

The Preparation of Combined Aluminium Oxide Coatings on Aluminium Substrate

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The preparation and properties of combined aluminium oxide coatings have been investigated. The coating has been prepared in two steps. First, aluminium substrate was anodically oxidized. In the next step the anodized film has been coated by the sol-gel method. The conditions of forming coatings without shrinkage were obtained empirically. It was found out that the film prepared by the sol-gel method has the same crystal structure as the oxide film prepared by the anodic oxidation. The thickness, phase analysis, and surface microstructure of obtained coatings were determined.

The coatings prepared by using of various methods can improve properties of functional coatings, for instance they can increase the corrosion resistance or improve mechanical properties [1]. In the present work, preparation and properties of aluminium oxide coatings formed by the combination of anodic oxidation and sol-gel process are discussed.

Anodic oxidation of metallic aluminium is an electrolytical process for production of porous alumina, which improves physical and chemical properties of coating and increases the field of application of aluminium [2, 3]. The porous layer only marginally improves the corrosion resistance of the underlying aluminium. Hence a method of sealing the pores is required. There are several possibilities how to carry out the process. The hydrothermal method is done by immersing anodized samples into boiling water. The so-called cold sealing uses the reactions of the porous alumina layer with nickel and fluoride ions [4–6]. The sol-gel method is a new up to now unpublished way of sealing of porous anodized aluminium. This procedure provides an ability to reach new properties of the combined alumina coatings.

The sol-gel method is based on the transformation of the metal alkoxide solution into gel during hydrolysis and polycondensation and continuing transformation into glass and ceramics [7]. The outstanding homogeneity of obtained materials, a relatively low reaction temperature (in our case lower than 400°C), and ability of forming new materials and composites are the main advantages of glass and ceramics preparation. The important sol-gel applications include thin glass or glass crystalline coatings. The layers on various substrates (glass, ceramics, metal) improve chemical and physical resistance or change the optical properties of the substrate. The most important advantage

of the sol-gel method is the ability to control the microstructure of the deposited film precisely, *i.e.* the pore volume, pore size, and surface area [8].

The aim of this work was to find out the conditions for preparation of combined aluminium oxide coatings without shrinkage and cracks. Dependence of the thickness, structure, phase composition, and the conditions of preparation of the layer was investigated as well.

EXPERIMENTAL

The coating has been prepared gradually, in two steps: first, aluminium substrate was anodically oxidized, next, the film has been formed by sol-gel dip coating technique [9].

Anodic oxidation has been carried out in 20 mass % sulfuric acid solution under following conditions: the bath temperature was kept in the range 18–20°C, the time of anodic oxidation was 15–40 min, and the current density was 1.5 A dm⁻². Aluminium pieces (purity 99.5 %) of dimensions 60 mm × 20 mm × 0.75 mm were used as substrate. Before anodic oxidation aluminium samples were degreased in an alkaline solution (Synalod 80, 50 g dm⁻³) at 70°C. In the next step the samples were etched in sodium hydroxide solution (100 g dm⁻³) at 50°C for 5 min, followed by the satin etching in the mixture of sodium hydroxide (90 g dm⁻³), sodium nitrate (109 g dm⁻³), and saccharose (1 g dm⁻³) at 50°C, brightening in nitric acid solution (400 g dm⁻³) at 50°C was realized. Between each stage of the pretreatment, samples were thoroughly rinsed.

Oxide film was formed by the anodic oxidation using the procedure described above. The samples were rinsed, dried, and dipped into aluminium oxide sol

