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Investigations of the surface morphology of Al_2O_3 layers by atomic force microscopy

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Amorphous alumina coating films, prepared on aluminium substrates by oxidation by the electrolytic method in ternary electrolytes, have been characterised by atomic force microscopy. The surface roughness and growth structure of the obtained Al_2O_3 films are related to the experimental conditions: temperature, current density, and deposition time. They are also related to the preparation method of the aluminium substrate surface. The columnar growth revealed by atomic force microscopy, with shape and size of columns depending on temperature and current density, has been confirmed by scanning electron microscopy.

Key words: *alumina coating films; atomic force microscopy (AFM); scanning electron microscopy; X-ray diffraction; tribological properties*

1. Introduction

Although properties of Al_2O_3 seem to be well known, alumina has been extensively studied both in the bulk and thin film forms [1] because of its possible applications. These are ranging from microelectronics, optical applications, and wear-resistant coatings to decorative purposes on massive aluminium. Thin films of alumina can be prepared by various deposition methods, e.g., evaporation [2, 3], sputtering [4], binary reaction sequence chemistry [5], and also by direct anodic oxidation of aluminium surfaces [6, 7]. An interesting feature of the thin films, both crystalline and amorphous, is that they often exhibit pronounced internal growth structure [8], which evolves during the growth (deposition) process and projects onto the film surface,

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giving rise to film surface topography and roughness. It is also well known that such structural features affect physical properties of thin films [8]. Therefore, properties of produced films can be controlled by an appropriate selection of the preparation method and conditions, e.g., chemical composition of the electrolyte and other parameters such as temperature and current density in the case of an anodizing preparation process. Tribological properties of alumina coatings used as the sliding connections are of great interest in practice. Thin oxide films, formed on the aluminium substrate by direct contact with oxygen, are inapplicable due to unsatisfactory mechanical properties [9]. A special surface treatment with electrolytes is therefore necessary to improve these properties, allowing the Al_2O_3 films to be extensively used in various industries: anti-corrosive protection, protective and decorative coatings, primer layers; elements of clutches, transmission gears, shears, and guides; elements of automatic equipment and hydraulic controllers; raceways of rolling bearings in pairs; pistons of engines and cylinder bearing surfaces in compressors [1].

Oxide films obtained by carefully performed anodic oxidation of aluminium exhibit a significant adhesion which makes the separation of the layer from the substrate practically impossible. They also exhibit high porosity resulting in the ability to absorb considerable quantities of lubricants, and in a great hardness ensuring a high wearability. A thin sliding film of polytetrafluoroethylene-graphite can be easily obtained on a coating prepared in such a way, which is important in terms of the friction properties of these connecting elements [1].

In this paper, studies of the surface morphology of alumina coating films by atomic force microscopy (AFM) are described. The obtained results are related to those obtained by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental details and characterization of the films

Hard anodic treatment in water solutions of sulphuric and oxalic acids is usually used to produce thin Al_2O_3 layers. Anodising in H_2SO_4 solution is performed at the electrolyte temperature of 264–281 K, with concentration up to 20%, and anodic current density of 1 A/dm^2. In the case of $(COOH)_2$ solution, the anodising parameters are: temperature 275–279 K, concentration up to 5%, anodic current density 1–3 A/dm^2. A great amount of heat is released in the oxide coating during oxidation from the exothermic chemical reaction of aluminium oxide formation and from the electric current. This heat has to be removed very quickly from the surface of the anodised object, otherwise the coating overheats. As a result of the overheating, tribological properties of the alumina layer are degraded and the coating becomes wear unresistant. This is a serious disadvantage of hard anodic treatment, complicating the formation of alumina coating films. This disadvantage can be overcome by appropriate changes in the chemical composition of the electrolyte.

In the present work a method of hard anodic treatment at higher temperatures has been developed [1, 9]. It does not require cooling, the heat being used to control the quality of the surface oxide layer and its properties. By anodizing at the appropriate amount of electrolyte, related to the surface area, oxidation without additional carrying away the heat is possible. According to the method proposed here, the oxidation was carried out in a ternary water electrolyte of sulphuric, adipic and oxalic acids (SAO). The temperature of the electrolyte during oxidation was in the range of 293–313 K, whereas the anodic current density was in the range of 2–4 A/dm^2. Under these conditions the oxidation process can be started at room temperature.

A TopoMetrix Explorer Atomic Force Microscope was used in the contact mode to study the morphology and roughness of thin films. Atomic force microscopy (AFM) images were obtained using a commercially available Si_3N_4 V-shape cantilever (force constant – 0.032 N/m) with a tip radius < 50 nm (Topometrix SFM probe model 1520-00). Forces of a couple of nN are used in contact mode AFM. There are two imaging methods in the contact mode AFM. The most common method of obtaining contact mode AFM images is the constant force method. In this method, the correction voltage for *z*-piezo restoring the cantilever to its orginal deflection is used as the *z*-data for imaging the sample surface topography (constant force or topography image). In the variable force method, the photo-sensor output (from deflection of the cantilever) is used as the *z*-data for obtaining a constant height (variable deflection) image.

The results of surface topography presented here were obtained in the “constant force” mode. Practically, however, the load force varies during surface scanning and the cantilever deflection photo-sensor output “error signal” was used to acquire error signal image simultaneously with topographical imaging. The AFM topographic images shown in this paper were neither filtered nor corrected.

