

Condensation mechanism of AgCl and NaCl island films on a nickel substrate

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The paper presents the results of exploring the temperature range of formation and thermal stability of the AgCl and NaCl liquid phase in the islands condensed to Ni substrate in vacuum. It is established that the change of the mechanism of condensation from vapour-crystal to vapour-liquid at the deposition of the films of these chemical compounds is observed when the temperatures of the substrate is lower than their melting temperature. The values of supercooling at crystallization on the nickel substrate of island films of substances under study are determined, which make 95 K for AgCl and 369 K for NaCl, respectively. It is shown that the method of studying supercoolings which uses vacuum condensates is applicable to a broad range of substances.

Приводятся результаты исследований температурного интервала образования и температурной устойчивости жидкой фазы в островковых вакуумных конденсатах хлоридов серебра и натрия на никелевых подложках. Установлено, что смена механизма конденсации от пар-кристалл к пар-жидкость при осаждении пленок этих химических соединений наблюдается при температурах подложки ниже температуры их плавления. Определены величины переохлаждений при кристаллизации островковых пленок исследуемых веществ на никелевой подложке, которые составили 95 и 369 К для AgCl и NaCl, соответственно. Показано, что метод изучения переохлаждений с использованием вакуумных конденсатов пригоден для широкого класса веществ.

1. Introduction

The study of the metastable phases formation and stability conditions (in particular, supercooled liquids) is of fundamental interest for the development of physics of phase transitions, the theory of homogeneous nucleation as well as for modern materials science since the physicochemical and structural properties of materials which are obtained by growing from a liquid melt are determined by the kinetics of crystallization and, in particular, the value of supercooling.

To date, the phenomenon of supercooling during crystallization was observed by various methods for substances of different nature, such as metals, alloys, organic materials, molten salts, etc. [1, 2]. The long-established fact is that the magnitude of supercooling during crystallization depends

on the elimination or suppressing the heterogeneous nucleation, i.e. formation of a new phase by impurities, contaminations or on the walls of the container which holds the melt. Accordingly, methods which ensure the greatest exposure to supercooling are based on either the use of high cooling rates, allowing both to forestall the process of heterogeneous nucleation and in some cases gives an opportunity to avoid crystallization and to obtain an amorphous (vitreous) material, or the removal of nuclei by a careful cleaning and multiple remelting of the substance under investigation as well as minimize or completely eliminate the influence of the environment.

Among the latter group of methods, most fruitful is the micro volume approach proposed by Turnbull [3]. The gist of Turn-

ball's approach is as follows: if the initial volume of liquid contains a limited number (n) of the heterogeneous crystallization nuclei, then by dividing this volume into a sufficiently large (larger than n) number of small droplets one obtains the situation in which separate droplets are not to have such nuclei at all. Under these conditions, the main influence on the values of the observed supercooling will be caused by the environment with the surface of the liquid contacts. Reducing the impact of the environment or its complete removal is achieved by various methods, for example, selection of special inert emulsions, conducting experiments in microgravity (in space or in a state of free fall), using a variety of fields to keep the samples in a suspended state, etc. [2].

Significant progress in obtaining the ultimate supercooling is achieved by using the methods based on studying the condensation mechanism of island films in vacuum on a substrate with a temperature gradient [4-7]. It was established experimentally that the condensation of a metal in vacuum (depending on the temperature of the substrate) goes by the mechanism of vapor-solid below a certain temperature T_g (which is called the temperature of changing the condensation mechanism) or by the mechanism of vapor-liquid at $T_g < T < T_k$ (T_k - the critical temperature of condensation). However, during the initial period of condensation the islands which form on the substrate are always liquid due to the decrease of the melting temperature with the decrease of size. Further on, in the process of their growth, when they reach the size r (determined by the size dependence of the melting temperature $T_m(r)$) for a given substance, they either crystallize or remain in the liquid state, now in a supercooled one. As shown in the electron-microscopic studies [4-7], the microstructures of the films formed through the liquid and crystalline phases are significantly different from one another, and the surface of these films scatter light differently. As a consequence, during the metal condensation on a substrate with a temperature gradient, a visual boundary between the areas of various condensation mechanisms is observed, as it follows from the above said, it corresponds to ultimate supercooling of the matter condensed under these conditions.

By means of this method, systematic studies on the condensation of pure metals (In, Sn, Bi, Pb, Au, Cu, Fe, Co, Ni) under different conditions and on various sub-

strates [4-6], as well as a number of alloys on their base (Bi-Pb, Bi-Sb [6, 7]), were carried out. These studies revealed that in island films, condensed under fairly pure conditions, supercooling during crystallization $\Delta T = T_s - T_g$ (T_s - the melting point) metal islands is determined only by the nature of their interaction with the substrate and reaches maximum values in almost non-interacting systems, such as metal - carbon, metal - oxide: $\Delta T = (0,3-0,4)T_g$. As the parameter which determines the effect of substrate material on the supercooling during liquid phase crystallization, the contact angle θ of wetting by the liquid island of the condensed metal of the substrate is used. According to [4-7], with the small contact angles the supercooling is small, and with the growth of θ (that is, with the worsening of wetting), the supercooling in the 1st approximation increases linearly and at $\theta \rightarrow 180^\circ$ tends to a value which is constant for all the metals considered, up to 0,4 of the melting temperature. It can be suggested that these phenomena are not limited to metals and their alloys but are also characteristic of substances of other nature as well; yet such research has not been conducted; this is why in the present work the possibility of determining the limit of supercooling by the method of vacuum condensates for simple chemical compounds has been studied.

