Characterization of zinc-rich layers on aluminium

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Outline

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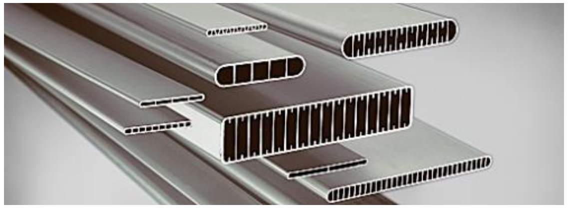
2. Sample preparation
3. GD-OES calibration
4. GD-OES results
5. SEM results
6. Modelling of Zn diffusion into Al substrate
7. Conclusions

Motivation



http://www.sapagroup.com/en/precision-tubing/hvacr/products/multi-port-extrusion/

- Heat exchangers
- Multi port extruded (MPE) profile
- Wall thickness less than 1 mm
- Possible challenge in practice: **pitting corrosion in Cl^-** environment

- Main market today: automotive industry, dominated by aluminium
- HVAC&R: growing market for aluminium use, dominated by copper.
  – Additional protection from pitting corrosion is needed

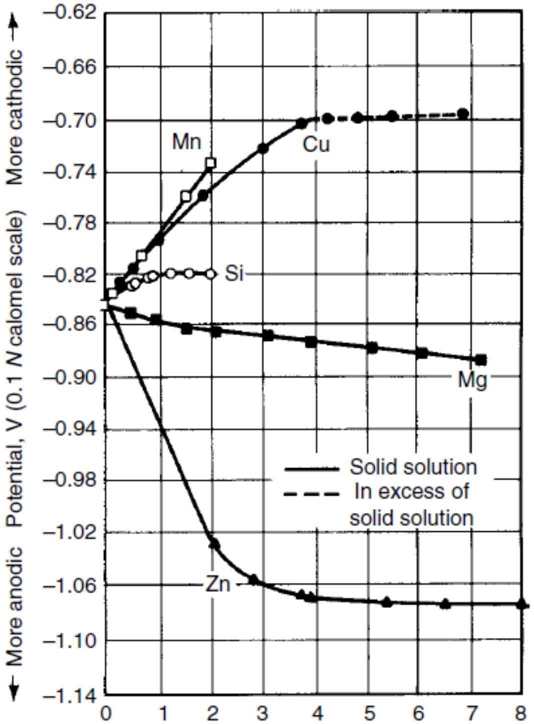
Motivation

Zn coating on Al

➢ Addition of Zn lowers Al potential

➢ Zn coating => **heat treatment** => creation of **Zn–rich layer**

➢ **Zn-rich layer** is expected to serve as a **sacrificial coating** and **reduce pitting** on Al substrate



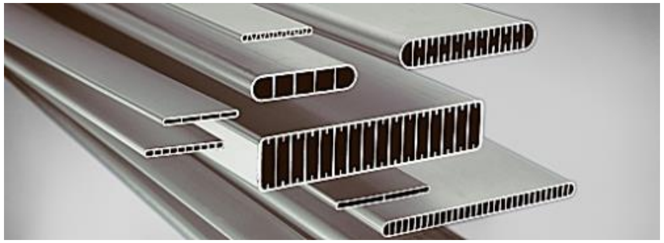
ASM Metal Handbook, Volume 13B - Corrosion: Materials. 2003

Objective

Objective: surface characterization of Zn rich layers on Al alloy

- **EDS**: poor resolution and analytical sensitivity, time-consuming
- **GD-OES**: nm depth resolution, good analytical sensitivity
  - Requires calibration.

Sample preparation



Samples: 3XXX Al MPE tubes. Composition:

