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Surface Segregation in Aluminium AA6xxx, Measured in GDMS(Glow Discharge Mass Spectrometer) and Calculated with Alsim/Alstruc

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DC-cast aluminium has surface segregations, and an important part of the casting technology is to reduce these, as they usually have a low melting-point. One of the objects of homogenisations is to reduce these segregations. The GDMS (Glow discharge mass spectrometer) and the spectrograph have been used to characterise such segregations, in DC-cast material and in especially net shape cast samples for spectrographic analysis, before and after homogenisation. Three types of modelling tools are used to discuss the results. Alstruc, gives the concentration of the remaining liquid as a function of the fraction solid at the scale of the dendrite for multi component alloys. Alsim, coupled with Alstruc, calculates macrosegregation, in this case without exudation. A simple diffusion model calculates the diffusion length of the low melting elements during homogenisation. Although the basic understanding of segregation is simple, *i.e.* the part of the liquid that solidifies last ends up in at other locations than the liquid that solidifies first, fairly advanced modelling schemes are needed to predict the segregation pattern and the composition of the last liquid that solidifies. The locations of low melting alloying elements after homogenisation are even more important: Some elements diffuse to the oxide surface, and some diffuse along concentration gradients within the sample.

Keywords: *AA6xxx, surface segregations, mass spectroscopy, modeling.*

1. Introduction

AA6xxx alloys are commonly used for extrusion. This is a process that takes place at 500-580°C. The quality of the extruded products is deteriorated if the material at the surface of the product begins to melt during the process. The extrusion billets often have a lowmelting layer at the surface after casting. It is almost smoothed out during homogenisation, and neutralised further during by intelligent design of the extrusion die.

2. Alloy composition and specimen preparation

Only two alloy were used in the present experiments: Both were AA6xxx-alloy from Sunndalsøra, DC-cast into extrusion billets, The material was received both as unhomogenised material and as industrially homogenised at 560°C. The compositions are given in Table 1.

The surfaces of the billets were not completely flat, so they was pressed flat in SINTEF's pilot scale extrusion press at room temperature before they were taken to the GDMS.

Table 1: Alloy compositions. (weight%, balance Al.)

Billet	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Zn**	**Cr**	**Pb**	**Zr**	**V**	**Ti**	**B**	**P**
G	0.44	0.19	0.001	0.05	0.37	0.003	0.0006	0.001	0.002	0.01	0.01	0.001	0.0002
L	0.44	0.19	0.01	0.04	0.38	0.011	0.003	0.001	0.001	0.01	0.01	0.001	0.0007

3. GDMS depth scans

Depth scans in the Glow Discharge Mass spectrometer was performed in two samples of the unhomogenised material and two samples of the homogenised material, without the use of standards. Fig. 1 shows an optical micrograph of the surface. Some of the results are shown in Fig. 2. Each spot represents approximately 1 µm in depth. The scale on the y-axis is uncalibrated mass fraction. This should be within a factor 3 of the true composition.

