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ZCO-55: *Dross Minimization in the Galvanizing Bath*
ZCO-66: *Zn-Mg Alloy Galvanizing Bath Management*

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Outline

- Overview of ZCO-55 and ZCO-66 contract (2011-2014)

ZCO-55 Dross Minimization in the Galvanizing Bath

Task 1: Bottom Dross Treatment

Task 2: Optimizing Thermal Field within Bath for Dross Minimization

Task 3: Determination of Fundamental Aspects of Dross and Skimmings Formation Using Bench Scale Experiments

ZCO-66 Zn-Mg Alloy Galvanizing Bath

Task 1: Description of flow, composition and temperature fields in the bath with particular emphasis on the strip-liquid bath contact zones

Task 2: Numerical determination of the Zn-Al-Fe-Mg phase diagram in the zinc rich corner

Task 3: Determination of the optimum ingot feeding schemes

Task 4: Assessment of on-line chemical analysis techniques

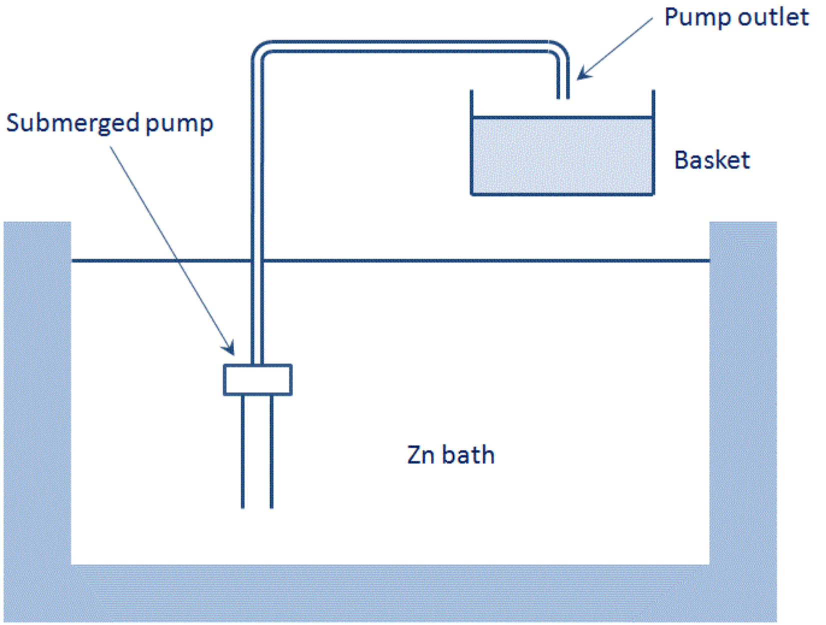
Task 5: Characterization of dross particles and skimmings from industrial baths using Mg rich solutions

- Strategy and work plan of ZCO-71 contract (2014-2017)

ZCO-55, Task 1: Bottom dross treatment

Summary of observations

- Exit stream from pump contains about 0.06% Fe, which is about double the average bath Fe content, indicating bottom dross enrichment;
- Basket drippings are essentially of the same or slightly lower Fe composition than the bath operating composition (0.030% Fe);
- Semi-solid material sampled from the top of the basket is rich in bottom dross at 1,23 % Fe;
- Drained bottom dross sampled from the top of a solidified basket is rich in bottom dross particles (up to 4.3 % Fe);
- Porosities are due to drained liquid phase;
- **Pumping of bottom dross is an effective operation.**



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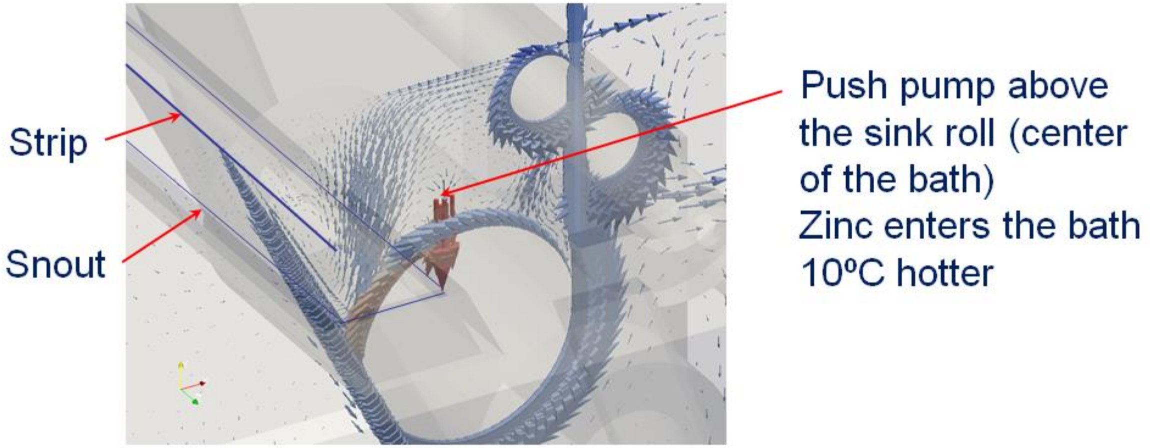
ZCO-55, Task 2: Optimizing thermal field

Summary of observations

- Without pumping: temperature near the sink roll < mean bath temperature (460ºC);
  dross concentration above the sink roll > mean value in the bath;
- Pumping higher temperature material determines an <u>increase of the temperature above the sink roll</u> and a <u>reduction in the level of dross</u> formed in this region;
- With pumping the level of dross formed around the sink roll decreases below the average bath level;
- Using two pumps results in lower temperature gradients than when using one pump with twice the temperature increase;
- Heating of the zinc near the sink roll is expected to determine the heating of the roll and a **significant reduction of dross buildup on the sink roll**.



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ZCO-55, Task 3: Fundamental Mechanisms and Characteristics of Dross Formation

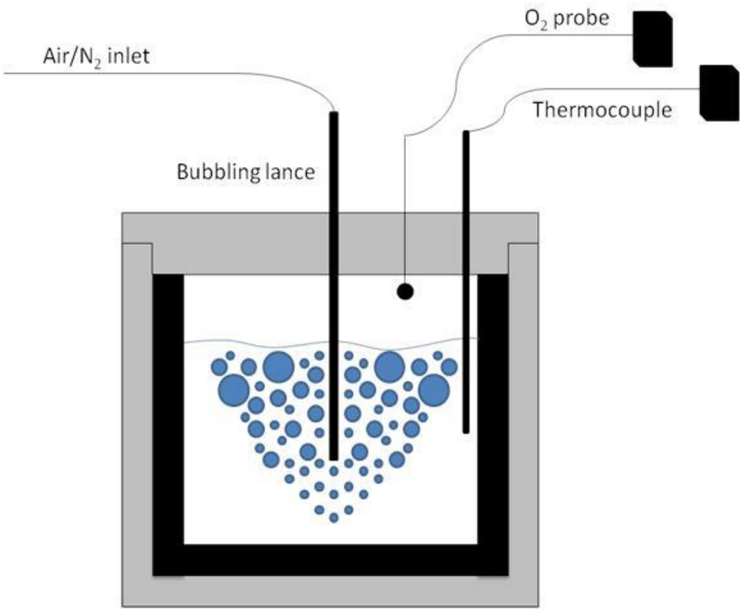
Bubbling tests

- Bubbling experiments using compositions with variable Al and Mg contents (up to 5% Al and 5% Mg)
  - Tata Steel, Salzgitter and Voest Alpine use bath composition of about 1.6% Al and 1.6% Mg
- Analysis of the skimmings generation rate
- 5 bath compositions were analyzed at 450, 460 and 470ºC
- Both air and nitrogen bubbling was analyzed

Bubbling procedure

- Bubbling air or nitrogen at predetermined rate
- Remove tube after 10 minutes and recover skimmings
- Quench the skimmings in water and weight the sample
- Analyze samples for Al, Mg and Fe content using atomic absorption spectroscopy
- Representative samples of liquid bath and skimmings were selected, mounted and polished for microstructural and compositional analysis using SEM and dispersive X-Ray analysis

