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AC-anodized and Ni-pigmented aluminum for selective solar absorption

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A phosphoric acid solution (0.5 and 1.0 M) modified with addition of $FeSO_4.7H_2O$ has been used to form porous Al_2O_3-films on technical purity aluminum via AC-polarization. By combining the anodizing conditions (voltage and time) porous aluminum matrices with different thickness have been formed. The nickel electrodeposition has been carried out in a $NiSO_4$ (pH 4.0) solution at different voltages and durations. Spectral characteristics of the colored electrodes have been recorded in the UV-VIS-NIR (200-2500 nm) and IR (2.5–20 μm) regions. It has been found, that during absorbance in the solar spectrum, the thickness has no significant influence due to the small values of reflected light. The emission capability in the infrared region, however, depends strongly on the layer thickness. The tests carried out show that the obtained coatings exhibit high absorption in terms of solar light and relatively low emission in the infrared. These technical features present them as very promising for use in low and medium temperature solar collectors.

Key words: alumina films, AC anodization, nickel electrodeposition, selective solar absorbance.

INTRODUCTION

In the late 19th century, at the very beginning of anodic oxidation studies, alternating current (AC) has been used to grow alumina coatings. The advantage of this regime over direct current polarization has been accounted for the use of two identical electrodes and much simpler technological equipment. AC-anodizing has been still abandoned because of the severe condition to ensure equal surface and composition of the electrodes, as well as a superior quality of contacts.

Nowadays, the series production of some aluminum-based parts, for instance panels for solar absorption, seems to provoke the revival of the AC-technology. Moreover, the anodic oxidation of aluminum alloys with a relatively high content of alloying elements has been found [1-4] to proceed more easily in AC than in DC mode.

The aim of the present paper was to investigate the possibilities to obtain efficient selective coatings on the base of alumina matrices grown by AC-anodization and filled by electrochemical deposition of nickel. From technological point of view, it was expedient to grow the porous matrices in phosphoric acid solutions over aluminum of technical purity. The alumina structures formed in phosphoric acid are known [5] to have comparatively larger pore diameters; the anodization in some modified electrolytes has been found [6] to lead to formation of thicker films at equal other conditions.

The incorporation of metals into the porous alumina films is normally carried out through their AC polarization in aqueous solutions of metal containing salts. Alongside with their decorative and anti-corrosion properties, porous matrices with incorporated metal particles exhibit selective absorption of solar light. Nickel is one of the mostly used metals for this purpose [7-15]. By varying the conditions of matrix growth and of nickel deposition, coatings with good selective absorption can be obtained. In general, the efficiency of a selective coating is determined [16-19] by high absorption within the solar spectrum (0.2 - 2.5 μm) and low emission in the far infrared region (2.5 - 25 μm).

EXPERIMENTAL

The working electrodes were cut from technical purity aluminum sheets (99.5% Al). The pretreatment of the electrodes was carried out at room temperature according to the following procedure: (i) degreasing with acetone, (ii) etching in sodium hydroxide (10%), (iii) neutralizing in nitric acid (30%) and (iv) washing with distilled water. The exposed working area of the samples was 60 x 25 mm.

Anodizing was carried out in 0.5 M and 1.0 M aqueous solutions of phosphoric acid, modified by the addition of 5 g dm^{-3} $FeSO_4.7H_2O$, as suggested

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in [6]. The porous matrices were simultaneously formed on both electrodes under AC-polarization (50 Hz) at 20 ºC. The process was carried out at two formation voltages (18 V and 50 V) for two different durations (15 min and 30 min). Through variation of anodizing voltage and time, porous alumina matrices with different thickness were formed. The time dependence of the current density was registered with a Mastech MS 8050 multimeter through a PC-based data acquisition system.

The electrodeposition of nickel was carried out by AC-polarization (50 Hz), at two polarization voltages (14 V and 50 V) for different coloring durations (2 - 8 min). The coloring electrolyte consists of 70 g dm^{-3} $NiSO_4.6H_2O$, 30 g dm^{-3} $MgSO_4.5H_2O$ and 15 g dm^{-3} H_3BO_3 (pH = 4.0). After coloring the samples were "sealed", by immersing them in boiling water for 2 minutes.

The spectral characteristics of the colored specimens were recorded in the UV-VIS-NIR region (200 - 2500 nm) by reflectance spectra at normal incidence using a Shimadzu UV-3100 with $BaSO_4$ sphere. Reflectance in the IR region (2.5 - 20 μm) was registered with a FTIR spectrophotometer equipped with mirror reflectance accessory.