In order to test the crystallinity of the obtained Al_2O_3 films, X-ray diffraction measurements were made with a Siemens DS 2000 powder diffractometer, using Ni filtered $Cu_{K\alpha}$ radiation and a scintillation counter. The X-ray diffraction patterns were recorded in a 2Θ angular range from 5 to 80 deg in a symmetrical reflection mode. The structures of cross-sections of Al_2O_3 films were also studied by Scanning Electron Microscopy (SEM) using a Philips XL30 type instrument.

3. Results and discussion

The X-ray diffraction patterns of three selected samples: A2, A3 and A4 are shown in Fig. 1. Films A3 and A4 were fabricated at higher temperatures (303 and 313 K) and higher current densities (3 and 4 A/dm^2), while film A2 was deposited at 293 K and 2 A/dm^2. The sharp diffraction peaks can be identified as originating from the Al substrate. The diffraction patterns of deposited Al_2O_3 consist of very broad peaks, typical of amorphous materials. The peaks, observed at about 10° for films A3 and A4, are sharper than those in the range of 12–24°, but more spread than the crystalline Al peaks. No such peak is observed in the A2 sample. This suggests that a fine-grained crystalline phase is formed at higher temperatures and higher current densities. The occurrence of different crystalline aluminium oxide phases in alumina films obtained by anodizing has been previously reported [10]. The positions of the first diffraction peaks revealed for films A3 and A4 are close to that reported in the ASTM 31-0026 card for a disperse alumina gel. No additional information about this structure is reported in the ASTM data base. To learn more about the local structure of Al_2O_3 films obtained by anodizing, more detailed wide-angle X-ray scattering studies on free-standing samples are necessary.

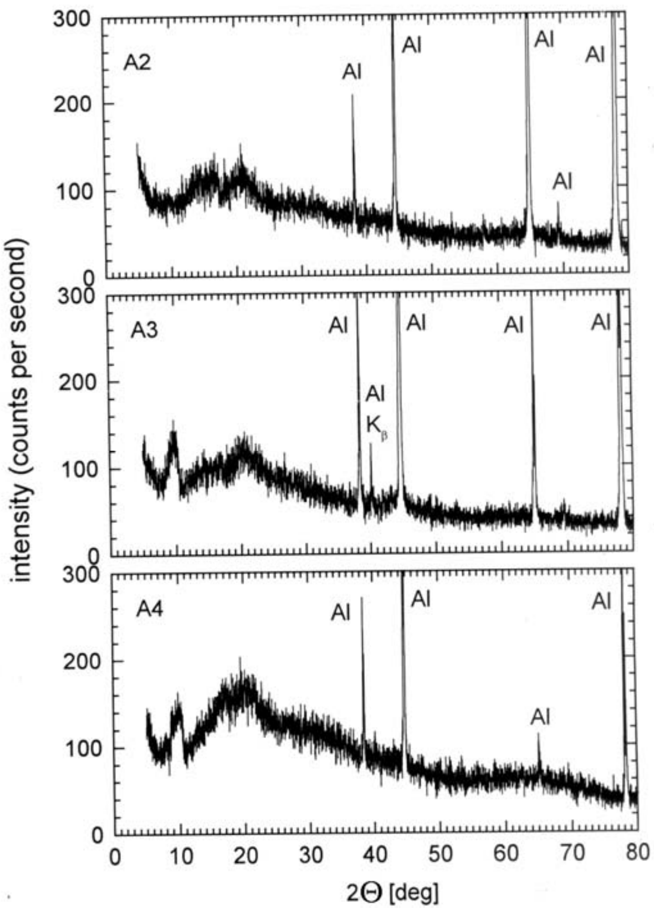

Fig. 1. X-ray diffraction patterns of the A2, A3 and A4 alumina films

Figures 2–6 show contact mode AFM error signal (a) and 3D topographic images of (5000×5000 nm^2 area) b) obtained for the alumina films surface. The error signal images, although containing no true height information, can give an additional, complementary information about film surface appearance and may resemble the micrographs observed in SEM or TEM images of replicated sample surfaces.