Schematic of bubbling apparatus

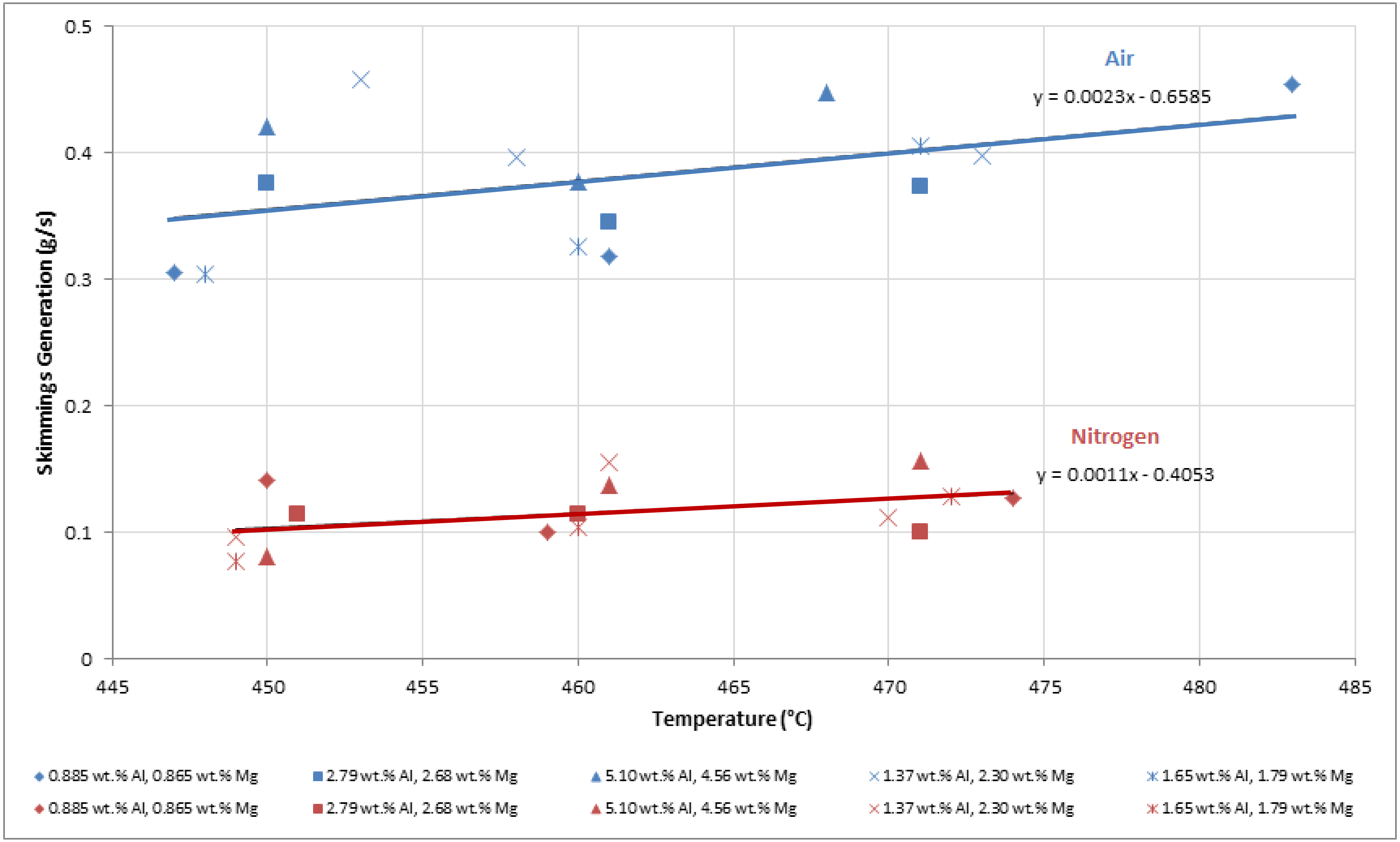


Zinc Alloy Compositions

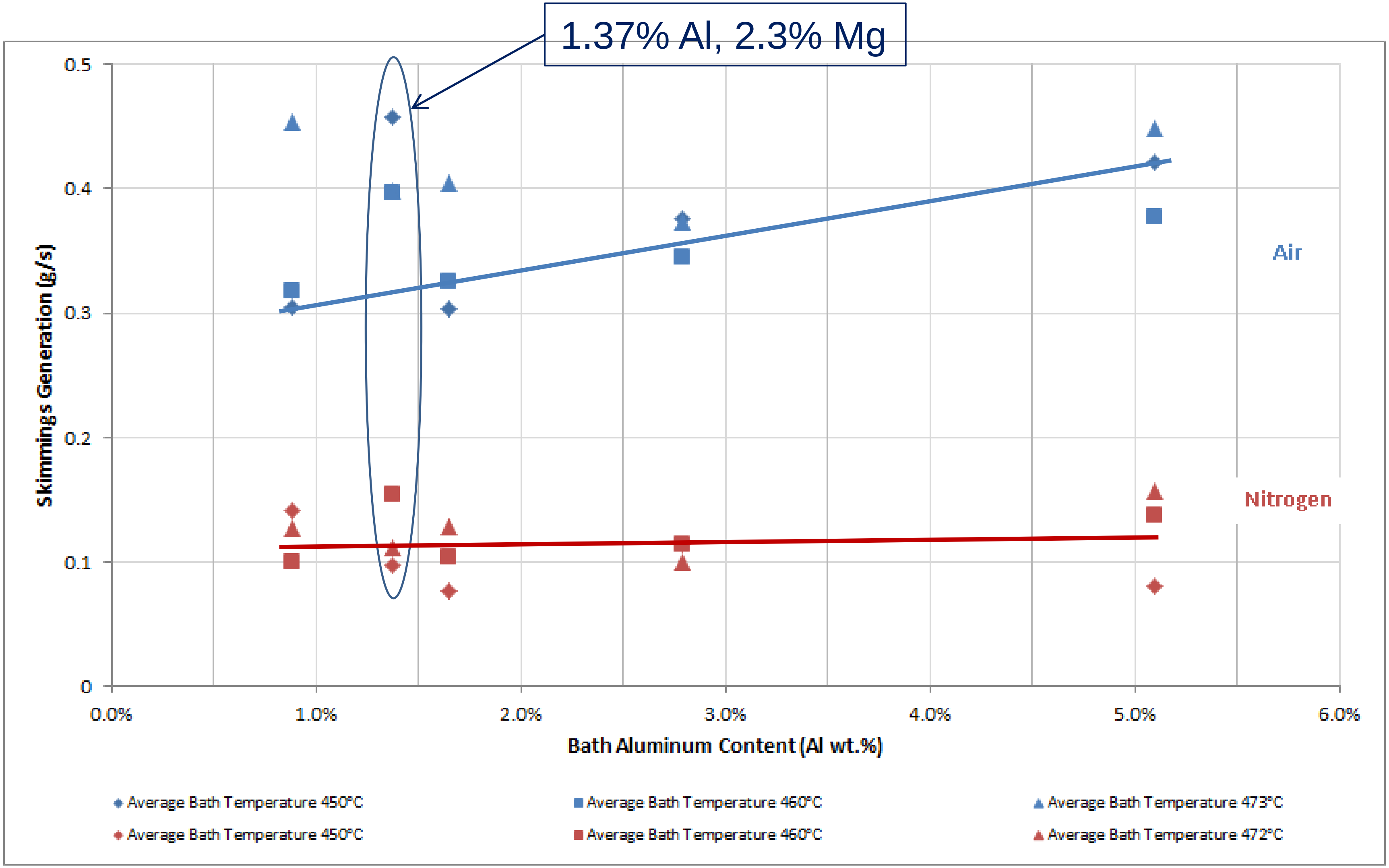
Alloy	% Al	%Mg	% Fe
1	0.885	0.865	0.004
2	2.79	2.68	0.050
3	5.10	4.56	0.030
4	1.37	2.30	0.016
5*	1.65	1.79	0.015

