The Teflon impregnation of anodic coating onto aluminium substrate

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Introduction

Aluminium and its alloys, due to their low density and good mechanical properties, especially after heat treatment, are widely applied in the aircraft and automotive industry. In order to enhance the corrosion resistance of aluminium and its alloys, thick oxide coatings are produced in the anodizing process. The anodic coatings improve also the adhesion of paints. However, their hardness and abrasion resistance is insufficient. Therefore, hard anodic coatings are produced onto aluminium and its alloys. The characteristic properties of hard anodizing are: low temperature of the bath (usually below 273 K), high current density (over 2.5 A·dm^{-2}) [1]. The thickness of hard anodic coatings should be over 51 μm [2]. Elements anodized in such a process are widely applied in the aircraft and automotive industry (*e.g.* pistons and cylinders of reciprocating engines, elements of hydraulic systems) [1]. However, the tribological properties of the hard anodic coatings need further improvement.

The characteristic properties of abrasion resistant material are high hardness and low friction coefficient. The former achieves 500 HV for the hard anodic coatings and depends on the chemical composition of the alloy. The latter in turn usually equals to *c.a.* 0.25. The significant improvement of the abrasion resistance may be achieved by means of decreasing of the value of friction coefficient. Therefore, hard anodic coatings are impregnated with teflon (polytetrafluoroethylene PTFE), graphite or molybdenum disulphide MoS$_2$. For instance introduction of teflon particles to the anodic coating enables achieving the value of friction coefficient as low as 0.13 [5, 17–19]. What is more, besides improvement of the tribological properties, teflon ensures good corrosion resistance and hydrophobicity of anodic coatings. The latter helps to avoid deposition of ice on transmission line wires (icephobic properties) [3–5].

Anodic coatings on aluminium are porous. The diameter of pores depends on chemical composition of the bath, temperature and voltage applied. It was shown that in moderately concentrated solution of H$_2$SO$_4$ (165 g·dm^{-3}) at 278 K the diameter of the pores is within the range from 17 to 20 nm [1, 5]. Hard anodic coatings are produced in more concentrated solutions, at lower temperature, thus, the diameter of the pores is smaller. On the one hand, it is stated, that the impregnation of anodic coating is basically introduction of teflon particles to the pores of the coating. However, the particles in commercially available teflon suspensions are bigger than the size of the pores, *i.e.* above 100 nm (DuPont, Dyneon 3M, RO-59 Inc.). Thus, they cannot penetrate into the porous anodic coating. The teflon coating on the Al$_2$O$_3$ is rather formed. Its adhesion to the anodic coating is weak – via the van der Waals bonding [6]. On the other hand, impregnation is sometimes miscalled sealing. The nature of the latter is chemical transformation of anhydrous aluminium oxide (γ-Al$_2$O$_3$, γ'-Al$_2$O$_3$, η-Al$_2$O$_3$), formed during anodizing, to boehmite AlO(OH) at elevated temperature (> 353 K) [1, 7]. It is usually realised in the water vapour, boiling deionized water, water solutions of Ni(II) and Co(II) salts as well as Cr(VI) [7, 8]. The sealing of the anodic coatings is often applied in order to improve the corrosion resistance, however, the tribological properties are deteriorated. Thus, sealing is not used for hard anodic coatings.

The impregnation of anodic coatings may be realised simply by immersion of the element into the suspension of teflon particles. The teflon coating is formed via electrostatic attraction between the aluminium oxide and the particles. It is known that the surface of metal oxides in water solutions is electrically charged due to protonation and deprotonation of terminal oxide ions exposed to the surface. The potential difference between solid and electrolyte is called zeta potential ξ. It depends on the pH value *i.e.* decreases monotonically with increasing pH. The pH value, for which the electrical charge is zero, is called the isoelectric point (IEP). For aluminium oxide, the zeta potential equals to 0 at pH = 8. The pH value depends on both the chemical composition of aluminium alloy and the chemical composition of the anodizing bath [1, 9]. Thus, the surface of Al$_2$O$_3$ is positively charged for pH < 8 and negatively for pH > 8. The electrical charge of teflon particles, which results from the surfactants (anionic or cationic) adsorbed onto their surface, should be negative or positive, respectively.

The impregnation process is conducted in the wide range of temperature (310–360 K) and concentration of the suspension (10 – 35% wt.), the time is usually between 10 and 30 minutes [10]. The best stability of the suspension against coagulation was observed for its low concentration (1–5% wt.). They should not also be heated close to their boiling point [3–5, 11, 12]. It was observed that application of ultrasonic waves is beneficial for both stability of the suspension and kinetics of the impregnation [9, 13].

