

Appearance Modeling of Multilayered Nano-structured Metal Oxides Formed in Interference Coloured Anodised Aluminium

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The creation of functional properties is highly sought after in current state of the art nanotechnology. The design of nano-structured metal surfaces aims at diversifying properties, with optical appearance being one of many. Colour is an important feature of the appearance and initiating from nano-structured metal surfaces, it is the result of the complex interplay between light and the surface's optical and microstructural features. In present work, an optical modeling procedure is developed for complex multi-layered nano-structured metal surfaces. The case study selected here is interference colouring of anodized aluminium. The conventional and best established electro-colouring processes produce all shades of bronze to black with superior UV light resistance due to the metallic nature (mostly Ni and Sn) of the electro-deposit of a few μm in the pores of the anodised layer. Producing grey and clear spectral colours is also possible when additional electrolysis steps for pore modification and re-anodising are included in the processing chain. The aspired optical effect is then interference (as opposed to light scattering for bronze-black colours) which requires only a very thin layer of deposit (<100 nm) at the modified pore bases, making the process more sensitive than for bronze colouring. The current work aims to evaluate a continuous line procedure to make interference colours on anodised aluminium starting from established technology for bronze colours, i.e., using a tin-based electrolyte for colouring and sulphuric acid for pore modification after conventional anodizing.

Keywords: *Optical modeling, electrocolouring, interference, nanostructures*

1. Introduction

The process of anodizing aluminium and its alloys has been known for nearly 100 years. Anodising is an electrolytic surface process that results in the formation of a regularly structured porous oxide film. This film protects the metal surface through a greater corrosion and wear resistance, provides a physical key for organic coatings and adhesives (allows mechanical interlocking in the pores), and offers a matrix to contain colorants (absorption and deposition of elements in the pores). In Europe, about 120 000 ton of anodized aluminium is produced each year for architectural and decorative applications. Anodized aluminium is particularly suited for outdoor building applications because it provides a very durable surface finish. It retains its initial appearance for a longer period of weathering than other architectural metals with the exception of expensive titanium. Furthermore, it is more resistant to ultra-violet light and erosion than painted metal, and also has an inherently better corrosion resistance. For painted sheet, the corrosion resistance is still often ensured by a chromate conversion layer under the paint, containing carcinogenic chromium VI+ and therefore remains an unwanted pretreatment. Colours on anodised aluminium can be obtained by various methods. Electro-colouring is the best suited for outdoor exposure applications because of the superior light fastness (UV resistance) compared to the other methods such as organic dyeing. The superior UV resistance is associated with the metallic nature of the colouring substance. The

conventional and best established electro-colouring processes produce all shades of bronze to black with superior UV light resistance due to the metallic nature (mostly Ni and Sn) of the electro-deposit of a few μm in the pores of the anodised layer. Producing grey and clear spectral colours is also possible when additional electrolysis steps for pore modification and re-anodising are included in the processing chain. The aspired optical effect is then interference (as opposed to light scattering for bronze-black colours) which requires only a very thin layer of deposit ($<100\text{ nm}$) at modified pore bases, making the process more sensitive than for bronze colouring. The batch interference processes described in the technical literature are mostly nickel-based and pore modification is preferred in phosphoric acid. Additionally, for interference colours a final colour fixation step is best practice for deposit and colour stability. Here potential issues arise because the chemicals involved can have ecological and economical disadvantages. The aim of this project is to make interference colours on anodised aluminium using only “green” technology. This technology is already established at COIL NV/United Anodisers (Landen, Belgium) for the continuous line bronze colouring processes. We aim to transfer this technology for the more complex interference colouring. Hence, the aim is to develop continuous line processes based on tin instead of nickel for colouring, sulphuric acid instead of phosphoric acid for pore modification, and eliminating the need for colour fixation. Some results of this “green” interference colouring method are presented. Colour is measured using TIS (Total Integrated Scattering) and microstructure is characterised using FEG-SEM/EDX (Field Emission Gun Scanning Electron Microscopy-Energy Dispersive X-ray analysis). The second objective is to develop an optical model that, based on the microstructure and composition data, can simulate and predict the colour of the samples. Having a model that can predict how the colour changes when differences in microstructure or chemistry are introduced gives us a powerful tool for product/colour diversification. Optical modeling of metal surfaces has received some attention in literature e.g.[1-5]. In the PhD thesis of Veerle Goossens (VUB, 2009) various steel surfaces have been optically modeled.

2. Colouring

The perception of colours on electro-coloured anodized aluminium is associated with the interplay of visible light with the porous substrate, i.e., reflection, absorption, scattering and interference phenomena. The spatial dimensions of the porous film structure are below the wavelength of visible light, hence influence the colour but not the directionality of the reflected light.