solution. This solution was prepared in two forms: alkoxide solution and colloid solution. Alkoxide solution is based on partially hydrolyzed aluminium oxide solution obtained by mixing aluminium alkoxide with about 0.4–1 mol of water per 1 mol of aluminium alkoxide in the presence of sufficient amount of alcohol. The final sol solution contained up to 10 mass % of alumina. The mixture is heated until clearing, which usually requires a temperature of 60 °C [8]. Then sufficient amount of additional water is added to bring the amount of substance of moles of water per 1 mol of alkoxide up to at least about 2 mol. A polymerized alumina glass can be prepared from the sol described above by heating up to the temperature of 400 °C [10]. The Yoldas process consists of hydrolyzing an aluminium alkoxide, $\text{Al}(\text{OR})_3$ (usually $\text{Al}(\text{O}i\text{Bu})_3$), in a large excess of water ($r = 100\text{--}200$, r being the mole ratio of water to $\text{Al}(\text{O}i\text{Bu})_3$) at 80–100 °C followed by peptization with a mineral acid (HNO_3) to yield a stable particulate sol. Gelation is generally achieved by concentration of the sol *via* evaporation [7].

In this work the Yoldas process was used. The samples were immersed into the sol and withdrawn vertically with the speed of $u_0 = 11.7 \text{ cm min}^{-1}$. Then the solvent was evaporated at temperature of 80 °C for 10 min. Dried samples were heated for 15 min at 400 °C in air [7].

The first series of experiments served like a proof of realization of combined alumina coatings on the aluminium substrate. It was found out that the prepared combined films cracked when heated. Therefore in the next series of experiments the conditions for preparation of combined alumina coatings which would neither shrink nor crack were investigated. Different combination of the time of anodic oxidation, concentration of the sol solution, speed of withdrawing the samples from the sol solution, and the conditions of heating were tested.

The time of anodic oxidation ranged from 15 min to 40 min. The mixtures of $\text{Al}(\text{O}i\text{Bu})_3$ with water with the mole ratio $r = 1:100$, 1:150, 1:200 were used. Speeds of withdrawing were $u_0 = 1.6 \text{ cm min}^{-1}$, 4.8 cm min^{-1} , and 11.7 cm min^{-1} , respectively. The conditions for drying were not changed. On the basis of DTA analysis of the samples it was found out that the optimal conditions for drying are 110 °C and time of 30 min. Calcination of the samples was realized for 15 min at the temperature of 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C, respectively. The various approaches of the heat treatment were used:

a) Gradual heating from ambient temperature to the goal temperature with the heating rate 10 °C min^{-1} or 30 °C min^{-1} , calcination at the determined temperature for 15 min, cooling – spontaneous or controlled (10 °C min^{-1} or 50 °C min^{-1} cooling rate).

b) No preheating (the sample was placed into the oven heated to the chosen temperature), calcination at the determined temperature for 15 min, cooling –

spontaneous or controlled (10 °C min^{-1} or 50 °C min^{-1} cooling rate).

c) No preheating, calcination at the determined temperature for 15 min (thermal shock realized only with giving into and taking out from the furnace), abrupt cooling to the ambient temperature.

The surfaces of the coating films were observed visually and by scanning electron microscopy (SEM) using the model Jeol JSM 35 or Tesla BS 300. Microstructure and phase content composition of alumina oxide coating were determined by the X-ray diffraction (XRD) using the model Dron UM1. Thickness of the surface film was determined gravimetrically and it was also measured on the cross-sections of the samples by X-ray microanalyzer Jeol JXA-840A.

RESULTS AND DISCUSSION

The experimental results are summarized in Tables 1 and 2. Quality of prepared anodic film on aluminium substrate was evaluated visually. In Table 1, properties of the films prepared by anodic oxidation of aluminium are presented. In Table 2, properties of films prepared by combination of electrolytic anodizing and sol-gel procedure are given.

In the first series of experiments we were concentrated upon the realization of combined alumina coatings on aluminium surface. Anodic oxidation has been carried out in sulfuric acid electrolyte (20 mass %) for 40 min ($j_A = 1.5 \text{ A dm}^{-2}$). The other conditions of the treatment of the oxide layer are given in Table 1.