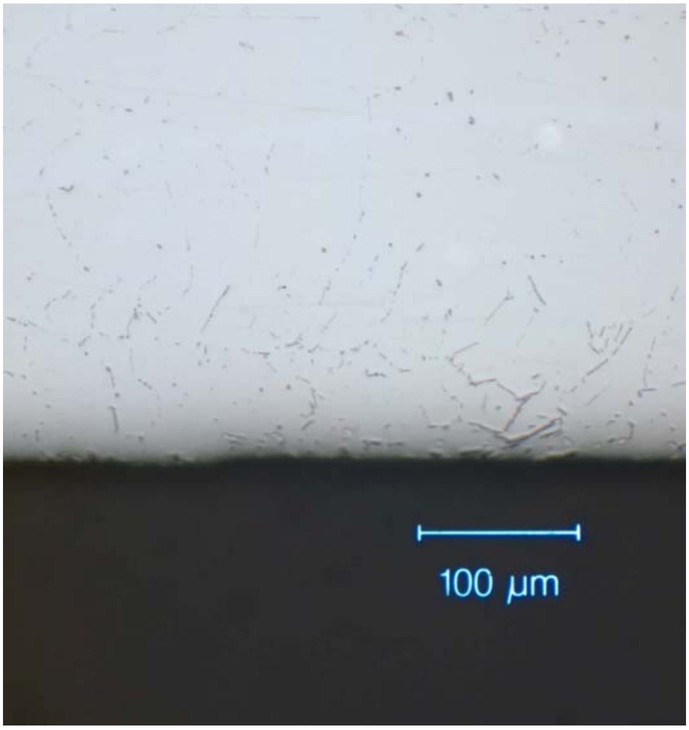


Fig.1. Optical micrograph of the surface in alloy G-HOM. Compare with the GDMS parameters: Scanning depth up to 500µm, the first part of the scan was 50 µm, inside that the composition was constant as measured with two parallels in GDMS.

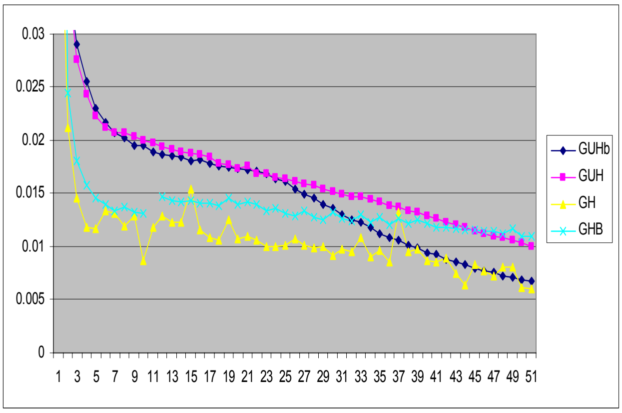


Fig. 2a. GDMS surface scan of Si.
Each spot represents roughly 1 μm thickness.
Diffusion rate 55 μm in one hour.

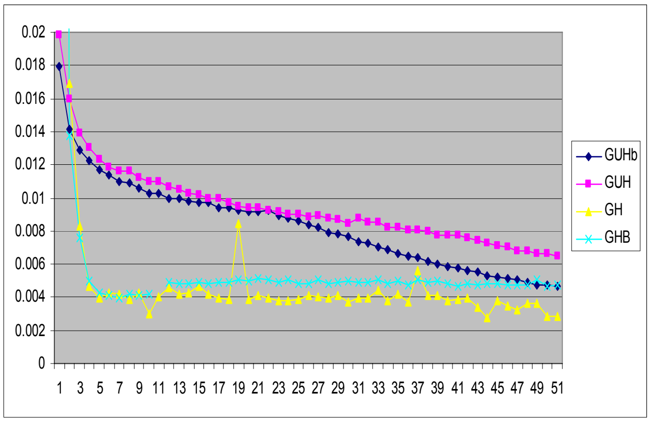


Fig. 2b. GDMS surface scan of Mg.
Each spot represents roughly 1 μm thickness.
Diffusion rate 40 μm in one hour.

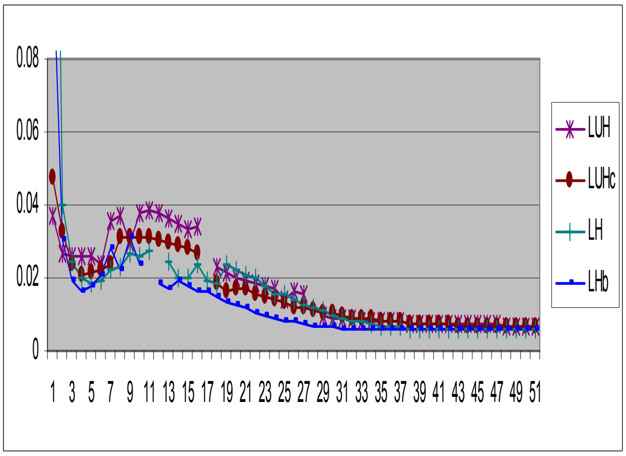


Fig. 2c. GDMS surface scan of Fe.
Each spot represents roughly 1 μm thickness.
Diffusion rate 0.6 μm in one hour.

