

Communication

## The Influence of Space Environment on Substructure of Light-Absorbing Thermoregulating Al Coatings

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**Abstract:** Porous light-absorbing and thermoregulating low-vacuum aluminum coatings (AC) precipitated by thermal evaporation were the object of this study. The small-angle X-ray scattering (SAXS), electron microscopy, precision hydrostatic weighing, and the dynamical technique for argon low-temperature desorption were used for our investigations. It was shown that AC pore formation in open space (OS) is conditioned by the reduction of molecular flow orienting impact and the increase of the diffusing-vacancy mechanism on coatings formation in zero-gravity conditions, which causes the formation of coarse and equiaxed pores with lowered polydispersity levels.

**Keywords:** open space; porous structure; anisotropy; oxygen

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## 1. Introduction

Black Al coatings (BAC) are widely used as the absorbing thermoregulating elements for spacecraft. As was shown in [1], due to vacuum of space, thermal regulation of satellites is passively managed by radiative exchange between its internal surfaces and the environment. Satellite temperatures in open space (OS) are often passively controlled by thermo-optical properties of suitable surfaces, *i.e.*, having convenient solar absorbance and emittance. BAC are mainly used because of their low cost, as well as the low risk of contaminating the spacecraft's instruments. At the same time, the authors of [1] and the authors of [2] analyzed AC, formed by means of electrochemical oxidation of Al surface, while in [3], Al vacuum condensates have been considered for their use as surfaces. The present paper reflects investigations initiated in [3] and continued in [4] researching the effect of OS conditions on the porous structure of Al coatings. Detection of the laws and mechanisms of pore formation in condensates and specific composite systems contributes to the setting of the required porosity characteristics at the formation of new challenging materials with specified properties. The formation processes and behavior of submicropores (SMP) at multiple-factor external influence are considered below.

## 2. Experimental Section

Al films of 1–40 nm width have been generated by means of crucible evaporation of 99.99% Al aluminum at the temperature range of 400–600 K, speed range of  $\Omega = 0.1\text{--}0.15$  nm/s and at normal incidence of molecular flow. Differences in dissection techniques of “black”, “grey” and “light” surfaces consists mainly in controllable variation of vacuum level from  $10^{-2}$  Torr to  $10^{-5}$  Torr in working volume of vacuum chamber as well as in slight change of settling velocity. To determine the structure degradation extent under joint exposure to OS aggressive factor: thermal cyclization ( $\pm 150$  °C), high ultraviolet (HUV) radiation, inflowing fluxes of atom oxygen, electrons, protons, solar radiation energy, *etc.*, black films were exposed for about a year at the MIR 1 orbital station open platform. Along with SAXS technique, electron microscopy (raster electron microscope JSM-840), precision hydrostatic weighing, and the dynamical technique for argon low-temperature desorption were used for determining the sample specific surface. The SAXS indicatrices were registered according to [5] by a “KRM-1” modified small-angle X-ray diffractometer using a five point cubic interpolation technique of the Cu  $K_{\alpha}$  X-ray beam. The nature of angular distribution, asymptotes, and integral parameters (invariants) of the SAXS indicatrices, which were used to determine the morphology of the electron density scattering inhomogeneities, were analyzed.

Specific surface value (S) was determined by the method of argon low-temperature desorption and calculated as  $S = 4.17 x_m$ , where 4.17—area ( $m^2$ ), occupied by  $1\text{ cm}^3$  of Ar, adsorbed by mono-molecular layer and  $x_m$ —volume of adsorbed monolayer, determined from adsorption (BET), which describes physical adsorption of gases and steam at the temperature close to their boiling temperature:

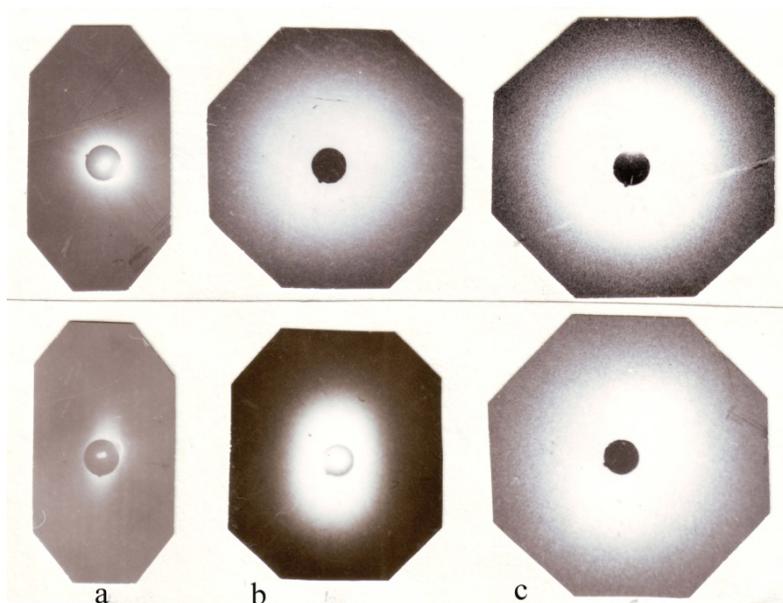
$$\{(p/p_s) \times (1 - p/p_s)\} = (1/x_m A) + [(A - 1)/x_m A] p/p_s \quad (1)$$

