

Surface Segregation in DC-cast Aluminium AA5182, Measured in GDMS(Glow Discharge Mass Spectrometer) and Discussed in View of the Phase Diagram

Anne Lise Dons¹ and Trond Furu²

¹SINTEF Metallurgi, Alfred Getz vei 2b, N-7465 Trondheim, Norway

²Hydro Aluminium RTD, N-6600 Sunndalsøra, Norway

Slabs often have thick layers of exudation at the surface. The GDMS (Glow discharge mass spectrometer) has been used to characterise such segregations.

Segregations occur if the part of the liquid that solidifies first, ends up on a separate place from the part of the liquid that solidifies late. With several active mechanisms, surface segregations are difficult to calculate. We have tried to compare the segregations with the composition of the liquid toward the end of the solidification

The microstructure model Alstruc [1] gives the development in the concentration of the remaining liquid as a function of the fraction solid in multi component alloys. It has a copy of the COST/Eural phase diagram for AlFeMnSiMg in its present version [2-5]. Alstruc calculations showed that the measured concentrations of Si, Mn and Mg and several other eutectic elements were reached in the liquid when 70-75% had solidified. But not for Fe: Here precipitation of particles had reduced the concentration to the original level.

A calculation with an old version of Alstruc, built on Phillips' phase diagram [6-7], gave a concentration of Fe that matched the measurements, but gave too high Mn-concentration.

Keywords: Aluminium, solidification, surface segregations, GDMS, modeling.

1. Introduction

DC-casting of aluminium with the use of grain refiner is designed to give as homogeneous a microstructure as possible. Even so, as a result of shrinkage during solidification, and a support free water cooled surface, some of the melt tends to escape to the surface, and (hopefully) solidify there. If this happens at an early stage of the solidification, and the water cooling is insufficient, the result is a massive leak, and tons of aluminium end at the floor. If it happens late, there is only a thin, bumpy layer of exudation at the surface. Such a layer, at the surface of an AA5182 rolling slab, is the subject of the present paper. It should be noted that the layer is almost removed before industrial rolling.

2. Alloy

The alloy was a DC-cast rolling slab with composition as given in Table 1.

Table 1 Alloy composition (wt%).

	Fe	Si	Mn	Mg	Cu	Al
wt%	0.17	0.10	0.35	4.11	0.044	balance

3. Microstructure

A specimen at the surface was cut perpendicular to the surface, ground on silicon carbide paper, and polished with OPS. It was examined in an optical microscope. The exudation layer was up to 500 µm thick, but extremely uneven, and completely missing in some places. Fig. 1 shows the uneven exudation layer to the right, and the normal structure to the left.

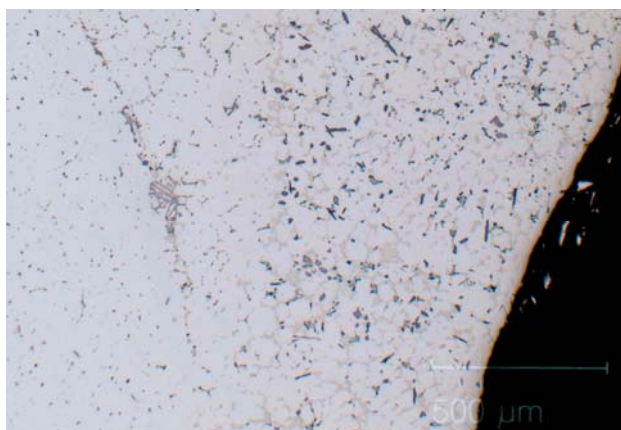


Fig. 1 Optical micrograph of A5182. Normal structure to the left, with a line of particles corresponding to a Bergmann zone. Exudation structure to the right.

4. Specimen preparation for GDMS

Pieces of approximately the size of a matchbox were cut from the surface of the slab. There were two samples, one roughly 2 cm thick and one roughly 4 cm thick, with saw markings on the back. The surface was uneven, so both samples were pressed in the pilot press at SINTEF until the roughly 0.5 mm tops and bottoms on the surface were flat. This was done at room temperature, with clean metal plates above and below the samples.

5. GDMS

The GDMS-investigation was done as sputtering series, without standards. The scan speed was roughly 1 μm per minute. The "concentration" is given as peak integral ratios, not corrected for the abundance of the isotopes. The left part of the curves represents two 20 minutes surface scans, with grinding to remove the first spot between the scans. Each spot represents a dept of roughly 0.5 μm . The right part of the scan is a scan on the sawn side, with the saw marks to the left. This is as close as we can come to the average composition of the slab with a minimum of effort. There were two parallel samples, one was the thin piece, 1-2 cm, and the other was the thick piece, 2-4 cm, before pressing. They gave roughly the same result, as shown in Table 2.