Element	Al	Zn	Mn	Fe	Si	Mg
Content (wt%)	98.92	0.005	0.72	0.21	0.09	0.019

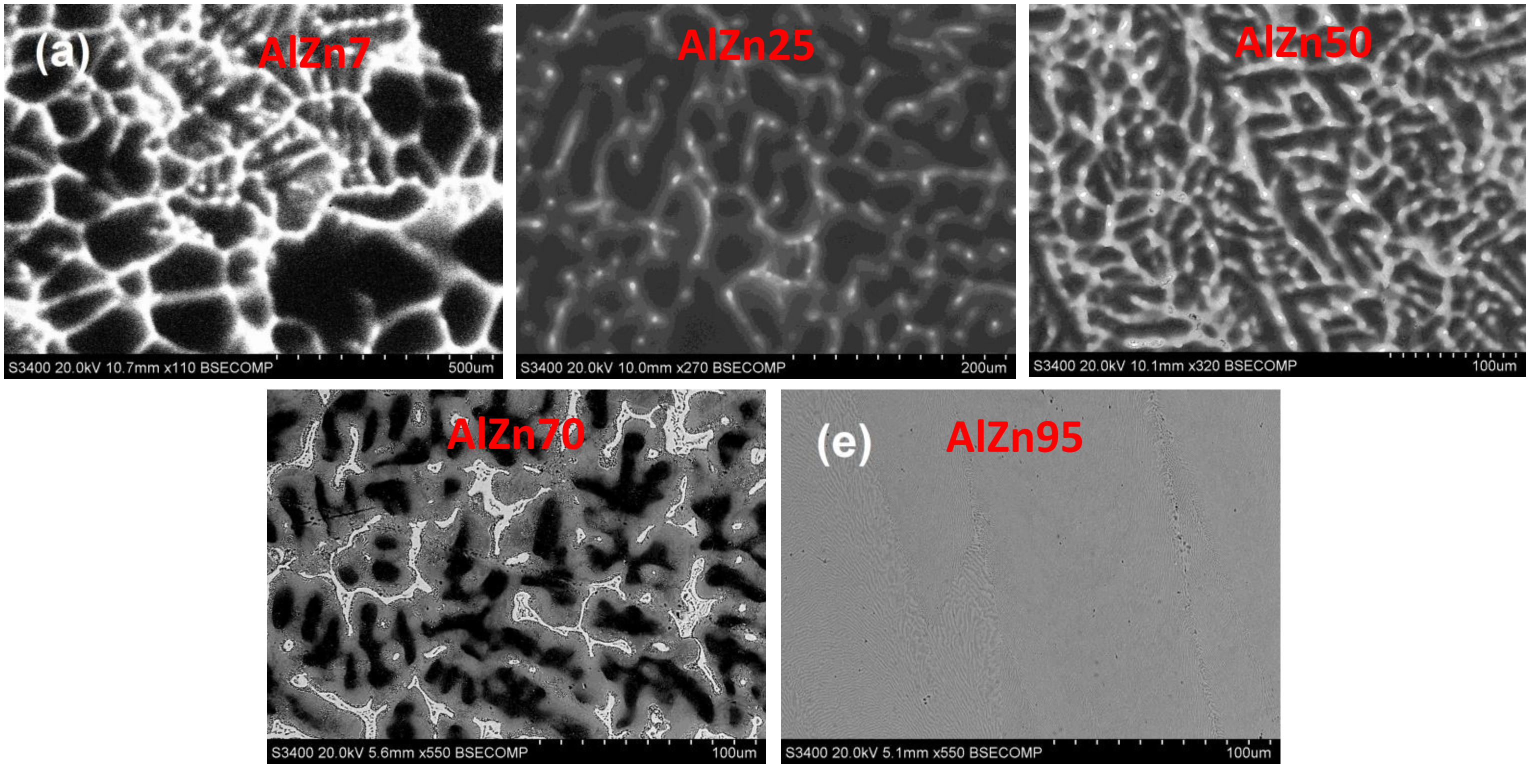
Zn coating: Zinc thermal arc spraying (ZAS) of ≈8±0.5 g/m^2 (measured by X-ray fluorescence (XRF) spectrometer)

Surface modification:

Heat treatment at various durations and temperatures for diffusion of Zn and forming the Zn-rich surface layer:

- 350-430 °C
- 1-5 hours

GD-OES Calibration of Al-Zn system. AlZn binary alloys



Alloy	AlZn7	AlZn25	AlZn50	AlZn70	AlZn95
Zn content (wt%)	6.8±0.5	26.4±1.8	49±1.5	71.6±2.4	94.5±0.8

GD-OES Calibration of Al-Zn system. Standards

Sample	Chemical composition (wt%)											
	Al	**Zn**	**Mn**	**Fe**	**Si**	**Mg**	**Ti**	**V**	**Ni**	**Cu**	**Cr**	**Pb**
Alloy1	98.93	0.02	0.69	0.2	0.1	0.01	0.015	0.07	0.003	0.0016	0.009	0.0006
Alloy2	98.91	0.0015	0.74	0.2	0.08	0.013	0.009	0.008	0.003	0.0013	0.0011	0.0009
Alloy3	98.9	0.0006	0.93	0.08	0.05	0.001	0.013	0.01	0.0025	0.0008	0.0002	0.0013
Alloy4	99.08	0.002	0.15	0.17	0.09	0.0025	0.01	0.01	0.003	0.46	0.0006	0.0008
Alloy5	99.16	0.19	0.33	0.08	0.08	0.12	0.017	0.01	0.0045	0.001	0	0
Alloy6	99.16	0.003	0.23	0.48	0.06	0.004	0.02	0.011	0.003	0.003	0.0007	0.0006
AA8112	98.2	0.035	0.11	0.66	0.52	0.014	0.028	0.028	0.02	0.26	0.024	0.008
7075AF	89.02	5.75	0.031	0.17	0.19	2.66	0.092	0.02	0.027	1.75	0.22	0.0073
2007AA	92.22	0.071	0.58	0.41	0.46	0.56	0.024	0.016	0.075	4.24	0.023	1.08
2011AC	92.77	0.047	0.023	0.26	0.12	0.015	0.017	0.017	0.024	5.62	0.019	0.53
5454AC	95.11	0.03	0.75	0.4	0.25	3.16	0.064	0.02	0.033	0.1	0.03	0.0035
SQ-10WP	99.99	0.0002	0	0.0004	0.0004	0.0002	0	0	0	0.0004	0	0
RA19/90	78.61	7.5	1.2	1.39	1.34	7.02	0.22	0.12	0.57	0.6	0.19	0.01
RA18/118	70.46	0.29	0.32	0.49	16.34	0.24	-	0.005	2.8	8.08	0.002	0.27