where:  $x$ —adsorption value, which complies with relation of equilibrium pressure  $p$  and elasticity  $p_s$  of adsorbate saturated steam (test results give  $p/p_s = 0.2$ );  $A$ —constant dependent from adsorption energy and temperature, equal to relation of molecule lifetime in the prime and consequential layer.

### 3. Results and Discussion

The sensitivity of condensate porous structures to their preparation conditions is vividly seen in AC of three typical outwardly differentiable types: black, gray and light. Their essential differences are demonstrated not only in the surface topological properties, but in their inner structural features and properties as well. Thanks to Al's large oxygen affinity and its high chemical activity in melted state, the observed differences can be varied within a wide range. The limited possibility of evaporated metal interaction with residual gases, avoidance of condensate doping by evaporator impurities and by hydrocarbon decomposition products provide favorable conditions for the formation of light AC with monodisperse and the most perfect structure, which actually shows the disperse line smearing. Because of low porosity (less than 0.05%), their dispersability is minimal (Figure 1(a)). SAXS anisotropy evidences the presence of typical ellipsoid shapes and submicropores (SMP) orientation along molecular flow, SAXS indicatrix asymptotic is described by Porod's law [6], and no fractal symptoms are present.

**Figure 1.** Small-angle X-ray studies for light (a), gray (b), and black (c) aluminum coatings (AC).



Vacuum deterioration with preserved molecular-flow condensation condition results in the generation of gray low-crystalline AC with typical column-like structure and high oriented porosity, causing SAXS anisotropy (Figure 1(b)). In their intensity level and SAXS angular range, gray films considerably exceed the light ones. This is because of SMP dispersity; their volume concentration is higher by the order of magnitude than that of light films (see Table 1). Typically, neither gray nor light condensates possess fractal features. Under low-vacuum condensation, when an atom free path in vacuum is a thousandth of a fraction of a meter, such complexes of an Al atom and its variously dispersed oxides are condensed to vapor-phase substrate (along with atomic flow) which are generated directly in vapor phase as a result of interactions between colliding atoms (aerosol mechanism).

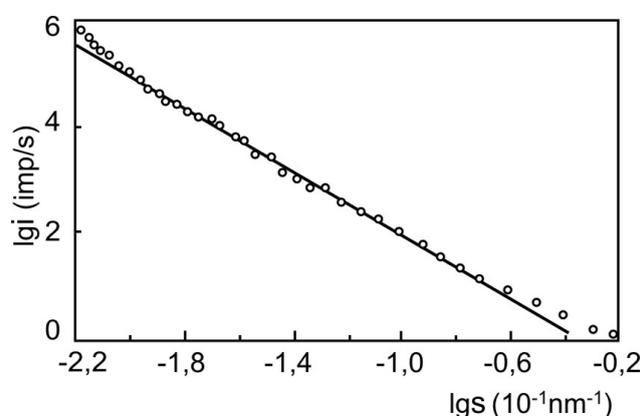
Typically, neither gray nor light condensates possess fractal features. Under low-vacuum condensation, when an atom free path in vacuum is a thousandth of a fraction of a meter, such complexes of an Al atom and its variously dispersed oxides are condensed to vapor-phase substrates (along with atomic flow) which are generated directly in vapor phase as a result of interaction between colliding atoms (aerosol mechanism).