* Supplied by Tata Steel, Ijmuiden, NL

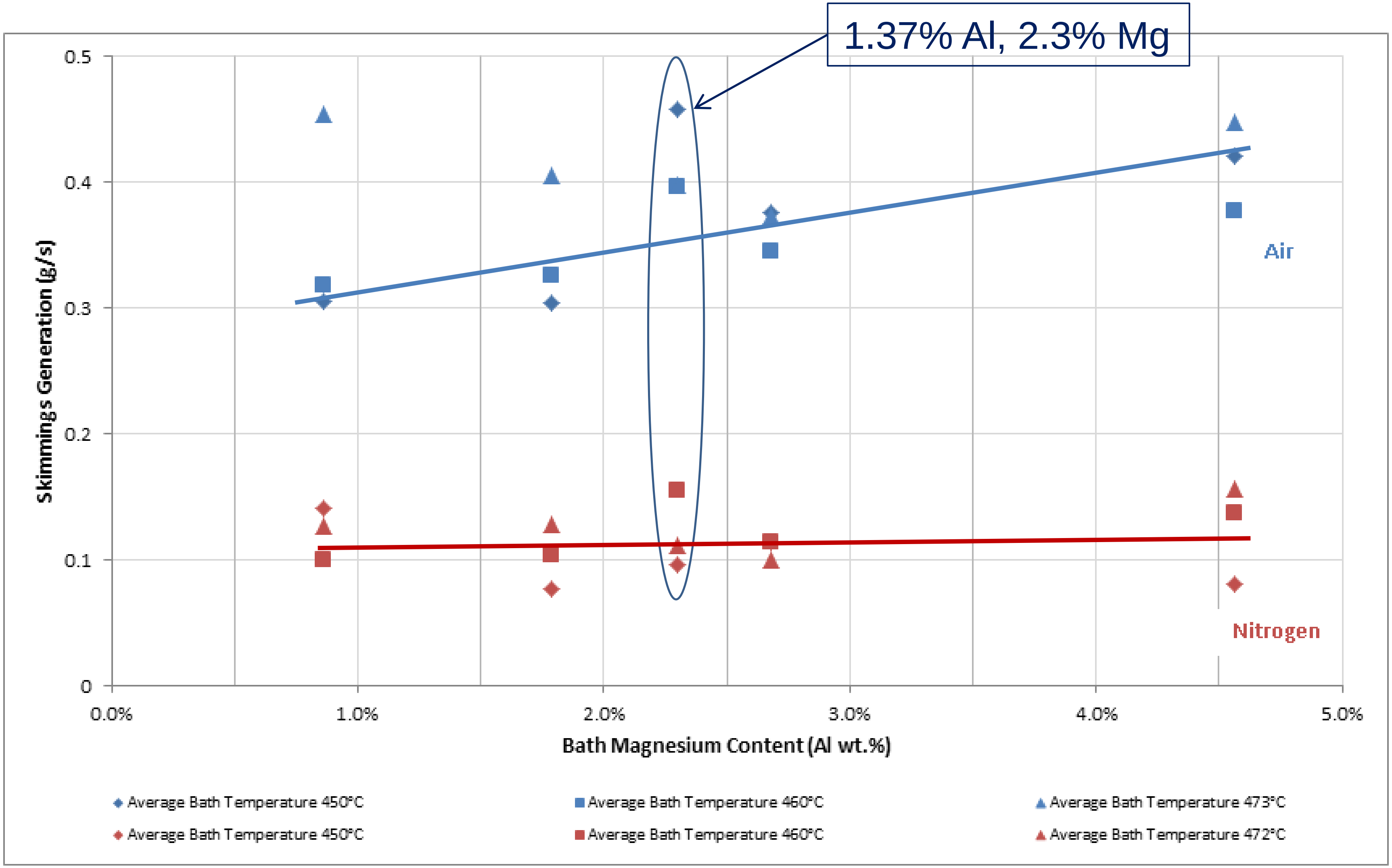
Temperature dependence of skimmings generation



Bath Al content dependence of skimmings generation



Bath Mg content dependence of skimmings generation



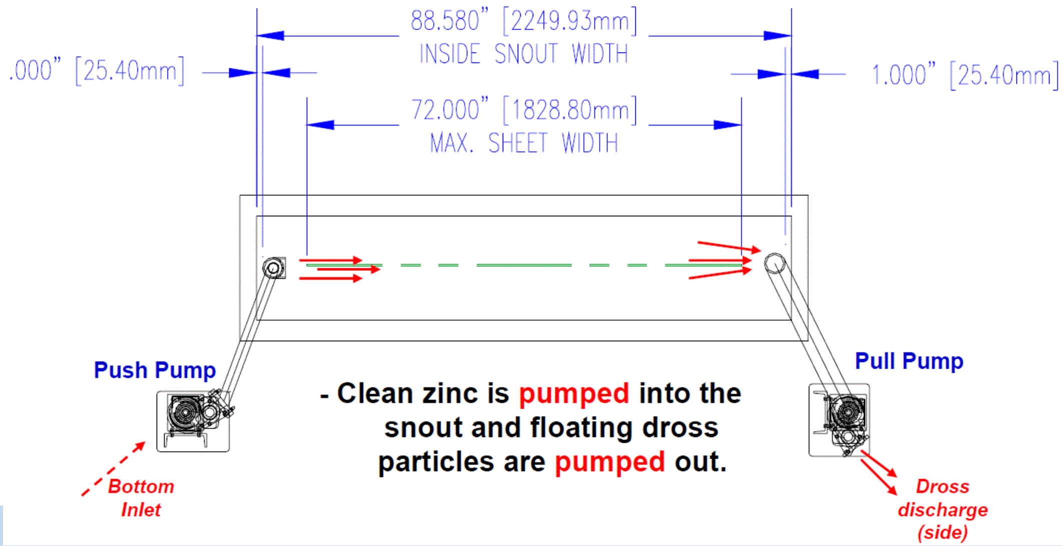
Summary of observations

- Skimming generation is significantly lower for nitrogen (0.12 g/s) than for air (0.4g/s)
- There is a slight correlation between skimmings rate and temperature (slight increase in skimmings rate with an increase in temperature)
- Data cannot identify a correlation between skimmings rate and Al or Mg content; For air bubbling we observe a slight increase in skimmings rate when increasing Al and Mg content

ZCO-66, Task 1: Effect of pumping in the snout region

Summary of observations

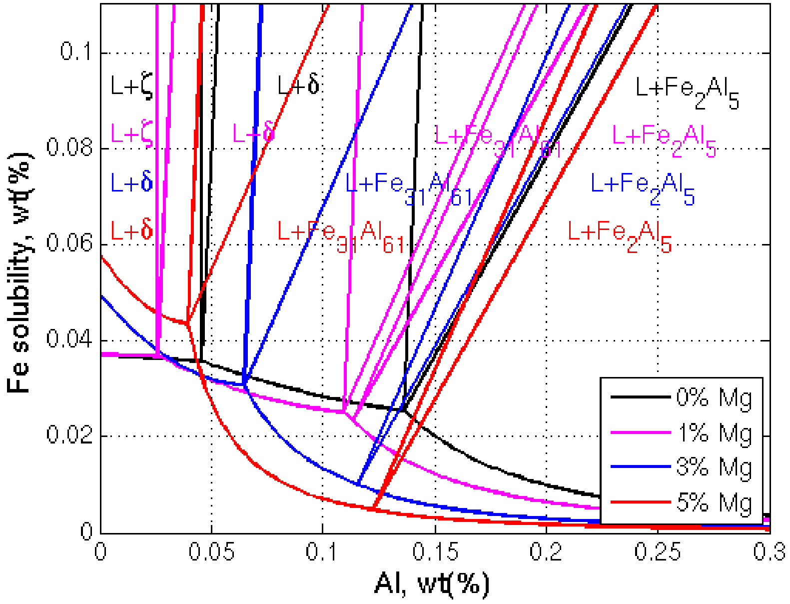
- Only small differences are observed in the snout region (push pump) and in the region of the pull pump discharge;
- The effect on the velocity distribution is limited to the region in close proximity with the pump;
- The flow from the pumps it’s not able to completely overtake the natural flow pattern determined by the movement of the strip;
- A more effective dross elimination from the snout region would be achieved by using pull pumps at the center of the strip on each side;
- The temperature inside the snout is modified by the use of the pumps. The effect is more significant around the push pump and on the ingot side of the strip.



