Corrosion Resistance and Quality of Sealed Porous Alumina Coatings*

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The sealing of porous anodic oxide films on aluminium by the use of sol-gel method has been proposed as an alternative to the hydrothermal sealing method or cold impregnation.

Corrosion resistivity of samples prepared by these various sealing methods was investigated using accelerated corrosion test (STN 03 8131) in the condensation chamber. The sealing quality and continuity of prepared samples were also investigated (tests ISO 3210 and ISO 2085). The obtained results were compared and evaluated. Hydrothermally sealed anodized samples on aluminium give qualitative, continuous coatings with high corrosion resistivity. The high corrosion resistivity and continuous coating is property of anodized coating treated by the sol-gel method. The corrosion resistivity of samples sealed by cold impregnation is low.

Aluminium is a highly reactive material. To improve its durability and resistance to corrosion it is often subjected to anodization whereby a thick oxide film, typically up to 25 μm in thickness, is grown on the aluminium by making it the anode in an electrochemical system [1]. Anodizing of aluminium produces a very porous anodic film. This film, depending on the anodizing conditions, has an enormous surface area per unit of projected area. This porosity and high surface area contributes to forming a surface with great chemical activity. Hence a method of sealing is required. Sealing has been defined as a process which by absorption, chemical reaction or other mechanism increases the resistance of an anodic coating to staining and corrosion, improves the durability of the colour produced in the coating or imparts other desirable properties [2].

There are several methods for sealing of anodized aluminium (organic solutions, steam, oil, lacquer). Traditionally sealing has been done by immersing anodized samples in boiling water, that is the hydrothermal sealing [3]. In recent years alternative methods were investigated because of expensive energy of hydrothermal sealing, for instance the cold sealing (cold impregnation) based on the nickel and fluoride ions at ambient temperature of solution [1].

To obtain specific properties of prepared material, the coating prepared by the sol-gel method was deposited on anodized aluminium [4]. 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 [5].

The qualities of film surfaces sealed by hydrothermal method, cold impregnation and by the sol-gel method on anodized aluminium, respectively, were tested. The quality of sealing (ISO 3210), corrosion resistivity coating (STN 03 8131), and the continuity of film (ISO 2085) were investigated.

The aim of this work was investigation of corrosion resistance of alumina coatings prepared by the anodic oxidation and by the sol-gel method on aluminium substrate and the comparison of the quality of combined coatings with hydrothermally or cold impregnation sealed anodized aluminium.

EXPERIMENTAL

Anodic oxidation of all samples was carried out in 20 mass % sulfuric acid solution under following conditions: the bath temperature was kept in the range θ_K = 18—20 °C, the time of anodic oxidation was τ_{AO} = 20 min, 25 min, and 40 min, respectively, and the current density was j_A = 1.5 A dm^{-2} Aluminium pieces (purity 99.5 %) of dimensions 5 cm × 5 cm × 0.75 cm were used. Between each stage of pretreatment described in [4], samples were thoroughly rinsed.

After forming the oxide film by the anodic oxidation the samples were rinsed, dried and sealed by three ways: hydrothermally, by the cold impregnation, and

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by the sol-gel method. Hydrothermal sealing was realized in boiling distilled water during $\tau_S = 15$ min. Cold impregnation was realized in solution containing nickel ion and fluoride ion in the ratio 2 : 1 (we used nickel oxalate and potassium fluoride because of these ions). The sealing by cold impregnation was carried out during $\tau_S = 10$ min at $\theta_S = 30\,°C$. After cold impregnation the samples were exhibited to the effect of atmosphere and after certain time the test ISO 3210 was realized. The influence of ageing time τ_{AG} on the quality of sealed surface was searched. The sol-gel film was prepared by dipping into alumina sol solution according to Yoldas [5]. For preparation of sol different mole ratios of aluminium butoxide $Al(OBu^s)_3$ to water $x_r = 1:100$, $1:150$, $1:200$ were used. The speed of withdrawing was constant $u_0 = 11.7$ cm min^{-1}. The exact conditions of preparation of Al_2O_3 film by the sol-gel method on anodic alumina have been described in [4].

The sealed samples were evaluated by the tests ISO 3210, STN 03 8131, and ISO 2085. Set of six samples for each type of sealing was used for testing.