Table 2 GDMS-results (uncalibrated wt%)

	Fe	Si	Mn	Mg	Cu	Al
GDMS inside slab	0.6	0.1	0.7	4.7	0.03	balance
GDMS Surface	2.0	0.4	0.7	12	0.1	balance

The values for Mn and Fe should be divided by approximately three to give correct weight%, according to our uncertified lab standards.

The depth scan shown in Fig. 2 reveals that Fe, Cu and Si, which have distribution coefficients of 0.1 or less, have tripled or quadrupled in concentration, while Mg with a distribution coefficient of 0.3 has more than doubled, and Mn, with a distribution coefficient of 0.7-0.9 is the same at the surface as inside the slab. This is as expected from earlier projects and literature data.

It can be seen from Table 2 and the GDMS-analysis in Fig. 2, that while all the five alloying elements increase their concentration toward the skin in the outer 1-3 spots, there is a dip before Mg and Si for some 40 points under the skin. Such dips are also observed after homogenisation, and are probably a result of diffusion toward the oxide layer. The diffusion length of Mg and Si at 500°C is roughly 25 to 50 μm in one hour.

The depth scan in Fig. 3 shows the same tendency for the major trace elements: The eutectic Cu and Ga have increased concentrations in the exudation layer, while the peritectic elements Ti and V prefer to stay in the main part of the billet. Minor trace elements showed the same tendency in Figs. 4-6.

Thus it should be possible to guess from the phase diagram, which elements that have increased concentrations in the surface.

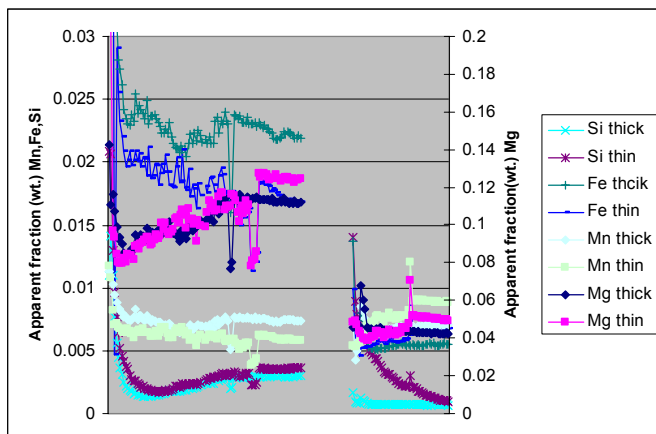


Fig. 2 GDMS of the main alloying elements. The left part of the curve is a scan from the surface and inward. The right part of the curve is a scan at 1-4 cm depth. Each point represents roughly 1 μm thickness. Mg has almost tripled, Si tripled and Fe quadrupled in the outer layer. The values for Mn and Fe should be divided by three to give approximately correct results.

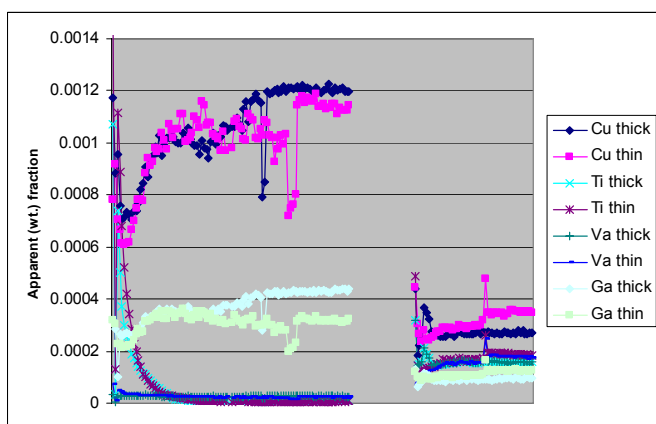


Fig. 3 GDMS of the main trace elements. The left part of the curve is a scan from the surface and inward. The right part of the curve is a scan at 1-4 cm depth. Each point represents roughly 1 μm thickness. Ga has tripled, and Cu quadrupled in the outer layer.

