

The influence of the deposition parameters on the porosity of thin alumina films on steel

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Abstract: The influence of the deposition parameters on the porosity of thin alumina films electrophoretically deposited on steel from aqueous suspensions was investigated. The effects of the applied voltage, deposition time, suspension temperature and the solid content of the aqueous suspension on the porosity of the obtained alumina films have been determined using optical microscopy coupled with image analysis. It was shown that the lowest film porosity was obtained from a suspension containing 20 wt.% alumina powder at the lowest applied voltage (30 V), for a longer deposition time (10 min) using a suspension temperature of 30 °C. This behavior can be explained by the smaller amount of hydrogen evolved on the cathode during the electrophoretic deposition process.

Keywords: alumina, cataphoretic deposition, deposition parameters, image analysis, porosity.

INTRODUCTION

The electrophoretic deposition process has been well known for many years as a method of forming films with various performances and for different applications. Electrophoretic deposition allows control of the film thickness, uniformity and deposition rate. Using this method for film production it was recognized that decreasing the particle size decreases the temperature of sintering.¹ Additional advantages of using this method are its simplicity, the low cost of the required equipment and the possibility of film formation on substrates of complicated shapes.^{2,3} Electrophoretic deposition is a process in which suspended solid particles are deposited directly from stable suspensions under the influence of an electric field.

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Two simultaneous processes lead to the formation of solid films: the movement of the charged particles under the applied electric field and the deposition of those particles onto the electrode. Electrophoretic deposition is a powerful method for the production of both thin and thick films.^{4–7} Cataphoretic deposition has been used for the formation of protective organic coatings on metal substrates,⁸ as well as for deposition of ceramic micro-laminates,^{6,9} conductive fibers/epoxy composites,¹⁰ organoceramics films¹¹ and bioceramic materials.¹² This method is also used for the processing of advanced microelectronic components.¹¹ The electrophoretic phenomena have been investigated both in non-aqueous media^{2,10,13} as well as in aqueous media.^{4,7,9,14} The non-aqueous media have much better performances compared to aqueous media (*e.g.*, low viscosity), but environmental problems arise with the use of organic media. Accordingly, electrophoretic deposition process should be performed from an aqueous solution whenever it is possible.

The aim of this work was to investigate the effect of deposition parameters, *e.g.*, applied voltage, deposition time, suspension temperature and solid content in the aqueous suspension, on the porosity of alumina films electrophoretically deposited on steel.

EXPERIMENTAL

Preparation of alumina aqueous suspension

The starting powder was commercial reactive alumina A-16 SG (Alcoa Chemicals, Bauxite, AR, USA) with equiaxed grains having an average particle size of 0.5 μm , a specific surface area of 8.5 m^2g^{-1} (typical values declared by the manufacturer). The powder was dispersed in water with the aid of the commercial deflocculant Dolapix ET 85 (Zschimmer&Schwarz, Lahnstein, Germany), an alkali free ester of carbonic acid, supplied as a yellow aqueous solution, and a binder (2 % solution of polyvinyl alcohol in distilled water). The concentration of the deflocculant was 1.4 wt.% and concentration of the binder was 1.0 wt.% with respect to the solid phase content of the suspension (the concentrations are based on solutions not on active substances). The pH value was adjusted to 4.0 by addition of 65 % nitric acid. Dispersion was realized in a ball mill for 2 h. The dispersion was allowed to stabilize in the mill without balls for 1 h. The solid phase contents of alumina powder in the aqueous suspensions were 10, 20 and 30 wt.%.

Electrodeposition of alumina films on steel from aqueous suspensions

A three-electrode cell arrangement was used for the cataphoretic electrodeposition process. The working electrode was a steel plate (5 × 5 mm, steel T-57 by ISO standard). The counter electrodes were platinum panels, which were placed parallel to the working electrode at a distance of 1.8 cm. The alumina films were electrophoretically deposited onto the steel from aqueous suspensions of alumina powder using the constant voltage method. The experiments were performed at different values of constant voltage between 30 and 90 V, for different deposition times of 2, 5 and 10 min and at different suspension temperatures between 20 °C and 40 °C.

