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Condensation-dependent porosity in film nanostructures

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The formation processes and behavior of submicro-, micro- and macropores in amorphous, poly- and single-crystalline condensed systems at multiple-factor external influence are considered. The pore formation mechanisms depending on physical and technological condensation conditions are discussed as well as effects of external factors on the porous structure stability.

Рассмотрены процессы образования и поведения пор в аморфных, поли- и монокристаллических конденсированных системах при многофакторных внешних воздействиях. Обсуждаются механизмы порообразования в зависимости от физико-технологических условий конденсации и влияние внешних воздействий на стабильность пористых структур.

The porosity problem in condensed systems is of considerable importance because it is connected directly with properties of films and coatings [1]. The porosity is a favorable factor in some cases while being undesirable in other ones where its effect is to be minimized. To date, the pores are considered in the physical materials science in two fashions: as a characteristic structure component defining the material properties and destination (high-porosity objects), and as three-dimensional structure imperfections along with zero-dimensional, single-dimensional, and bidimensional structure defects. In developing the existing concepts, the authors have proposed to consider pores in a more general manner as phase-structure inhomogeneities; this concept is applicable both to crystalline and amorphous materials. Such an approach makes it possible to describe the morphology, thermodynamic and kinetic characteristics of porous systems independently on the origin thereof. However, it requires to consider the whole set of internal and open pores as a system forming a united system with the matrix [2].

We have shown in previous works that the submicro-, micro- and macroscale pores are characteristic phase-structure inhomogeneities and, in many cases, also an inherent structure component in condensed systems due to the formation regularities of amorphous and crystalline structures under substance condensation [1, 2]. The wide variety of the substance deposition methods causes a multiple-factor dependence of the pore formation mechanisms during the condensation. To study those mechanisms, a combination of methods was used, including X-ray small-angle scattering (SAS), X-ray structure analysis, optical, electron, and X-ray shadow microscopy, high-precision measurements of hydrostatic density, mercury porosimetry, sorption, and transpiration methods [3]. It is just the high-sensitivity, high-resolution SAS method that has been found to be the most effective, because it provides the integral information on the dispersity, volume concentration, shape, and orientation of pores unavailable by other methods, as well as, due to development of high-vacuum small angle X-ray diffractometer, makes it possible to study the kinetics of the pore formation in its initial stages directly under various external influences, such as isochronic and isothermal heating, thermal cycling, gas saturation, VUV irradiation, and external loading. The samples were tested at the earth surface as well as in outer space (using orbital stations).

By purposeful investigations of a wide class of condensates including metals, alloys, chemical compounds, and various composites obtained by thermal evaporation, electron bombardment, electrolysis, pyrolysis, gas transport, ion-plasma sputtering, etc., the main mechanisms of the condensation-dependent pore formation were established. Those mechanisms act in combinations depending on the formation conditions of the deposit structure. The following mechanisms are most typical: diffusion-vacancy, sorption, "shadowing" effect, loose jointing of the structure elements, pore formation at the growth steps, inhomogeneous growth due to the topology of condensation surface, micro-shrinkage, shock, drop, and aerosol mechanisms. The mechanisms are due to regularities and specific features of the condensation process [1, 2]. Depending on one specific mechanism or other, it is just intragrain or intergrain pore formation processes, or else the fractal structure formation that predominate. A comparative consideration of the porosity characteristics as functions of physical and technology parameters of the evaporation and condensation processes for a wide class of condensates made it possible to establish the general physical regularities of the porosity formation in films and coatings of various origins. These regularities consist in what follows.

The main factors defining the condensation-dependent pore formation are: competition of diffusion and sorption processes, gas release and gas absorption, orienting actions during the cooling, correlations between the overcooling extent, evaporation and condensation rates, the substrate surface chemical composition and topology as well as difference between thermal dilatation parameters of the substrate and condensate. Depending on the above factors, the porosity may amount from some fractions of a per cent to several tens per cent, the pore sizes being within a range from several fractions of nanometer up to tens of micrometers. The orienting action is due to the prevailing condensation mechanism. So, under electrolysis, the orienting factor is the direction of the continuous release of gas bubbles, and the pores are elongated along the deposit thickness but flattened in the deposit plane parallel to the electrolyte surface [2]. Under anodic oxidation, there is an erosion porosity where the main orienting factor is the direction of continuous delivery of the etching electrolyte to the pores, and the porosity level increases as the oxidation regime becomes more hard [2].