The migration rate of teflon particles towards the anodic coating during electrophoresis may be increased using externally applied electric field. Its strength is proportional to the voltage applied between the counter electrode and the impregnated element. The latter is positively polarised when the electrical charge of teflon particles is negative and the other way round. The bigger value of the charge and smaller distance between the electrodes, the higher efficiency of the process [14, 15].

Aforementioned methods concern impregnation of the anodic coating. However, there is also a possibility of preparation of impregnated anodic coating in one step relying on anodizing in for instance sulphuric acid solution containing suspended teflon particles. Since teflon is soft material, the hardness of such coatings

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is insufficient. It is improved by introduction of hard particles for example SiC to the bath. They are incorporated to the anodic coating together with teflon particles and composite material characterized with high hardness and low friction coefficient is obtained [11].

Anodic coatings are always dried after impregnation. Usually, after initial drying in air, they are annealed at the elevated temperature, often above 523 K. The time of heat treatment is between 0.5 and 24 hours [3–5, 10, 16]. Annealing enhances the adhesion of teflon to the anodic coating.

The aim of this work was determination of the influence of the conditions of impregnation of anodic coatings on their abrasion resistance and corrosion resistance in alkaline and acidic media. The analysed parameters were voltage and time of electrophoresis.

Experimental

Anodic coatings were produced onto aluminium (technical purity, EN-AW 1050) with following chemical composition: Fe – 0.3% wt., Si 0.25% wt., Zn 0.05% wt., Ti, Mg, Mn < 0.05% wt. The specimens were degreased and etched in alkaline solution (NaOH, 100 g·dm^{-3}). The anodizing process was performed in sulphuric acid, 158 g·dm^{-3} at 273 K, applied current density was equal to 2.5 A·dm^{-2}, anodizing time – 45 min. The thickness of the coatings obtained was equal to 32 μm. After anodizing, the specimens were rinsed in deionized water and impregnated in suspension of teflon particles in water. The diameters of applied particles were lower than 200 nm, pH = 10 (Dyneon 3M), T = 290 K. The value of zeta potential for applied suspension was obtained from the measured electrophoretic mobility values (Malvern Instrument Ltd.). During impregnation process, the aluminium specimen was polarized positively (anode), the counter electrode made of stainless steel – negatively (cathode). After impregnation, the specimens were dried in air and subsequently annealed at 373 K for 20 minutes. The influence of applied voltage (5 and 10 V) as well as time of electrophoresis on the abrasion resistance was determined using Taber method (TABER® Rotary Platform Abrasion Tester). Flat specimens 100×100 mm were rotated with 60 rpm, using CS-17 abrading wheels, under 9.81 N load. Weight loss was determined after 1000, 2000, 3000, 5000 and 10000 revolutions.

Corrosion resistance of impregnated coatings was determined in aqueous solutions of NaOH (0.05 M) and HCl (0.5 M) at 300 K. Flat specimens (40×50 mm) were anodized, impregnated (T = 293 K, t = 30 min, U = 25 V) and annealed (t = 30 min, T = 373 K). Prior to the corrosion experiment, their edges were secured with the tape resistant to chemicals. Hydrogen evolved during corrosion processes was collected in the burette. Its volume was recorded as a function of time.

Results and analysis

In order to impregnate anodic coating via electrophoresis, one should know the electrical charge of the teflon particles in suspension. It was measured prior to the impregnation experiments. From the results obtained it may be concluded that zeta potential of applied particles is −22 mV at pH = 10.8. It ensures sufficient stability of the suspension. It was also observed that the change of pH in the range between 2.9 and 10.9 does not bring about to coagulation of the particles. All in one, impregnated element should be polarised positively vs. counter electrode. The applied electric field pushes negatively charged teflon particles towards anodic coating. When the impregnation was finished, the coatings were rinsed with deionised water in order to remove loosely adherent particles from the surface. The surface after annealing at 373 K was examined with naked eye. After immersion in water, poor wetting of the impregnated coating when compared to non-impregnated one was observed. It proved the presence of teflon onto the surface of impregnated coating (Fig. 1b,c).