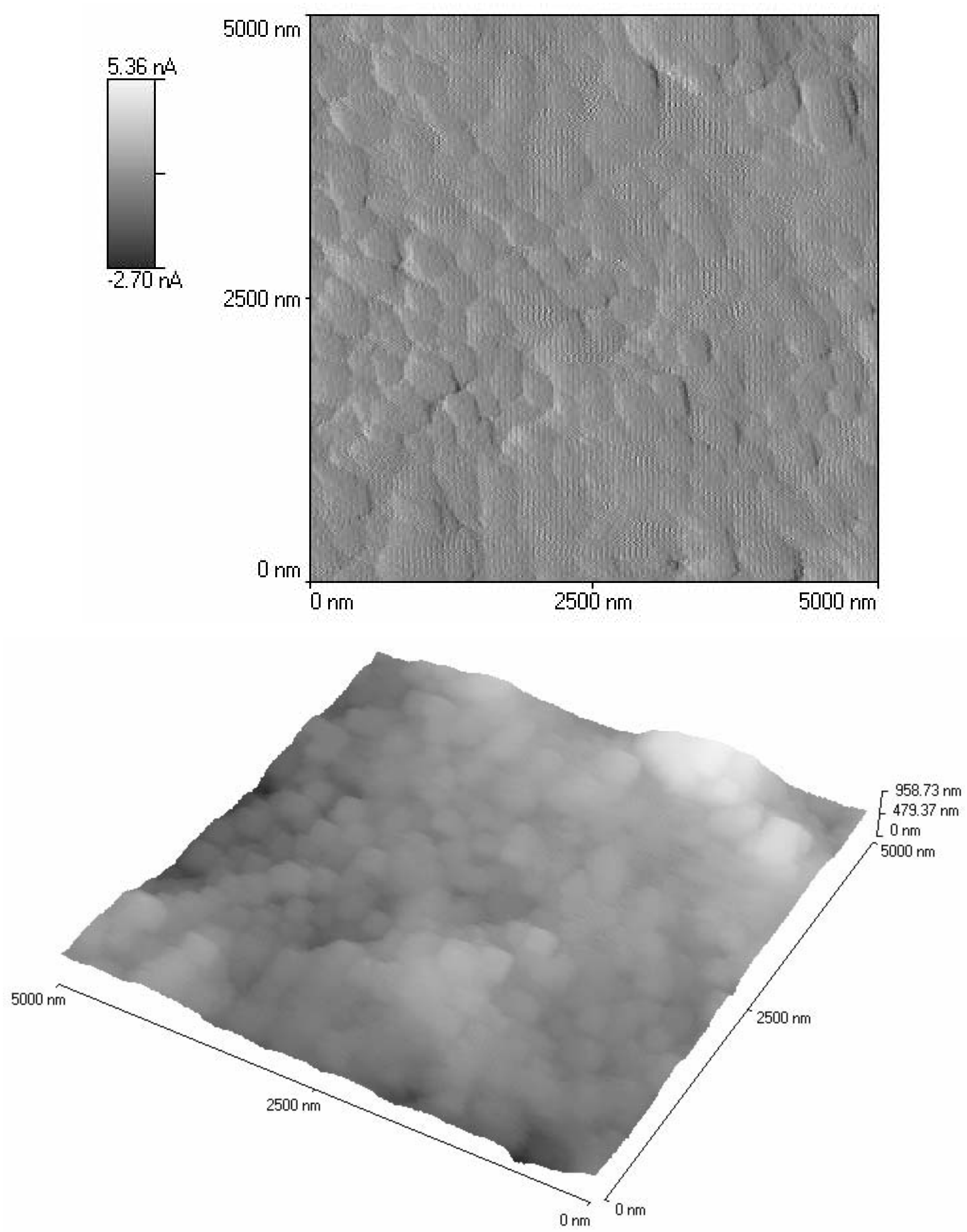

Fig. 2. Simultaneously acquired AFM contact mode: a) error signal, b) 3D-topography images of the A2 alumina film obtained at anodizing temperature T = 293 K, anodizing current density I = 2 A/dm^2, and anodizing time t = 60 min