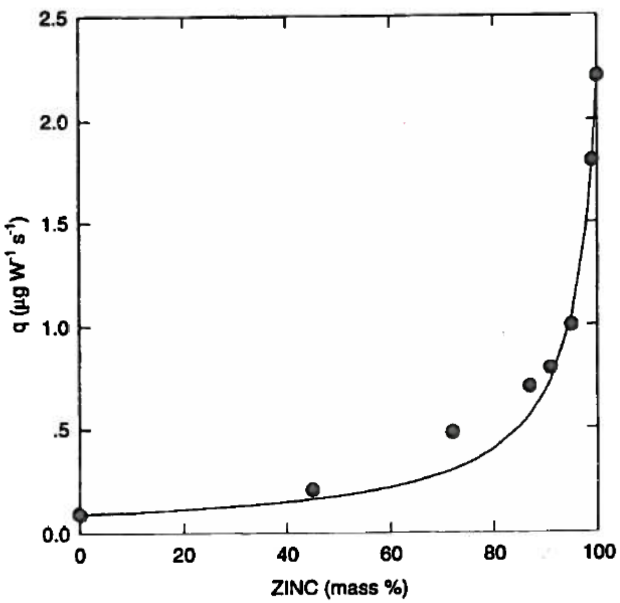
Standard	Chemical composition (wt%)							
CE650	**Al**	**Ti**	**O**	**N**	**C**	**W**		
	38	22	34	0.27	4.9	0.4		
1766-NBS	**Fe**	**Mn**	**Al**	**Si**	**Ni**	**Cu**	**C**	**Cr**
	99.8	0.067	0.012	0.01	0.021	0.015	0.015	0.024

GD-OES calibration of Al-Zn system

Spectral lines

Element	Al	Zn	Mn	Fe	Si	Mg
Line (nm)	396.152	481.053	403.448	371.994	288.158	285.213

AlZn alloys sputtering rates

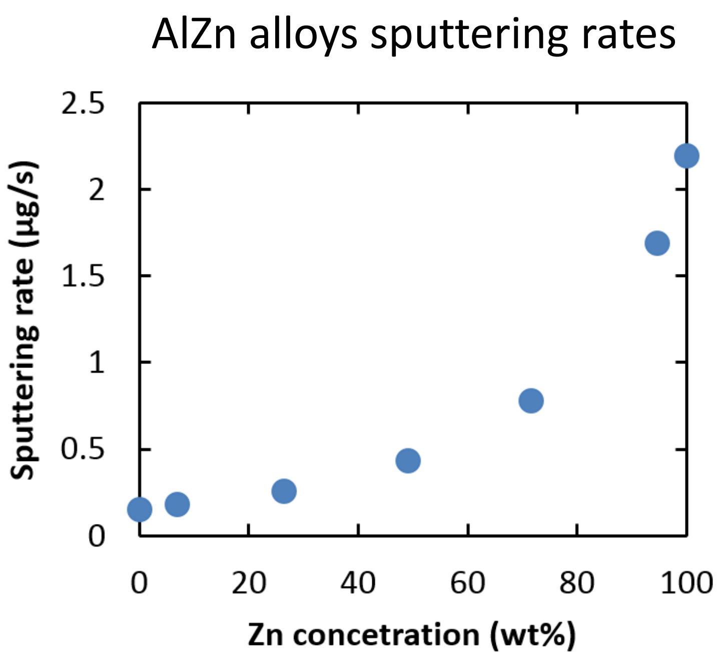


- 396.152 nm Al spectral line has high self-absorbance
- Al and Zn have large difference in sputtering rates
  - This introduces errors in calibration for alloying elements through sputtering rate measurements

R. Payling. In R. Payling, D. G. Jones, and A. Bengtson, editors, Glow discharge optical emission spectrometry, pages 267–68. New York: J. Wiley, Chichester, 1997.

GD-OES calibration. Sputtering rates of the standards

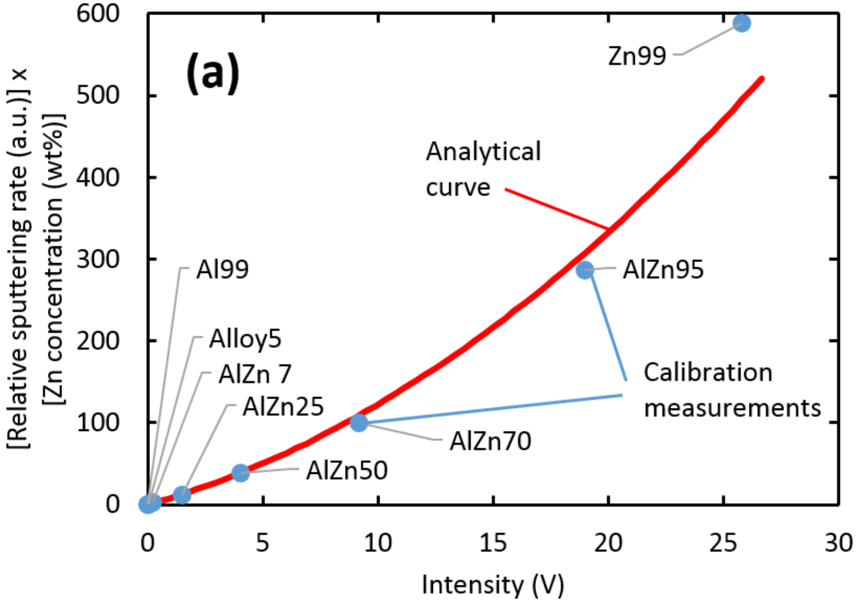
Standard	Sputtering rate (μm/min)	Relative sputtering rate
AlZn7	3.1	0.32
AlZn25	3.8	0.46
AlZn50	5.3	0.78
AlZn70	7.7	1.4
AlZn95	12.4	3.03
Alloy1	2.9	0.3
Alloy2	2.9	0.3
Alloy3	2.9	0.3
Alloy4	2.9	0.3
Alloy5	2.8	0.28
Alloy6	2.9	0.3
AA8112	3.2	0.33
7075AF	4.0	0.42
2007AA	4.1	0.44
2011AC	4.2	0.45
5454AC	3.4	0.34
SQ-10WP	2.9	0.3
RA19/90	-	0.45
RA18/118	-	0.49
CE650	1.3	0.18
1766-NBS	3.4	1
Al99	2.8	0.28
Zn99	22.1	5.89