RESULTTS AND DISCUSSION

Formation of porous anodic oxides and nickel electrodeposition

The AC-anodizing kinetics in the modified phosphoric acid electrolytes followed the well-known current density vs. time dependence observed during potentiostatic DC-anodization in phosphoric acid. Initially, the formation of a compact barrier layer of aluminum oxide takes place, followed by partial dissolution of the compact layer by the acidic electrolyte and nucleation of pores. Finally, a balance between oxide formation and dissolution at the pore bases is reached, thus imposing steady current density conditions.

The incorporation of nickel into the alumina matrices obtained under various conditions in the phosphoric acid solutions led to the coloration of the coatings in beige, brown, or black shades. The choice of the appropriate conditions both for matrix growth and nickel deposition permitted to produce highly reproducible black-colored coatings.

Spectral characteristics

The reflectance spectra of colored anodic films were recorded at normal incidence of the light in two different wavelength ranges.

UV-VIS-NIR range from 200 to 2500 nm

Reflectance spectra of two samples (Nr. 2 and Nr. 6) obtained through anodization and coloration at boundary conditions are shown in Fig. 1.

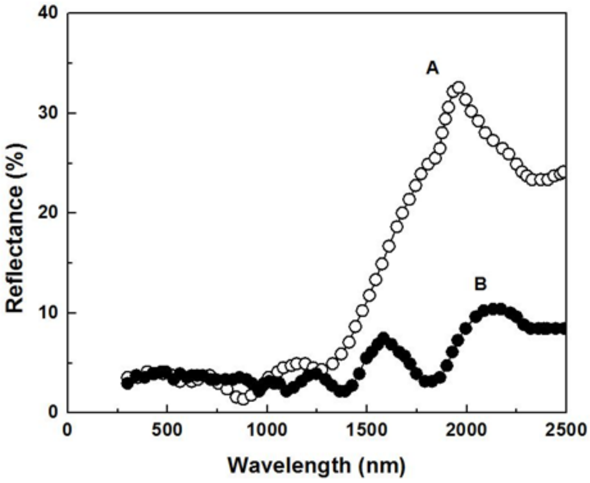

Fig. 1. UV-VIS-NIR reflectance spectra of two samples: (A) Sample Nr.2, anodized in 1 M H_3PO_4 (30 min, at 50 V), colored for 8 min at 50 V; (B) Sample Nr. 6, anodized in 0.5 M H_3PO_4 (15 min, at 18 V), colored for 2 min at 14 V.

The solar absorption coefficient (α_S) was calculated in accordance with the European Standard EN 410 (1998) using the formula:

$$\alpha_S = 1 - \rho_S = 1 - \frac{\sum_{i=1}^{n} S_i \rho(\lambda) \Delta\lambda}{\sum_{i=1}^{n} S_i \Delta\lambda}$$

$$\Delta\lambda = 300 - 2500\, nm\,. \qquad (1)$$

Here, S_i is the spectral distribution of solar energy, $\rho(\lambda)$ is the spectral reflectance coefficient and $\Delta\lambda$ the wavelength range. The results obtained for the solar absorption coefficient α_s of different samples are summarized in Table 1.

IR range from 2.5 to 20 μm

Reflectance spectra of the same samples (Nr.2 and Nr.6) in the wavelength range from 2.5 to 20 μm are presented in Fig. 2.

The heat emission coefficient (ε_t) was calculated in accordance with the European Standard EN 673 (1997) from the data on surface reflection and on heat emissivity of a black body at 373 K by using the formula:

$$\varepsilon_t = 1 - R_n = 1 - \frac{1}{30} \sum_{l=1}^{i=30} R_i(\lambda_i) \qquad (2)$$

Here, R_n is the average value of standard reflectance and R_i (λ_i) - the reflectance at λ_i. The values of the heat emission coefficient ε_t of the samples at 100 °C (ε_{100}) are summarized in Table 1 in dependence of the anodizing and coloring conditions.