Bronze and black colours (*Fig.1*)

This is considered as the ‘conventional’ process. DC-anodising in sulphuric acid (stage 1) is followed by AC metal deposition (stage 2). Optical effect: relatively substantial amounts of metal deposit (a few weight percent and a few μm height) are present and with significantly different lengths in different pores. Incident light is scattered and absorbed in the structure. This is a Rayleigh type scattering because the pore dimensions (order 20 nm) are smaller than the wavelengths of visible light (350-700 nm). The blue end of the light spectrum is scattered and ultimately absorbed by the structure more than the red end of the spectrum resulting in brown/bronze coloured light emerging. The higher the deposit height, the more multiple scattering and loss of light intensity, and hence the darker the shade of the colour.

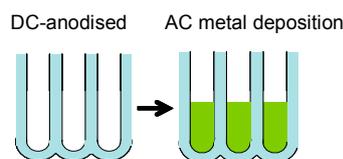


Fig.1 - Bronze and black colours: 'conventional' process: DC-anodising in sulphuric acid (stage 1) + AC metal deposition (stage 2)

Grey and clear interference colours (Fig.2)

- 1st generation interference processes = greys: This is a two-step anodising procedure: DC-anodising in sulphuric acid for the basic pore structure (stage 1), followed by anodising in phosphoric acid or sulphuric acid under different conditions compared to the first step to modify the pore structure adjacent to the barrier layer (stage 2). This is then followed by AC deposition of metal in the modified pores (stage 3).

- 2nd generation interference processes = clear colours: The procedure is the same as for the grey colours, but after AC metal deposition there is an additional re-anodising step (stage 4) (DC or AC in dilute acid solution for example) to cause further porous film growth beneath the deposits (metal deposition and re-anodising can be combined in one process, but this requires a very critical balance between the solution parameters).

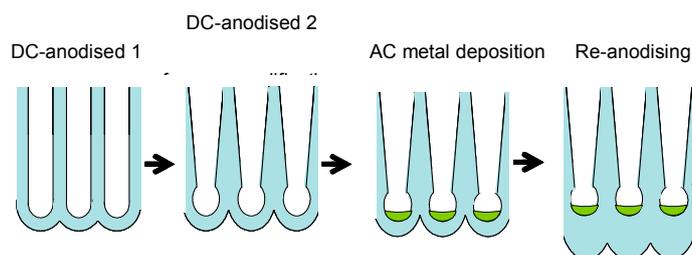


Fig.2 - Grey and clear interference colours: DC-anodising in sulphuric acid (stage 1) + anodizing in phosphoric acid or sulphuric acid (stage 2) + AC metal deposition (stage 3; final step for greys)+ re-anodising step (stage 4; additional step for clear colours)

Optical effect: Grey and clear colours are produced by thin-film interference phenomena. In this case, the pore structure of the anodic film is designed so that a relatively small amount of metal electro-deposit is constrained to a uniform thin layer adjacent to the aluminium substrate. Reflections from the surface of this layer and the surface of the aluminium (or other) interface interfere to produce colours dependent on the thickness of the deposited layer and underlying barrier layer. Interference colours are possible for a separation between the reflecting parallel planes in the order of the wavelength of light (a few hundred nm). The way the parts of the light reflected from the upper and lower planes recombine and the optical path difference between them, controls whether constructive or destructive interference occurs, the former resulting in a colour. As more metal is deposited the separation between these two surfaces is increased and the colour changes. The height of the metal deposit in the pores, the porosity at the pore base and the amount of re-anodising beneath the deposits determine the colour.

3. Experimental

A 5xxx series alloy, typical for outdoor building applications, was used in this project. The substrates were first thoroughly cleaned using standard degreasing, alkaline etching and acid

neutralisation steps before being anodised in a H_2SO_4 solution under DC current conditions to produce a porous anodic layer of around 12 microns. The samples then went through a pore modification step (still in the same H_2SO_4 solution) but under applied AC voltage conditions (sample 1 for 3 min and sample 2 for 5 min) to change the pore dimensions at the base. The third step was kept constant, i.e. electro-colouring in a Sn-sulphate solution at room temperature under applied AC current conditions to deposit Sn into the porous anodic film before being sealed in boiling demineralised water. Field-emission-Scanning Electron Microscopy and Energy Dispersive X-ray analysis (FEG-SEM/EDX) were used for the visualisation and elemental analysis of the microstructures with a 10 nm lateral resolution. These tools allowed a detailed visualisation and characterisation of coloured cross-sections and were instrumental to collect the input data for the optical model. The $L^*a^*b^*$ values as defined in 1976 by CIE (Commission Internationale de l'Eclairage) were determined with Total Integrated Scattering (TIS), using a Hunterlab Ultrascan XE instrument with a D65 light source which produces an uniform spectrum ranging between 360-700nm, quite similar to natural day light.

4. Results and discussion

FEG-SEM and TIS results

In table 1, the dimensions of the pore-modified section and the colour $L^*a^*b^*$ values are collected.