The first test ISO 3210 is based on the use of the chromic acid—phosphoric acid mixture to determine coating mass. This mixture consists of phosphoric acid ($c = 35$ mol dm^{-3}), chromic acid ($\rho = 20$ g dm^{-3}), and distilled water. The test is done at temperature $\theta_I = 37\,°C$. Time of immersion is $\tau_I = 15$ min. Coefficient K is decisive for determining the quality of sealed surface and should not exceed the value $K = 30$ mg dm^{-2}.

$$K = (m_1 - m_2)/S \qquad (1)$$

The m_1 is mass of sample before and m_2 after immersion into phosphoric acid—chromic acid solution per area unit S.

The second test STN 03 8131 is realized in condensation chamber at temperature $(35 \pm 2)\,°C$ and 100 % humidity. The mass changes Δm and the microstructure of surface films were followed as a function of time after 1, 2, 3, 7, 10, 14, 16, 21, and 28 days with expectation of mass stabilization. The mass changes Δm were obtained by weighting in the determined range according to the test and the microstructure of surface films was evaluated visually.

The third one, ISO 2085, investigates film continuity. A chemical method of detecting breaks in the anodic coating involves immersion in copper sulfate solution. The reagent does not affect an anodic film, black copper spots appear where no anodic film is present. This method will also detect cracks in the coating caused by overheating or bending.

RESULTS AND DISCUSSION

At first, the test ISO 3210 was used. The results are shown in Table 1. We can see that hydrothermally sealed anodized samples exhibit high quality of sealed

Table 1. Dependence of the Coefficient K on the Way of Sealing. (τ_{AO} is the Time of Anodic Oxidation, τ_{AG} is the Time of Ageing)

Method	τ_{AO}/min	K/(mg dm^{-2})
Hydrothermal sealing	20	20.0
	25	24.6
	40	17.6
	τ_{AG}/h	K/(mg dm^{-2})
Cold impregnation (sealing)	5	33.5
	24	20.2
	168	16.3
	336	12.1
	672	9.75
	n(Alkoxide):n(Water)	K/(mg dm^{-2})
Sol-gel sealing	1:100	240
	1:150	216
	1:200	245

surface. The value of coefficient K does not exceed the recommended one (30 mg dm^{-2}) for this type of samples. The dependence of coefficient K on time of anodic oxidation was important for hydrothermal sealing. The influence of time of ageing τ_{AG} on the quality of prepared surface was dominating for samples anodically oxidized and sealed by cold impregnation. The best results of coefficient K for this type of samples were reached after $\tau_{AG} = 24$ h. The film prepared by the sol-gel method was dissolved during the testing process. The obtained results for all types of sealing are caused by the different mechanism of hydrothermal, cold, and sol-gel sealing. During hydrothermal sealing the original anodic Al_2O_3 is partly transformed into a hydrated oxide boehmite $AlO(OH)$ and the volume of coating increases rapidly. As to cold sealing, this gradual diffusion process is long-term. The Al_2O_3 prepared by the sol-gel method is glassy, so the coating was dissolved in phosphoric acid—chromic acid solution.

Next, test according to STN 03 8131 was carried out. The mass change per area unit $\delta m_s = \Delta m/S$ was counted from measured values. Microstructure of samples was investigated according to STN 03 8101. We can see the results of mass change in Figs. 1—3. They show the dependence of δm_s on time. The programme MICROCAL ORIGIN was used for evaluation of the obtained results applying the equation

$$y = P_1(1 - \exp(-P_2 x)) \qquad (2)$$

where P_1 and P_2 are parameters of the tested function. We can rewrite eqn (2) as the dependence of mass change per area unit δm_s vs. time t, while P_1 means the supposed value of maximal mass change per area
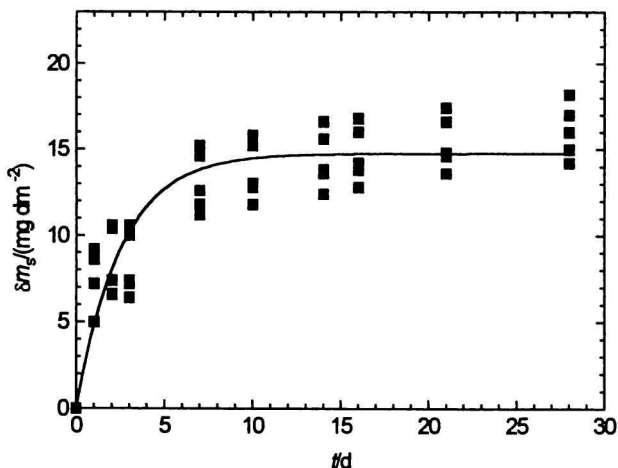
Fig. 1. Dependence of mass change per area unit ($\delta m_s = \Delta m / S$) on time for anodized aluminium ($\tau_{AO} = 20$ min) sealed by the *sol-gel* method. $n(Al(OBu^s)_3): n(H_2O) = 1:100$.
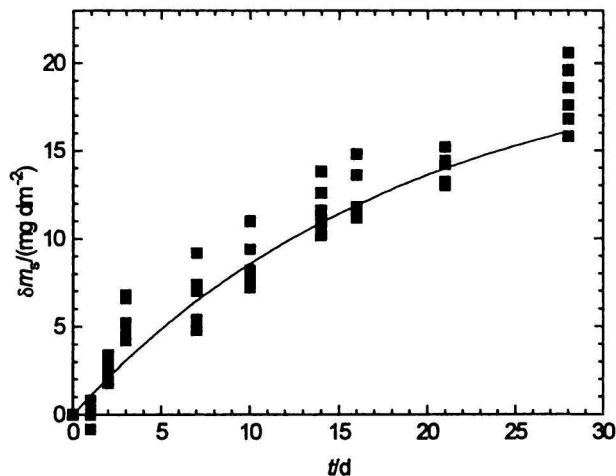