The thickness of deposited alumina films, δ , was determined by weighing the cathode before and after deposition and applying the equation:

$$\delta = G / (\rho S) \quad (1)$$

where S is the surface area of the working electrode, $\rho = 3.96 \text{ g cm}^{-3}$ is the powder density and $G = w_2 - w_1$ (where w_2 and w_1 are the weight of the cathode after and prior to deposition, respectively).

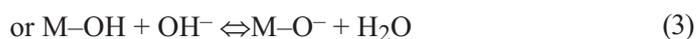
Surface characterization of the alumina films electrodeposited on steel

Optical microscopy coupled with quantitative image analysis was used for surface characterization of the alumina films electrodeposited on steel. A stereo microscope (model LEICA M6, LEITZ, Goslar, Germany) with excellent depth of the field sharpness and with variable magnitude up to 200× was used as the source of visual information, being very suitable for non-destructive measurements of the fragile alumina deposits. The picture was transferred to a computer by a CCD (charge couple device) camera (Sony Hyper Had), where it was digitized using MIRO-DC10 Frame Grabber. The statistical analysis of the results obtained from optical microscopy coupled with quantitative image analysis enables the determination of the pore number and the percentage of the film surface covered by pores. The finer microstructure of the alumina films was investigated using scanning electron microscopy (SEM) (PHILIPS XL 30), after vapor deposition of a conductive carbon layer on the surface of the alumina deposits.

RESULTS AND DISCUSSION

Electrophoretic deposition of alumina films on steel from aqueous suspensions

The surfaces of colloidal particles may be positively or negatively charged, depending on the pH:^{1,15}



At low pH values, Al_2O_3 , particles are positively charged.

According to the proposed mechanisms, electrophoretic deposition of alumina occurs in several steps:^{4,15-18}

– The charged particles attract oppositely charged ions (*i.e.*, counterions) around themselves; this “atmosphere” plus the particle is the “lyosphere” (*e.g.*, $[\text{M-OH}_2]^+\text{X}^-$). The positively charged oxide particles migrate toward the cathode;

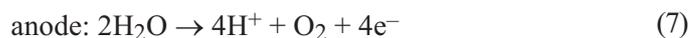
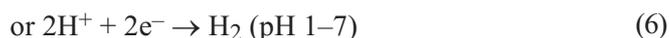
– The rate of migration that the particles can achieve, v , is given by the equation:

$$v = zE/6\pi\eta r \quad (4)$$

where E is the applied electric field, η is the suspension viscosity, r is the particle radius and z is the particle charge, indicating a linear dependence of the migration rate on the applied electric field;

– When an ion reaches the cathode, it discharges.¹⁵ As the particle is close enough to the cathode, attractive forces dominate and coagulation/deposition occurs;

– Simultaneously, hydrogen evolves on the cathode and oxygen on the anode:



– The evolved hydrogen leaves the cathode through the coating, resulting in pores inside the deposited alumina film, thus causing its porous structure.

The alumina film thickness is a function of deposition time, alumina powder content in the aqueous suspension and the suspension temperature, as was shown in previous papers.^{14,16–18} Increasing the applied voltage increases the rate of particle migration, according to Eq. (4), and consequently increases the film thickness. The rate of hydrogen evolution reaction, as an undesirable process, increases with applied voltage, also. Increasing the suspension temperature increases the film thickness because increasing the suspension temperature increases the rate of particle migration due to decreasing viscosity of the alumina powder suspension. Increasing the deposition time also increases the film thickness due to more particles reaching the cathode surface and depositing on it.¹⁶

The effect of alumina powder content in aqueous suspension on the alumina film porosity

The effect of applied deposition voltage and alumina powder content in the aqueous suspension on the percentage of the alumina film surface covered by pores is represented in Fig. 1.

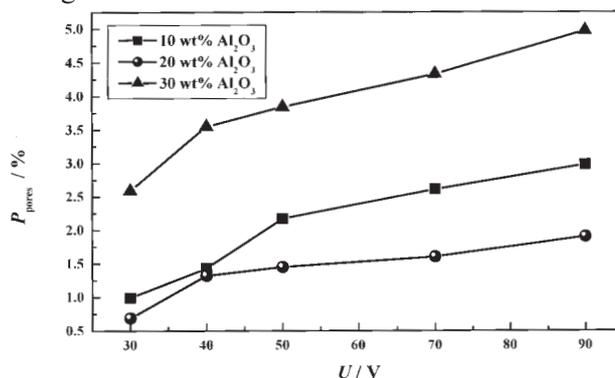


Fig. 1. The percentage of alumina film surface covered by pores vs. applied deposition voltage for different contents of alumina powder in the suspension (deposition time 10 min).