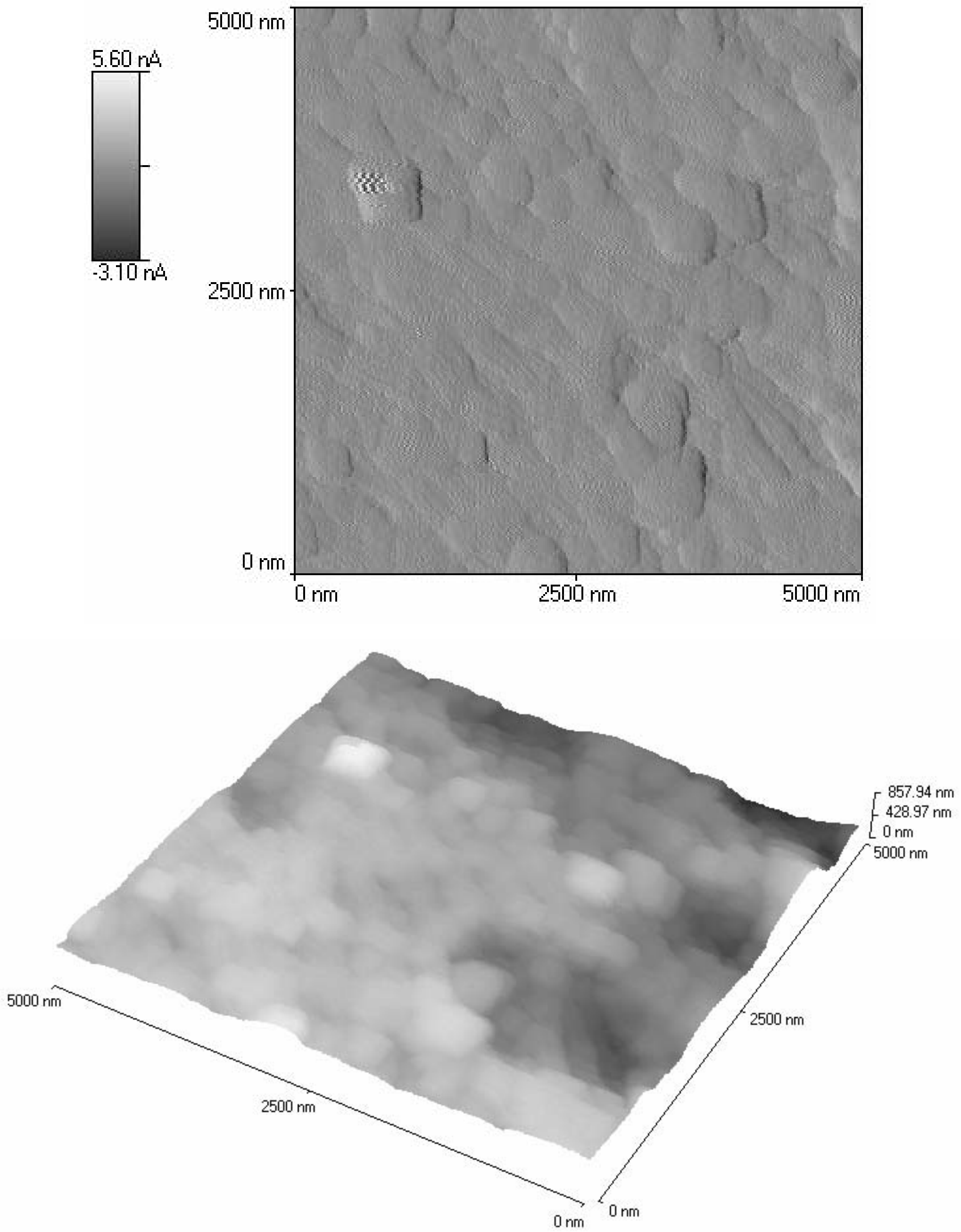

Fig. 3. Simultaneously acquired AFM contact: a) error signal, b) 3D-topography images of the A23 alumina film obtained at anodizing temperature T = 293 K, anodizing current density I = 3 A/dm^2, and anodizing time t = 40 min

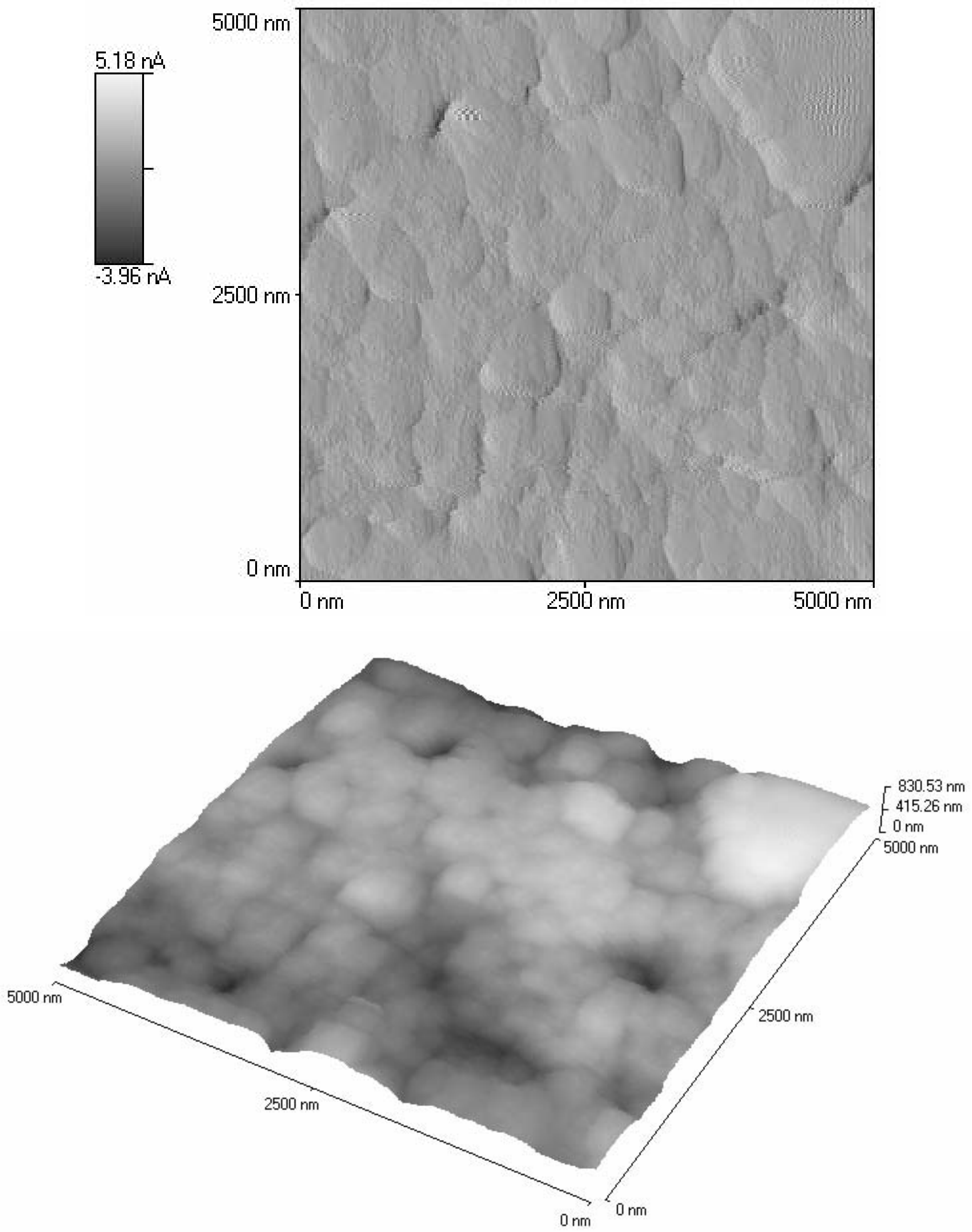

Fig. 4. Simultaneously acquired AFM contact mode (a) error signal, b) 3D-topography images of the A32 alumina film obtained at anodizing temperature T = 303 K, anodizing current density I = 2 A/dm^2, and anodizing time t = 80 min