**Table 1.** Submicroporosity of aluminum coatings ( $2R_n$ —mean square size of submicropores (SMP), nm).

	Total volume concentration of SMP, $C_n$ , %	Volume concentration of SMP with different sizes fractions, % ( $2R_n$ is pore size, nm)			$2R_n$ , nm
		$2R_n < 8\text{nm}$	$8 \leq 2R_n < 30\text{nm}$	$2R_n \geq 30\text{nm}$	
“black”	initial	8.85	5.45	2.10	15
	after annealing	6.55	3.40	1.70	18
“gray”	initial	0.6	0.5	0.1	10
	after annealing	0.77	0.60	0.12	13
“light”	initial	0.048	0.002	0.006	35

In addition, the oxidation of structural element surfaces during sediment formation, as well as immuring of hydrocarbon molecule absorbed layers, their decomposition products and residual gases result in the suppression of adatom migration mobility and inhibition of SMP coalescence. By combination of molecular-flow condensation in oil vacuum with high volume condensation, porous black films are obtained which have unique properties permitting them to be employed as light-absorbing thermoregulating coatings (TRC). The extremely high dissipability of black AC stems from their specific fractal structure. Since pore preferential orientation is absent, the SAXS indicatrix asymptotic is close to  $\sim s^{-3.1}$  ( $s$ —wave vector), which corresponds to  $D = 2.9$  fractal dimension (Figure 2).

**Figure 2.** Small-angle X-ray scattering (SAXS) indicatrix asymptotic for black AC.



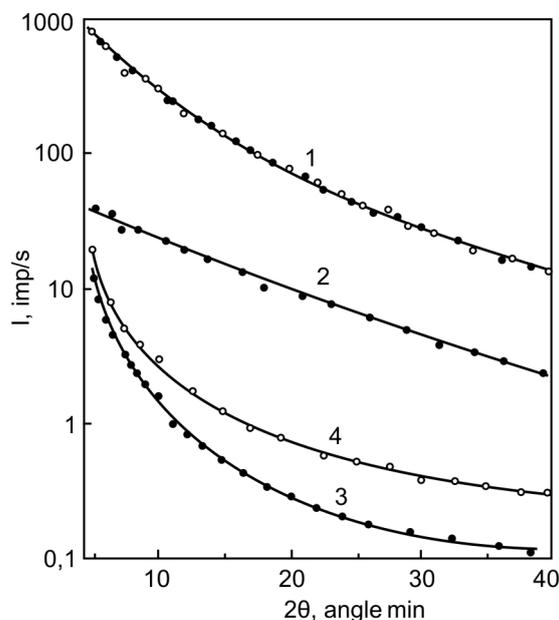
In light AC with a thickness of  $8\ \mu\text{m}$ , which possess fractal properties, a decrease of hydrostatic density is observed (from  $2.62$  to  $2.55\ \text{g/cm}^3$ , see Table 2) which is induced due to an annual full-scale exposure in OS and considerable reduction of scattering power (Figure 3, curves 3 and 4) caused by intensively growing process of formation of gas-diffusion-deformation SMP.

The pattern of the black condensates' structure is determined by interaction processes between different Al atoms and between Al atoms, residual gases and admixtures from evaporator, running both at substrate and vapor phase at conditions of low-vacuum condensation, when the length of the atom's free path is a sub-centimeter.

**Table 2.** Characteristics of Al coatings.

Samples	Specific surface, $10^3 \text{ m}^2/\text{g}$	Hydrostatic density, $\text{g}/\text{cm}^3$	Open porosity, %	Total porosity, %	Mean square size of SMP, nm
“black”	50	2.24	21.5	38.5	15
“grey”	1.5	2.12	2.5	24.0	10
“light”	0.05	2.62	2.0	6.4	35

**Figure 3.** SAXS indicatrix for AC: 1—black; 2—gray; 3, 4—light, ●—initial state; ○—after one year of exposure in an open space.



Thick (more than  $1 \mu\text{m}$ ) black condensates appear to be the items with developed specific surface, which, similarly to the data of argon low-temperature desorption, can reach  $\sim 50 \text{ m}^2/\text{g}$  (see Table 2). The intensity level of their SAXS is several degrees higher as compared to light films, obtained in a higher ( $1 \times 10^{-5}$  torr) vacuum (Figure 3). Considerable differences are also observed in steepness and asymptotics of SAXS indicatrices. Based on intensity level criteria, grey films are in intermediate position between black and light condensates.

SAXS in condensed polycrystal films of metals and alloys are mostly caused due to sub-micro-porosity of condensation origin. An analysis of indicatrices integrated parameters shows that the submicroporosity  $C_n$  of black films is 8.85% at root-mean-square size of micropores of  $2R_n \sim 15 \text{ nm}$  (see Table 1). The average size of micropores in grey films is slightly less ( $2R_n \sim 10 \text{ nm}$ ) and their bulk concentration is  $\sim 0.60\%$ .