The weight gain of the specimens after impregnation was determined. It was in the range between 1.5 and 7.7 mg·dm^{-2}. It corresponds to the thickness of the coating between 30 and 180 nm (density of teflon is 2.2 g·cm^{-3}). It was observed that the longer time of impregnation, the higher thickness of the coating. Increasing voltage influences the coating thickness at the same manner. The decrease of the coating thickness after 35 min of impregnation at 10 V probably arose due to partial removal of the coating during rinsing after impregnation. It should be noted here that the coatings obtained are hygroscopic, therefore the coating mass and thickness were estimated rather than accurately determined.
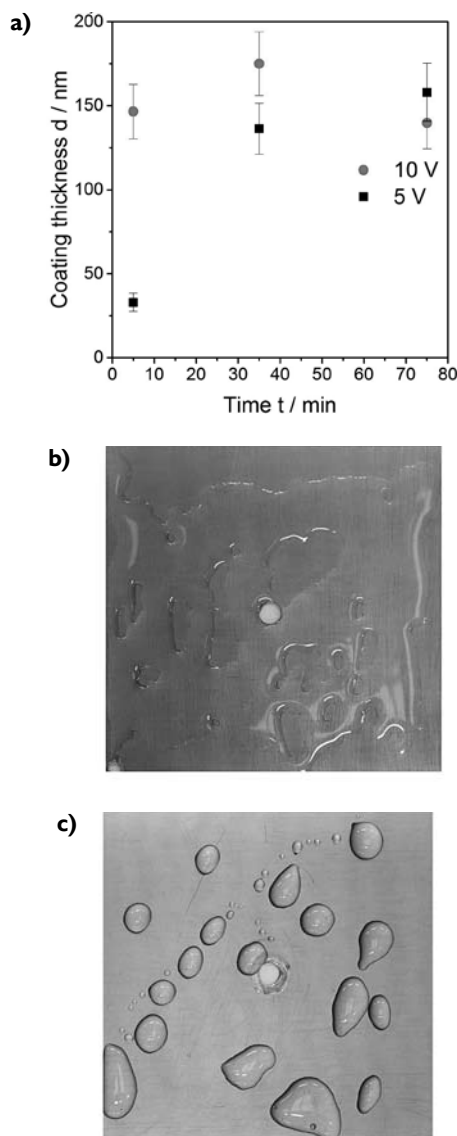

Fig. 1. The thickness of anodic coating vs. time for different impregnation voltage a), the surface of the anodic coatings after immersion in water: b) non-impregnated,
c) impregnated (10 V, 35 min)

The Taber method is widely used for determination of the abrasion resistance of anodic coatings on aluminium and its alloys in the aircraft industry [1, 2, 17]. It was observed that the weight loss for 5 anodic coatings produced at the same conditions, after 10 000 revolutions differs within the range ± 2 mg. This value was presented in Fig. 2 as the error bar after 10 000 revolutions.

Analysis of the results obtained showed that impregnation of anodic coatings deteriorates their abrasion resistance. The non-impregnated coating is the most abrasion resistant (Fig. 2). The increase of impregnation time, which means thicker teflon deposit, leads to higher weight loss during abrasion test. It is probably due

to weak adhesive forces between the anodic coating and teflon particles. They are easily removed during abrasion, thus higher weight loss when compared to non-impregnated specimen is observed. The longer time of impregnation, the higher value of the weight loss. At the same time, higher voltage during impregnation improves the abrasion resistance of the impregnated coatings. The results obtained suggest beneficial influence of the higher voltage. The weight loss of the coatings produced at 10 V at various times are similar. Therefore, the influence of time of impregnation is less pronounced when compared to impregnation at 5 V. Probably, the reason is the fact that the coating reaches its maximal thickness and further physisorption of the teflon particles is hampered. In addition, higher voltage may improve the adhesion of the coating to the substrate.

The corrosion resistance of the impregnated and non-impregnated coatings was determined both in NaOH and HCl solutions. It was observed that due to their porosity, the teflon coatings obtained at 10 V do not protect against corrosion in NaOH and HCl solutions. In order to improve the anticorrosive properties, the voltage equal to 25 V was applied during electrophoresis. Again, in the aggressive alkaline medium (0.05 M NaOH) impregnation did not increase the corrosion resistance (Fig. 4a). The bubbles of hydrogen evolved caused peeling of the teflon from anodic coating. The difference between impregnated and non-impregnated specimens may be explained in terms of experimental error. Better corrosion resistance of impregnated coating, which means smaller volume of hydrogen evolved when compared to non-impregnated one, was observed in 0.5 M HCl (Fig. 4b).
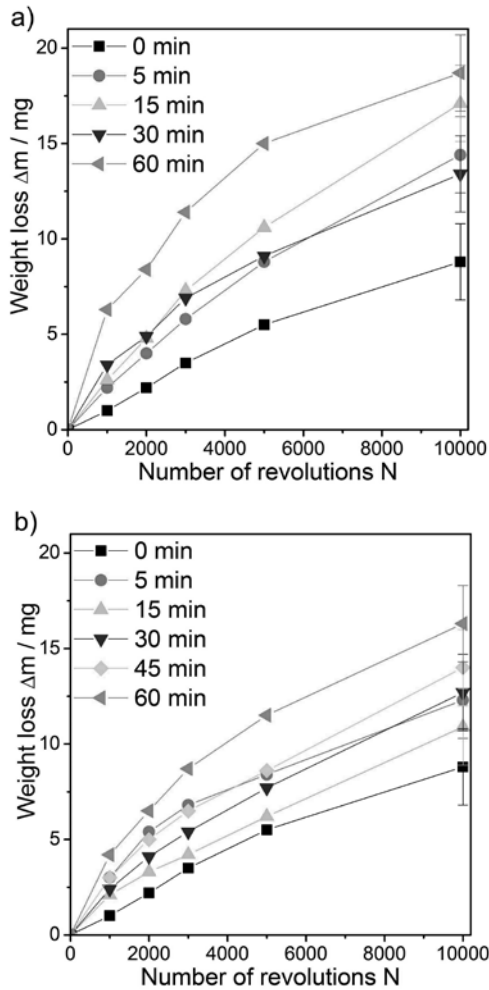