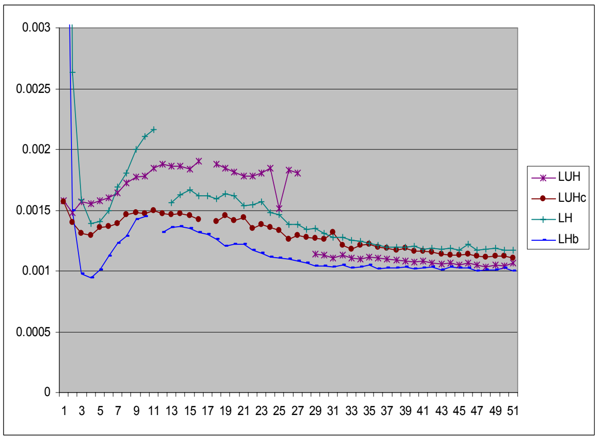
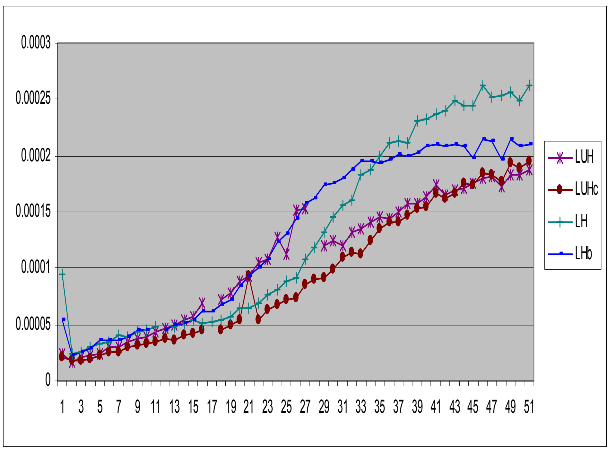


Fig. 2d. GDMS surface scan of Mn.
Each spot represents roughly 1 μm thickness.
Diffusion rate 2 μm in one hour.



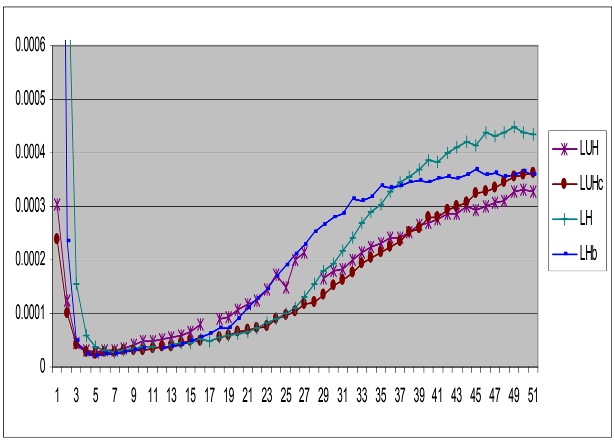


Fig. 2e. GDMS surface scan of V.
Each spot represents roughly 1 μm thickness.
Diffusion rate 0.6 μm in one hour.

Fig. 2f. GDMS surface scan of Ti.
Each spot represents roughly 1 μm thickness.
Diffusion rate 2 μm in one hour.

4. Results

The results can be divided in principle be divided into three groups:

- fast diffusing eutectic elements
- slow diffusing eutectic elements
- slow diffusing peritectic elements

The first group had increasing concentration towards the surface after solidification This layer had almost disappeared into the billet and/or out into the oxide layer after homogenisation. Figs. 2a and 2b. Sometimes, there was a dip toward the surface in the unhomogenised sample, on the outside of the bump.

Slow diffusing eutectic elements are shown in Figs. 2c-d. There is no marked difference in the segregations before and after homogenisation.

We have not analysed any fast-diffusing peritectic elements. The slow-diffusing ones are shown in Figures 2e and 2f. Here the concentration decreases toward the surface, but increases again in the outer oxide layer.

