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Trace Elements In Aluminium Alloys: Their Origin And Impact On Processability And Product Properties

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The present paper focuses on the challenges regarding pick-up of trace elements in the processing chain of aluminium production and the quantities of these elements that will eventually end-up in the final products. Measuring the trace elements in aluminium is not straight forward when using techniques like Optical Emission Spectroscopy since the trace elements are often present in very small amount varying from several ppm to a few ppb's. The paper gives an overview of the complementary analysing techniques. The effect of some elements at trace levels on processability of extruded profiles, rolled sheets and foundry alloys as well as the impact on critical properties are also presented. It is shown that some elements may have significant influence on properties even for very low concentrations.

Keywords: Trace elements, Raw materials, Processability, Product quality, Analysing techniques

1. Introduction

Trace elements or impurities are commonly present in aluminium and its products and can originate from different sources. Well known sources accountable for the trace elements in aluminium are the raw materials such as alumina and coke, processing conditions and equipment. Future predictions suggest that an increasing level of trace elements can be expected in aluminium products as a result of change in raw material quality. These changes include anode qualities and an increasing volume of recycled aluminium. Introducing recycled products can be challenging since these products may be enriched by certain elements due to various end-user processes such as different surface treatments including laquering, anodising, coatings as well as non-aluminium contaminant in the Al-scrap.

A trace element is defined as an element that is not intentionally added to the aluminium. In principle, trace elements can be any element from the periodic system and are usually present in (very) small concentrations. Despite these small quantities, some trace elements have shown to impact the properties and processes of aluminium and aluminium products significantly. In some cases diffusion of these elements may cause segregations. This might give locally higher values which can have significant impact on the processability and product properties. Segregation of trace elements to the surface which may have a significant impact on the surface appearance such as high or low gloss and colour of the product. Another example is segregation of elements at heterogeneities such as grain boundaries deteriorating the properties of the product. Additionally the interaction between different trace elements or between trace elements and alloying elements (particles, precipitates) may change the mechanisms such as the solidification of primary phases, precipitation of dispersoids or the precipitation sequence in age hardenable alloys.

In order to improve the consistency in processability and product properties, knowledge about the consequences of various trace elements is needed. Experiments with controlled chemical compositions have to be carried out in order to find the critical levels. These critical levels are the cut-off point at which the trace elements can be considered harmful with respect to processes, microstructures and consistent final properties. The objective of the present paper is to give an overview of the areas that may lead to different trace element levels and their influence upon processing and products qualities. Finally the critical prerequisites that must be controlled for obtaining predictable and consistent products are discussed.