It can be seen that films obtained from suspensions containing 20 wt.% alumina powder have the lowest porosity for all deposition voltages. This can be explained by 20 wt.% alumina powder giving the optimal ratio of number of suspended particles and number of water molecules, thus enabling the best packing of particles on the cathode during the deposition process. The films obtained from 10 wt.% and 30 wt.% suspensions have greater porosity which may be due to the larger amount of evolved hydrogen (in the case of the 10 wt.% suspension) and due to some agglomerates detected in the alumina deposits (in the case of the 30 wt.% suspension), which is probably the result of inadequate dispersion of the particles in suspensions with high solid alumina powder content. Therefore, the effect of ap-

plied voltage on the morphology of alumina films was investigated in further experiments only for the films obtained from 20 wt.% suspensions.

The effect of applied voltage on the alumina film porosity

Bearing in mind that the hydrogen evolution reaction on the cathode is slower at lower deposition voltages, experiments were conducted in the range of 30 – 90 V, with the aim of determining the optimal deposition voltage for alumina film formation. Increasing the applied voltage increases the number of pores (Fig. 2a) and the percentage of the alumina film surface covered by pores (Fig. 2b) for all deposition times.

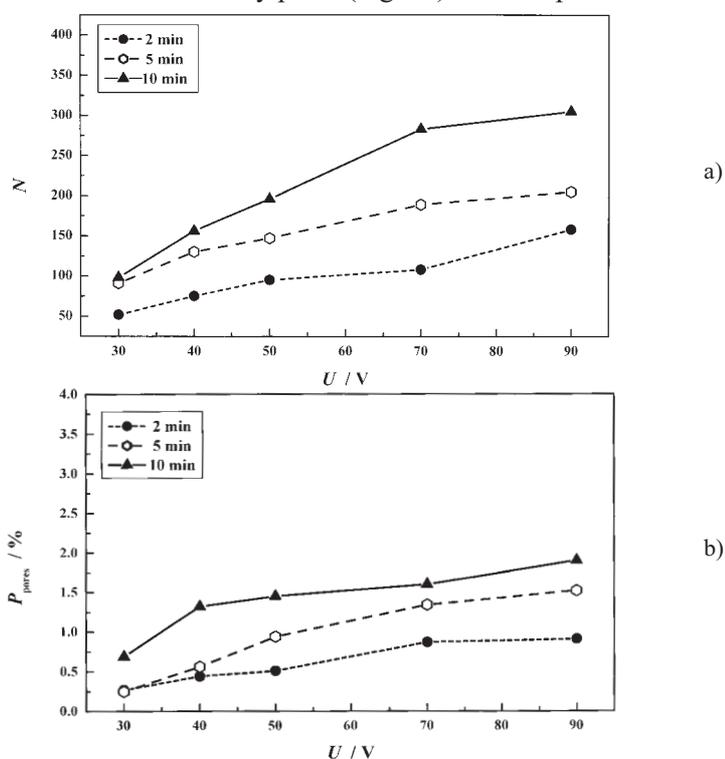


Fig. 2. Number of pores (a) and the percentage of alumina film surface covered by pores (b) vs. the applied deposition voltage, for 20 wt.% alumina suspension and different deposition times.

These results can be explained by the fact that the amount of evolved hydrogen is higher at higher voltages. This evolved hydrogen deposits from the cathode through the coating, leaving pores inside the deposited alumina film, thus causing its porous structure. Thus, the number of pores and the percentage of the film surface covered by pores have minimum values for the film obtained at an applied voltage of 30 V.

The effect of deposition time on the alumina film porosity

The effect of deposition time on the alumina film thickness and porosity was investigated for films deposited from 20 wt.% suspensions at 30, 40 and 50 V (Figs. 3 and 4, respectively).