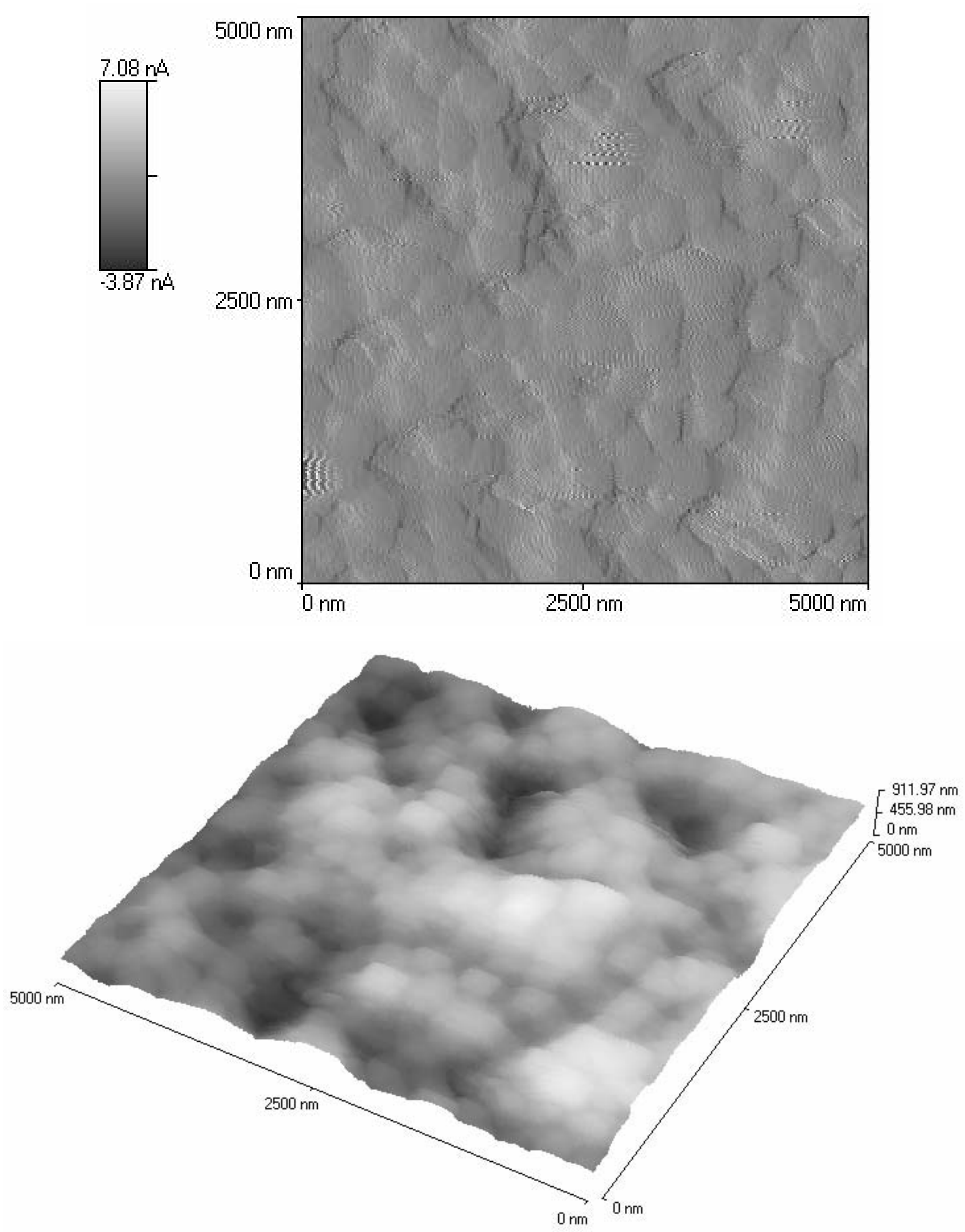

Fig. 5. Simultaneously acquired AFM contact mode (a) error signal, b) 3D-topography images of the A3 alumina film obtained at anodizing temperature $T = 303$ K, anodizing current density $I = 3$ A/dm^2, and anodizing time $t = 60$ min