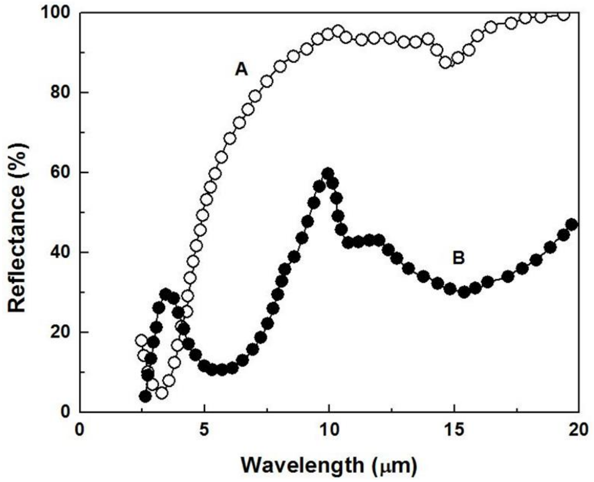

Fig. 2. IR reflectance spectra of two samples: (A) Sample Nr.2, anodized in 1 M H_3PO_4 (30 min at 50 V), colored for 8 min at 50 V; (B) Sample Nr.6, anodized in 0.5 M H_3PO_4 (15 min at 18 V), colored for 2 min at 14 V.

Table 1. Light absorbance and heat emission of samples obtained at different conditions

Sample Nr.	AC-anodization		Nickel deposition		H_3PO_4	α_s	ε_{100}
	U [V]	t [min]	U [V]	t [min]	[mol.dm^{-3}]	%	%
1	18	15	0	0	1.0	14.5	8.5
2	50	30	50	8.0	1.0	96.4	68.4
3	50	30	50	2.0	1.0	80.5	48.0
4	18	15	14	2.0	1.0	85.6	21.0
5	18	15	14	2.5	1.0	92.0	24.0
6	18	15	14	2.0	0.5	95.7	16.6
7	18	15	14	2.5	0.5	93.6	25.8

Both the conditions of matrix growth and of nickel deposition proved strongly to affect the optical properties of the coatings. The nano porous structure of the anodic films caused interference interactions in the whole wavelength range of investigation, judging by the waves observed in the reflectance spectra. The interference upon absorption in the solar spectrum range (Fig. 1) had no negative consequences because of the low intensity of the reflected light. The emission capability in the infrared region, however, strongly depended on the thickness of the layer. Relatively thick interference layers caused a noticeable increase of the heat emission in the IR range, as seen from the data for samples Nr.2 and Nr.6. The solar absorption coefficients of both samples are over 90 %, but the thicker sample (Nr.2), anodized for 30 min at 50 V, had a high heat emission coefficient, ε_{100} = 68.4 %, while the thinner sample (Nr.6), anodized for 15 min at 18 V, had a coefficient ε_{100} = 16.6 %.

It can be summarized that the deposition of nickel particles into a dielectric alumina matrix provides high light absorption in the solar spectrum range (over 90 %). With sufficiently thin matrices, the heat emission in the IR range can be reduced below 20 %. Hence, the requirements for an efficient selective coating are fulfilled.

Solar absorption calculation test

It was of interest to determine the absorptive capacity of the produced coatings in terms of solar radiation in the wavelength range from 300 nm to 2400 nm. For the purpose, the spectral data obtained for sample Nr.6 in Table 1 were used with ASTM G173-03 reference spectra derived from SMARTS v. 2.9.2 (AM1.5) spectral radiation from the solar disk plus sky diffuse light and diffuse light reflected from the ground on a south facing surface tilted 37 deg from the horizontal position [20]. In the chosen wavelength range, a solar spectral absorbance of 960.5 W m^{-2} was calculated. The highest possible absorbance being 1000.9 W m^{-2}, a solar absorption coefficient of the selective coating amounting to 96.0 % was calculated. Using the same procedure, a solar absorption of 94.2 % was calculated for a commercially available selective coating on copper base.

Stagnation temperature natural test

The stagnation temperature (T_p) is defined as the maximum temperature achieved by a solar collector under specific conditions. This temperature is reached when the total heat losses in the collector exactly balance the energy absorbed by it. High stagnation temperatures are a reliable indication that the solar collector would have superior performance in cold environment even at high temperatures of the heated fluid. Under stagnation conditions, no heat is delivered to the load and a solar collector dissipates all the absorbed energy. In terms of Duffie *et al.* [21] it means

$$U_L\left(T_p - T_a\right) = \tau\alpha G \,, \tag{3}$$

where (τ) is the transmittance of the glazing, (α) is the absorbance of the absorber plate, (U_L) is the total collector heat loss coefficient, (T_p) is the temperature of the solar collector absorber plate, (T_a) is the surrounding air temperature and (G) is the solar radiation in the plane of the solar collector. Using this expression, the temperature of the absorber during stagnation (T_p) has been estimated.