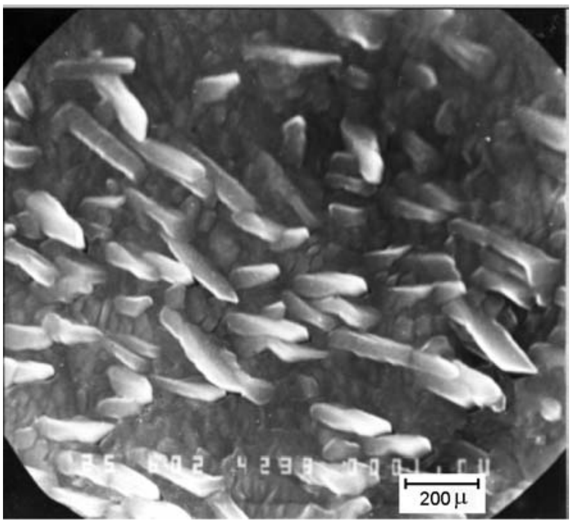

Fig. 1. Columnar structure of Al condensates oriented nearly along the molecular flow direction.

In vacuum condensates being deposited under on-earth conditions without any chemical interaction, the orienting factor is the molecular flow direction while overcooling extent, condensation rate and molecular flow incidence angle, working atmosphere composition and pressure, substrate surface structure and topology are the main parameters defining the porous structure character. The dominating role of the pore formation mechanisms is established depending on those parameters. For example, the oriented porosity of amorphous and crystalline condensates is a result of the directional condensation and columnar structure formation (Fig. 1) while the pore formation is favored by factors suppressing the migration mobility of adatoms and facilitating the sorption processes.

Under significant overcooling in earth conditions, the incidence angle β of the molecular flow is the most effective factor; as it increases, the porosity rises sharply, and the mutual shadowing effect as well as the non-dense joining and fusing of the structure elements become the decisive mecha-

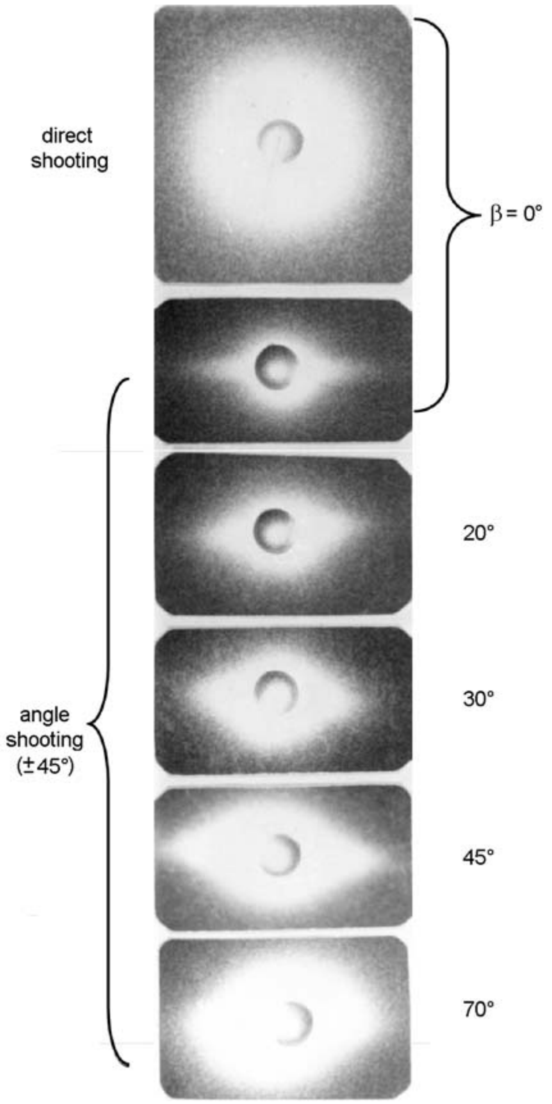

Fig. 2. SAS anisotropy caused by submicropores in Ni films condensed at various incidence angles β of molecular flow.

nisms. The porosity increasing with β causes a considerable increase in the SAS intensity (Fig. 2) and a simultaneous decrease of the condensate hydrostatic density [1, 2]. As the overcooling extent and condensation rate decrease, the role of diffusion-vacancy mechanism becomes more and more important and the porosity is reduced significantly. Its increase at elevated temperatures is caused by the secondary coalescence of the condensation-dependent submicropores that compensate the molecular flow effect. This interrelation is typical for all condensates and it shifts towards higher temperatures as the overcooling extent increases; as the condensate purity increases, the dependence shifts towards lower overcooling extents [1, 2].