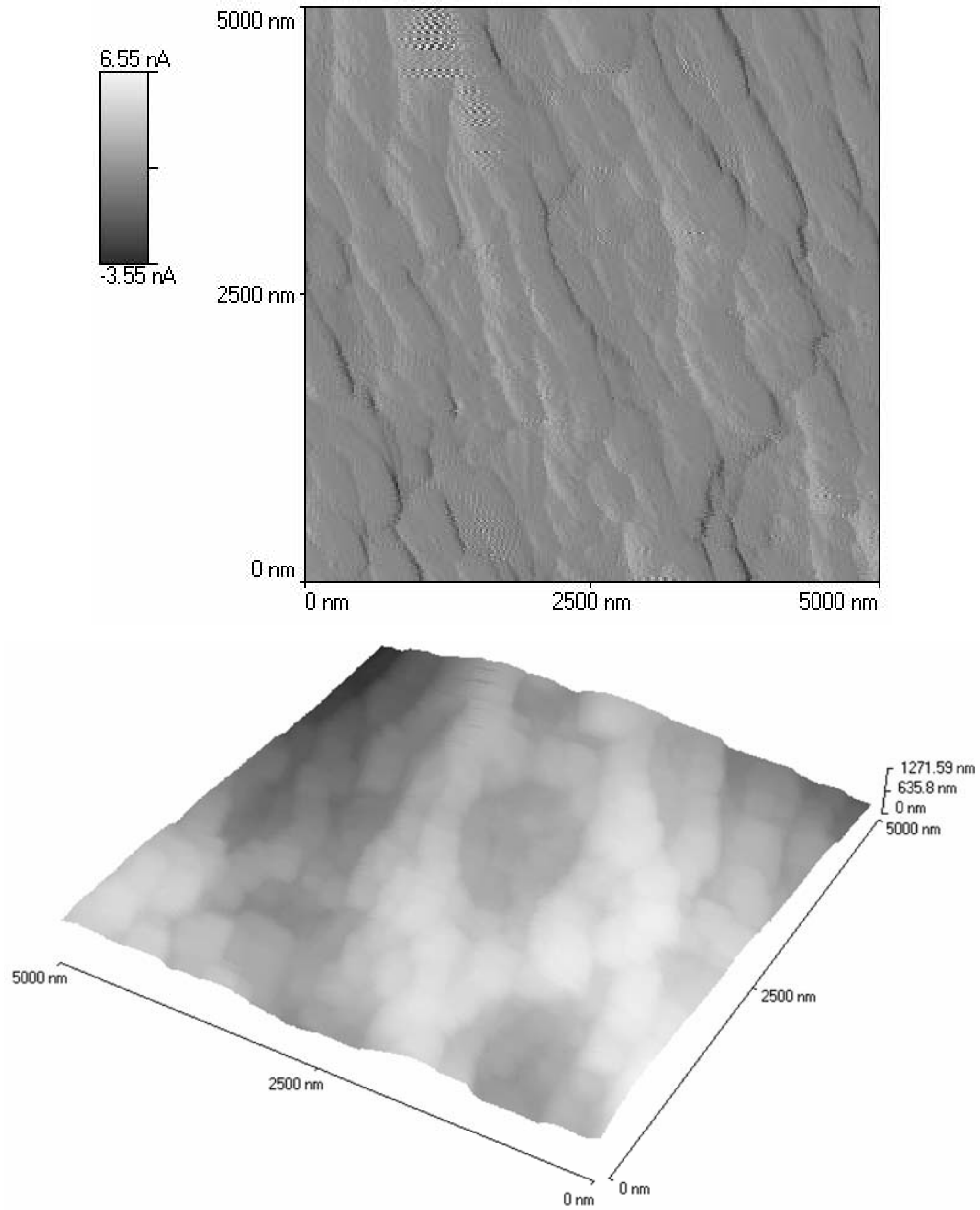

Fig. 6. Simultaneously acquired AFM contact mode (a) error signal, b) 3D-topography images of the A4 alumina film obtained at anodizing temperature T = 313 K, anodizing current density I = 4 A/dm^2, and anodizing time t – 60 min

Table 1 shows a summary of the parameters of the anodising process and the AFM parameters, characterising the surface roughness for several alumina films and also for the parent Al substrate. Surface roughness has been evaluated from topography images using microscope software. The shape of the tip was not taken into account. Surface roughness parameters, known and commonly used, are the average surface roughness R_a and surface root mean square rms. An additional parameter, however, the relative surface area R_{SA}, defined as the ratio of the surface described in 3-dimensional space by the AFM to the 2-dimensional scan range, can give better insight into surface roughness. AFM results for the films obtained at an electrolyte temperature ~293 K are shown in Figs. 2 and 3. These films were prepared at 2 A/dm^2 and 3 A/dm^2 current densities and their thickness were ~25 μm and ~29 μm, respectively. The images of the alumina films obtained at an electrolyte temperature of 303 K and anodising current densities of 2 A/dm^2 and 3 A/dm^2 are shown in Fig. 4 and 5, respectively.

Table 1. Summary of the anodizing process parameters and AFM results for several alumina films and for the Al substrate[1]

Sample	T (K)	I (A/dm^2)	d (μm)	t (min)	R_{SA}	rms (nm)	R_a (nm)
A2	293	2	25	60	1.296	190.52	144.74
A23	293	3	29	40	1.251	174.37	142.45
A32	303	2	33	80	1.331	293.20	197.12
A3	303	3	44	60	1.428	233.71	178.91
A4	313	4	67	60	1.765	480.52	390.43
Al					1.434	658.42	555.44

[1] T – anodizing electrolyte temperature, I – anodizing current density, d – obtained alumina film thickness, t – anodizing time, R_{SA} - relative surface area, rms – surface root-mean-square, R_a – average surface roughness (roughness parameters – without any flattening).

Presented in Figure 6 is the AFM surface topography of the alumina film prepared at the current density of 4 A/dm^2 and at the highest temperature in these experiments, 313 K. It differs considerably from the remaining samples. The line scans across of the AFM topography images for the alumina film and the initial Al substrate are shown in Figures. 7 and 8.

Film thickness increases when both the anodizing current density and temperature are raised. The results presented in AFM images clearly show that alumina films prepared at 293 K and 303 K reveal quite different surface topographies. The surface topographies of the films shown in Figs. 2 and 3, obtained at 293 K, exhibit not very flat and uniform surfaces with many holes (depressions), ranging from one to several columns in diameter. On the other hand, the surface of the films prepared at 303 K (Figs. 4 and 5) are more uniform, with the diameter of holes (or pores) of the order of one column (or smaller). The columnar sizes are estimated to be in the range 0.4–1 μm and were more nonuniform in the films obtained at 293 K.