Table 1 - Summary of the FEG-SEM and TIS results (PM= Pore modified section)

N°	Colour	$L^*a^*b^*$	PM d1 (nm)	Further barrier growth d0 (nm)
1		64.9 -5.9 23.8	250	0
2		64.4 1.3 15.8	450	60

An optical model as presented in Fig.4 was developed to simulate and predict the reflective properties and hence the colour of the electro-coloured anodised surfaces as a function of the differences in microstructure (pore modification characteristics, underlying barrier film growth). The model is built by breaking up the cross-section of a real sample into a number of layers having significantly different optical constants: the substrate is represented by pure Al at the base, followed by a barrier layer of Al_2O_3 , a mixed layer of Al_2O_3 and metallic Sn (to represent the pore modified part of the cross-section with the Sn deposit), and finally a top layer representing the porous anodic layer containing Al_2O_3 and void (or hydroxide if the samples have been sealed). The pure Al_2O_3 layer inserted between the substrate and the pore-modified section represents any further growth (during the electrolytic colouring step) of the compact barrier layer. The percentage of void present is directly proportional to the porosity of the anodic films. Previous calculations based on pore geometry have shown that the anodic films formed under our experimental conditions were made up of around 44% void and were about 12 microns thick.

The model of Fig.4 was used to simulate

Sample 1 with real colour: 

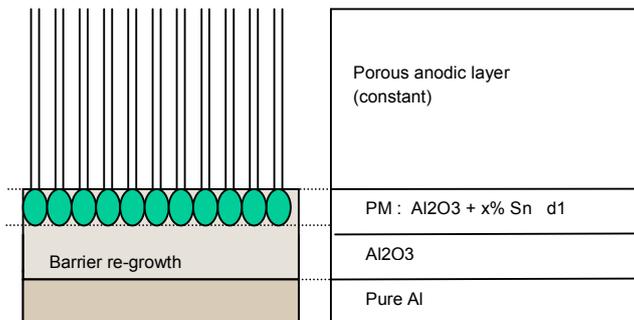


Fig.4 – Optical model for electro-coloured anodized aluminium (simplified model)

Four different series of simulations were obtained by changing in the model the pore-modified section thickness (i.e., $d_1=100, 250, 300, 450\text{nm}$) and by changing the percentage of Sn deposited in the pore-modified section (i.e., X varied from 100 to 0% Sn deposition). The simulated colours are shown in Fig.5.

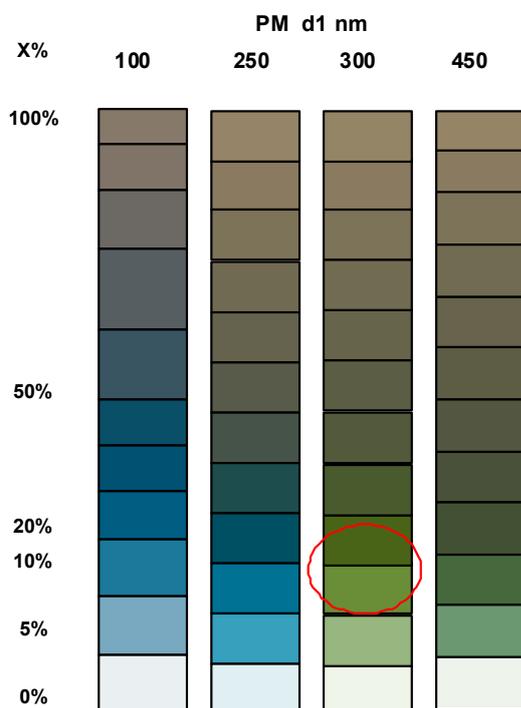


Fig.5 – Simulated colours based on the optical model of Fig.4 for the green sample 1

The best match between the real colour and the simulated colour is seen for a simulated PM section of around 300 nm and a PM filling with Sn between 10 and 20 %. This PM thickness value corresponds to the value determined from the FEG-SEM image of around 250 nm. It can be noted that the

thickness of the pure Al_2O_3 layer was taken to be zero in this case as there was no barrier re-growth observed. The percentage of Sn deposition may be confirmed by XRF quantification.

The same optical model was used to simulate Sample 2 with real colour: 

In this case, the model included also a barrier re-growth layer ($d_0=60$ nm) under the pore-modified section.

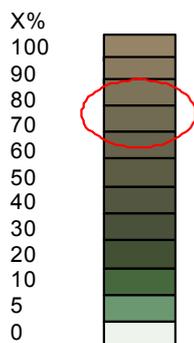


Fig.6 - Simulated colours based on the optical model of Fig.4 for the beige sample 2

In this case, the model parameters giving the nearest match are 500 nm of pore modification with 70-80% Sn deposit. On the FEG-SEM image the PM section was around 450 nm for this sample 2, hence this corresponds quite well to the simulated value.

5. Conclusions

We can conclude from the above results that it is possible to produce clear interference colours using environmentally friendly components such as Sn and H_2SO_4 . Further, we can conclude that the developed optical model of Fig.4 is able to predict the colour of a surface as per its microstructure to a very good degree of accuracy. It is highly sensitive to minute changes (porosity, percentage of metal deposition, presence of barrier re-growth, etc) on a nano-scale and thus has a very good potential as a tool to relate process conditions to the resulting microstructure and hence to the final colour characteristics of the metal surface.

6. References

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