Table. Variation of hydrostatic density ρ in SiO-doped Ni condensates due to the porosity development

SiO, %	$\rho \cdot 10^3$ kg/m^3	
	As-deposited	Annealed at 600°C
0	8.810	8.810
0.5	8.805	8.788
1.6	8.797	8.717
2.8	8.660	8.410
3.9	8.585	7.947
4.6	7.940	7.760
5.6	7.050	6.370

The secondary thermally activated processes that are developed in condensates under predomination of diffusion-vacancy mechanism may give rise to structure inhomogeneity by thickness resulting from formation of pores or other phase-structure inhomogeneities differing in orientation from the initial one [2]. The development of condensation-dependent porosity is favored significantly by insoluble and poorly soluble impurities that hinder the development of secondary processes. This is evidenced not only by the SAS data but also by the high-precision hydrostatic weighing (see Table).

Along with dispersing of the structure elements, the increase of insoluble impurity concentration, e.g., SiO in Ni condensates, results in reduction of hydrostatic density due mainly to intensive pore formation without changing of the lattice period remaining close to the reference value for the metal. This means that such impurities, being not dissolved in the crystal, are distributed chaotically within the condensate volume as local segregates, thus restricting the mobility of metal atoms being condensed and deteriorating the perfection of the condensate structure. In the course of diffusion during the condensation as well as under thermal activation in the post-condensation period, the foreign dispersed particles scattered chaotically in the volume act as constant runoffs for vacancies and thus stimulate the pore formation processes. In turn, the surfaces of pores formed cause an additional supersaturation of the lattice with vacancies and form efficient runoffs for point defects, thus favoring the pore formation.

Along with the diffusion-vacancy mechanism, the adhesion at the insoluble inclusion/matrix interfaces contributes considerably to the pore formation processes. The pore are generated due to de-cohesion along the boundaries of microinclusions localized both within the structure elements and at the grain boundaries. The role of that mechanism is increased due to the volume or grain-boundary diffusion and is particularly pronounced under high-temperature heating as well as at temperature changes. The pore formation may be favored considerably by the presence of non-relaxed stresses around the microinclusions in dispersion-hardened materials. Doping with insoluble impurities reduces the formation energy of stacking defects and thus gives rise to interplanar sliding, and concentration of high stresses and facilitates the pore formation processes [2, 4].

The reinforcing of metal matrix with foreign dispersed particles is among effective stabilization methods of physical-mechanical, magnetic, electric, and dielectric properties of films and coatings. In the dispersion-hardened alloys, it is just structural factors that play a decisive part in the hardening. In such alloys, the matrix is the main load-bearing element while the role of hardening phase is reduced mainly to the contribution to formation of dislocation structure under exploitation at elevated temperatures. A specific role in this case is played by pores that, along with the dispersed particles, may act as the hardening phase, as it is observed, for example, in quenched aluminum where the hardening is due to three-dimensional accumulations of vacancies and submicropores originated from the grown nuclei of dislocation loops [2, 4]. According to the Ashby-Aurovan criterion, the rounding stress of a pore by a dislocation, τ, can be estimated as $\tau = A(G\mathbf{b}/2\pi\Lambda)\cos\Theta\ln\{2R[1 + (\Lambda/2R - 1)\sin\Theta]/r_0\}$, where $A = \{1 + [\nu/(1 - \nu)]\sin^2\alpha\} = 1/(1 - \nu)$ for edge dislocations and $A = 1$ for screw ones; α is the angle between the Burgers vector $\mathbf{b}$ and the dislocation line in the absence of stresses; Θ, the angle between the dislocation line under stress and the sliding line; R — the pore radius; Λ, the average interpore distance along the dislocation line blocked by the pores; r_0, the inner radius of the dislocation core; ν and G, the Poisson coefficient and the shear modulus, respectively. The shear stress attains its maximum in Θ range from 15 to 30°. Therefore, for the most Λ and N values, an arbitrary selected value $\Theta = 20°$ makes it possible to obtain the stress required to move the dislocation between the pores of pre-specified size: $\tau = A(G\mathbf{b}/2\pi\Lambda)0.94\ln[1 + (0.34\Lambda)]/r_0$.