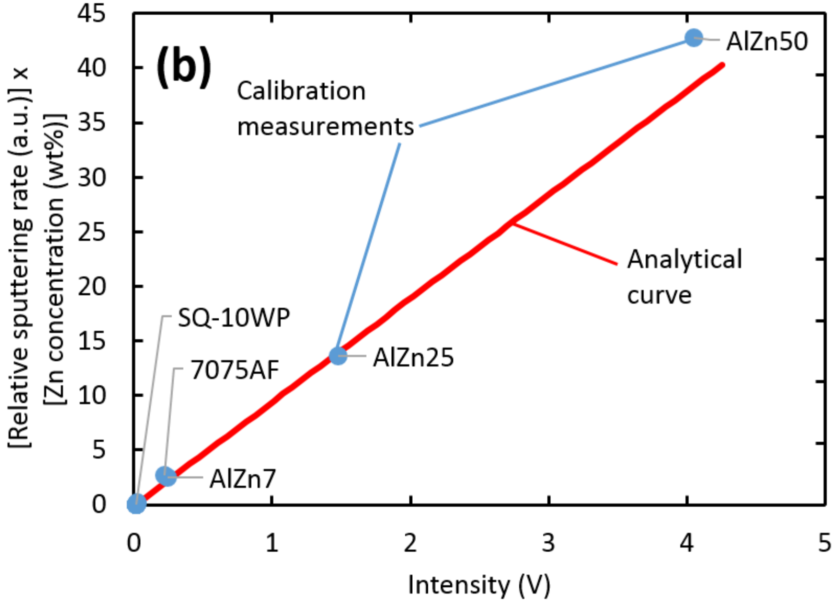


Error: 3-7%

Results. Calibration for Zn

Two Zn calibration curves: for Zn coatings (with Zn concentration up to 100 wt%) and Zn rich layers (Zn concentration below 50 wt%)

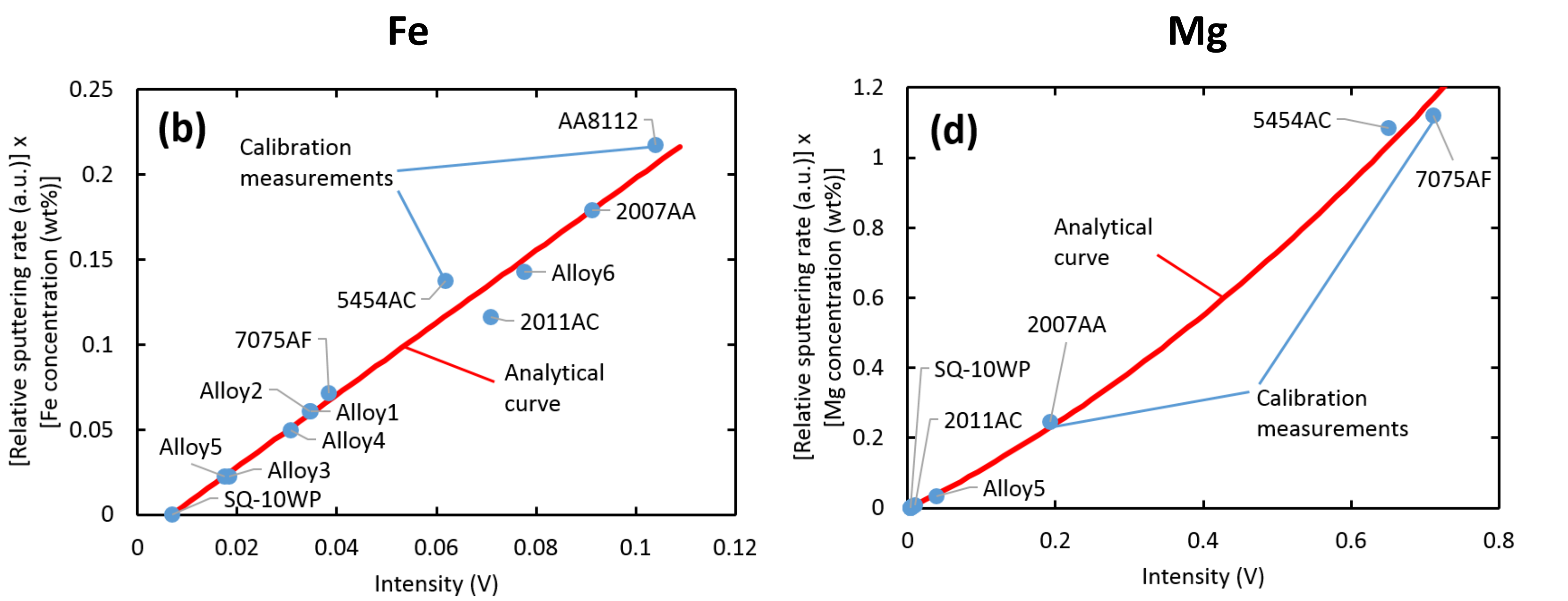




Detection limit: $DL = 3\sqrt{2}SD = 0.12\ wt\%$

SD is the standard deviation of replicated measurements of Zn signal in the Zn-free standard