ZCO-66, Task 2: Zn-Al-Mg-Fe phase diagram

Summary of observations

- Thermodynamic calculations were carried out for 0%, 1%, 3% and 5% Mg content
- ζ phase is formed at low Al content only for 0% and 1% Mg; for 3% Mg, ζ phase forms up to 456˚C; no ζ phase for 5% Mg;
- When increasing Mg content we have $Fe_{31}Al_{61}$ forming at Al concentration between those corresponding to δ and η (Fe_2Al_5) phases; $Fe_{31}Al_{61}$ forms at temperatures up to 462˚C for 1% Mg, up to 472˚C for 3% Mg and up to 479.4˚C for 5% Mg;
- The minimum Al content for which η (Fe_2Al_5) phase forms is slightly lower for 1% Mg than for 0% Mg and then increases when increasing the Mg content (it remains in the range 0.11% to 0.14% Al).
- Analytical model created and implemented into the bath management simulation



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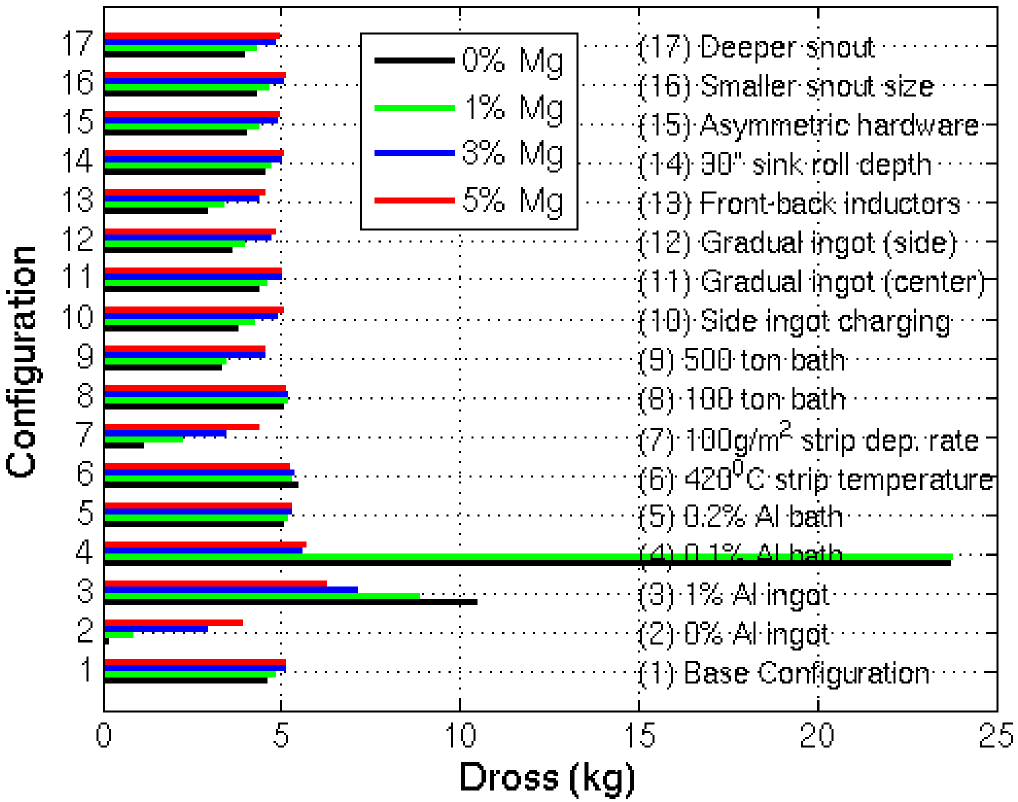
ZCO-66, Task 3: Optimum ingot feeding scheme

Summary of observations

- Base configuration: dross quantity increases slightly as the Mg content increases
- Sensitivity with respect to the Al content in ingot decreases for larger Mg content
- At 0.1% Al the quantity of dross increases drastically for 0% and 1% Mg, but very little for 3% and 5% Mg
- The 100 ton bath produces almost the same amount of dross for any Mg content
- The 500 ton bath produces less dross
- Side ingot charging produces slightly less dross
- Gradual ingot charging has little effect on dross formation
- Front-back inductors produce less dross for any Mg content
- Hardware position has little effect on dross formation



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ZCO-66, Task 4: Assessment of on-line chemical analysis techniques

Summary of observations

- The amplitude of several atomic emission lines was measured in a molten Zn bath containing up to 5.4% Al and Mg in equal proportions and the LIBS system calibrated
- There seems to be a hysteresis in Fe solubility during the temperature cycle (also observed in previous work)
- Because of the dependences of the line ratios on temperature and Al and Mg concentrations were linear to a good approximation, it would be simple to build a calibration relating line amplitude ratios and temperature to the concentration of the elements of interest
- The calibration is not universal because it depends on experimental parameters that can vary between installations. However, once a system is installed, it is relatively easy to reconstruct the calibration.
- LIBS system could be used for on-line monitoring of baths containing Mg

ZCO-66, Task 5: Characterization of dross particles and skimmings

- Analysis of samples from Salzgitter-Mannesmann Forschung GmbH
- 165 tons bath, 410ºC average temperature, 150 m/min line speed
- Nominal bath composition: 1.6% Al, 1.7% Mg
- Analysis of 28 bath samples, 18 skimmings samples and 17 coated steel coupons

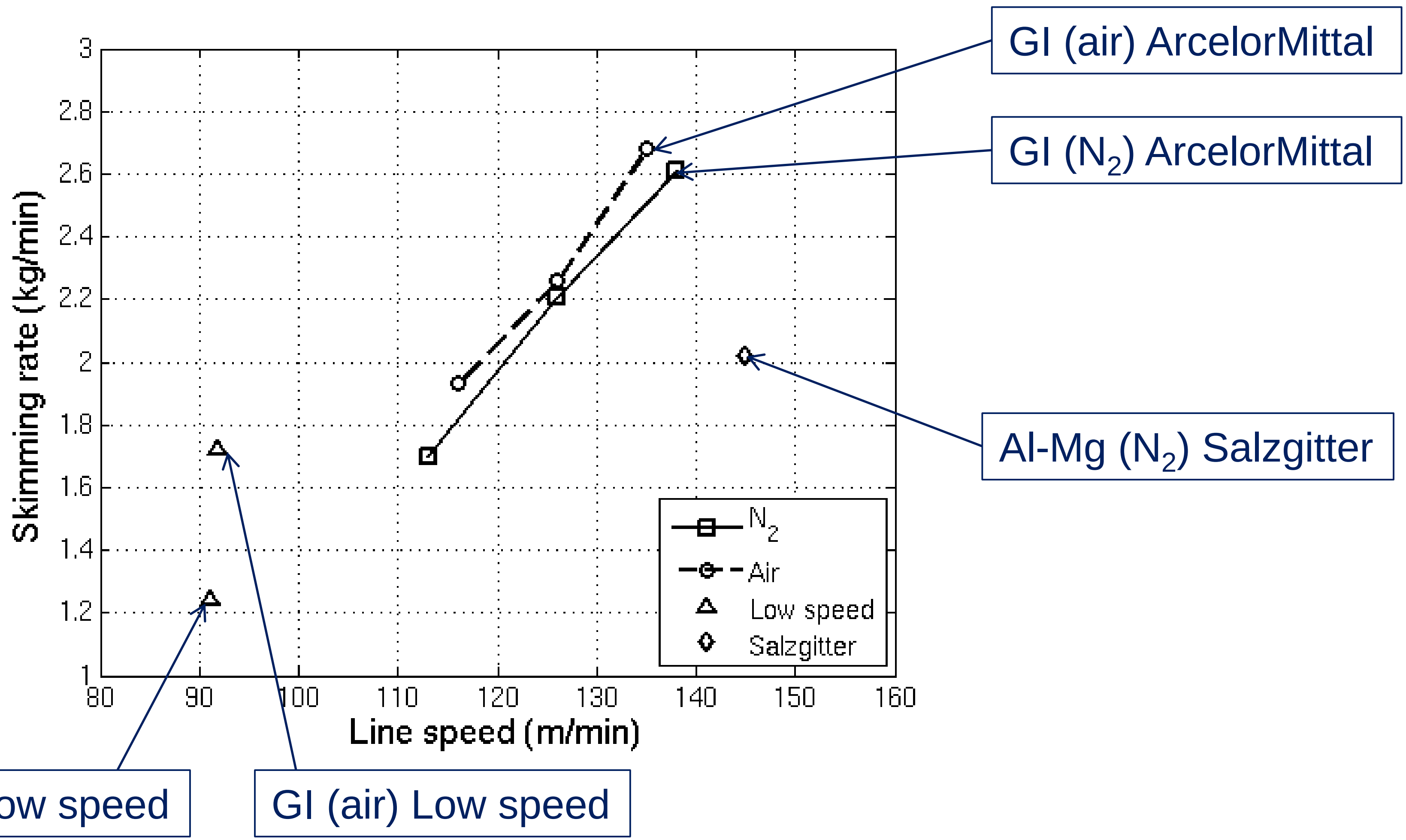
Average chemical analysis

	%Al	% Mg	% Fe
Bath	1.517	1.576	0.01
Skimmings	1.725	1.583	0.102

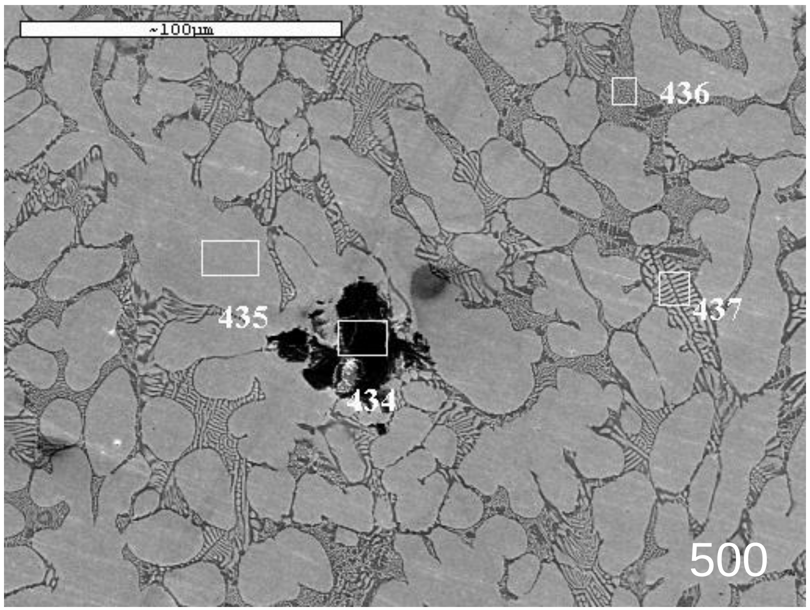
- Slightly higher Al and Fe content in the skimmings
- Almost the same Mg content in bath and skimmings