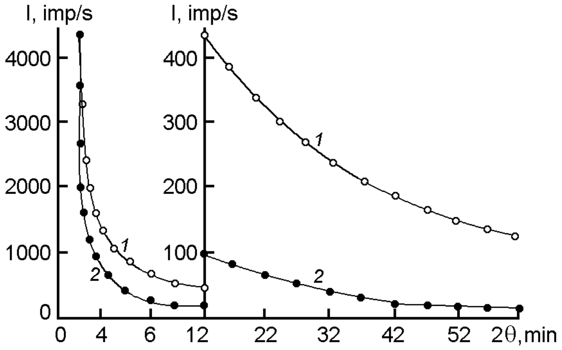

Fig. 3. SAS caused by pores in Cu films condensed on earth (*1*) and in outer space (*2*).

For N pores of $2R$ diameter, the average inter-barrier distance Λ is $\Lambda = [1 + (2RN)^{0.5}] - 2\pi R/4$. Using the criteria proposed, the expected increase of the yield limit due to homogeneously distributed spherical pores of the same diameter can be estimated.

So, the minimum pore density required to increase the yield limit for aluminum is about 10^{12} cm^{-3}. If the pore distribution is inhomogeneous, this density attains 10^{13} to 10^{14} cm^{-3} at the average pore diameter of about 10 nm. The theoretically calculated increase of the yield limit amounting 1.6 kg/mm^2 is rather close to experimental values of 1.32 to 1.65 kg/mm^2. The minimum size of a pore able to attract a near-neighboring dislocation is determined by setting the relationship for interaction energy E_{int} to zero. For example, for the pores of $2R$ diameter arranged symmetrically around a screw dislocation, $E_{int} = [-G\mathbf{b}^2 2R/4\pi][(\pi^2/12) + \ln(2R/2r_0)]$. At $2R \neq 0$, $(\pi^2/12) + \ln(2R/2r_0) = 0$, $2R = 2r_0\exp(-\pi^2/12) = 0.878r_0$. Thus, the pores with diameter equal to the dislocation core radius form an appreciable hindrance to the dislocation motion. This has resulted in the conclusion that the efficiency of pore hardening depends to a lesser extent on the pore size than on the density thereof, i.e., on the pore spacing. The estimations obtained have been taken into account when selecting the technological parameters of the film condensation process [2, 4].

The condensates deposited in outer space contain less disperse and relatively equiaxial pores distributed more homogeneously than in on-earth analogs; the same is true for the surface relief. This is concluded basing on the consideration of SAS in aluminum condensates [5]. In Fig. 3, the SAS intensity level and indicatrice slope (being defined mainly by submicropores) in films obtained in earth conditions are seen to be higher as compared to those for "spatial" analogs; while the scattering anisotropy at different sample orientations relative to the X-ray beam is considerably lower in "earth" samples than in "cosmic" ones. This can be explained by reduced orienting action of the molecular flow under microgravitation and predomination of the diffusion-vacancy mechanism. The role of shadowing effect is compensated also under condensation on alternatively moving substrate both on earth and in space. The condensation rate reduction and especially gas saturation (in particular, hydrogen implantation) under the amorphous film deposition results in a ramified network of lowered density areas (LDA) having no pronounced orientation. The network model is such that the branched LDAs of no more than 2 nm in diameter separate more homogeneous areas (grains of polyclusters) of a size corresponding to the average LDA spacing (about 10 nm). As the gas partial pressure rises, the LDA dispersion and equiaxiality extent increase considerably [2].

The pore formation processes are most pronounced under predominance of chemical factor and sorption processes with minimum role of the diffusion-vacancy mechanism. This is realized when the volume condensation is combined with deposition from a molecular flow, e.g., in low-vacuum blacks (aluminum) where the porosity attains 40 to 60 % with a developed (up to 100 m^2/g) specific surface and a high (over 95 %) light absorption coefficient in visible and IR spectral regions. Such labyrinth type fractal structures are used in high-capacity electrolytic condensers, heat-regulating light-absorbing coatings as well (due to polymodal pore distribution) as molecular sieves for gas chromatography [1, 2].

Under combined action of thermal, chemical, and radiation factors, e.g., during formation of ion-plasma condensates, the pore formation intensity increases sharply in parallel with the gas working pressure and charged particle flow [6]. For example, in tungsten coatings obtained by magnetron sputtering at low currents in xenon and argon media as well as in Al–Cu antifriction coatings, porous structures characterized by branched internal free volume (Fig. 4a), fractional dimensionality, and polymodal pore distribution are formed. Due to the system of partially communicating open pores of different dispersity and shape, those coatings show antifriction properties, since they are provided by effective lubricant access to the contact zone of friction surfaces. In such condensates where the individuality of pores becomes relative, fractal features are observed.

