EFFECT OF COMPOSITION ON THE WETTING PROPERTIES OF NANOMETER FILMS OF Al–Me ALLOYS (Me=Mn, Fe, Ni) OBTAINED BY ION-ASSISTED DEPOSITION

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The present study investigates the effect of composition and morphological characteristics on the wetting behavior of nanosized films of Al and its lightly doped Al–Me (Me = Mn, Fe, Ni) alloys produced by means of ion-assisted deposition on glass. The surface structure of the film/glass system was studied using atomic force microscopy. The wettability of the samples by distilled water was assessed using the sessile drop contact angle method. Within a bi-Gaussian surface model context, the surface profiles of the thin-film coatings were considered as a superposition of the lower and upper Gaussians, corresponding to the plain areas and the protrusions respectively. The deposition of aluminum and its alloys was found to significantly reduce the hydrophilicity of the glass substrate, with the contact angles ranging from 70° to 80°. The change wetting properties of the films are explained by the mechanisms of homogeneous, heterogeneous and mixed wetting of films by water.

Keywords: ion-assisted deposition; atomic force microscopy; bi-Gaussian surface; wettability; aluminum alloys.

Introduction

There is scientific and practical interest in the synthesis of aluminium alloy films using physical deposition methods from the vapour phase [1], due to the potential to form coatings with a wide range of properties. The properties of the film depend on the deposition method, the nature of the substrate and the chemical composition and morphology of the surface. Relevant developments in the scientific foundations of coating surfaces are related to the investigation and modelling of the physical features of nanocrystalline films and aluminum-based alloy coatings. This will enable the management of the surface characteristics of materials and facilitate the regulation of their physicochemical and performance properties.

This study examines the effect of composition and surface morphology on the wetting properties of nanometre-thick aluminum and Al-Me (Me = Mn, Fe, Ni) alloy films on glass substrates, obtained by ion-beam-assisted deposition (IBAD). The results of the structural and morphological analysis of the metallic films at various stages of growth are presented. Analysis was conducted using the bi-Gaussian surface model.

Materials and research methods

Metallic films on glass substrates were manufactured using a resonant ion source of vacuum electric plasma. Aluminum and Al-2.1 at.% Mn, Al-1.5 at.% Fe and Al-1.4 at.% Ni alloys were used as electrodes. The IBAD method is described in [2]. The crystallization rate (cooling of atomic-collision cascades) in experiments was on the order of 10^{12}-10^{13} K/s. In ion-assisted deposition mode, the accelerating voltage U between source and target was 3 kV. An average deposition rate of coatings was of ~0.1-0.2 nm/min. The deposition time and average thickness of the different films are listed in Table 1.

The surface nanorelief of film was investigated on an NT-206 atomic-force microscope (AFM) with CSC-38 probes using SurfaceScan control software. Images of areas of 20 × 20 μm were proceeded with SurfaceXplorer and SurfaceView programs. Additionally, a discrete relative position parameter of the mean line according to the height of the rough layer was calculated as $\mu = R_v/R_t$. Experimentally measured histograms of the distribution of heights of protrusion and depths of depressions of the surface nanorelief were approximated using a double Gaussian function with a common central value. The measurement error of discrete roughness parameters was 5-15%.

Table 1. Parameters describing the morphology, roughness and wettability of aluminum foils and Al–Me alloys deposited on glass

Parameters	Specimens				
	Al	Al–Mn	Al–Fe	Al–Fe	Al–Ni
t, h	10.0	9.1	6.0	10.0	6.0
d, nm	90	80	50	90	50
R_a, nm	31.51	23.87	23.74	38.52	17.09
R_q/R_a	1.63	1.67	1.58	1.51	1.80
$\frac{R_{ku}}{R_{sk}}$	5.88	5.67	5.41	5.53	-9.19
μ	0.42	0.38	0.39	0.44	0.41
$\frac{\sigma_1}{\sigma_2}$	1.88	1.46	2.52	1.14	2.08
θ, °	73.20	74.40	78.20	81.90	81.30

The sessile drop method was used to determine the contact angle θ (CA) of distilled water on a film surface at equilibrium. When measuring the wettability of films, the drop volume was 9.3 μL, the stabilization time was 60 s. The measurement error of θ was not more than 5%.

Results and their discussion

The ion-assisted deposition of Al and Al–Me alloys leads to the formation of thin-film nanostructures with a developed microrelief. The relief of coatings does not exhibit any dominant periodic structures of the same scale. With an increase in deposition time, the roughness of films also increases. For 90 nm thick film of Al–Fe alloy, the roughness parameters reach maximum values: R_a=38.52 nm and R_q=58.33 nm.