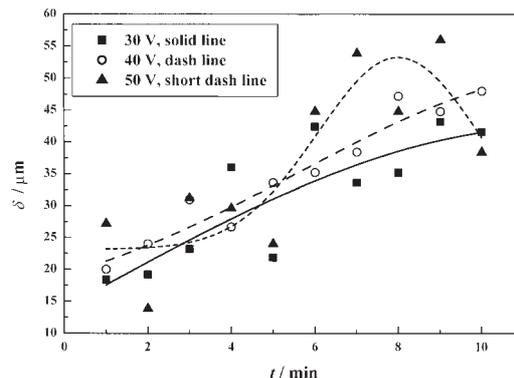


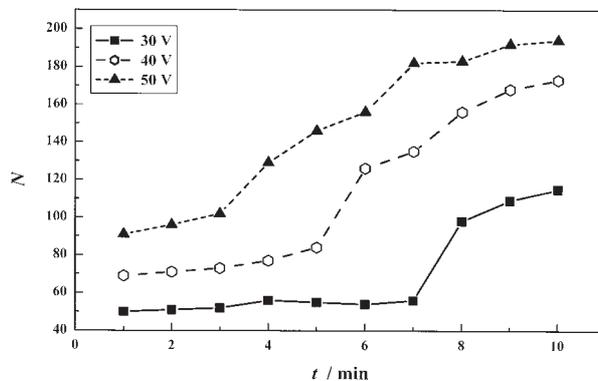
Fig. 3. The time dependence of the alumina film thickness for 20 wt.% alumina suspension at different applied voltages.

At lower applied voltages (30 and 40 V), increasing the deposition time increases the film thickness (Fig. 3), due to the greater number of particles reaching the cathode and depositing on it. For longer deposition times, at higher deposition voltage (50 V), the film thickness achieves a maximum and then decreases due to the larger amount of evolved hydrogen, which accumulates on the cathode and causes more pores in the deposited film. This explains the greater number of pores (Fig. 4a) and the larger percentage of the alumina film surface covered by pores (Fig. 4b) for alumina films electrophoretically deposited at higher voltages and for longer deposition times.

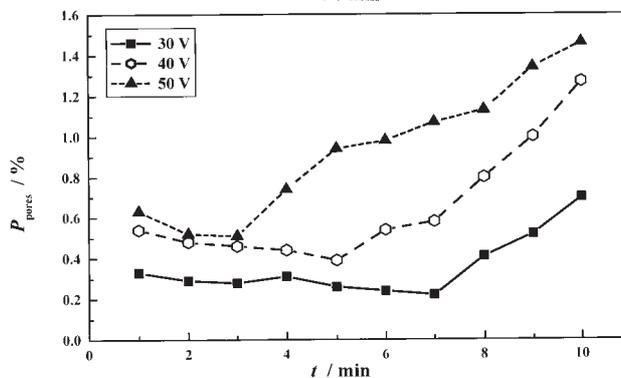
Since increasing the deposition time does not increase the film porosity significantly at the lowest deposition voltage of 30 V, (Figs. 4a and 4b), but significantly increases the film thickness, (Fig. 3), it can be concluded that the optimal deposition time is 10 min, for an applied voltage of 30 V and a 20 wt.% suspension. The SEM micrograph of an alumina film obtained under these conditions is represented in Fig. 5.

As mentioned earlier, during electrophoretic deposition, two simultaneous processes occur on the cathode, *i.e.*, hydrogen evolution and alumina particle deposition. The influence of these two processes on the alumina film porosity could be seen more clearly during the initial deposition time. The effect of deposition time on the percentage of alumina film surface covered by pores, for deposition time of up to 1 min, was investigated for a film deposited from a 20 wt.% suspension at 30 V (Fig. 6).

It can be noticed that the alumina film porosity decreases at the beginning, achieves a minimum value and then increases. This behavior can be explained as



a)



b)

Fig. 4. Number of pores (a) and the percentage of alumina film surface covered by pores (b) vs. deposition time, for 20 wt.% alumina suspension at different applied voltages.