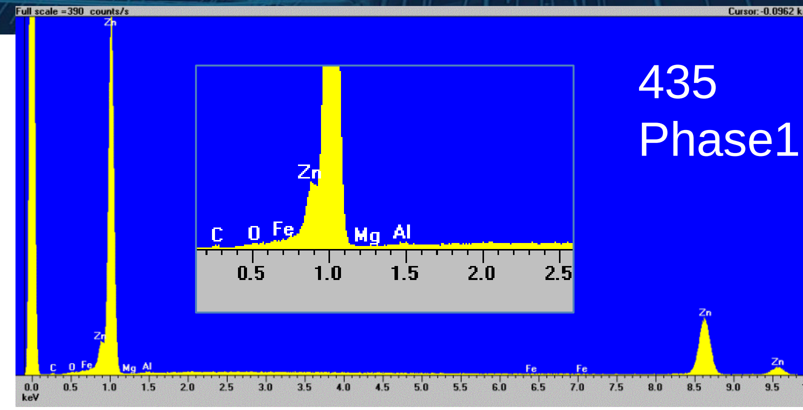
Skimmings rates for variables conditions

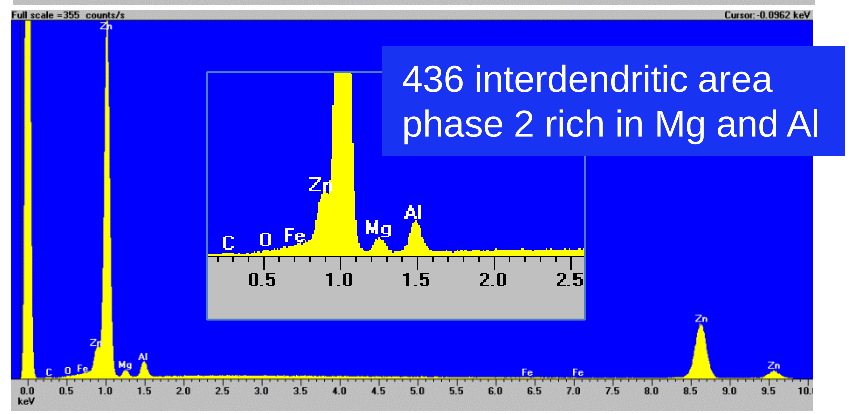
Comparison with Cleveland ArcelorMittal measurements

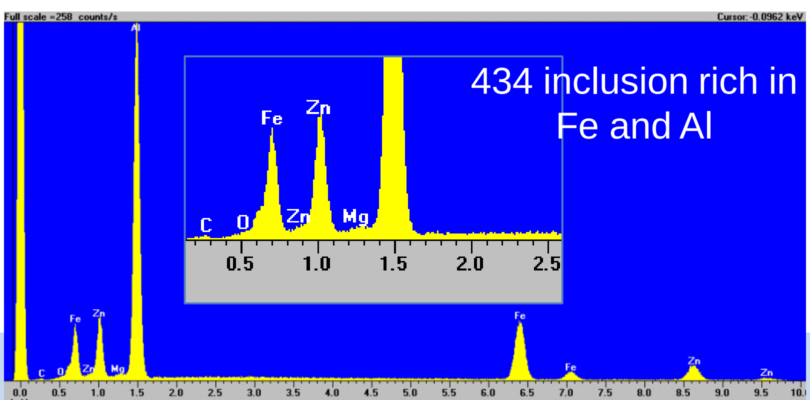


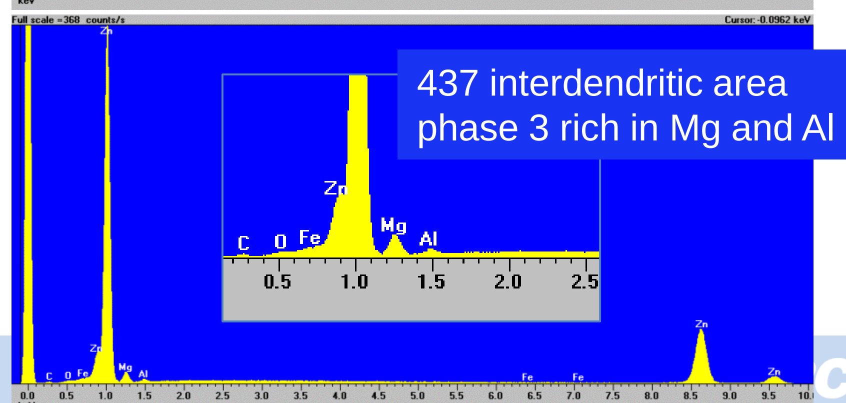
Micrograph and XRD spectra of Salzgitter bath sample B1



