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# High current anodization of magnesium and magnesium alloys

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A thesis submitted for the degree of Doctor of Philosophy,  
The University of Auckland, 1996.

## **Abstract**

### High current anodization of magnesium and magnesium alloys

*Ellen Angharad Carter*

Pure magnesium and three magnesium alloys containing different amounts of aluminium (2–9%) plus zinc and manganese were anodized with constant current density in sodium hydroxide solution with and without fluoride or phosphate ions. Electric field strengths of resultant anodic films were calculated from galvanostatic transients. These transients showed three characteristic features: linear voltage increase, noisy high voltage signals accompanied by sparking, and sawtooth-like events characterized by instantaneous voltage drops followed by slower voltage increases. Each feature was linked to certain physical processes occurring in the metal/film/solution system.

Oxidation of magnesium and magnesium alloys formed anodic films with bilayer structures: a passive barrier layer adhering to the metal electrode, topped by a porous secondary layer. Cation injection into the barrier film across the metal/oxide interface was the rate determining step for film growth. Interstitial cations migrated through the film under the influence of the electric field. At the film/solution interface they reacted with electrolyte species and either thickened the film or dissolved in solution.

Electric field strength was constant for particular metal/solution combinations and was independent of applied current density. Changing the electrode material altered the resultant electric field strength: pure magnesium produced oxides with lower electric field strengths than films formed on the three magnesium alloys. Changing the electrolyte had no discernable effect on the electric field strength. Charge efficiency of the film growth process was investigated by oxygen gas evolution; efficiency decreased during sparking.

Ion beam analysis (Rutherford backscattering, fluorine depth profiling and nuclear reaction analysis) coupled with X-ray photoelectron spectroscopy, scanning electron microscopy, X-ray diffraction studies and Raman spectroscopy gave information about the anodic film surface. These techniques showed that oxides formed on magnesium-aluminium alloys were thinner than those formed on pure magnesium caused by aluminium dissolution. Fluorine depth profiling revealed that concentration profiles for fluorine in anodic oxides formed in fluoride-containing solution altered depending on the aluminium content of the electrode material.



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## **Symbols and abbreviations**

<i>a</i>	half jump distance between interstitial sites in oxide lattice
aq	aqueous
A	ampere
	area
	constant
Å	angstrom
$A_r$	atomic weight
AC	alternating current
B	byte
	constant
<i>c</i>	constant
C	constant
CAFE	corporate average fuel economy
CE	counter electrode
<i>d</i>	deuterium particle
<i>d</i>	spacing between crystal planes
D	measure of spread of a sample
DC	direct current
<i>e</i>	electron
<i>e</i>	charge on electron
<i>E</i>	potential difference between metal and reference electrode
<b><i>E</i></b>	electric field strength
$E_B$	binding energy
$E_{eq}$	equilibrium potential of hydrogen evolution at the cathode
$E_K$	kinetic energy
Eqn	equation
eV	electron volt
<i>F</i>	Faraday constant = 96487 C mol <sup>-1</sup>
Fig.	figure
FWHM	full width at half maximum
<i>g</i>	gas
	gram
<i>G</i>	Gibbs free energy
$\Delta G_f^\ominus$	Gibbs free energy of formation
GPS49	standard sample used for calibration of ion beam accelerator
<i>h</i>	Planck constant = 6.626196 x 10 <sup>-34</sup> J s
<i>i</i>	current
I	current
IBA	ion beam analysis
<i>j</i>	current density
$J_M$	flux of cation vacancies
$J_O$	flux of oxygen vacancies
<i>k</i>	Boltzmann constant = 1.380622 x 10 <sup>-23</sup> J K <sup>-1</sup>
$k_x$	constant (where x = 0, 1, 2, ...)

$K_s$	solubility constant
l	liquid
$L$	film thickness
L	litre
m	mass
	metal
	metre
M	metal
$M_i^*$	interstitial metal cation
$M_M^x$	metal cation occupying metal cation site in crystal lattice
max	maximum
min	minimum
	minute
mol	mole
$n$	integer
	number of mobile ions per unit volume
	number of moles
	order of the Bragg reflection
N	measure of the separation of outlier
	number of atoms per unit area of metal surface
NHE	normal hydrogen electrode
NRA	nuclear reaction analysis
$O_O^x$	oxygen anion occupying oxygen anion site in crystal lattice
$p$	pressure / Pa
p	p-type electron
	proton
PE	potential energy
ppm	parts per million
$q$	charge on ion
$Q_e$	charge used in oxygen production
$Q_o$	total Faradaic charge passed
$r^2$	linear correlation factor
$R$	gas constant = $8.31434 \text{ J K}^{-1} \text{ mol}^{-1}$
$R_{EL}$	electrolyte resistance
$R_{PB}$	Pilling-Bedworth ratio
$r_i$	ionic radius of element $i$
RBS	Rutherford backscattering
RE	reference electrode
s	s-type electron
	second
	solid
SCE	saturated calomel electrode
SEM	scanning electron microscope
	scanning electron microscopy
SENRS	simulation and evaluation of nuclear reaction spectra

SIMS	secondary ion mass spectrometry
std. dev.	standard deviation
$t$	time
$T$	temperature / K or °C
$V_M$	metal atom vacancy in metallic lattice
$V$	volt
	voltage / V
	volume / m <sup>3</sup>
$V_i$	molar volume of element $i$
$V_m$	molar volume / m <sup>3</sup> mol <sup>-1</sup>
$V_M'$	metal cation vacancy in crystal lattice
$W$	potential energy barrier height / eV
WE	working electrode
$x$	length
$x_i$	atomic percentage of element $i$ in the alloy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
$z$	number of electrons

### ***Greek symbols***

$\alpha$	alpha particle
	transfer coefficient
$\beta$	fraction of non-aluminium ions
$\chi$	charge on metal ion
$\delta$	charge on ion ejected from barrier layer
$\Delta$	change
$\varepsilon$	fraction of charge used in oxygen production
$\phi$	potential difference across film
	work function
$\phi_m$	metal potential
$\phi_s$	solution potential
$\Delta\phi_f$	potential drop across film
$\Delta\phi_m$	metal/film interfacial potential difference
$\Delta\phi_{ref}$	reference potential
$\Delta\phi_s$	film/solution potential difference
$\gamma$	gamma ray
	surface roughness factor
$\eta_{CE}$	overpotential at the counter electrode
$\lambda$	wavelength
$\mu$ PDSM	micro powder diffraction search/match
$\nu$	frequency of simple harmonic motion vibration
$\theta$	angle of incidence <i>or</i> angle of reflection
	fraction of cations released by barrier layer that precipitate to form outer layer
$\sigma$	charge density / C m <sup>-2</sup>
$\Omega$	ohm