Results. Calibration for Fe and Mg



285.213 nm Mg spectral line is a resonance line with high self-absorption

Results. Alloying elements in the base alloy

Compare results for Al 3XXX alloy with composition measured by Spark OES with accuracy of 2%

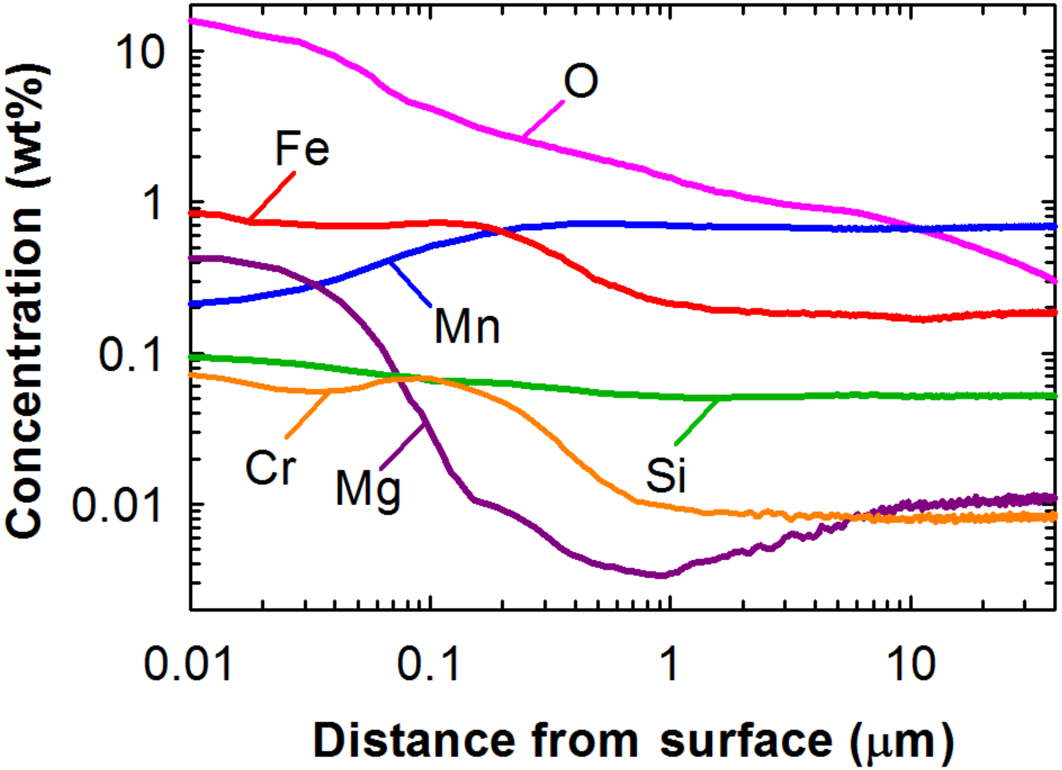
$$Deviation = \frac{Content(Spark\ OES) - Content\ (GD - OES)}{Content\ (GD - OES)} \times 100\%$$

Element	Content (wt%) Spark OES	Content (wt%) GD-OES	Deviation relative to spark OES
Mn	0.72	0.687±0.018	4
Fe	0.21	0.198±0.012	6
Si	0.09	0.072±0.006	20
Mg	0.019	0.016±0.002	13

- The deviations for Mn and Fe are quite small
- Mg calibration curve is non-linear, the calibration curve is intended for concentrations up to 3 wt%.
- Si spectral line has low sensitivity [1]

[1] R. Payling, D. G. Jones, and S. A. Gower. Quantitative-analysis with dc-glow and rf-glow discharge spectrometry. Surface and In-terface Analysis, 20(12):959–966, 1993.

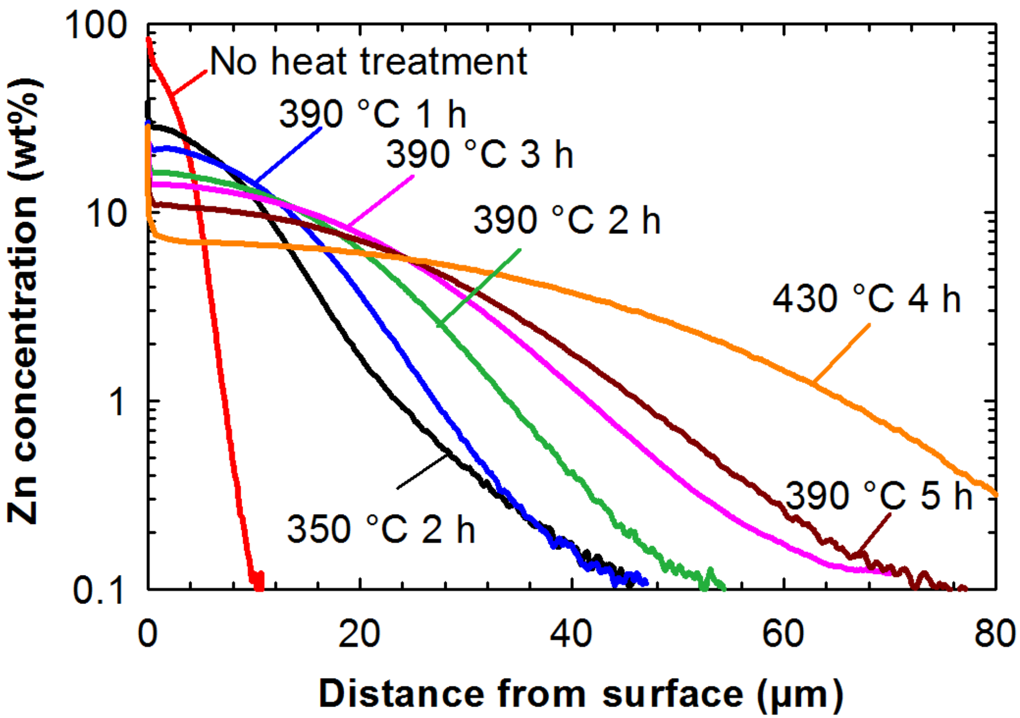
Results. GD-OES profiles: Base alloy, no Zn coating



Contamination from extrusion die?