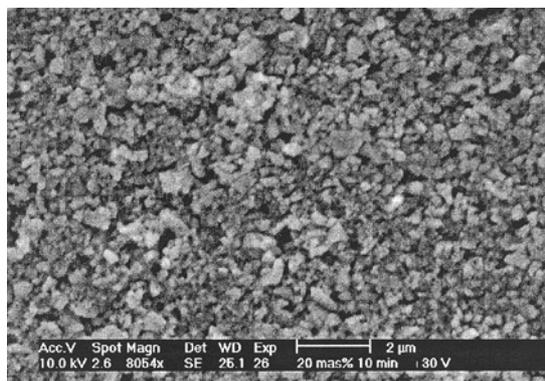


Fig. 5. SEM micrograph of an alumina film surface electrophoretically deposited on steel (20 wt.% alumina suspension, 10 min, 30 V).

follows. At the very beginning of the deposition process, the alumina particles are attracted to the cathode surface. However, a large percentage of film surface is covered by pores due to the large number of pores existing in the film as a result of the hydrogen evolution reaction on the cathode. After a few seconds, the pores are

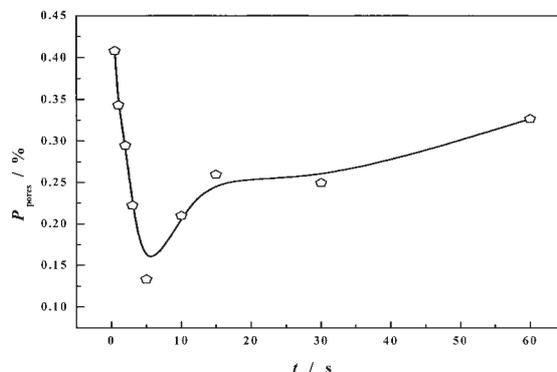


Fig. 6. The percentage of alumina film surface covered by pores vs. deposition time for 20 wt.% alumina suspension at an applied voltage of 30 V (deposition time of 1 min).

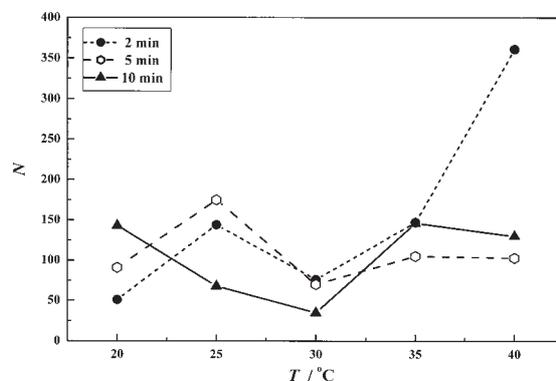
filled with alumina particles and, consequently, the film porosity decreases and achieves a minimum value. This means that the process of alumina particles deposition becomes dominant with respect to the hydrogen evolution reaction. During further deposition, the film porosity increases, but not significantly, due to the larger amount of evolved hydrogen, as was also evident from Fig. 4b.

The effect of suspension temperature on the alumina film porosity

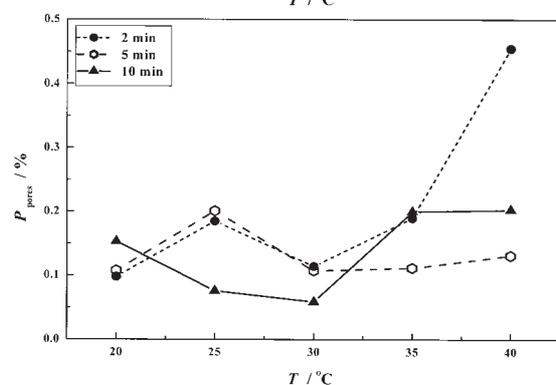
The majority of the work in the field of electrophoretic deposition of ceramic films has been done at room temperature,^{19–22} although some experiments have been performed at higher temperatures, up to 38 °C.⁴ In this work, the suspension temperature was varied from 20 °C to 40 °C. At temperatures lower than 15 °C, the rate of film formation is low. On the other hand, at temperatures higher than 40 °C, water and organic compounds evaporate intensively, changing the pH value and affecting quality of the suspension.

The temperature dependence of the number of pores (Fig. 7a) and the percentage of the alumina film surface covered by pores (Fig. 7b) show a minimum at 30 °C for all deposition times.