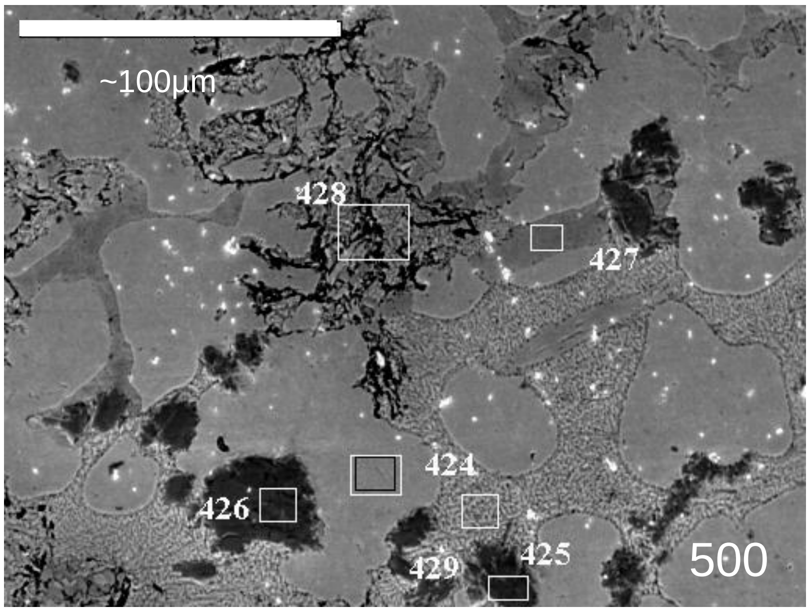


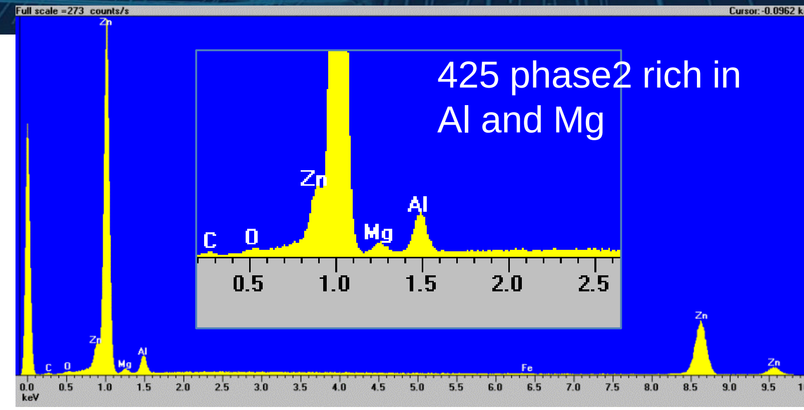


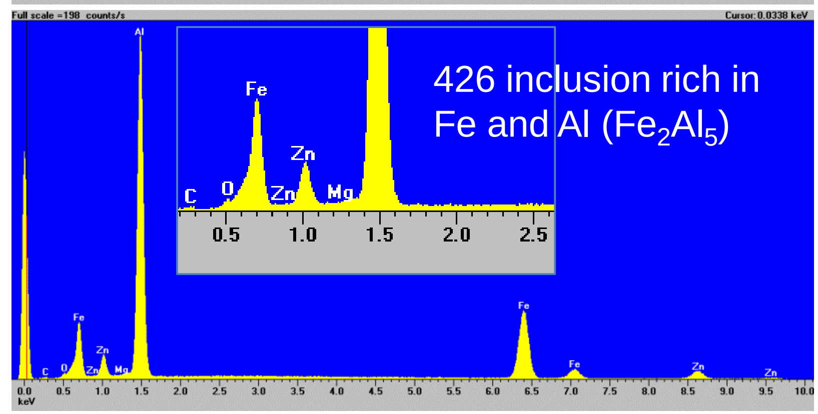


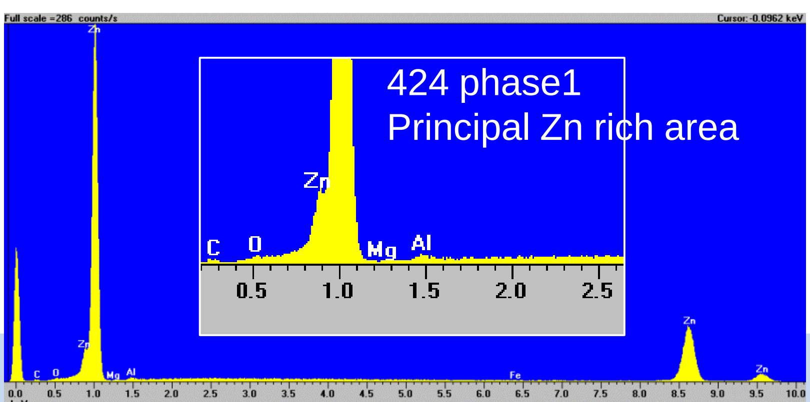


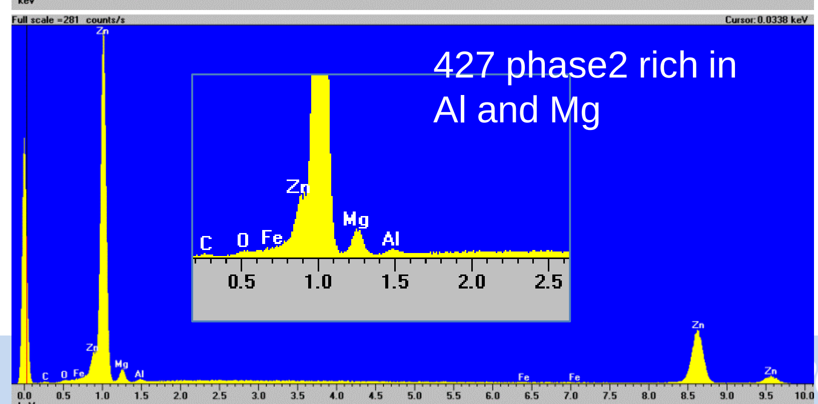
Micrograph and XRD spectra of Salzgitter skimmings sample S1