Fe and Cr

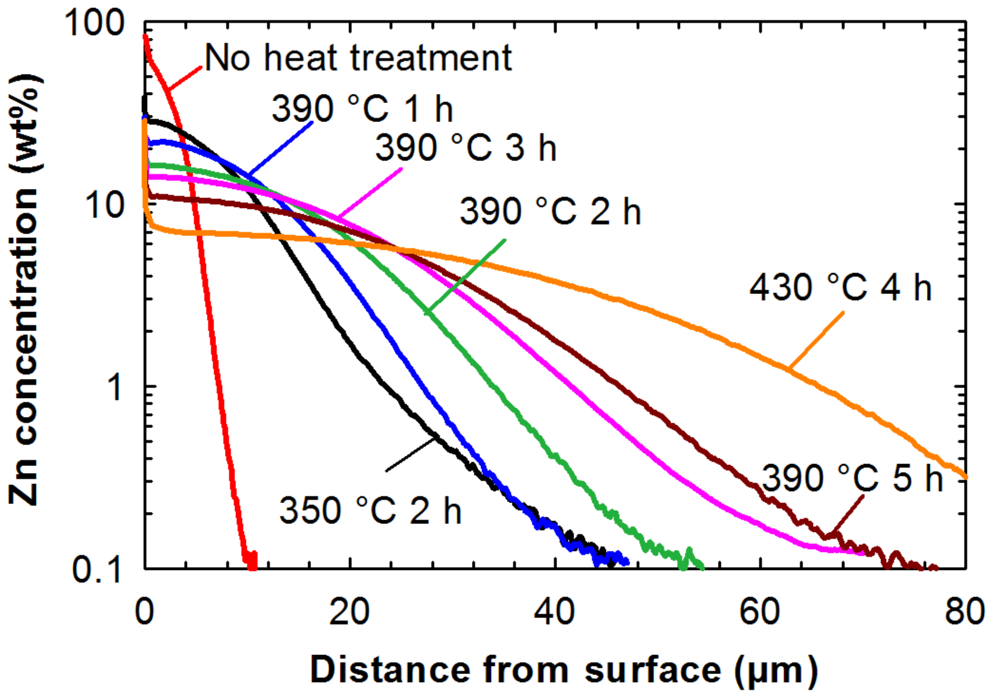
Results. ZAS samples: Zn concentration profiles



- Zn concentration does not exhibit 100 wt% for as sprayed coating
- High Zn concentration on the surface after heat treatment

