Thorough electrochemical kinetic and energy balance models clarifying the mechanisms of normal and abnormal growth of porous anodic alumina films

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ABSTRACT

Thorough kinetic and energy balance models of growth of porous anodic alumina were formulated. Insight into film growth mechanisms showed that all local processes interact with those in the rest surface and the processes rates and parameters vary along Al surface, imperceptibly in normal and perceptibly in abnormal film growth. Al was anodised at 0.51 and 1.02 M H_2SO_4, 0–25 °C and anodic potential 23.5–25 V. The normal growth or abnormal one presenting island-like and strong burning were discerned and related with peculiar chronoamperometric plots. Island-like burning emerges at random places in the two Al faces above threshold conditions after a current density boundary in the second transient stage. Among this stage and quasi-steady state the plots show intense maxima and poor reproducibility. More afar from them this burning near a side is transformed to strong at corresponding positions in Al faces at this stage after a higher current density boundary. Plots rise fast coming from fast rise of current in burnt area due to avalanche-like hastened processes. Burning is a joint kinetic, Joule heating, thermochemical and heat transfer local effect yielding higher local current density and real anodising temperature. It emerges after the self-regulated mechanism of normal film growth collapses when local starting parameters, like thickness of barrier layer and/or attached electrolyte layer, etc. distributed in Al surface exceed limiting values which vary with conditions, experimental details and position. New methods to avoid burning can be elaborated that are vital for proper Al anodising.

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1. Introduction

In industry Al materials and parts are coated by porous anodic alumina films (PAAF) for mechanical, civil, architectural, aerospace engineering, etc. applications. Basic demand is the as uniform as possible growth of proper thickness films without mostly macroscopic defects [1–3]. The applications of PAAF in other areas like rechargeable batteries, magnetic memories, nuclear reactors, fuels cells, templates for synthesising emitters, nanoscience and nanotechnology, catalysis, etc. [4–9] and the currently developing technology [10–16] where the long range regular porous nanostructure is crucial put even more strict demands. But during Al anodising, e.g. in the main pore forming electrolytes H_2SO_4, $H_2C_2O_4$ and H_3PO_4, a highly undesirable, usually damaging, phenomenon called burning emerges which is easily discernible macroscopically. Film growth is abnormal degrading the coatings. It is a major problem in laboratory and industry mostly for hard anodising. Burning is local

very fast Al consumption and oxide film growth, where Al is thinning and the oxide film thickens and becomes whitish, darker, black, brown, generally coloured. At a given voltage, the rise in current no tending to decline shows burning causing among other effects uncontrolled breakdown and dissolution of film [1]. Burning occurs also at constant current [17–22]. In burnt areas rupture of film continuity and cracks appear [1,20,21]. Earlier it was suggested that in burning area the electrolyte is heated, at potentiostatic anodising the current density rises and the progressively increasing heating causes current flood, film is highly degraded due to its attack by hot electrolyte and becomes soft [1–3]. Also it was linked with high starting voltage above critical values, poor bath stirring, electrical contact problems, Al alloy composition, thin parts, fresh bath, etc. [1–3,23]. It appears at places where localized heating occurs [19]. Definition of burning conditions and key thresholds for hard anodising was tried but these vary and are not efficiently usable.

Now burning is related with high local current density that rises notably the local temperature [19,20,24,25]. It is linked with

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Nomenclature

a_2 and a_3 activation (half jump) distances of O^{2-} and Al^{3+} transport inside the barrier layer (nm)

AM_{Al} atomic mass of Al

A_2 $N_{2,m,a}v_{2,a}n_2FN_A^{-1}$ (mA cm^{-2} or A m^{-2})

A_3 $N_{3,m,a}v_{3,a}n_3FN_A^{-1}$ (mA cm^{-2} or A m^{-2})

B_2 n_2a_2 (nm)

B_3 n_3a_3 (nm)

c_a concentration of H_2SO_4 anodising electrolyte (M)

c_i concentration of ionic i species in pores, attached layer and adjacent layer up to reference electrode or in bath bulk solution during anodising (mol μm^{-3})

$C_{p,Al}$ molar heat capacity of Al (J mol^{-1} K^{-1})

d_{Al} density of Al (2.7 g cm^{-3})

D, D_b, D_c and D_a diameter of the hemispherical section surface across the barrier layer, pore base diameter, cell width and average D across the barrier layer in steady state (nm)

D_i diffusivity of ionic species i in pores, attached layer and adjacent layer or bath bulk solution (μm^2 s^{-1})

$2^{-1}(D_c - D_b)$ barrier layer thickness (nm)

Δm difference of Al anode mass after and before anodising (g or mg)

ΔH_a average across the barrier layer change of enthalpy between ordinary and transient oxide lattice structures involved in ionic charge transport in this layer (J mol^{-1})

ΔP $P_{an} - [jS(R_{pfs} + R_{attl} + R_{bs}) + \hat{E}_{diff,pfs}h + \hat{E}_{diff,attl}h_{attl}]$

E local low field intensity in electrolyte from pores depth to reference electrode ($E = E_{ohm} + E_{diff}$) (V μm^{-1})

E_{ohm} and E_{diff} low field intensities due to applied external potential drop and to diffusion potential drop emerging during the passage of ionic current in electrolyte (V μm^{-1})

$\hat{E}_{diff,pfs}$ and $\hat{E}_{diff,attl}$ mean E_{diff} along the pores and across the attached layer (V μm^{-1})