5. Models

Three types of modelling was used: Modelling of the solidification path in the phase diagram, modelling of diffusion at the homogenisation temperature, and modelling of macrosegregation. The models are shortly described in the following:

5.1 Alstruc

Alstruc [1] can do a step by step Scheil type solidification calculation for a multi component aluminium alloy, or a calculation where diffusion in the solid state is included. It uses a phase diagram where intermetallic particles are described with either solubility products or free miscibility. The solubility data and the diffusion coefficients are curve fitted from data in [2-7]. Fig. 3 shows solidification paths, i.e, the composition of the remaining liquid as a function of the fraction solid.

5.2 Diffusion "model"

A rough estimate of the diffusion to the surface during the homogenisation was obtain by estimating the diffusion range in 1 hour according to

$$d = \sqrt{(2 D t)}, \qquad (1)$$

where d is the diffusion distance, D is the diffusion constant, and t is the time. The homogenisation time was four times as much, roughly 4 hours, and corresponds to twice the distances quoted in Fig. 2.

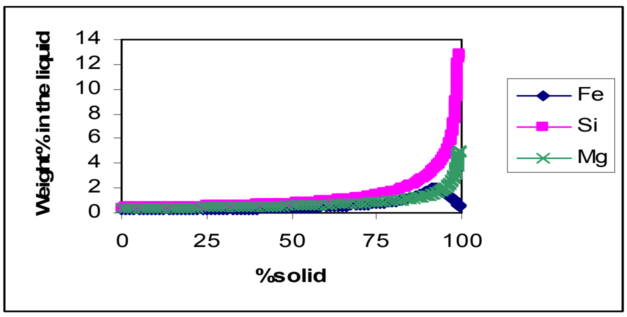


Fig.3a. Si and Mg increase in the remaining liquid during the solidification. Fe decreases when intermetallic particles start to form.

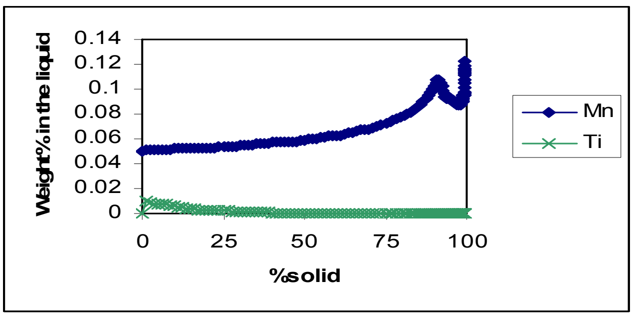


Fig. 3b. Mn increases moderately, while Ti decreases as the solidification proceeds. V follows Ti (not shown). (Alstruc calculations)

5.3 Macrosegregation model

Alsim [8] is a model dedicated to DC casting of Al. It calculates heat, fluid flow, stresses, and deformation during aluminium casting. Mechanical analysis can be carried out in the solid regions and in the coherent mushy zone. The model was recently extended to include macrosegregation. It has been coupled to the Alstruc phase diagram through a .dll (a dynamically linked library) [9,10]. The primary solid and the secondary phases are considered as one "common solid phase". Altruc is called for each node at each time step with the current alloy composition, and the enthalpy. The fraction solid and the temperature are returned. The model was used to estimate how high or low the surface concentration would be as a result of macrosegregation formation driven by solidificaton shrinkage and thermo-solutal convection, exudation was neglected. The calculation geometry is shown in Fig. 4a. Some results are shown in Fig. 4b-d.

5.4 Comments on the Alsim calculations

The Alsim calculations had a mm mesh, and are not on the same scale as the GDMS profiles. With 7% shrinkage, the space will be filled from neighbour areas, where the liquid is more or less enriched in alloying elements. Alsim gives an estimate, but the geometry is simplified.

6. Discussion

Comparing the GDMS results more closely with the Alstruc results, we see that the average surface composition corresponds to the composition of the remaining liquid after approximately 70-75 % has solidified. The composition might correspond to the remaining melt composition even later in the solidification process mixed with early material. However, this should give a lower surface concentration of iron than the measured. The results might be due to Fe-rich particles leaking out, or a supersaturated liquid. Comparing the measurements with the Alsim calculations, we see that solidification shrinkage and convection induced macrosegregation does not explain the measured high surface segregations: There must be microsegregation or exudation, or the galculation geometry is all wrong.