The least favorable conditions for the formation of small micro-pores are created at the formation of light condensates. The average size of micropores under such conditions reaches  $2R_n \sim 35$  nm and their bulk concentration is less than 0.05%.

Strongly evident polydispersity of submicropores is the subject of much attention. However, in black and grey films, the main volume fraction of SMP is formed of pores with a size of  $2R_n < 8$  nm. It is mostly typical for grey films, which are condensed at higher speed rates (see Table 1). In contrast to light films, invariant curves of SAXS indicatrices for black and grey films have several strongly evident maximums, which show that these condensates possess several types of size-distribution of pores, *i.e.*, polymodal distribution.

The distinctive feature is that, at the observed sharp difference in sub-micro-porosity level, the hydrostatic density of black films is higher than that of grey films ( $2.24$  g/cm<sup>3</sup> towards  $2.12$  g/cm<sup>3</sup>, see Table 2). However, as shown in the data of oil absorption measurements, the open porosity of black films is considerably higher (21.5%) than grey (2.5%) and light ( $\leq 2.0\%$ ). Specific surface does not exceed the value of  $0.5\text{--}1$  m<sup>2</sup>/g for grey condensates and is less than  $0.05$  m<sup>2</sup>/g for light condensates. Thus, measurement data on hydrostatic density, specific surface and oil adsorption as well as analysis of SAXS nature validate that the main contribution to the total porosity is made by open submicro-, micro- and macropores; the total bulk concentration of which reaches 38.6%.

The pores of grey films have a lengthened shape and are mostly aligned along the molecular flow incident direction, *i.e.*, standard alignment towards the film. However, in black condensates, pores form multi-branch network of channels, allocated in the deposit space without well-defined preferred alignment, but having an open outlet outside of the side inversed to the evaporator. Such channels are formed due to loose coalescence and self-shading mechanisms border poly-disperse granular elements of the condensate structure, the surface of which is blocked with adsorbed layers of oxide and other products of interaction between deposit and residue gases as well as admixtures, coming from the evaporator.

It can be assumed that the poly-disperse porous structure featured with low reflectivity which is observed in black films is considered for electromagnetic radiation as a complicated labyrinth where most of the incoming light in a wide range of waves—from infrared to UV spectral region—is adsorbed, which contributes to the black color of condensates.

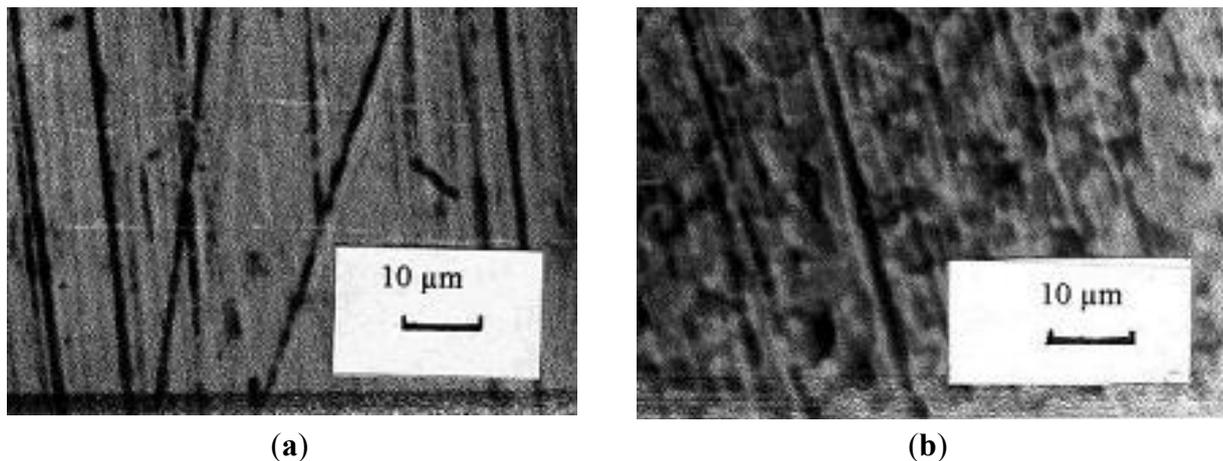
Due to an hourly anneal of black and grey films at  $T_{\text{anneal}} = T_{\text{melt}}$  and a vacuum of  $10^{-4}$  torr, no visible change of total porosity has been detected and the characteristics of the structures generated from diffraction extension has been determined. However, based on the processed data on SAXS indicatrices, the pattern of the effect of the above-mentioned anneal on submicroporosity  $C_n$  on each type of films is different: in black films the  $C_n$  rate is reduced while in grey condensates a tendency for an increase in sub-micro-porosity has been observed (see Table 2). It is especially notable at the analysis of change in bulk concentration of micro-pores of different sizes. Therefore, the anneal of grey films results in the growth of concentration of both large and small SMPs in such a range that their mean square average weighted size increases.