$\hat{E}_{diff,pfs}h$ and $\hat{E}_{diff,attl}h_{attl}$ diffusion potential along the pores and across the attached layer during anodising (V)

E_{bl} mean high field strength across the barrier layer (V nm^{-1})

f_B Bjerrum activity coefficient

F Faraday's constant (96487 C mol^{-1})

h_f, $h_{f,a}$, h, h_{attl} and h_{bs} film thickness, average film thickness, length of pores ($\approx h_f$), thicknesses of the attached layer and thickness of adjacent layer up to reference electrode (μm)

j, j_a and j' current density, average current density and this in non-burning surface region (mA cm^{-2} or A cm^{-2})

$j_{extr} = j_{min}$ extreme (minimum) of j predicted by kinetic Eq. (11) at $T_{an} = T_{an,extr}$ (mA cm^{-2})

j_i flow rate of ionic species i (mol μm^{-2} s^{-1})

κ $\sum u_i$ = Electrical conductivity of electrolyte (Ohm^{-1} μm^{-1})

k Faradaic constant of oxide production, $MM_{Al2O3}(6F)^{-1}$ = 1.761×10^{-4} g C^{-1}

k' rate constant of film thickness increase 6.9833×10^{-5} cm^3 C^{-1}

$k_{ht,ox}$, $k_{ht,pfs}$, $k_{ht,attl}$ and $k_{ht,tot}$ thermal conductivity of oxide, pore filling solution and attached layer and total heat transfer coefficient (W cm^{-1} K^{-1})

l index in parameters   generally local parameter in a small or large Al surface area for normal film growth or average parameter in burning region or local parameter in small area in burning region

l_{Al} mean thickness of Al metal remaining unconsumed during anodising (mm)

me metal

$m|o$ metal|oxide interface

$m_{Al,sod}$ and $m_{Al,F}$ consumed Al mass found by selective oxide dissolution and by Faraday's law (g or mg)

$m_{ox,sod}$ and $m_{ox,mb}$ oxide mass found by selective oxide dissolution and by the mass balance method (g or mg)

MM_{Al2O3} molar mass of Al_2O_3

n surface density of oxide cells/pores near the Al substrate surface in steady state (cm^{-2})

n_2 and n_3 valences of O^{2-} and Al^{3+} ions

N_A avogadro constant (6.022×10^{23} mol^{-1})

$N_{2,m,a}$ and $N_{3,m,a}$ average across the barrier layer surface concentrations of mobile O^{2-} and Al^{3+} (cm^{-2})

v velocity of solution imparted by convection

$v_{2,a}$ and $v_{3,a}$ average across the barrier layer vibration frequencies of O^{2-} and Al^{3+} ions or the number of chances per s the ions may jump the energy barrier (activation energy) if they have sufficient energy (s^{-1})

$o|e$ oxide|electrolyte interface

ox oxide

p_a average porosity of the film (dimensionless)

P_{an} anodic potential vs. SHE (V)

$P_{an} - P_{cath}$ potential difference between anode and cathode or anodising voltage (V)

$P_{an} - P_{ref}$ potential difference between anode and reference electrode (V)

Q passing electric charge (C)

R universal gas constant (8.314 J K^{-1} mol^{-1})

R_{pfs}, R_{attl} and R_{bs} resistance of solution in pores, attached layer and next layer up to reference electrode (Ohm)

S_{Al} one face entire geometric surface area of Al specimen (cm^2)

S_g geometric surface area of Al specimens that is oxidised during anodising (cm^2)

S_a average hemispherical surface across the barrier layer for all barrier layer units along S_g $\approx 2^{-1}S_g$ $(2.093 + 2^{-1}\pi nD_b^2)$ (cm^2)

t anodising time (min or s)

tn_{an} and tn_{ca} transport numbers of O^{2-} and Al^{3+} across the barrier layer (dimensionless)

$tn_{an,a}$ and $tn_{ca,a}$ average tn_{an} and tn_{ca} when j and/or T_{an} vary during anodising and/or along the Al surface

T temperature of bath bulk solution (°C or K)

T_{an} and $T_{an,extr}$ real anodising temperature in the barrier layer region and the T_{an} where Eq. (11) presents an extreme (minimum) of j (°C or K)

u_i, $u_{i,pfs}$, $u_{i,attl}$ and $u_{i,bs}$ specific ionic conductance (conductivity) of i species and this conductivity in pore filling solution, attached layer and adjacent bath solution layer up to reference electrode at each plane parallel to film surface (Ohm^{-1} μm^{-1})

$\hat{u}_{i,pfs}$, $\hat{u}_{i,attl}$ and $\hat{u}_{i,bs}$ average $u_{i,pfs}$, $u_{i,attl}$ and $u_{i,bs}$ in the pores and in the attached and adjacent layers (Ohm^{-1} μm^{-1})

U_i and U_i^0 equivalent conductivity (mobility) of ionic i species in pores, attached layer and bath bulk solution and this mobility at infinite dilution (Ohm^{-1} μm^2 mol^{-1})

$W_{2,a}$ and $W_{3,a}$ average real activation energies of O^{2-} and Al^{3+} transport across the barrier layer (J mol^{-1})

W_2' $W_{2,a} + \Delta H_a$ (J mol^{-1})

W_3' $W_{3,a} + \Delta H_a$ (J mol^{-1})

z $(-W_3' + B_3FE_{bl})/(-W_2' + B_2FE_{bl})$ (dimensionless)

z_i charge of ionic i species in pores, attached layer and bath bulk solution (dimensionless)