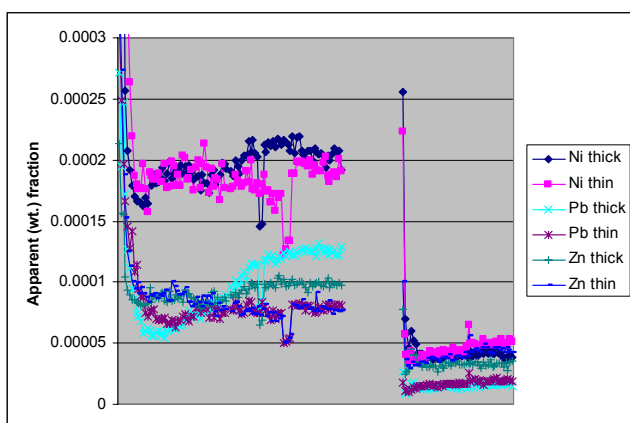


Fig. 4 GDMS of the minor trace elements. The left part of the curve is a scan from the surface and inward. The right part of the curve is a scan at 1-4 cm depth. Each point represents roughly 1 μm thickness. Zn has tripled, Pb and Ni quadrupled in the outer layer.

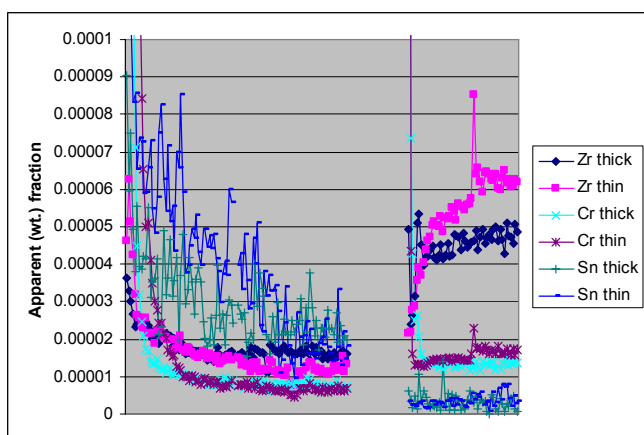


Fig. 5 GDMS of more minor trace elements. The left part of the curve is a scan from the surface and inward. The right part of the curve is a scan at 1-4 cm depth. Each point represents roughly 1 μm thickness. Sn has quadrupled in the outer layer, while the peritectic Zr and Cr went down.

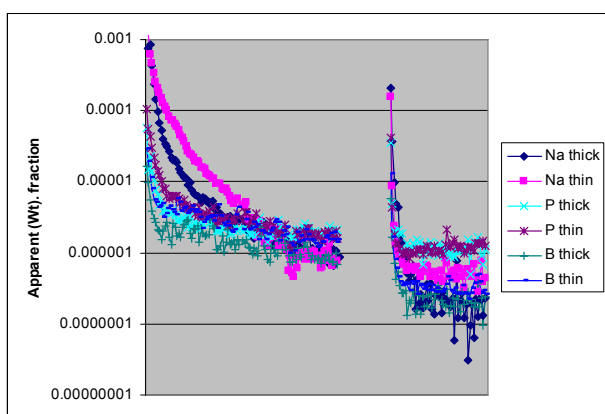


Fig. 6 GDMS of Na, P and B: Important, but rare trace alloying elements. Logarithmic scale. The left part of the curve is a scan from the surface and inward. The right part of the curve is a scan at 1-4 cm depth. Each point represents roughly 1 μm thickness. The concentrations have tripled in the outer layer.

6. Summary of the GDMS results

The exudation layers have concentrations of eutectic elements that are up to 4 times as high as the average of the alloy. The peritectic elements have low concentration in the exudation layer. At some stage the melt has leaked out to the surface. Assuming that only liquid, and not already precipitated particles leaked out, this must be a melt representing the last 25-30% that should have solidified in the vicinity. (Not the last 25-30% of the slab). This can be seen from a rough calculation: If the solid aluminium is pure, and all the alloying elements are in the remaining liquid, the concentration will be quadrupled when 25% have solidified.

7. The new and old versions of Alstruc

Alstruc [1] is a PC-model that calculates fractional solidification in the phase diagram, with solid state diffusion. The concentration of eutectic elements in the liquid increases at first, but then decreases as intermetallic particles begin to form while the temperature decreases. The current version of Alstruc gave too low Fe- and Mn- concentrations in the liquid at 10-12% Mg, with 75% solid, to match the GDMS-results, as a result of precipitation of intermetallic particles. As in shown in Fig. 7, the calculated maximum was even lower than the bulk composition, not three times as measured. The current Alstruc is built on the last version of the Thermocalc/Eural/SINTEF equilibrium phase diagram [2-5]. This has considerable lower solubility of Fe in an Mg-rich liquid than the old Phillips' phase diagram [6,7]. There is an old version of Alstruc, called 3T, which is built on Phillip's diagram [6,7]. Fig. 8 shows its calculated concentrations in the remaining liquid as a function of the fraction solid. The composition at 75% solid corresponds reasonably well with the observed exudation layer for Fe, but the calculated Mn is twice that of the bulk composition.