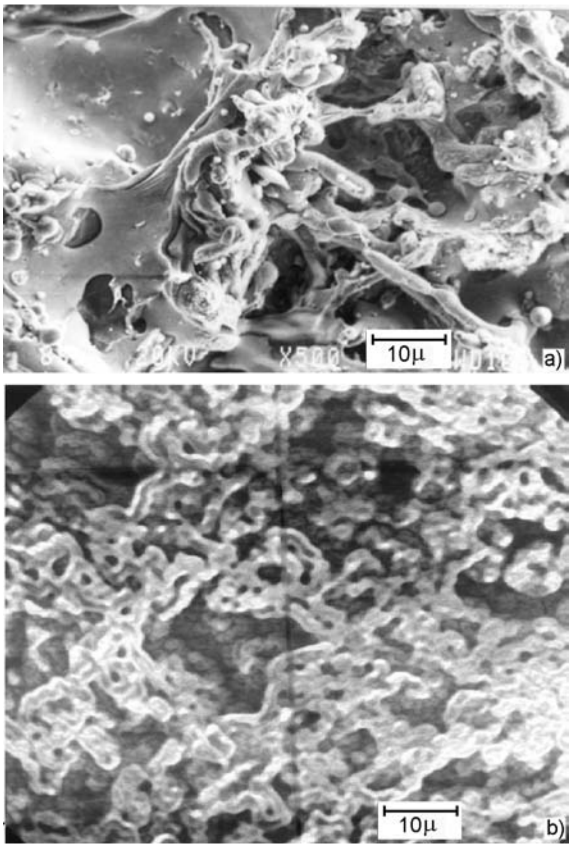

Fig. 4. Microstructure of ion-plasma Al–Cu condensates (a; the scale is shown in the Figure) and pyrolytic MnO_2 films (b; 1 cm corresponds to 4 μm) [6].

The fractal dimensionality of such structures that characterizes the internal roughness or the porous space branching can be varied from 2.1 to 2.85 by varying the gas working pressure and composition as well as the condensation rate and the sputtering current. The fractal features have been revealed also in highly porous amorphous films of boron and hydrogenated silicon, low-vacuum PbS condensates, as well as in polycrystalline granulated aluminum blacks prepared by combining the volume condensation with the condensation from a molecular flow [1, 2]. The formation of oriented and labyrinth structures under low vacuum may be accompanied by the fractal dimensionality anisotropy between the condensate plane and the normal thereto. This is of importance when the mass and heat transport in the coatings are considered.

The porosity as a characteristic feature of pyrolytic films prepared by chemical reactions under heating in air-free conditions is due mainly to evolving the pyrolysis gases which loosen the porous structure of films being grown and are in part released leaving open pores (Fig. 4b) and in part form gas bubbles being under a considerable internal pressure. The pyrolitic films also have characteristic fractal features which are due to developed surface relief, labyrinth and crater-like pore shapes. When epitaxial condensates grow on single crystal cleaves (e.g., PbS on NaCl) under a considerable overcooling, texturized polycrystals are formed and the pore orientation coincides with the texture direction (Fig. 5a). As the overcooling extent reduces and a single crystal is formed, according to Curie-Wulf rule, the pores become faceted with the cleavage planes [100], negative crystals form (Fig. 5, b–d), and the epitaxial layer structure becomes more perfect. Under thermal stresses arising during the cooling from 285°C (or higher) down to ambient temperature, due to the thermal expansion coefficient difference between the condensate and substrate, the plastic strain of condensate results in an increased dispersity degree and pore concentration caused by fragmentation of the "negative crystals" and additional faceting thereof with the sliding planes [111] (Fig. 6, e–g).

The concentration of pores in polycrystalline and epitaxial condensates can be estimated by comparing the SAS intensity levels for films condensed at different substrate temperatures (Fig. 6a). The substantial difference in those levels is caused by significant difference in the film porosity that attains several tens per cent in polycrystalline condensates formed under a considerable overcooling while being at several per cent in epitaxial ones. The pore formation processes are the least intense when the deposition takes place in a closed volume with an intense exchange interaction between the growing layers and vapor phase at optimum evaporation-to-condensation temperature ratio that provides conditions close to the thermodynamic equilibrium. This is illustrated by small-angle diffraction patterns shown in Fig. 6b where the SAS intensity level caused by pores is seen to decrease as the temperature is elevated. The porosity minimization is favored

