСТИЦ ЛЕГКОПЛАВКИХ МЕТАЛЛОВ В МНОГОСЛОЙНЫХ ПЛЕНКАХ «УГЛЕРОД-МЕТАЛЛ-УГЛЕРОД»

С.И. Петрушенко, С.В. Дукаров, В.Н. Сухов

Приводятся результаты исследований фазовых переходов плавление–кристаллизация в тонких пленках легкоплавких металлов, находящихся между более тугоплавкими слоями аморфного углерода. Установлено, что вследствие плохого смачивания в исследуемых контактных системах уже при первом нагреве тонкие слои легкоплавких металлов распадаются на отдельные островки. Такие пленки представляют собой модель системы «легкоплавкие частицы в тугоплавкой матрице». С помощью двух независимых in situ методик (измерения электросопротивления и электронографических исследований в процессе нагрева и охлаждения) получены величины переохлаждения при кристаллизации наночастиц жидкой фазы в многослойных пленках (C-Bi-C, C-Pb-C, C-Sn-C), равные 115, 135 и 160 К соответственно.

ПЕРЕОХЛОДЖЕННЯ ПРИ КРИСТАЛІЗАЦІЇ ЧАСТОК ЛЕГКОПЛАВКИХ МЕТАЛІВ У БАГАТОШАРОВИХ ПЛІВКАХ «ВУГЛЕЦЬ-МЕТАЛЛ-ВУГЛЕЦЬ»

С.І. Петрушенко, С.В. Дукаров, В.Н. Сухов

Наводяться результати досліджень фазових переходів плавлення–кристалізація в тонких плівках легкоплавких металів, що знаходяться між товщами шаром аморфного вуглецю. Встановлено, що внаслідок поганого змочування в досліджуваних контактних системах вже при першому нагріві тонкі шари легкоплавких металів розпадаються на окремі островки. Такі плівки є моделлю системи «легкоплавкі частки в тугоплавкій матриці». За допомогою двох незалежних in situ методик (вимірює електросопротивлення та електронографічних досліджень у процесі нагріву і охолодження) отримано величини переохлодження при кристалізації наночасток рідкої фази в багатошарових плівках (C-Bi-C, C-Pb-C, C-Sn-C), рівних 115, 135 і 160 K відповідно.