=> Original as sprayed coating is non-uniform

Results. ZAS samples: Zn concentration profiles

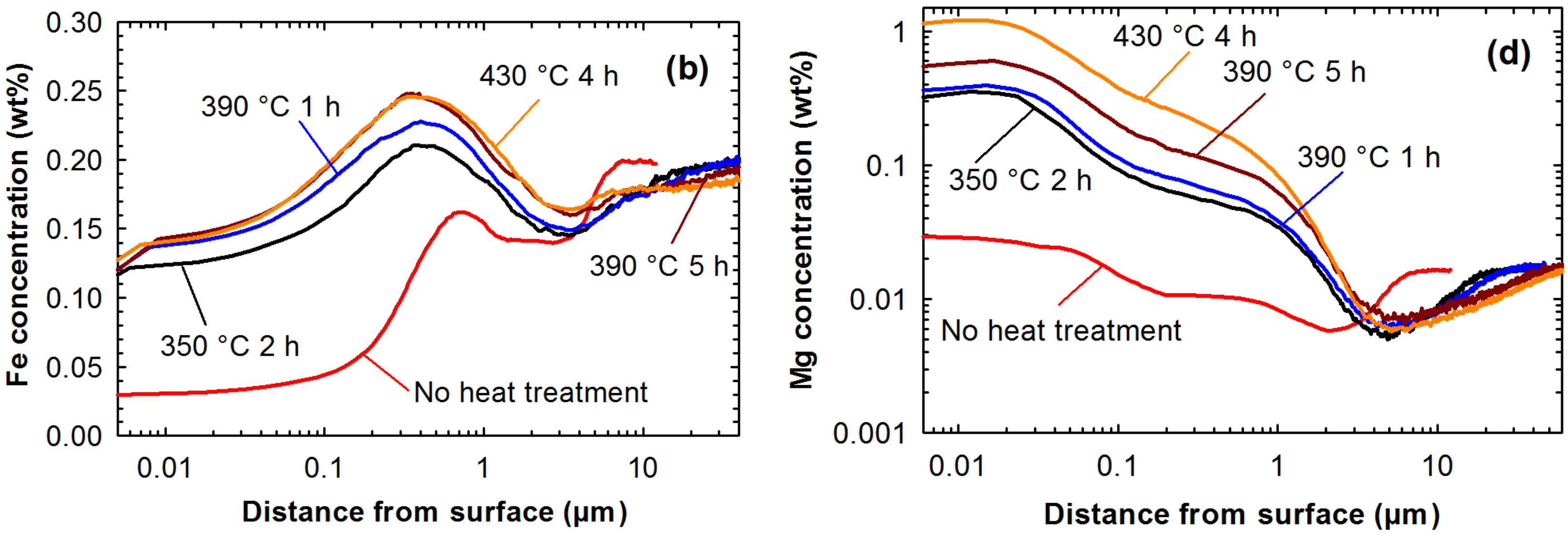


Heat treatment	Zn-rich layer thickness (µm)	Zn coating weight (g/m²)
No heat treatment		7.5
350 °C 2 hours	33.5	8.7
390 °C 1 hour	34.3	8.9
390 °C 2 hours	42	8.7
390 °C 3 hours	52.6	9.3
390 °C 5 hours	58.6	8.3
430 °C 4 hours	80.9	8.4

The layer thickness was estimated by assuming the depth at which Zn concentration dropped to 0.3 wt%

⇒ Average Zn weight is 8.7 g/m² for HT samples.

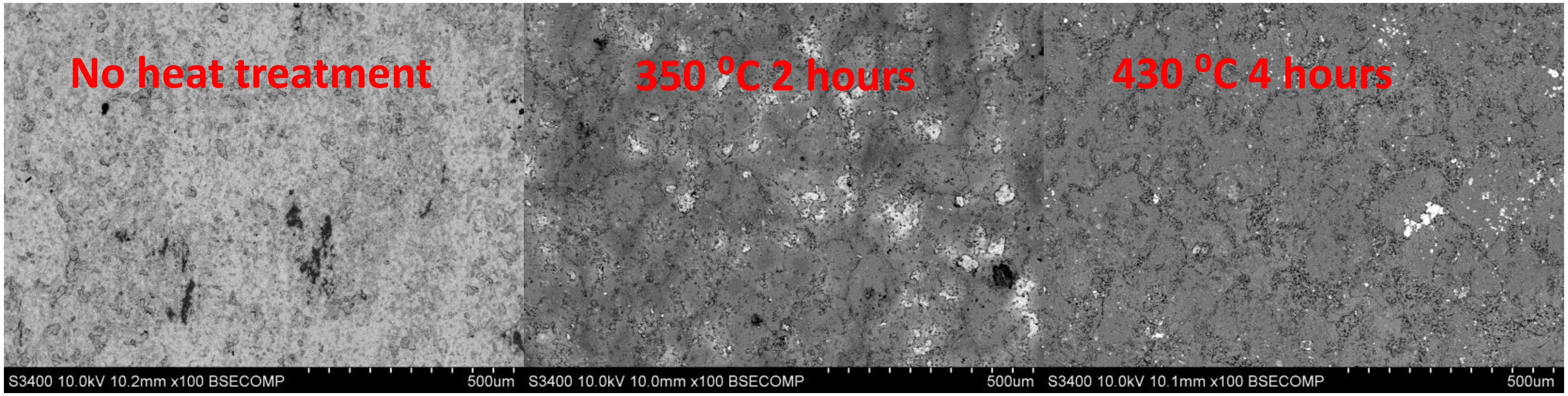
Results. Mg and Fe concentration profiles



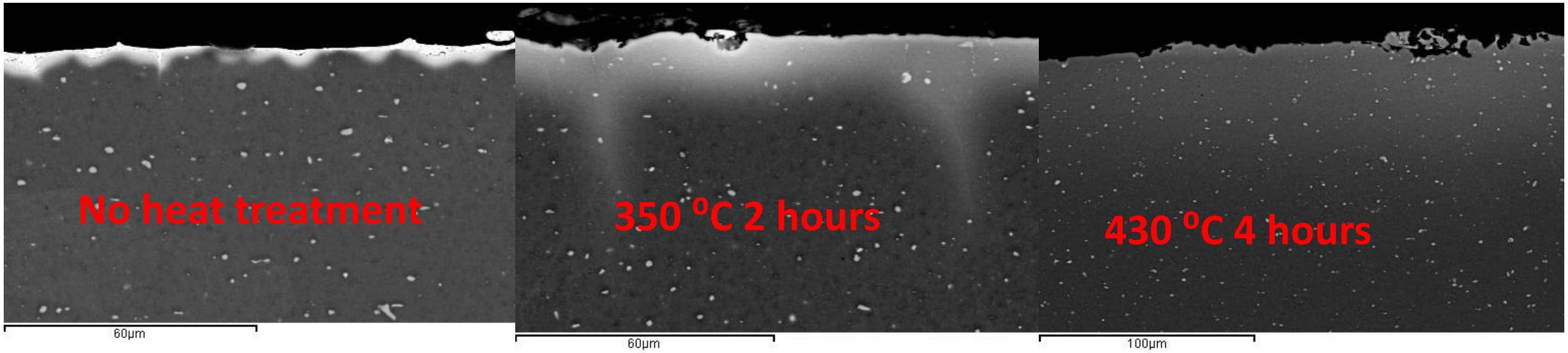
- Fe and Mg are enriched at the surface
- They have lowest concentration level at 5-6 µm depth which corresponds approximately to Zn coating thickness
- Mg and Fe become depleted deep into the Zn-rich layer