A separation improvement of three maximums at SAXS indicatrices' curves was also observed, and their bias to smaller dispersion angles certifies closer-cut separation at an anneal of three dimension-type SMPs contained in films.

Along with the enlargement of SMPs, a decrease in their non-equiaxity degree was also observed. In black films, the decrease of sub-micro-porosity at the anneal is conducted mostly due to reduction of small micropores' amount and growth of volume fraction of large pores (see Table 2); at the same time, the polymodality of the dimensional distribution of submicropores vanishes.

Differences in the changing characteristics of submicroporosity of examined types of films at low-temperature anneal can be explained by the conditions of grey deposit formation which most probably contribute to more intensive flow of coalescence process of surplus vacancies at the anneal with the creation of SMPs of diffusion-vacancy nature as compared to black condensates. In black films, the key role at low-temperature anneal results in the coalescence of SMPs of condensation nature. However, the creation of new micro-pores of diffusion-vacancy mechanism did not occur. BAC condensates have extremely developed specific surface, which, according to the data on low-temperature argon desorption, extends to 50 m<sup>2</sup>/g, whereas general porosity amounts to 38% (see Table 2). The index of 38.5% specifies the general porosity of the BAC, *i.e.*, the total value of open porosity (21.5%) and inner porosity (Table 2). This is determined by the method of precise hydrostatic weighing based on the coating density defect:  $(\Delta\rho/\rho) \times 100\% = 17\%$  (2.7 g sm<sup>3</sup>—aluminum apparent density; 2.24—black aluminum hydrostatic density). The sample's density is determined by means of hydrostatic weighing without regard to open pores being filled with process fluid (CCl<sub>4</sub>). According to electron microscope findings, the coatings have a chaotic polydisperse “granulated” structure formed by highly size-differing aggregates of loosely ingrown particles. The observed polymodality of pore volume size distribution stems from the concerted action of several pore formation mechanisms, including the diffusion-vacancy one, its role being mostly felt under high migratory ability of condensing atoms. In such structures, the pores look like a ramified network of channels with open exit from the evaporator-facing side. These channels are mostly formed by loose in-growth and self-shadowing mechanisms and fringe the polydisperse granule-like structural elements the surfaces of which are blocked by the adsorbed oxide layers and by alternative products of sediment interaction with residual gases, as well as the impurities landing from the evaporator. The system of open micro- and submicropores provide high (above 95%) values of solar energy factor, thus bringing the condensate optic properties closer to the absolutely black body—thanks to solar radiation absorption by the porous system “labyrinths”. The broad scope of open pore sizes ensures high (up to 0.97) absorption factor within the wide range of visible and IR wavelengths. The experiments have shown that such a structure is extremely stable to external exposures. This is particularly important for TRC operating under multiple-factor exposures, for instance in OS [7]. Such processes are carried out under the impact of the described space environment factors, liable to observable volumetric-structural change. Under such circumstances, microscopic snapshots (Figure 4) clearly reflect that, due to porosity, the progression of the coatings' surface geometry is being changed. Upon visual inspection, a significant forming (warping) of light AC has been indicated, which is structurally the least resistant to OS conditions. Regarding the behavior of pores in materials subjected to multiple-factor external actions, only the OS is a convenient natural medium for such studies. The repeated full-scale tests have shown that a prolonged exposure in OS results in density decrease of condensates and metallurgical foils due to porosity development (Figure 4). For example, the density decrease of high purity Al films after one-year of exposure attains 2.5%.

**Figure 4.** Surface microstructure of the light AC before (a) and after (b) one year of exposure in an open space.



#### 4. Conclusion

Specific features of condensation pore formation in space are conditioned by a reduction of molecular flow orienting the impact and increase of diffusing-vacancy mechanisms on condensate formation in zero-gravity conditions. This causes the formation of coarse and equiaxed pores with lowered polydispersity levels. The main factors of an OS, which cause space-structural changes due to pore formation process in condensates and foils of fine metals at their long-term occurrence in OS, appear to be thermal fluctuations in HUV and proton radiation conditions.

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