Combined alumina coatings were of good quality when the second film was prepared by the Yoldas process [8]. When we used the colloid method we did not succeed in preparation of compact film without cracks (see Fig. 1). Cracking of the surface film may be caused by different values of the coefficient of thermal expansion. The value of coefficient of thermal expansion of aluminium is $23.8 \times 10^{-6} \text{ °C}^{-1}$, the coefficient of thermal expansion of the anodized film is only about 20 % of that of aluminium and for the polycrystalline alumina the coefficient of thermal expansion is $7 \times 10^{-6} \text{ °C}^{-1}$ [2]. The problem of cracking was solved by changing of experimental conditions.

At first, the influence of chosen heat regimes on microstructure of anodically oxidized aluminium substrate was studied (see Table 1). The time of anodic oxidation as well as different heat regimes with various temperatures of calcination were altered. Varying time of anodic oxidation the thickness of the anodic oxide coating was changed.

We can conclude that heating did not influence coating microstructure. The heat shock (realized by giving the sample into furnace, its calcination and immediately taking it out from the furnace) caused the failure of surface coating. The spontaneous cooling regime from the temperature of calcination to the laboratory temperature has positively influenced the mi-

Table 1. Dependence of the Quality of Alumina Coating Prepared by Anodic Oxidation of Aluminium Substrate on the Conditions of Preparation

t_{AO}/min	$\theta_{calc}/^{\circ}\text{C}$	Heat treatment	Surface evaluation	
40	400	H, —	S	
		—	S	
		H, C	S	
		C	S	
		350	H, —	S
			—	S
	H, C		S	
	300	C	S	
		H, —	S	
		—	S	
	250	H, C	S	
		C	S	
		H, —	S	
		—	S	
		H, C	S	
		C	S	
	200	H, —	S	
		—	S	
		H, C	N	
		C	N	
		150	H, —	N
			—	N
	H, C		N	
	180	C	N	
H, —		N		
—		N		
15	400	H, —	S	
		—	S	
		H, C	N	
		C	N	
		350	H, —	S
			—	S
	H, C		N	
	300	C	N	
		H, —	N	
		—	N	
	250	H, C	N	
		C	N	
		H, —	N	
		—	N	
		H, C	N	
		C	N	
	25	400	C	S
		350	C	S
		300	C	S
	30	400	C	S
		350	C	S

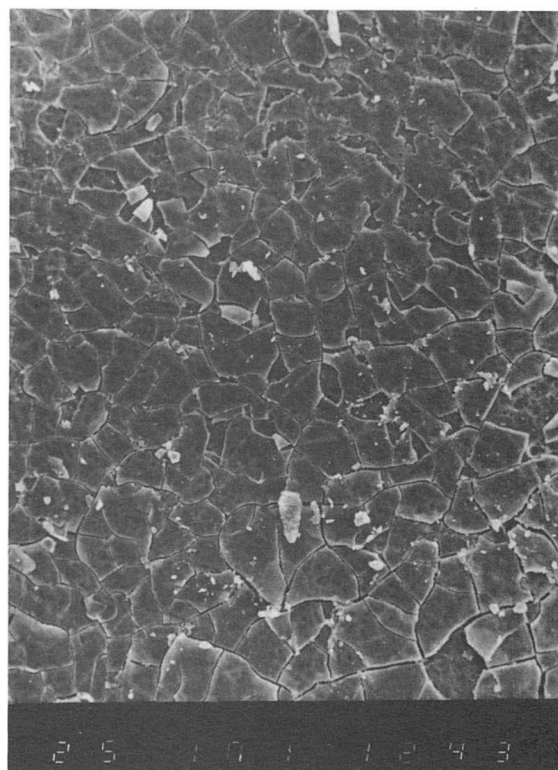
t_{AO} – time of anodic oxidation, θ_{calc} – calcination temperature, H – heating, C – cooling, — – direct giving of the sample into the furnace and cooling at ambient temperature, S – shrinkage, N – good quality film without shrinkage and cracks.

crostructure of prepared samples. These microstructures were evaluated visually and by scanning electron microscopy (SEM) (Fig. 2).