This behavior can be explained by the proposed mechanism of the alumina deposition process, which occurs in several steps, as mentioned earlier. Increasing the suspension temperature decreases the viscosity of the aqueous suspension and, consequently, increases the rate of particle migration, according to Eq. (4). On the other hand, the rate of the hydrogen evolution reaction, as an undesirable process, also increases with increasing temperature. At 30 °C these two processes, particle migration/coagulation and hydrogen evolution, are in equilibrium, which results in deposited films with the minimum porosity. It can also be noticed that the minimum values of pore number and percentage of alumina film surface covered by pores were obtained after a deposition time of 10 min. Namely, for longer deposition times (10 min) many more particles reach the cathode. In addition, the possibility that they pack better on the cathode is greater, so the film porosity decreases.



a)



b)

Fig. 7. Dependence of the number of pores (a) and percentage of alumina film surface covered by pores (b) on the suspension temperature, for 20 wt.% alumina suspension and different deposition times.

At temperatures lower than 30 °C, the migration of the particles is too slow although the rate of the hydrogen evolution reaction is low, which causes bad packing of alumina particles and formation of higher porosity films. On the other hand, at temperatures higher than 30 °C, the migration of the particles is fast but so too is the rate of hydrogen evolution. As a consequence, a larger amount of evolved hydrogen diffuses through the film, leaving more pores inside the films and causing more porous structures.

CONCLUSION

Statistical analysis of the results obtained from optical microscopy coupled with quantitative image analysis gives information about the porosity of alumina films (pore number and percentage of the film surface covered by pores) and enables the optimal values of the applied voltage, alumina powder content in the suspension, suspension temperature and deposition time to be determined for the electrophoretic deposition of alumina films on steel.

The percentage of alumina film surface covered by pores has a minimum value for films obtained from suspensions containing 20 wt.% of alumina powder

due to the optimal ratio of the number of suspended particles to the number of water molecules, which enables the best particle packing on the cathode during the deposition process. Increasing the applied voltage and deposition time increases the film thickness but also increases the film porosity. The minimum values of pore number and percentage of alumina film surface covered by pores were obtained for films deposited at 30 V. This can be explained by the fact that at this voltage the lowest amount of hydrogen is evolved at the cathode, which departs from the cathode by going through the film. Hence, the lower the amount of hydrogen, the less pores are left inside the film, resulting in films with a less porous structures. On the other hand, increasing the deposition time significantly increases the film thickness due to many more particles reaching the cathode, but it does not increase significantly the film porosity. This means that for longer deposition times (10 min) at a lower deposition voltage (30 V), alumina films of the greatest thickness with low porosity can be formed.

The minimum values of the pore number and percentage of alumina film surface covered by pores were obtained at 30 °C. This can be explained by the equilibrium between the migration of particles and coagulation, on the one hand, and hydrogen evolution at the cathode, on the other. At lower temperatures, migration is too slow, and at higher temperatures, hydrogen evolution is too fast, giving in both cases films of higher porosity.

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ИЗВОД

УТИЦАЈ ПАРАМЕТАРА ЕЛЕКТРОФОРЕТСКОГ ТАЛОЖЕЊА ПРАХА АЛУМИНИЈУМ-ОКСИДА ИЗ ВОДЕНИХ СУСПЕНЗИЈА НА ПОРОЗНОСТ ДОБИЈЕНИХ ТАНКИХ ФИЛМОВА НА ЧЕЛИКУ

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Испитиван је утицај параметара таложења, и то напона таложења, времена таложења, температуре суспензије и концентрације чврсте фазе у суспензији, на порозност катафоретски таложених танких филмова из водене суспензије праха алуминијум-оксида на челику. Порозност добијених филмова одређивана је применом методе оптичке микроскопије уз анализу слике. На основу добијених резултата показано је да је најмања порозност превлаке алуминијум-оксида на челику добијена при таложењу из водене суспензије концентрације 20 мас%, при напону таложења 30 V, за време таложења 10 минута и при температури суспензије 30 °C. Овакво понашање могуће је објаснити мањом количином издвојеног водоника на катоди током електрофоретског таложења.

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