2. Experimental and results

The study of the condensation mechanism and, consequently, of the supercooling at crystallization was carried out for AgCl and NaCl films on the nickel substrate. The selection of the objects is conditioned by the fact that among simple compounds, which are virtually not decomposed at thermal evaporation [8], and in sufficiently thick layers films are formed which have properties identical to bulk material [9]. These chlorides have relatively low vapour pressure near the melting temperature, which allows to consider that the temperature of condensation mechanism change turns out to be lower than T_k at acceptable film deposition speed. Samples to be studied were prepared by means of vacuum condensation of the substances on the polycrystalline nickel wedge tape with a temperature gradient, this tape was heated by letting an electric current go through it. The temperature of the tape was measured with the help of thin chromel-alumel thermocouples which

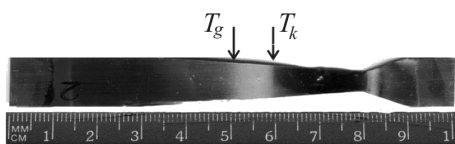


Fig.1. A photo of a wedged nickel substrate on which NaCl film is condensed. T_g – the temperature of the change in the mechanism of condensation from vapour-liquid to vapour-crystal, T_k – the critical temperature of condensation.

have been spot welded to its underside. The thickness of the films was controlled by a quartz resonator in the process of their application and was about 100-500 nm in different experiments. Immediately before the condensation of salts on the tape, a fresh layer of nickel 20-30 nm thick, which is the solid substrate in this study, was applied by thermal evaporation. After the condensation, and the cooling process of the substrate are complete, in all samples a visual boundary which separates the regions with different light scattering is observed, it is all results from a different surface morphology of the films (Fig. 1).

Electron microscopy images of the sodium chloride films, condensed at various temperatures, are shown in Fig. 2. As one can see, the NaCl films on both sides of the observed border (T_g), like the previously studied metal condensates [4-7], have a significantly different microstructure. Below the

temperature corresponding to the boundary, the films are almost continuous (Fig. 2a, b) and above it, they consist of individual particles, the shape of which is close to the spherical segment (Fig. 2d, e, f, Fig. 3). It allows to draw a conclusion that the boundaries observed which corresponds to the temperature of the condensation mechanism change T_g and is the temperature, to which the chemical compound is supercooled at crystallization from the melt under the given condition.

The conclusion that the NaCl film at a temperature above T_g inserted in a liquid state was confirmed by electronic-microscopic photos taken at an angle to the substrate plane, which shows clearly that the islands are in the form of sodium chloride crystallized droplets (the photos are shown in Fig. 3). Using the method of oblique observation [6, 10], we assessed the value of the contact angle super-cooled melt NaCl nickel surface on such micrographs, and it equals $\theta \approx 67^\circ$. For AgCl films the contact angles for different islands are characterized by a considerable scatter and are about 60° .

As a result of the investigations carried out, it has been established that for AgCl and NaCl films on a nickel substrate the temperature change in the mechanism of condensation of T_g is 633 K and 705 K, respectively, and the relative supercooling