We found out no shrinkage after 40 min anodic

Table 2. Visual Evaluation (S – shrinkage, N – no shrinkage) of Combined Alumina Coatings in Dependence on Time of Anodic Oxidation t_{AO} and Temperature of the Sol-Gel Film Calcination θ_{calc}

t_{AO}/min	$\theta_{calc}/^{\circ}\text{C}$	Surface evaluation
15	350	S
	300	N
	250	N
	220	N
20	350	S
	300	N
	250	N
	220	N
25	350	S
	300	S
	250	S
	220	N
30	350	S
	300	S
	250	S
	220	S

**Fig. 1.** Microstructure of combined aluminium oxide coatings prepared by anodic oxidation at the temperature 20°C for 40 min at the current density 1.5 A dm⁻² and by the sol-gel method at the temperature of calcination 400°C (× 100 magn.).

oxidation at the temperature of calcination ranging between 150–200°C followed by spontaneous cool-

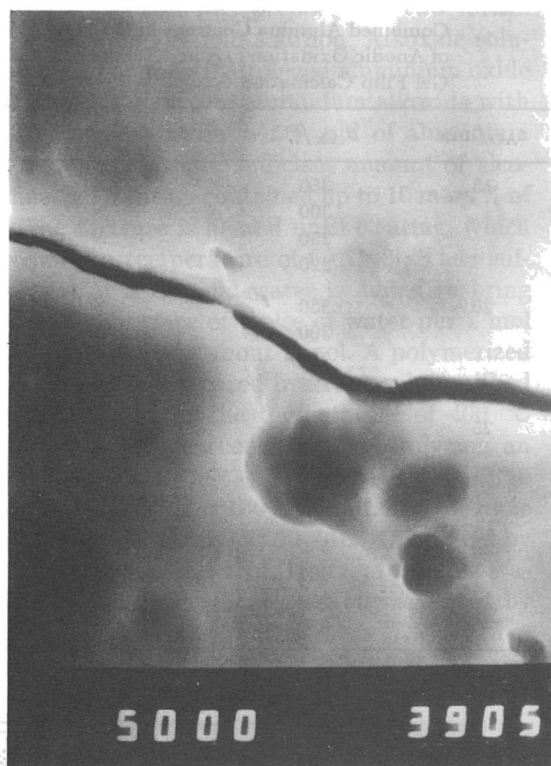


Fig. 2. Microstructure of the surface of combined alumina coatings for anodic oxidation time 15 min and calcination temperature 400°C for the sol-gel process ($\times 5000$ magn.).



Fig. 4. Microstructure of surface coating without shrinkage for 20 min anodic oxidation and temperature of calcination for the sol-gel process of 250°C ($\times 5000$ magn.).

ing. The film prepared by anodic oxidation for 40 min cracked if it was calcinated at 400°C. Besides the conditions of calcination the influence of thickness of the anodized layer on the quality of the film was investigated as well. Thinner anodic film was prepared by

15 min anodic oxidation followed by calcination at the temperature 400°C and spontaneous cooling. No shrinkage of the alumina film has been observed.