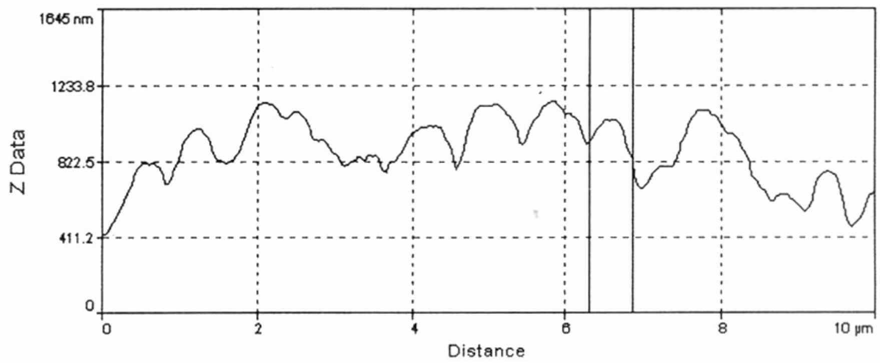

Fig. 7. Line scan across the AFM topography image for the A4 alumina film

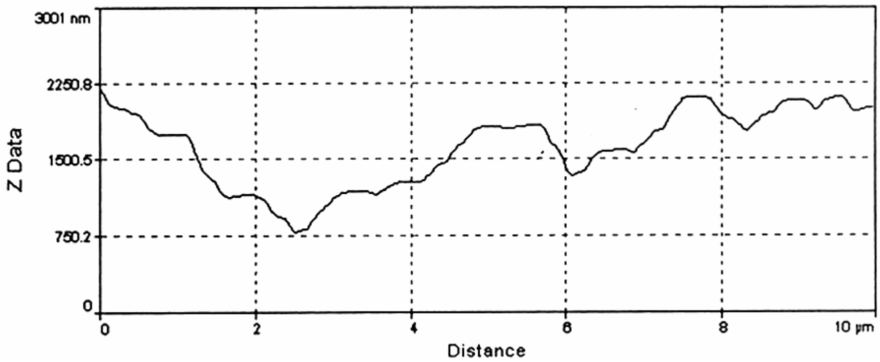

Fig. 8. Line scan across the AFM topography image for the Al substrate

The first results show that the experimental conditions (temperature and current density) are crucial for the final state of the fabricated coatings and especially for the aluminium substrate surface preparation. Prior to anodising, it is essential to clean the surface of dirt, grease oil and, in particular, any skin formed during rolling, drawing or pressing. Anodizing seems to be the growth process which itself can strongly affect the initial roughness of the substrate due to the chemical action of the electrolyte. From AFM images shown in the present paper, one can conclude that the large initial roughness of the aluminium substrates has been slightly cured during the growth of the alumina films in the anodizing process. In all cases, the topography of the alumina films resembles the rough topography of the initial Al substrate, although the roughness parameters, e.g. R_{SA}, for films prepared at 293 K and 303 K are lower than the roughness parameters for the initial Al surface. For films obtained at 303 K, however, these parameters are closer to R_{SA} and for film anodized at 313 K they exceed it.

The anodized alumina thin films exhibit a very distinct columnar growth structure, as can be shown in the SEM images of the film cross-sections. Examples of SEM images of the alumina film cross-sections are shown in Fig. 9, for the A2, A3 and A4 samples, where the columnar growth structure is clearly visible.

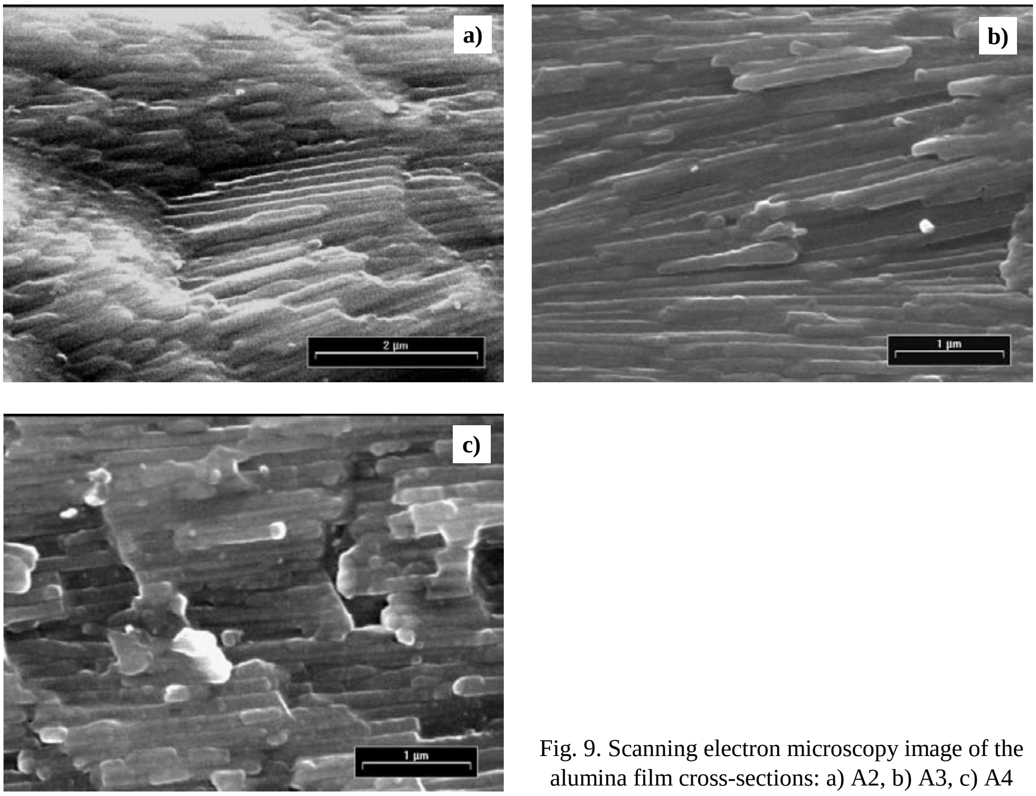

Fig. 9. Scanning electron microscopy image of the alumina film cross-sections: a) A2, b) A3, c) A4