SEM of ZAS heat treated samples

Plan view



Cross section

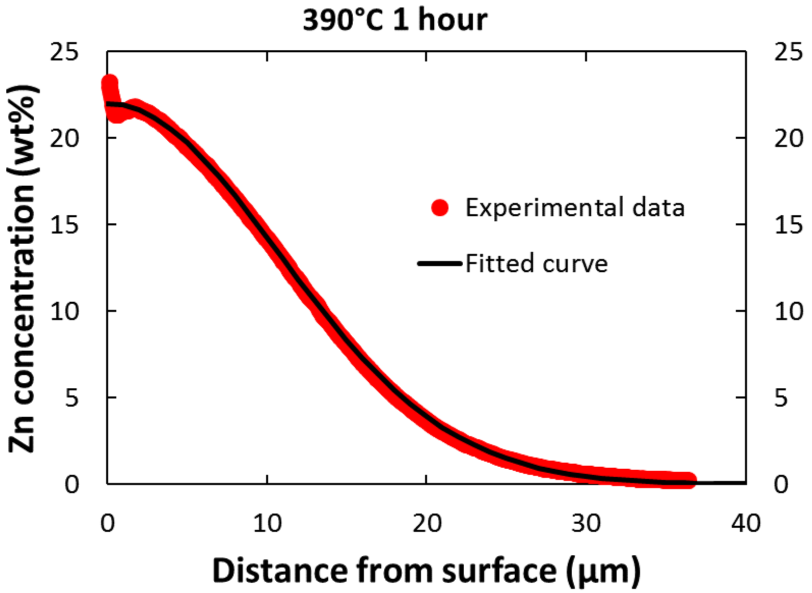


- Non-uniform Zn concentration
- Diffusion of Zn along grain boundaries
- Zn-rich layer thickness agrees with GD-OES values
- Nevertheless can be modelled by use of Fick’s law and an effective diffusion coefficient

Modelling of Zn diffusion into Al substrate

- Solution to 2nd Fick's law $C = \frac{1}{2} C_0 \left\{ \operatorname{erf} \frac{h-x}{2\sqrt{(Dt)}} + \operatorname{erf} \frac{h+x}{2\sqrt{(Dt)}} \right\}.$
- Describe initial Zn coating as a layer with concentration $C_0 = 100\ wt\%$ with depth of $h = 3\ \mu m$

  (based on GD-OES results)

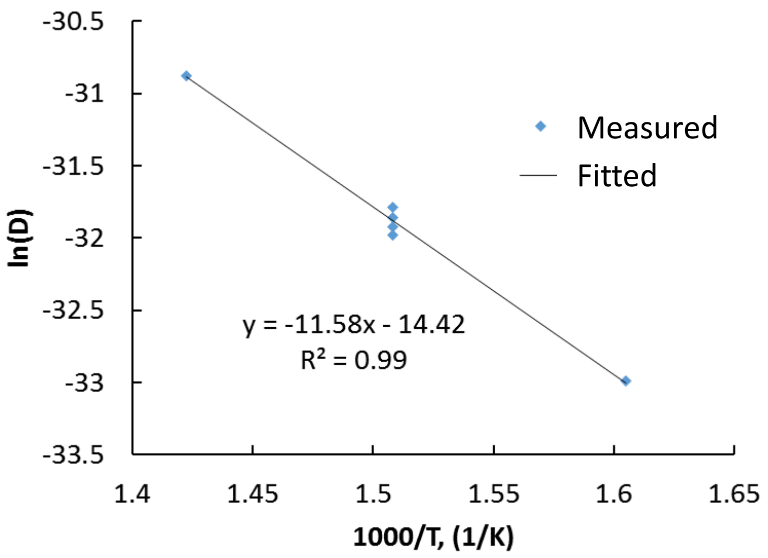


The experimental data (GD-OES profile) was fit by least square fit, by changing the diffusion coefficient *D* and maximizing R^2 (coefficient of determination)

In this case: $D = 1.57 \cdot 10^{-14}\ m^2/s$, $R^2 = 1$

Modelling of Zn diffusion into Al substrate

Heat treatment	D, (m^2/s)
390 1 hour	1.57E-14
390 2 hours	1.46E-14
390 3 hours	1.37E-14
390 5 hours	1.29E-14
350 2 hours	4.70E-15
430 4 hours	3.90E-14



Diffusion coefficient: $D = D_0 \exp(-E_a/kT)$

$$\ln(D) = \ln(D_0) - (E_a/kT) = b - ax$$

Plot $\ln(D) = f(1/T)$

$$D_0 = 0.055\ (cm^2/s)$$
$$E_a = 96.2\ (kJ/mol)$$

This allows simulation of Zn profiles for any heat treatment conditions

Conclusions

- The sputtering rates of the major components in the AlZn system differ widely with concentration. This does not seem to be a drawback in GD-OES calibration by using a few standards covering the full concentration range.
- Calibration of secondary alloying elements in such alloys is also possible and the accuracy depends on the nature of the spectral lines and the errors introduced by measurements of the sputtering rate of the standards.
- The GD-OES results based on Zn profiles agree well with the Zn content of samples and standards obtained independently by other methods (XRF and SEM)
- Despite the nonideal nature of the surface in terms of roughness and lateral variations in the initial Zn concentration, effective diffusion coefficient of Zn in Al was obtained by fitting the GD-OES depth profiles to the solution of Fick's second law at different temperatures. This allows prediction of Zn profiles expected for initial values of Zn load followed by application of different heat treatment temperatures.

Acknowledgements

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Thank you for your attention!