According to DTA and TG curves (Fig. 3) water

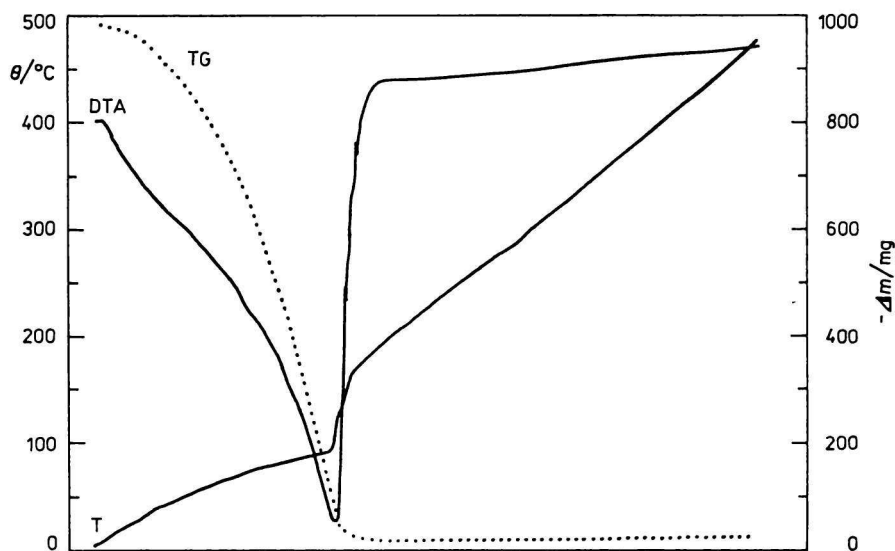


Fig. 3. DTA, TG, and T record of Al_2O_3 sol prepared according to Yoldas.

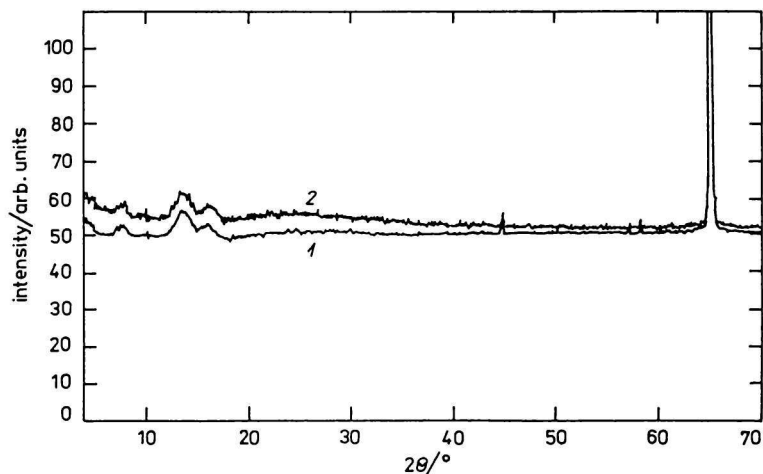


Fig. 5. X-Ray diffraction patterns of anodically oxidized (1) and sol-gel dip deposited (2) aluminium substrate.

and organic molecules of solvent have been removed in the temperature range 120–220 °C (part I–II). In the next series of experiments the anodized layer was covered by sol-gel film. However, when we used the thermal treatment described above, the surface film cracked. Therefore we investigated different conditions of alumina coatings on aluminium substrate which would yield a good quality surface film. The time of anodic oxidation was in the range of 15–40 min, the temperature of calcination was 250–400 °C. According to the experimental results shown in Table 2, we can conclude that optimal time of anodic oxidation equal to 20 min and calcination temperature of 250–300 °C is convenient for preparation of combined alumina coatings without shrinkage (Fig. 4). Statistic evaluation of obtained results confirmed that for preparation of good quality combined coatings the temperature of 250 °C is optimal.

XRD pattern of heat-treated anodized aluminium substrate is shown in Fig. 5. Mixture of transition aluminas was identified, especially the peaks of transition δ - Al_2O_3 . The peaks of aluminium metal are evident, too. Because of preferential orientation of planes only some peaks were recorded. It is evident that the crystal structure of alumina prepared by anodic oxidation is the same as that of alumina prepared by the sol-gel method.

The thickness of the films was determined by different ways. The thickness of sol-gel alumina film was determined gravimetrically (at the density of alumina 3.99 kg m^{-3}). It has been found that the procedure used in this work gives the film with the thickness of $(0.20 \pm 0.05) \mu\text{m}$. (Principle correctness of this result has been confirmed by SEM investigation of cross-section of the film.)

Thus it can be stated that combined alumina coatings prepared by a two-step process involving the anodic oxidation of aluminium substrate and the sol-

gel method have been developed. Surface film without shrinkage was formed at the time of anodic oxidation of 20 min and the temperature of calcination of 250 °C, followed by spontaneous cooling. The silver dull surface coating without shrinkage was obtained. Nowadays we investigate the properties of this coating type. X-Ray analysis has shown that a thin polycrystalline film consists of a mixture of transition aluminas. The thickness of the sol-gel coating determined gravimetrically is approximately $0.2 \mu\text{m}$.

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