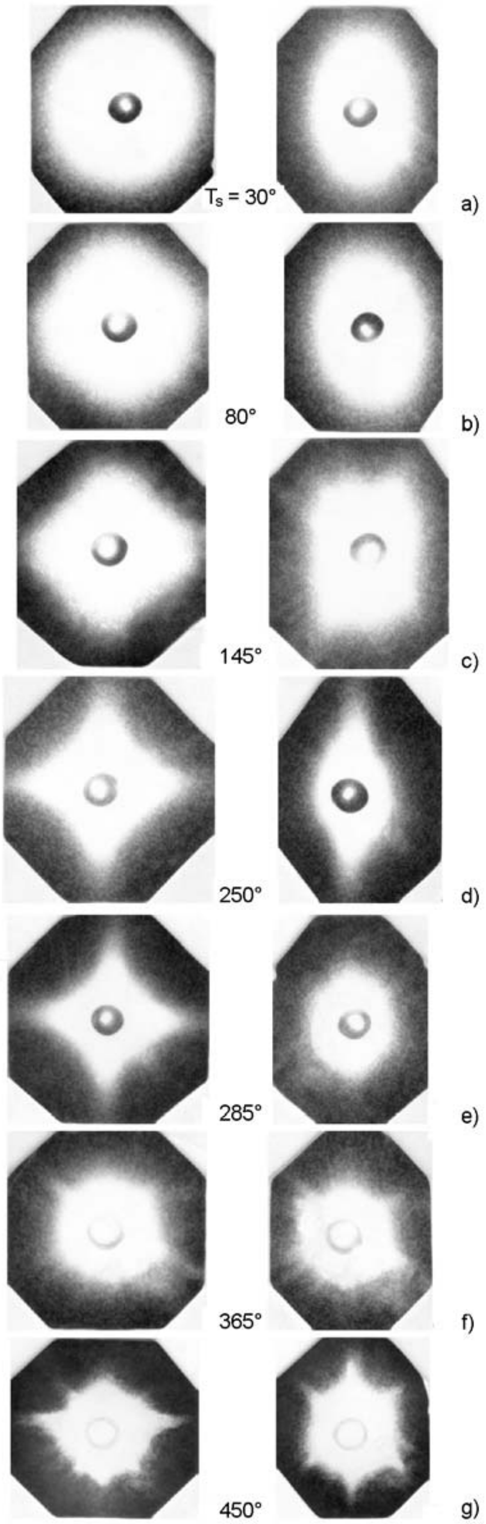

Fig. 5. SAS caused by pores in PbS condensates deposited onto NaCl cleavages. Left, normal shot; right, inclined shot (45°).

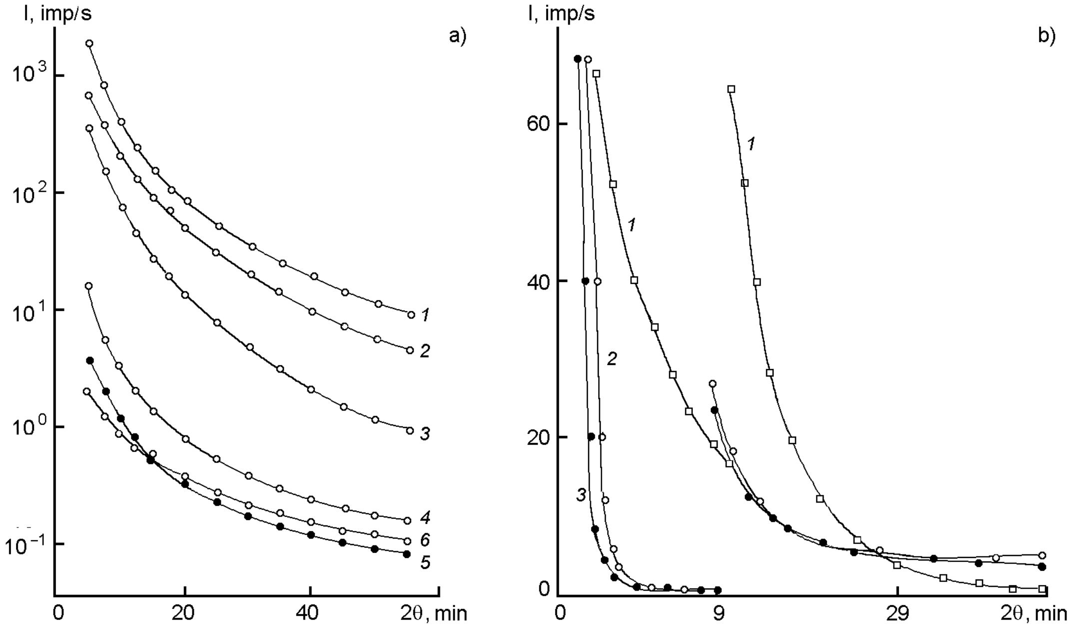

Fig. 6. SAS indicatrices for epitaxial PbS films condensed in an "outer" vacuum (a) and for epitaxial CdTe films condensed in a quasi-closed volume (b) at various substrate temperatures (°C): 240 (*1*), 400 (*2*), 500 (*3*).