Homogenisation is used to smooth out the segregation. The analysis shows that this is the case for the fast diffusing and low melting elements Si, Mg and Cu, but not for all alloying elements. It is therefore important to cut off or hide the surface layer during extrusion.

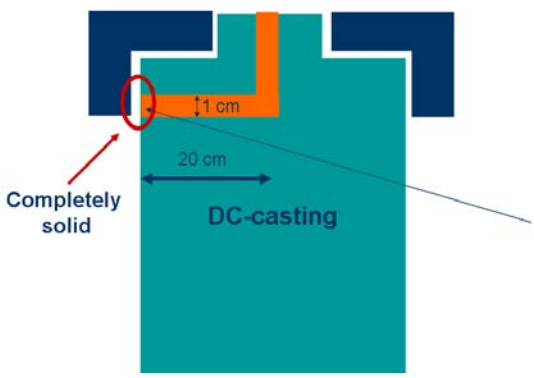


Fig 4a. The orange part is the calculation geometry.

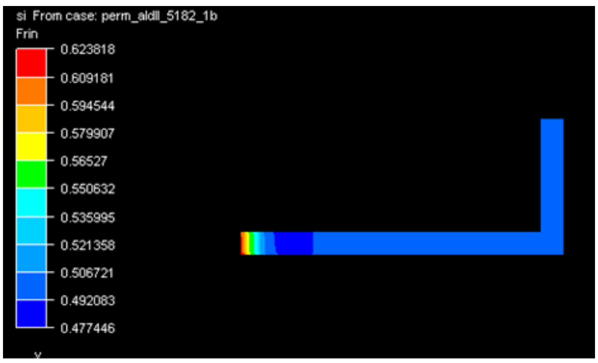
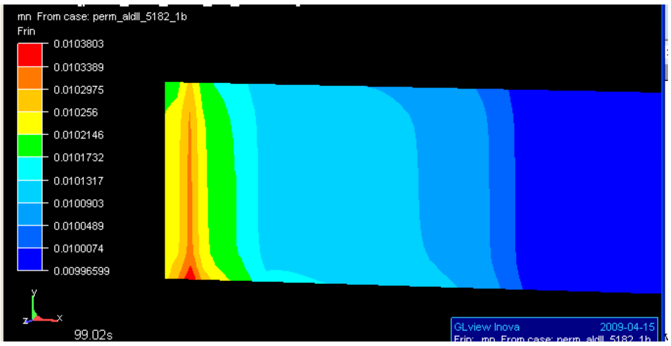


Fig.4b. Alsim results for Si (eutectic). The maximum is roughly 20% above the average.



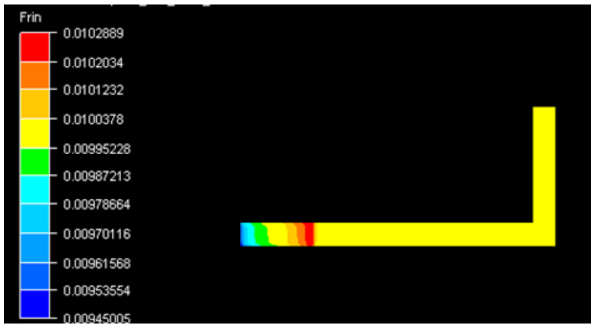


Fig. 4c. Alsim/Alstruc for 0.1%Mn, Maximum is 4% above average. Component thickness 1 cm. Only 2-3 cm in the tip are completely solid.

Fig.4d. Alsim results for a peritectic element. Minimum is roughly 5% below average. Component thickness 1 cm. Only 2-3 cm in the tip are completely solid.

7. Conclusion

Exudation and/or microsegregation leaves a surface layer rich in eutectic elements and poor in peritectic element on AA6063 billets. This layer is only partly removed by the usual industrial homogenisation.

Acknowledgements

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