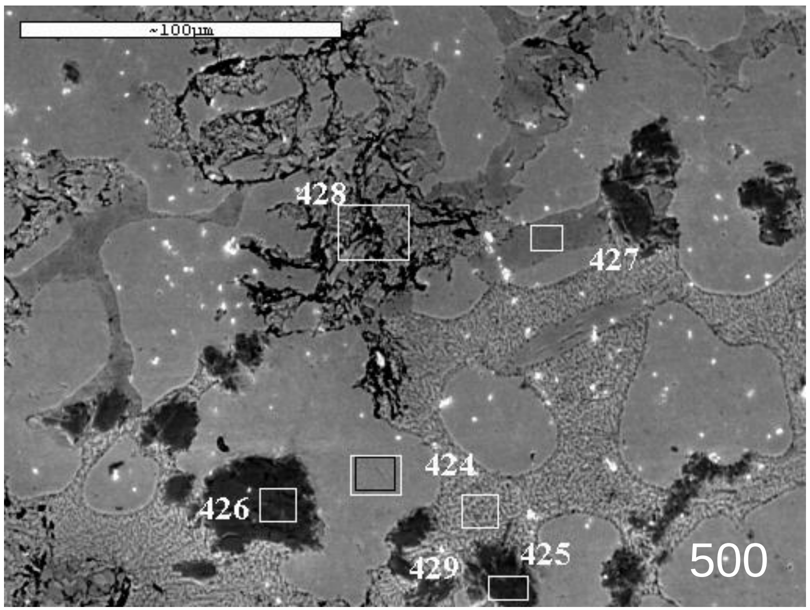


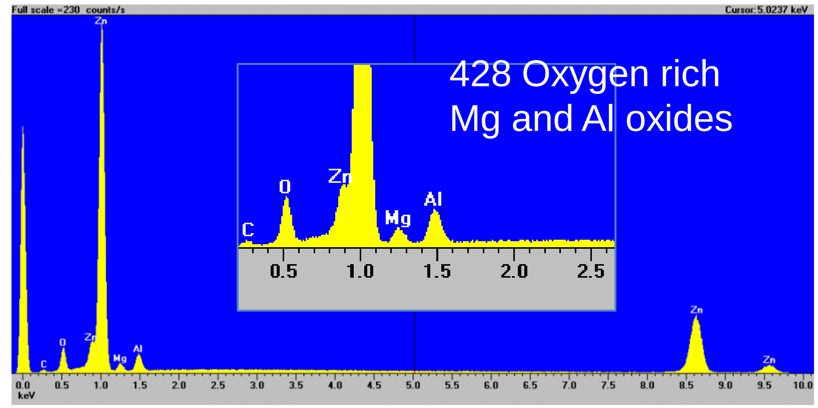


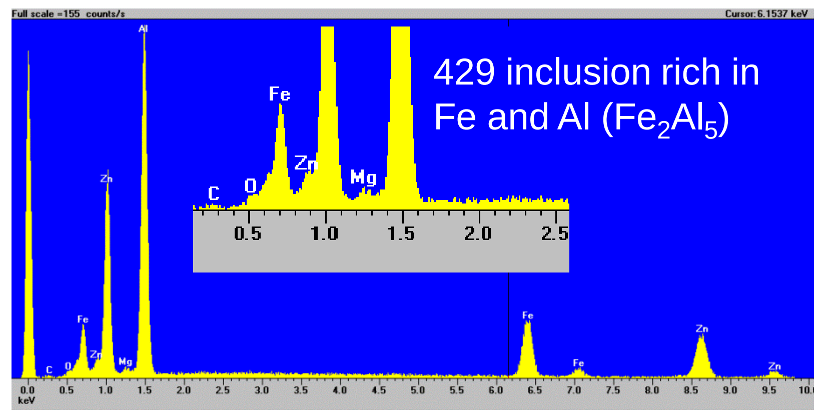




Micrograph and XRD spectra of Salzgitter skimmings sample S1







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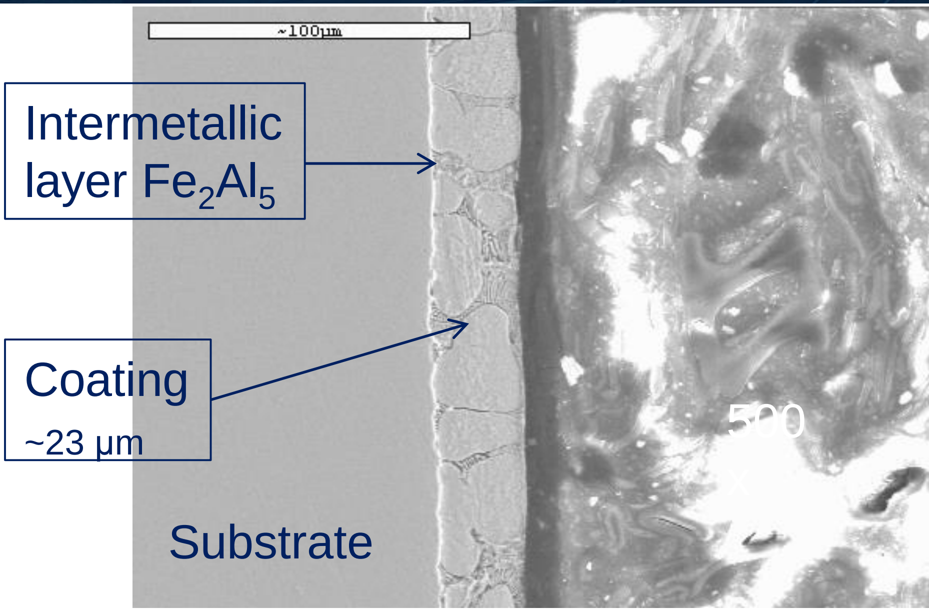
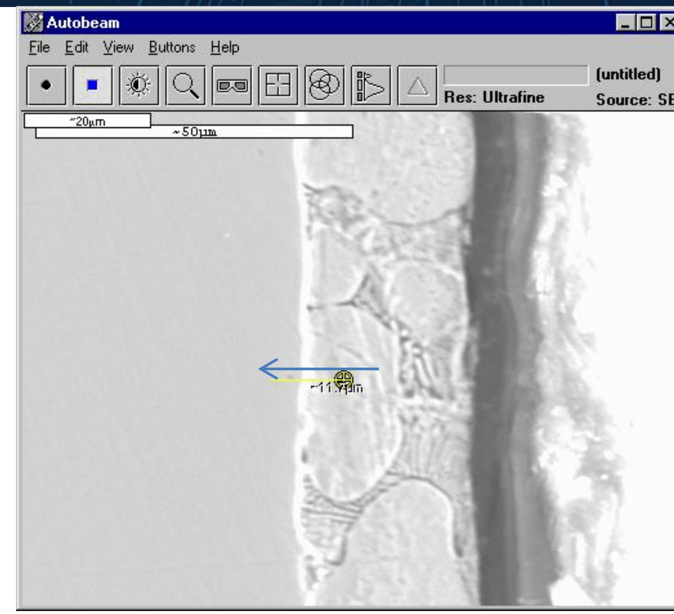
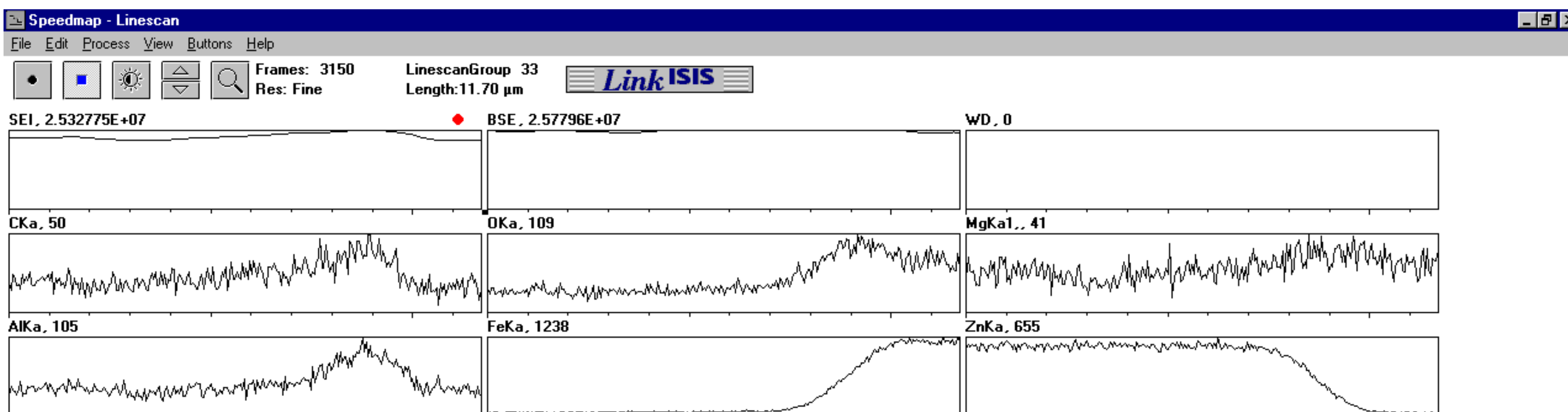
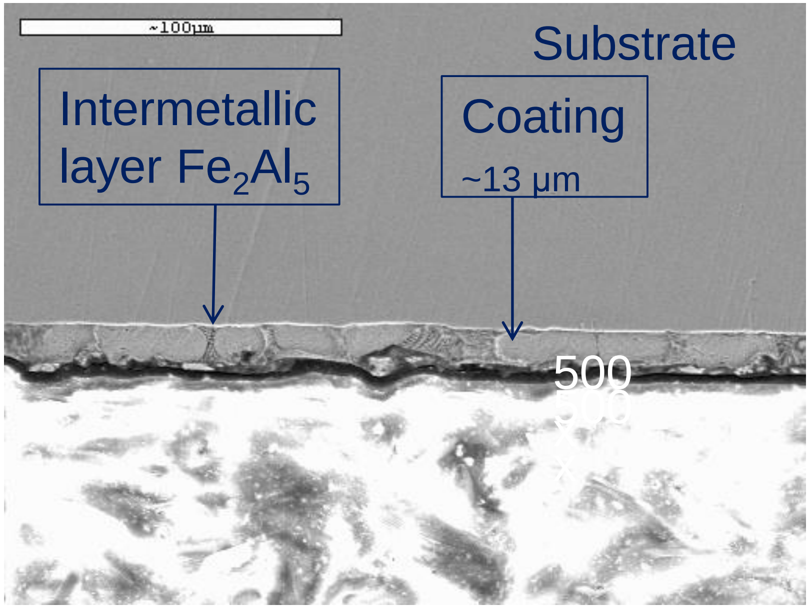
Micrograph of Salzgitter coating C5 and line scan