by predomination of a gas having a high migration ability (e.g., hydrogen) and depletion of the condensate in volatile components [2].

The condensate porous structure evolves under external actions. The amorphous films are densified under heating due to the free volume reduction in the course of structure relaxation. This process takes place, however, without any visible vicissitude features, i.e., gradually down to crystallization, while the implanted gas favors the stabilization of the porous structure [2]. In poly- and single-crystalline condensates, in contrast to the amorphous ones, the vicissitude of thermally activated processes is pronounced clearly. First, the submicropores are coalesced, the total porosity level being unchanged, and then, as the heating temperature or duration increases, the pores are cured resulting in densification. The effective activation energy of those processes is close to that of boundary and surface self-diffusion. This is associated with the presence of easy diffusion ways, such as extended grain boundaries, pores, and other structure imperfections [1]. In epitaxial films, the determined values of effective activation energy are more similar to that of volume self-diffusion [1, 2]. The recrystallization of polycrystalline films due to heating accelerates the pore curing due to displacement of intergrain boundaries that "sweep out" the intragranular submicropores that coalesce in part and become concentrated mainly at intercrystallite boundaries in the ternary joint sites, thus taking a high thermal stability [2]. But the higher are the condensation rate, dispersity and submicropore concentration in the initial structure, the lower is its post-heating porosity, according to the well-known principle: the more is the system nonequilibrium, the faster and more complete are the spontaneous equilibration processes under heating. Therefore, to minimize the porosity, it is not the condensation temperature but its rate that is to be increased, and the post-condensation heating is to be used [2].

The pore sintering is hindered by insoluble and poorly soluble dispersed impurities. As the content thereof increases, the effective activation energy of pore sintering approaches that of the volume self-diffusion. Due to heating of epitaxial films, the pores become larger and take a more equiaxial shape; this trend becomes more pronounced as the temperature elevates. In this case, the more reduced becomes the dislocation density and the larger become the coherent scattering areas, the more equiaxial shape is taken by the pores, both when the boundary diffusion plays the main part in polycrystalline films and when the volume self-diffusion is increased in epitaxial condensates [1, 2].

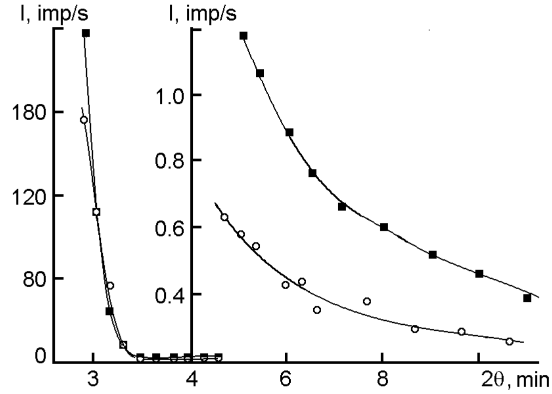

Fig. 7. Effect of VUV irradiation (22 h) at ambient temperature on SAS in Al condensates. °, initial state; ×, after irradiation.