Analytical analysis of AFM images of submicron cone-shaped morphology of film/glass system allowed to determine the transverse and longitudinal characteristics of geometry of film surface, see Table 1. The experimental distribution of protrusions and depressions of the surface roughness of thin films of Al and Al–Me alloys on glass was found to be deviated from normal. Firstly, the form of the linear regression equation $R_q = 1.25R_a + 1.56$ (COD=1.0) differs from the known relationship for a normal random profile by the presence of an constant intercept term. Secondly, the asymmetry parameter R_{sk} takes non-zero values (range of values was from -1 to 3) along with the fact that the kurtosis R_{ku} is higher than 3 (range of values was from 7 to 16). In general, except for the 50 nm film of Al–Ni alloy, the protrusions/depressions frequency distributions of coatings have positive asymmetry, i.e. relatively high heights in shallow depressions. Thirdly, it was obtained that the complex parameter for the films is $\mu < 0.5$. Therefore, the topography of nanostructured films of aluminum and its alloys deposited on glass substrates can be considered as an inverted topography of stratified surface ($\mu > 0.5$) and use a bi-Gaussian surface model [3]. This approach introduces the double Gaussian approximation to fit the experimental distribution histograms of the heights and depressions of the nanorelief of the thin film surface on glass. As previously found in [2], this enables us to obtain additional information about the surface state and estimate the proportion of structural elements such as high irregularities (peaks) and depressions in the surface nanorelief of thin Al and Al–Me alloy films on glass.

When the bi-Gaussian model is applied to films obtained by IBAD, the surface is presented as a superposition of two relief components with different roughness values. The 'upper' Gaussian function corresponds to the protrusions and has increased roughness. It is truncated at a certain height by the 'lower' Gaussian function, which describes the flat areas [2].

It was found that applying Al-containing coatings to the glass substrate surface in a potential mode significantly reduces its hydrophilicity (θ=22.0°). When aluminum is alloyed with manganese and iron to produce films with thicknesses of 50 nm (Al–Fe alloy) and 80 nm (Al–Mn alloy), the relief smoothing does not affect the CA (within the measurement error), as shown in Table 1. However, in the case of nickel alloying, wettability deteriorates during the smoothing process. The CA increases by 11% for Al–Ni alloy film with a thickness of 50 nm, reaching 81.3°. Increasing the deposition time of the Al–Fe alloy coating from 6 to 10 hours results in the formation of a 90-nm-thick film with the highest roughness values and a CA of 81.9°.

It was found that the hydrophilic behavior of 90-nm-thick Al films, as well as 50–80-nm-thick Al–Me alloy films, is described by the homogeneous wetting regime of Derjaguin–Wenzel, see Fig. 1. The upper and lower components of the relief are in the Wenzel state and are wetted by water.

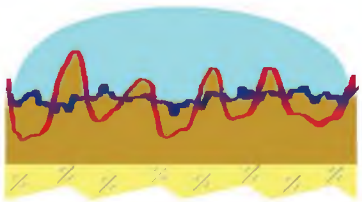

Fig. 1. Bi-Gaussian wettability in the Derjaguin–Wenzel state, where the lower (blue curve) and upper (red curve) components of the bi-Gaussian surface of a film on a solid dielectric substrate are in the Wenzel state

A morphological transition to a Gaussian surface was revealed when the Al–Fe alloy film reached a thickness of 90 nm. As the roughness of the relief increases, the deviation of the frequency distribution of the heights and depressions of the irregularities from the normal becomes minimal (σ_1/σ_2 =1.14). The surface hydrophilic-hydrophobic balance is maintained: the contact area of water droplets on the film surface, and therefore the wetting angle, remain almost unchanged compared to a 50-nm-thick film, as θ only increases by 5%. This suggests that the lower component of the alloy film surface relief is in a metastable Cassie state, with its roughness acting as air traps. Conversely, the upper component of the surface relief is in the Wenzel state, meaning the cone-shaped heights are wetted by water. This results in mixed wetting, i.e. the Cassie–Wenzel hybrid condition. In such cases, it is expected that water will penetrate deeper into rough surfaces.

Conclusion

It has been found that the submicron cone morphology and wetting properties of Al films and Al–Me alloys with a thickness of less than 100 nm are closely related. The CAs of the film range from 70° to 82°. The description of coatings in the framework of the model of the bi-Gaussian surface allowed to identify general patterns of formation of nanostructure elements of films and their influence on hydrophilic-hydrophobic balance of the surface.

The wetting behavior of 90-nm-thick Al and Al–Me alloy films with thickness of up to 80 nm is described by the Derjaguin–Wenzel mechanism. When the Al–Fe alloy is deposited using IBAD for an extended period of time, resulting in a film thickness of 90 nm, the degree of non-Gaussian relief is minimal and the bi-Gaussian surface transitions to a Gaussian surface (Cassie–Wenzel mechanism).

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