This does not necessarily mean that the modern phase diagram is wrong with respect to Fe. Industrial DC-casting is not an equilibrium process. Maybe Phillips describes a metastable equilibrium where the stable Al_3Fe is replaced by the metastable Al_mFe ? If the alloy contains Al_mFe instead of Al_3Fe , that will be an explanation.

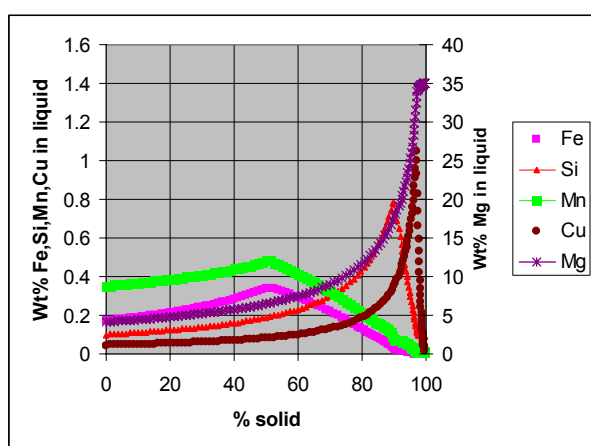


Fig. 7 Concentration of Mg, Fe, Si and Mn in the remaining liquid as a function of the fraction solid, according to Alstruc. Fe is down to 0.2 % before Mg reaches 10%.

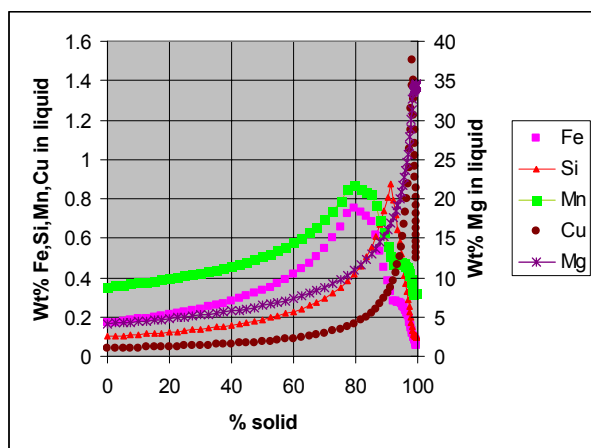


Fig. 8 Concentration of Mg, Fe, Si, Cu and Mn in the remaining liquid as a function of the fraction solid, according to Alstruc3T.

8. SEM-investigation of the intermetallic particles

A specimen from the bulk material was investigated in SEM with EDS. We used 10 -15 kV and k-lines, looking at the larger particles. The main phase was α -Al(Mn,Fe)Si, with 30%(M+Fe) and 3-5%Si. There was also some Al_3Fe , with < 1% Si in it, and more than 35%(Mn+Fe). There was probably a group of Al_mFe , with 30% (Mn+Fe), but these may have been be small Al_3Fe .

9. Conclusions

- Exudation is an interesting method of separating the remaining liquid from the mushy zone.
- Industrial DC-casting is not an equilibrium process.
- Particles do not start to precipitate as early as in the new Alstruc, nor as late as in the old Alstruc.

Acknowledgements

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References

- [1] A. L. Dons, E. K.Jensen, Y. Langsrud, E. Trømborg and S. Brusethaug: Metallurgical and Materials Transactions A, Volume 30A (1999) 2135-2146.
- [2] H.Feufel et Al: Journal of Alloys and compounds (1997) 247.
- [3] Thermochemical database for light metal alloys, Volume 2. Ed: I Ansana, A.T.Dinsdale, M.H.Rand. Luxembourg office for official publications of the European Communities, Belgia, 1998.
- [4] P. Kolby, C. Sigli and C. J. Simensen: The 4th International Conference on Aluminium alloys, 1 (1994) 508-512, Ed: T.H. Sanders and A. A. Starke, The Georgia Institute of Technology, Atlanta, Georgia, USA
- [5] Per Kolby, Kai Tang: Private communications.
- [6] H.W.L.Phillips: *Annotated equilibrium diagrams of some aluminium alloy systems*. The institute of metals, London, 1959.
- [7] H.W.L.Phillips: *Equilibrium Diagrams Of Aluminum Alloy Systems*. The Aluminum Development Associations, London, 1961.