This columnar structure can also be revealed on the alumina film surface as the dome-shaped ends of the columns projecting over the surface and can be imaged by AFM. The presented images show that the AFM technique is a very useful tool for studying thin film morphology, providing information that is equivalent to that obtained by SEM. However, as can be seen in the AFM topography images, especially for the films shown in Figs. 2 and 3, the observed columnar structure may be dominated by the large film surface irregularities mentioned above. Surface topography resembles some initial Al surfaces and the surface roughness R_{SA} is larger than that of the initial Al substrate. It was observed that error signal imaging can gives more details and the surface structure can be seen in areas that appear to be deep dark valleys in the topographic images. In general, alumina film surface topography and roughness can be attributed to the internal film growth structure, initial aluminium substrate irregularities, and to the specific anodizing process itself.

It is known that data obtained directly from AFM images overestimates lateral dimensions, because the obtained image is a combination of the tip and sample interactions. The tip broadening effect, even if it is not immediately obvious in images, is present in all AFM images. If the probe tip is larger than the surface features, then surface roughness measurements will appear smaller than they should be. In this paper, however, the obtained images are acceptable. They contain most of the features of the alumina films surface structure confirmed by the SEM.

The structure of Al_2O_3 oxide layers deposited on aluminium alloys stimulates the application of these layers in machine construction. Special properties of the deposited oxide coatings (e.g., morphology and an increase of the surface area due to micro- and macropores) give a wear and tear resistance guarantee for the upper layer and indicate their preferential use in sliding matchings. The main application of such an oxide layer is cylinder bearing surfaces in non-lubricated air-compressors. In this case, the oxide layer matches with rings made of a material containing polytetrafluoroethylene (PTFE), with a graphite filler in the amount of 15wt. % (TG15-type material). In the period of sliding mating of the oxide layer and TG15-type material the sliding film appears on a surface of the oxide layer in consequence of a frictional transfer of material. The creation of such a sliding film provides very good conditions for the mating of such a matching (friction coefficient $\mu = 0.08$).

The influence of the anodizing process parameters for the application of such an oxide layer in cylinder bearing surfaces in non-lubricated air-compressors was presented in [1] and [9].

4. Conclusions

A method of hard anodic treatment at elevated temperatures has been developed, which does not require an additional cooling. The heat produced during treatment is used to control oxide coating properties. The AFM contact technique was used to study the morphology and roughness of the alumina coating films produced by electrolytic deposition. An X-ray diffraction test has shown that the prepared films are generally amorphous. A small precipitation of a fine-grained crystalline phase, similar to the dispersive alumina gel, has been observed for films obtained at higher temperatures and higher current densities.

Columnar growth of the films has been revealed by the AFM technique and supported by SEM. Differences in surface roughness and in the size and shape of the columns have been clearly observed in the AFM error signal and 3-dimensional topography images. Those differences can be related to the parameters of the anodizing process. Oxide coatings appropriate for application were obtained under carefully selected deposition conditions, which ahead preparation of the films special properties of the deposited oxide coatings (like e.g. structure, with the large surface area due to the micro- and macropores created during the electrolytic process. The following parameters have proved to be optimal for the production of alumina caotings: a current density of 3 A/dm^2 and temperature of 303 K. An increase of the rate of deposition of oxide coating can be achieved by raising the current density to 4 A/dm^2, but then the temperature should also be raised to 313 K [1, 9].

The properties of the films obtained in this way, such as structure, morphology, and an increase in surface area due to the presence of micro- and macropores on the surface during cooperation, are suitable for the creation of sliding plastic films with TG15 protecting oxide coatings from wear. Films of increased porosity are of great interest from the point of view of their potential applications as sliding joints.

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References

[1] SKONECZNY W., TOKARZ A., Wear, 169 (1993), 209.
[2] VANFLETEREN J., VAN CALSTER A., Thin Solid Films, 139 (1986), 89.
[3] BUNSHAH R.F., SCHRAMM R.J., Thin Solid Films, 40 (1977), 211.
[4] VUORISTO P., MANTYLA T., KETTUNEN P., Thin Solid Films, 204 (1991), 297.
[5] OTT A.W., KLAUS J.W., JOHNSON J.M., GEORGE S.M., Thin Solid Films, 292 (1997), 135.
[6] STARK I., STORDEUR M., SYROWATKA F., Thin Solid Films, 266 (1993), 185.
[7] PATEL R.D., TAKWALE M.G., NAGAR V.K., BHIDE V.G., Thin Solid Films, 115 (1984), 169.
[8] THORNTON J.A., Annu. Rev. Mater. Sci., 7 (1977), 239.
[9] SKONECZNY W., KACAŁA Z., Exploitation Problems of Machines, 3 (1994), 443.
[10] ROSENBLUM B., *Tribo-Stimulated Emission From Oxide Covered Metal Surfaces*, University Microfilms International, Ann Arbor, MI, USA, 1976.

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