From the point of view of the absorber coating, the temperature of the absorber (T_p) depends on the absorbance of the absorber plate, α_s, and on ε, the heat emission of the absorber coating in the infrared region, which is a part of U_L. The higher the ratio α/ε, the better is the collector performance. This ratio was used to compare different absorber coatings. A simple side by side test for stagnation temperatures was carried out to practically compare the optical properties of sample Nr.6 with the commercial selective coating on copper base. Samples with small film resistance temperature detectors (RTD's) sealed on their back sides were placed side by side in a well insulated wooden box. The transparent cover was common for both samples. The *natural stagnation temperature t*est was carried out with two types of covers:

(i) with a single cover of a standard 4 mm float glass (Fig. 3, curves A);

(ii) with a cover of double glazed stack with low coating on the inner glass, commonly used in today's fenestration units (Fig. 3, curves B).

As seen in Fig. 3 sample Nr. 6 proved to behave as well or even better than the commercial specimen, showing higher stagnation temperatures.

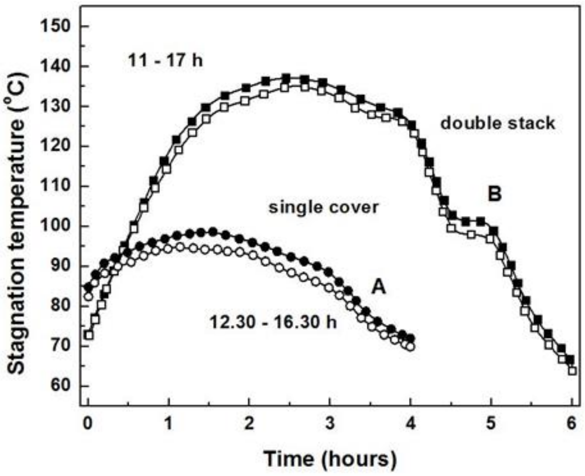

Fig. 3. Stagnation temperature vs. time: (A) single cover; (B) double glazed stack. The filled symbols denote sample Nr. 6, while the empty ones - coating on a copper base.

CONCLUSION

Phosphoric acid solutions modified with addition of ferrous ions proved to be suitable for the formation of porous alumina matrices on technical purity aluminum under AC-polarization conditions. The careful choice of polarization conditions enabled the obtainment of reproducible black-colored coatings through electrochemical deposition of nickel into the pores of the matrix.

Optimal results for the absorbance (α_s) of the coatings within the UV-VIS-NIR range (200 - 2500 nm), as well as for their emission (ε_{100}) within the IR range (2.5 nm – 20 μm) are reached for samples with low thickness of the absorbing interference layer. The high selectivity of the low thickness coatings is testified by the measured high absorbance of solar light and low heat emission in the IR range.

A side by side natural test for stagnation temperatures ascertained the superiority of the developed selective coating over a commercial coating on copper base. Spectral characteristics and test measurements of the developed coating indicate its suitability for low and medium temperature solar collectors. The main positive features of the coating are associated with low production costs and good radiation parameters at commonly used temperatures: a solar absorption coefficient of 94 - 96 % and a heat emission coefficient of 14 - 18 %.

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СЕЛЕКТИВНИ ПОКРИТИЯ НА ОСНОВА НА ПРОМЕНЛИВОТОКОВО АНОДИРАН И ОЦВЕТЕН С Ni АЛУМИНИЙ

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(Резюме)

Използван е разтвор на H_3PO_4 (0.5 и 1.0 M) модифициран с добавка на $FeSO_4.7H_2O$ (5 g dm^{-3}) за формиране на поресто Al_2O_3-филми върху технически алуминий в условия на AC-поляризация (50 Hz). Чрез комбиниране на условията на анодиране (напрежение и време) са формирани порести алуминиеви матрици с различна дебелина. Електроотлагането на никел е извършено от разтвор на $NiSO_4$ (pH 4.0) също при AC-поляризация с различно напрежение и продължителност. Снети са спектралните характеристики на оцветените образци в UV-VIS-NIR (200-2500 nm) и IR (2.5–20 μm) области. Намерено е, че при абсорбцията на слънчевия спектър дебелината на филмите не оказва съществено влияние, поради малките стоиности на отразената светлина. Емисионната способност в инфрачервената област обаче зависи силно от дебелината на слоя. Проведените тестове показват, че получаваните покрития имат висока абсорбционна способност по отношение на слънчевата светлина и сравнително слабо излъчване в инфрачервената област. Тези техни характеристики ги представят като много подходящи за използването им в ниско и средно температурни слънчеви колектори.