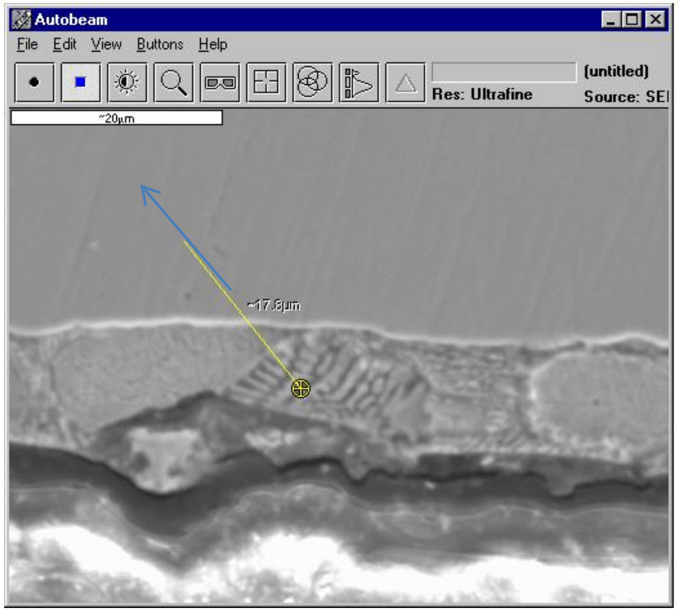


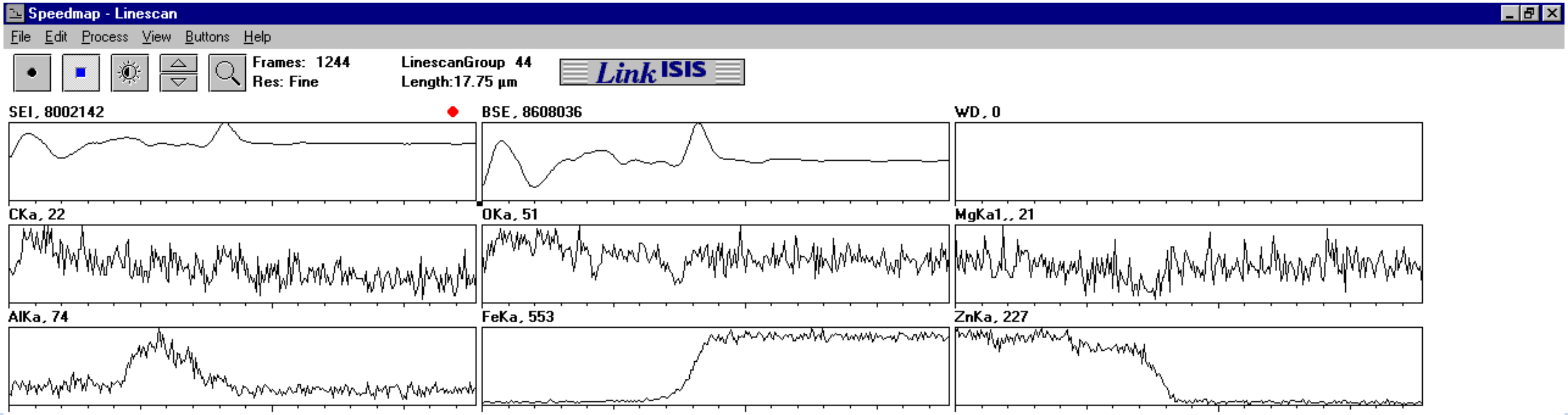




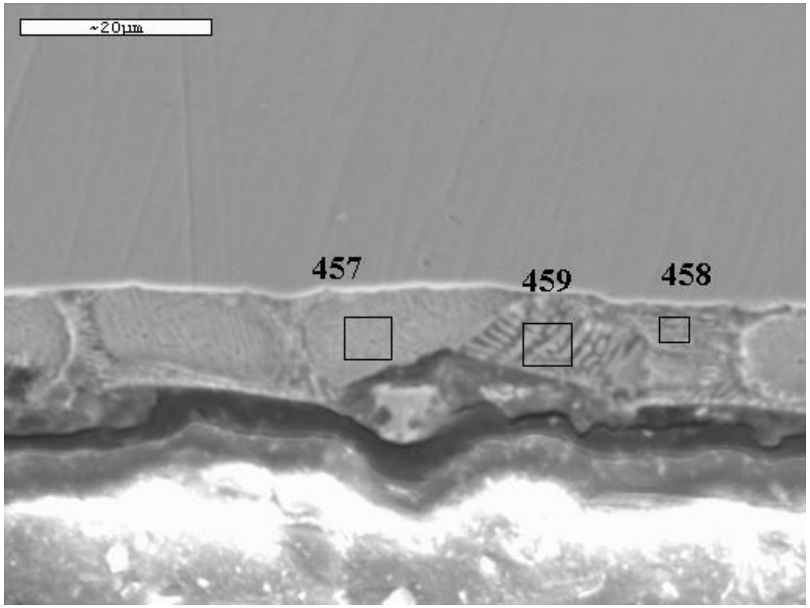
Micrograph of Salzgitter coating C11 and line scan



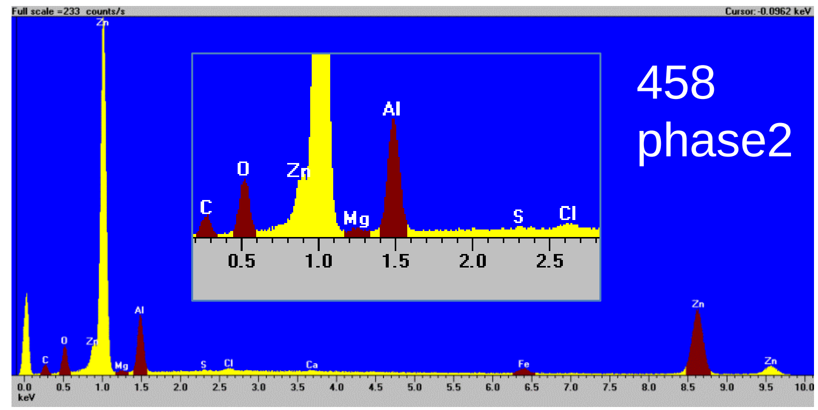




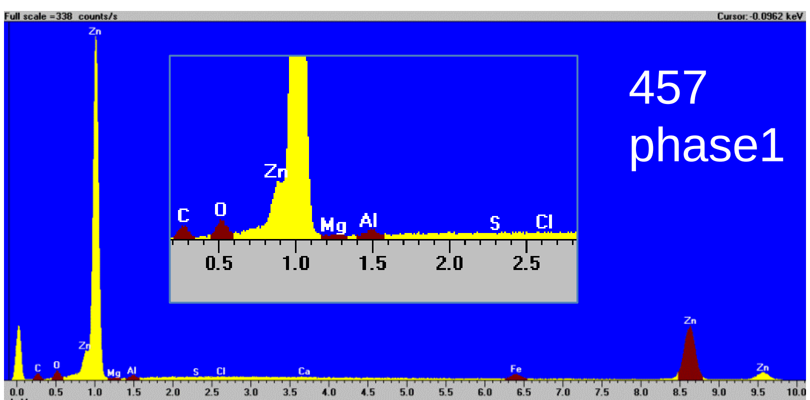
Micrograph of Salzgitter coating C11 and XRD analyses

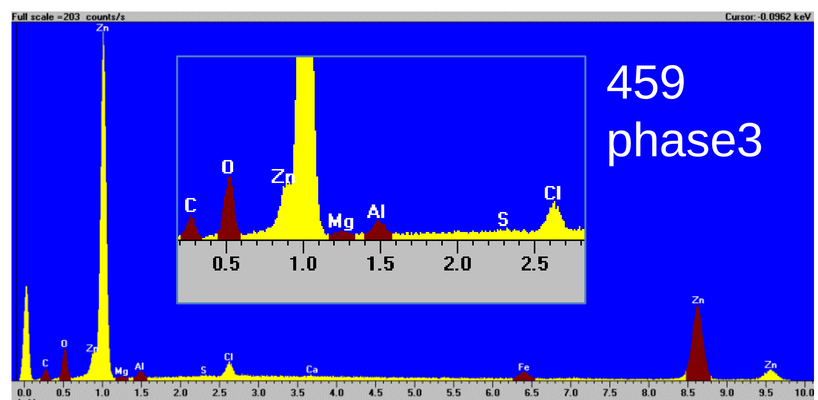


Eutectic phase area (higher Al, Mg)



Zn rich area





ZCO-66, Task 5: Characterization of dross particles and skimmings

Summary of observations

- Analysis of 28 bath samples, 18 skimmings samples and 17 coated steel coupons
- Chemical analysis of bath and skimmings samples was carried out
  - There is a slightly higher Al and Fe content in skimmings when compared with the bath
  - Mg content in bath and skimmings is almost the same
- Skimming rates for Al-Mg baths (Salzgitter) are lower than those for GA and GI lines (Cleveland ArcelorMittal)
- Micrographs of bath and skimmings samples were analyzed by SEM secondary electron imaging and selected areas were analyzed by dispersive X-ray analysis
- Micrographs and line scan were performed for three coating samples of different thicknesses

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ZCO-71: *Galvanizing Bath Management for Advanced High Strength Steels (2014-2017)*

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Objective

- Development and application of numerical simulation models to study the effect on galvanizing bath management of (1) Mn presence, (2) pre-oxidation pre-treatment (Fe dissolution rate) and (3) strip entry temperature

- Input from GAP members is needed to determine the operating conditions of interest

Work Plan

- Task 1: Mn effects on galvanizing bath management
- Task 2: Effects of pre-oxidation pre-treatment cycles on galvanizing bath Fe management
- Task 3: Effects of strip entry temperature and galvanizing bath management on coating quality

Task 1: Mn effects on galvanizing bath management

- Modeling work:
  - Full galvanizing bath model including Fe, Al and Mn concentration distribution
  - Solve typical galvanizing bath operating conditions for given levels of Mn content
  - Detailed modeling in the snout and sink roll areas
  - Quantify dross generation as a function of operating conditions
  - Bath management recommendations
- Input data:
  - Typical Mn bath levels to be studied
  - Operating temperature range (thermal cycling with or without ingot melting)
  - Coating composition data (with Mn, with Mn and Si)

Task 2: Effects of pre-oxidation pre-treatment cycles on galvanizing bath Fe management

- Modeling work:
  - Models for Fe dissolution rate based on pre-oxidation pre-treatment
  - Full galvanizing bath model including Fe, Al and Mn concentration distribution
  - Investigate impact on bath management of the increased Fe inputs after pre-oxidation pre-treatment
  - Dross generation as a function of sheet pre-treatment
  - Bath management recommendations
- Input data:
  - Fe source term as from ZCO-65 program at Case Western University
  - Data from the Tolket online sheet cleanliness measurement
  - Influence on Fe activity of the bath Al level and temperature

Task 3: Effects of strip entry temperature and galvanizing bath management on coating quality

- Modeling work:
  - Model for lower strip entry temperature typical of over-ageing treatments
  - Model for higher strip entry temperature (extended over-ageing or inadequate rapid jet cool capacity)
  - Assessment of bath equilibrium and bath management under such conditions
  - Dross generation analysis
  - Bath management recommendations
- Input data:
  - Range of strip entry temperatures to consider
  - Bath operating conditions (composition, line speed, …)

Thank you

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