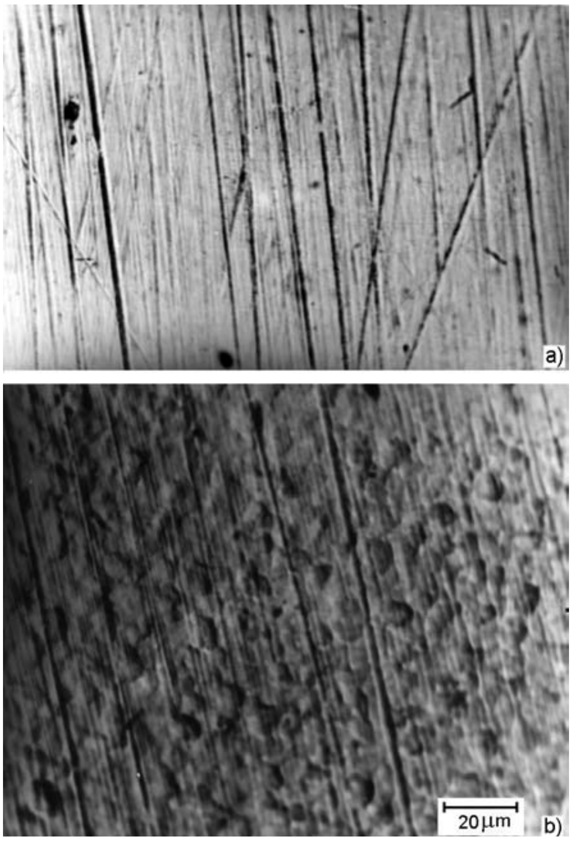

Fig. 8. Surface microstructure of Al films: initial (a) and exposed in outer space for 1 year (b).

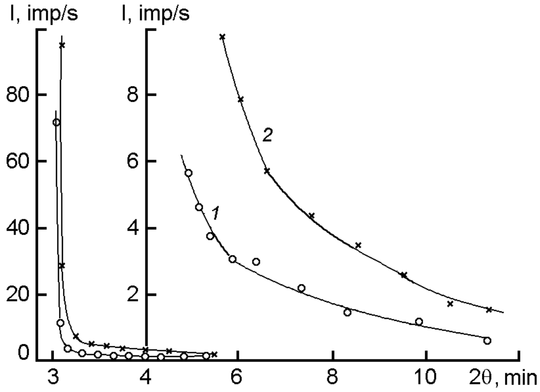

Fig. 9. SAS change in Al films resulting from outer space exposure for 1 year: as-deposited (*1*) and after the exposure (*2*).

It is just the pore formation caused by a low-energy (sub-threshold) vacuum ultraviolet (VUV) irradiation at room temperature, in particular, in Al condensates that is of most interest and has been revealed for the first time. It is seen in Fig. 7 how the SAS intensity level increases under VUV irradiation due to formation of submicropores. At a high quantum flow density (10^{22} quanta per m^2/s) and quantum energy near 10 eV being sufficient to increase the diffusion activity of gas atoms sorbed during the deposition and vacancies of condensation origin, the processes observed can be supposed to be due to the VUV-stimulated formation of gas-vacancy complexes that are converted into nuclei of submicro- and micropores [2]. This conclusion is based on the fact that a long-term VUV irradiation of aluminum foils (where the gas content is at least one order lower than in condensates) causes neither any appreciable density decrease nor a SAS pattern change. But if hydrogen is introduced into the foil at a concentration up to 10^{-4} at.%, already a 2 h long VUV irradiation results in a sharply increased XLS intensity and an appreciable (up to 1.5 %) density decrease of the foil.

As to behavior of pores in materials subjected to multiple-factor external actions, it is just the outer space (OS) that is a convenient natural medium for such studies. The repeated full-scale testing have shown that a prolonged exposure in OS results in density decrease of condensates and metallurgical foils due to porosity development (Figs. 8, 9). For example, the density decrease of high-purity aluminum films after one-year exposure attains 2.5 %. Due to combined action of the OS factors causing the pore formation in condensed films and coatings, the SAS intensity increases substantially within the whole angular range of scattering (Fig. 9). This evidences the continuous and combined running of the pore generation and growth processes during the whole time of the sample exposure in OS.

Comparing the results of outer space tests and imitation tests on earth under multiple-factor actions, it has been established that among the all OS factors, it is just the thermal cycling (from −150 to 200°C), VUV irradiation in the atomic oxygen flows, and hydrogen saturation resulting from the continuous proton irradiation that influence most heavily the porosity characteristics of metals and alloys. In its turn, confirmed has been one of the main conclusions from the previous studies, namely, that the sensitivity of condensates and other materials to thermal cycling and VUV irradiation is due mainly to gas saturation thereof. The materials become sensitive to thermal cycling and VUV only due to hydrogen saturation. It has been shown also that, using the results of modeled tests on earth, it is quite possible to forecast the changes in materials at prolonged service in natural conditions.

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Конденсаційна пористість у плівкових наноструктурах

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Розглянуто процеси утворення і поведінки субмікро-, мікро- і макропор у аморфних, полі- та монокристалічних конденсованих системах при багатофакторному зовнішньому впливі. Обговорюються механізми пороутворення у залежності від фізико-технологічних умов конденсації і вплив зовнішніх чинників на стабільність пористих структур.