Fig. 3. Dependence of δm_s on time for anodized aluminium ($\tau_{AO} = 40$ min) sealed by the *cold impregnation* method.
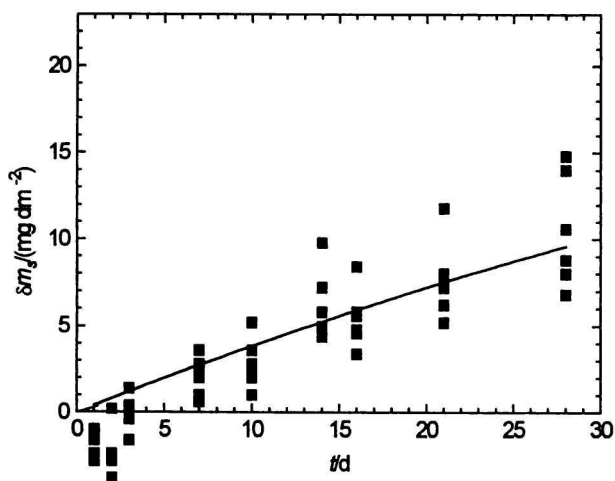

Fig. 2. Dependence of δm_s on time for anodized aluminium ($\tau_{AO} = 40$ min) sealed by the *hydrothermal* method.

unit $\delta m_{s,\,max}$ and P_2 is the rate constant k.

$$\delta m_s = \delta m_{s,\,max}(1 - e^{-kt}) \qquad (3)$$

This equation was chosen because of the presumed corrosion behaviour of samples. We assumed that after certain time corrosion-resistive coatings are stable as to mass change per area unit and we needed exponential function beginning in point [0, 0]. We have found out by statistical evaluation of the obtained dependences that $\delta m_{s,\,max}$ exists. $\delta m_{s,\,max}$ is the value to which mass changes per area unit are limitedly put near.

As we can see from Table 2, the values $\delta m_{s,\,max}$ are approximately 15 mg dm^{-2} for sol Al$_2$O$_3$ of the composition $n(Al(OBu^s)_3):n(H_2O) = 1:150$ and 1:200.

If the solution ratio $n(Al(OBu^s)_3):n(H_2O) = 1:100$, mass stabilization begins at 20 mg dm^{-2} Fig. 1 shows the typical course of anodized aluminium sealed by the sol-gel method.

The values $\delta m_{s,\,max}$ are 15 mg dm^{-2} ($\tau_{AO} = 40$ min) and 10 mg dm^{-2} ($\tau_{AO} = 20$ min) for hydrothermal and 23 mg dm^{-2} ($\tau_{AO} = 40$ min) and 10 mg dm^{-2} ($\tau_{AO} = 20$ min) for cold sealing, respectively. The behaviour of sealed surfaces in the condensation chamber is similar. During first three days initial decrease of sample mass occurs and after this time we can observe mass gains (Figs. 2 and 3).