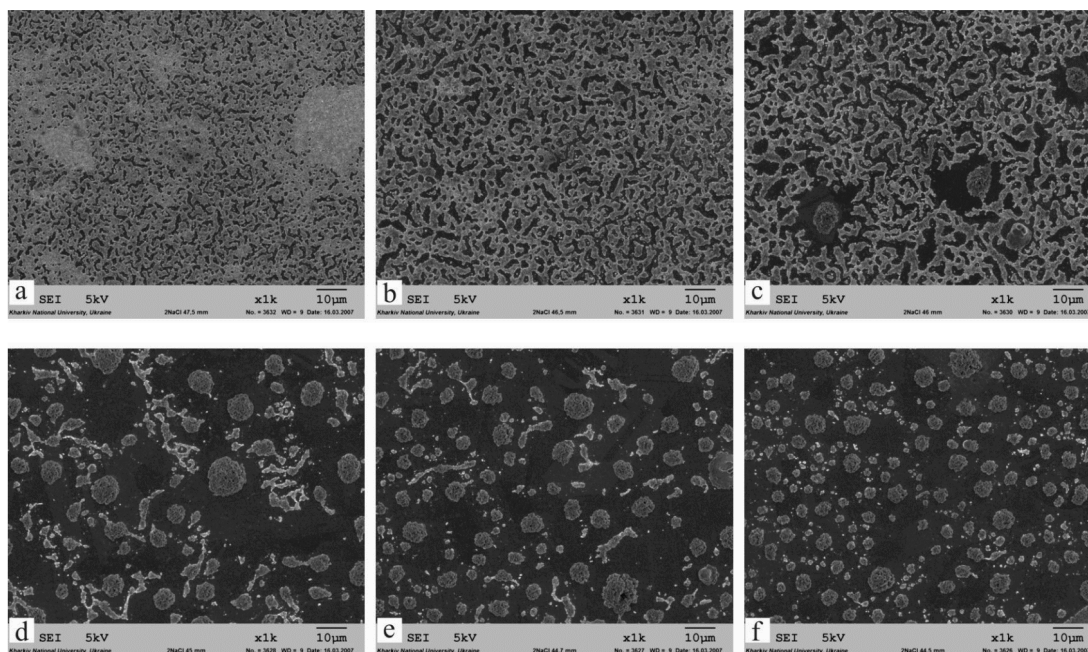


Fig. 2. Micrographs of NaCl films condensed at different temperatures on a nickel substrate: a) 698 K and b) 703 K – the vapour-crystal condensation mechanism; d) 710 K, e) 712 K, f) 713 K – the vapour-liquid condensation mechanism; c) 705 K – corresponds to the boundary of transition.

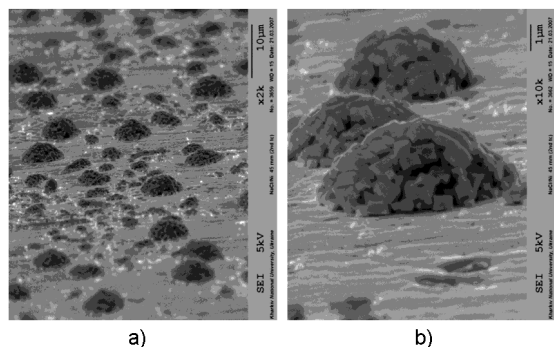


Fig. 3. Micrographs of crystallized NaCl droplets condensed at 710 K on a nickel substrate (the substrate is placed at an angle of 70° to the optical axis of the microscope).

is $\Delta T/T_s = 0.13$ and 0.34 . The resulting values for the AgCl ratio of the relative supercooling and the contact angle are in agreement with the known laws for metals and alloys [4-7]. At the same time, taking into account the obtained values of the angles of wetting, one should have expected smaller supercooling. Here, however, one should take into account the fact that existing dependence of the relative supercooling and the contact angle, the values of θ are used, which correspond to a temperature higher than the melting temperature of the material. It is not possible to obtain these values for sodium chloride vacuum condensates on nickel because of a lower critical temperature of condensation than the value of T_s for vapour pressure of NaCl at the melting temperature. As a result, analyzing the results for the NaCl/Ni system, we have to use the value of the contact angle at the maximum supercooling, which may be significantly lower than the values of the equilibrium phases as shown by the example of metals [6, 11]. However, the obtained results for sodium chloride are also consistent with the relations for the island condensates crystallization of metals and alloys on various substrates [4-7]. A characteristic feature of previous studies is the fact of decrease in the supercooling value, which usually indicates the presence of heterogeneous nucleation centres during using any environment or larger size samples. A similar situation occurs for sodium chloride. In [12, 13] for a number of drops of alkali-halide compounds size of about 5 microns, formed by condensation of salt vapours in an inert gas, relative supercooling values within $0.15 < \Delta T/T_s < 0.25$ were obtained. The observed in [12, 13] crystallization temperature of the NaCl droplets is 906 K and the

corresponding supercooling value ($\Delta T/T_s = 0.16$) is considerably smaller than the value obtained in this work.

Thus, it has been shown that the method of studying the supercooling during crystallization using the vacuum condensates is applicable to a wide class of substances and indicates that the relative supercooling is determined only by the conditions of crystallization as well as crystallized metal, alloy or chemical compound.

3. Conclusions

The condensation mechanism of AgCl and NaCl films on a nickel substrate was studied and the temperature change in the condensation mechanism T_g for these compounds was identified (633 and 705 K, respectively). Suggestedly the temperature T_g is the boundary temperature for the liquid phase existence, the supercooling values during crystallization of island AgCl and NaCl films on a nickel substrate (95 and 369 K) were obtained.

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Механізм конденсації острівцевих плівок AgCl і NaCl на нікелевій підкладці

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Наводяться результати досліджень температурного інтервалу утворення та температурної стійкості рідкої фази в острівцевих вакуумних конденсатах хлоридів срібла і натрію на нікелевих підкладках. Встановлено, що зміна механізму конденсації від пара-кристал до пара-рідина при осадженні плівок цих хімічних сполук спостерігається при температурах підкладки нижче температури їх плавлення. Визначено величини переохолоджень при кристалізації острівцевих плівок досліджуваних речовин на нікелевій підкладці, які склали 95 та 369 К для AgCl і NaCl, відповідно. Показано, що метод вивчення переохолоджень з використанням вакуумних конденсатів придатний для широкого класу речовин.