Fig. 2. Weight loss of the coatings vs. number of revolutions for different impregnation time, applied voltage: a) 5 V, b) 10 V (temperature of impregnation = 290 K, annealing conditions: t = 30 min, T = 373 K)

The morphology of the impregnated coating before and after abrasion is presented in Figure 3. The surface roughness of the area abraded is lower than the untouched part of the coating.
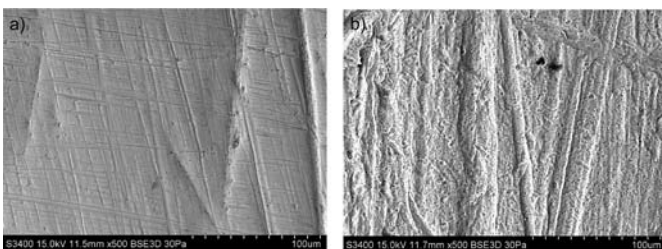

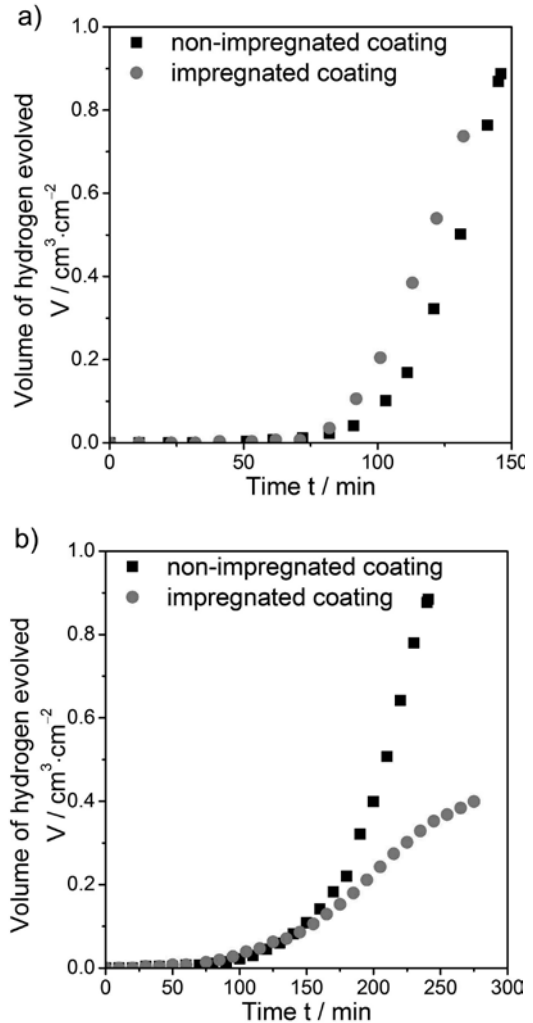Fig. 3. The surface of the impregnated coating (10 V, 35 min): a) abraded area, b) non-abraded area

Fig. 4. The volume of the evolved hydrogen during corrosion in 0.5 M HCl at 300 K for impregnated and non-impregnated coating, conditions of impregnation: T = 293 K, t = 30 min, U = 25 V, annealing at 373 K for 30 minutes

Summary

It was shown that electrophoresis may be successfully applied for the impregnation of anodic coatings on aluminium alloys. The teflon coatings are porous and their adhesion to anodic coating is weak. It causes their lower abrasion resistance when compared to non-impregnated coatings. It was shown that increasing voltage during impregnation is beneficial for abrasion resistance of impregnated coatings. Since the coating are porous, the corrosion resistance of impregnated anodic coating in alkaline solution is the same as the non-impregnated one. However, the increase in the corrosion resistance was observed in the less aggressive, acidic solution. The improvement of the anticorrosive and tribological properties may be achieved after

annealing at higher temperature than it was applied. The effect of sintering of the teflon particles is desired. However, it cannot be applied for precipitation hardened aluminium alloys.

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