The visual evaluation confirms obtained results. The sol-gel anodized samples do not change their microstructure. We found out blooming on hydrothermally sealed samples for time of anodic oxidation $\tau_{AO} = 20$ min, 40 min. Anodic coatings sealed by cold impregnation have been damaged for both times of anodic oxidation $\tau_{AO} = 20$ min, 40 min. It is a consequence of the mechanism for cold sealing. As fluoride ions enter the pores, a place exchange mechanism occurs causing a shift in the local pH which is sufficient to cause nickel ions to precipitate. The nickel hydroxide blocks the pore mouths. A slow step then occurs whereby water from the atmosphere diffuses into the film, hydrating the film and causing general pore blocking. In this case, in the condensation chamber, corrosion reaction takes place. We can observe it from decreasing of mass and from the visual evaluation. Then anodic Al$_2$O$_3$ reacts with water to fill the pores. This reaction is realized after corrosion reaction.

As to the sol-gel type of sealing on anodized aluminium, a new mechanism is put forward. Al$_2$O$_3$ coating prepared by the sol-gel method copies anodic Al$_2$O$_3$ and partially the pores of anodic Al$_2$O$_3$. The mass of samples is increased by the reaction of com-

Table 2. The Values of Eqn (2)

Method	$\delta m_{s, \, max}/(\text{mg dm}^{-2})$	Error of $\delta m_{s, \, max}$	k/d^{-1}	Error of k
HT 40 min	14.3609	8.4888	0.0311	0.0252
HT 20 min	9.3386	2.2307	0.0616	0.0265
SI 40 min	23.1787	2.2904	0.0493	0.0079
SI 20 min	13.3148	8.8159	0.0345	0.0325
SG 1:100	19.9167	0.3318	0.4251	0.0308
SG 1:150	14.9797	0.3041	0.1281	0.0071
SG 1:200	14.7912	0.4029	0.3863	0.0449

The abbreviations of the used sealing methods: HT – hydrothermal sealing; SI – cold impregnation; SG – sol-gel method.

bined coating with humidity. This reaction means the passivation of coating without marks of damage and is connected with mass gains. After certain time the mass of combined coating Al_2O_3 on aluminium substrate remains constant.

As to the hydrothermal sealing at the beginning it is the decreasing of mass and later the mass rises. The values $\delta m_{s, \, max}$ are lower in comparison with the sol-gel method: 15 mg dm^{-2} ($\tau_{AO} = 40$ min) and 10 mg dm^{-2} ($\tau_{AO} = 20$ min) but there are high deviations of $\delta m_{s, \, max}$ and of rate constant (Table 2). The deviations of $\delta m_{s, \, max}$ and of rate constant (Table 2) were obtained using the programme MICROCAL ORIGIN for eqn (3). The mass gain in this case is caused at the first waste arisen by corrosion reaction and next by reaction of sealed anodic Al_2O_3 with air humidity.

Finally, the test ISO 2085 has been realized. The evaluated sealed surfaces have been divided in continual coatings, partially continual coatings, and uncontinual ones. The continual coatings are coatings without damage and released copper, partially continual ones are partially damaged coatings, and uncontinual coatings contain unsealed pores. Aluminium substrate anodized for 40 min sealed hydrothermally is taken like standard. The samples are according to this test continual as well as anodized aluminium treated by the sol-gel method. Anodized aluminium sealed by the cold impregnation is partially continual coating. The copper appears on this surface. It is caused by gradual diffusion of nickel ions into pores of Al_2O_3. The exchange of nickel and copper ions proceeds.

We can conclude (Table 3) that hydrothermally sealed anodized samples from aluminium are convenient for all types of tests. This type of sealing gives qualitative, continual coatings with high corrosion resistivity. The high corrosion resistivity and continual coating are properties of anodized coating treated by the sol-gel method. But the quality of sealing evaluated according to the test ISO 3210 is very low. In comparison with hydrothermally sealed anodized aluminium, the corrosion resistivity of anodized aluminium deposited by sol-gel is higher as it can be seen from Figs. 1 and 2 and from Table 2. The same

Table 3. Evaluation of the Quality of Anodized Samples Sealed by Various Ways

Testing method	Sealing method	Observation
ISO 3210	Hydrothermal	High quality
	Cold impregnation	Average quality
	Sol-gel	Low quality
STN 03 8131	Hydrothermal	Average quality
	Cold impregnation	Low quality
	Sol-gel	High quality
ISO 2085	Hydrothermal	High quality
	Cold impregnation	Low quality
	Sol-gel	High quality

was seen from visual evaluation of microstructure of searched samples. As to the results from the test ISO 3210 there must be realized more tests to state excellent corrosion resistance of anodized aluminium sealed by usage of the sol-gel method. Anodized aluminium sealed by cold impregnation gives results in accordance with theory of this type of sealing [1]. The coating is stable after 24 h, partially continual and its corrosion resistivity is low.

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