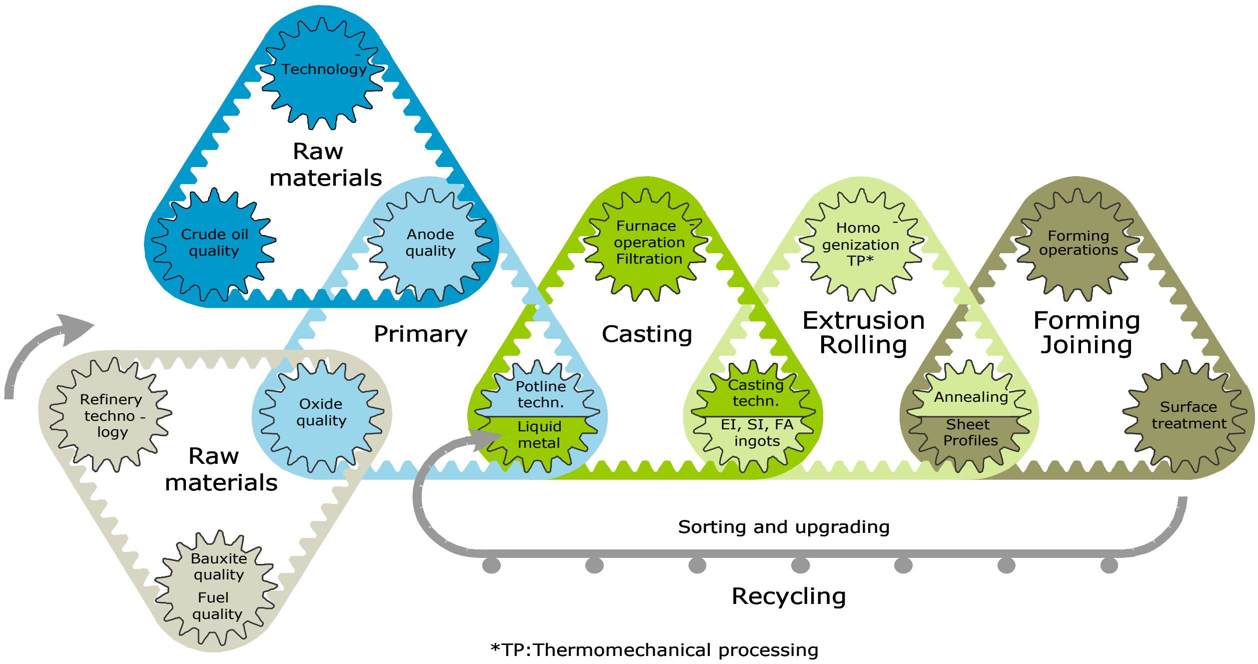


Figure 1: The value chain of cast (FA), rolled (SI) and extruded products (EI).

2. Trace Element Pick-up

2.1 Raw materials and processes in primary production

Each process step is a potential source for the pick-up of trace elements. It is immediately influenced by the choice of the raw material sources that are used for the production of aluminium. Raw materials include alumina as well as the coke and pitch used in the anodes. The alumina is obtained from bauxite ores consisting of 40-60% of alumina (Al_2O_3) and Si, Fe, Ti compounds together with a wide range of other elements. The bauxite normally lies closely to the surface and is strip-mined. The largest bauxite mines are found in Australia, China, Brazil, Guinea, and Jamaica. The region from where the bauxite originates is of great importance since this will determine to some extent which trace elements will be present as well as the concentration at which each trace element is present in the bauxite. Some bauxite sources are known to be relatively rich in Zn compared to the bauxite from other parts of the world, while the Ga level from these sources are correspondingly lower, see Fig. 2.

The primary alumina obtained from the bauxite is used in the pot-rooms to produce the aluminium, and it is treated with the fumes collected from the electrolysis cell. The primary alumina reacts with the fluorides in these fumes and is called secondary alumina thereafter. However, these fumes also contain other trace elements that have evaporated during the electrolysis process and thereby can enrich the alumina. The secondary alumina is transported to the electrolysis cell and dissolved in an electrolyte consisting of liquid cryolite (Na_3AlF_6) and other fluoride containing compounds.

The anodes used in the electrolysis cells are made of coke, pitch and crushed anode butts. The coke is a by-product of oil production and can vary in quality. The quality of the coke depends on the regions were the crude oil is obtained (Middle East, Venezuela, Mexico, Africa, Norway and the US Gulf).

Low (cheap) quality coke can have relatively high levels of trace elements like V and Ni, while the better and more expensive coke quality has generally lower levels of trace elements. The pitch is a by-product from coal tar and is used as a binder in the anodes. The pitch is often enriched in elements like Zn and Pb.

The electrolysis cells materials and the processing condition and parameters of the cell are very important sources for trace element pick-up. Some elements like Cu, Mn, Fe are known to originate from the equipment and tools used in the potrooms. The equipment such as stubs of the anodes and the bars in the cathodes used in the potroom are made of steel. The high temperatures and the corrosive environment can cause erosion of these steel parts. The level of Fe is monitored and high levels are often a sign of leakage of a cell or that a cell needs re-lining. A higher level of Fe automatically leads to a higher level of other alloying elements added to the steel. Fig. 3 shows the concentrations of Cu, Cr and Mn as a function of Fe for two different primary aluminium sources.

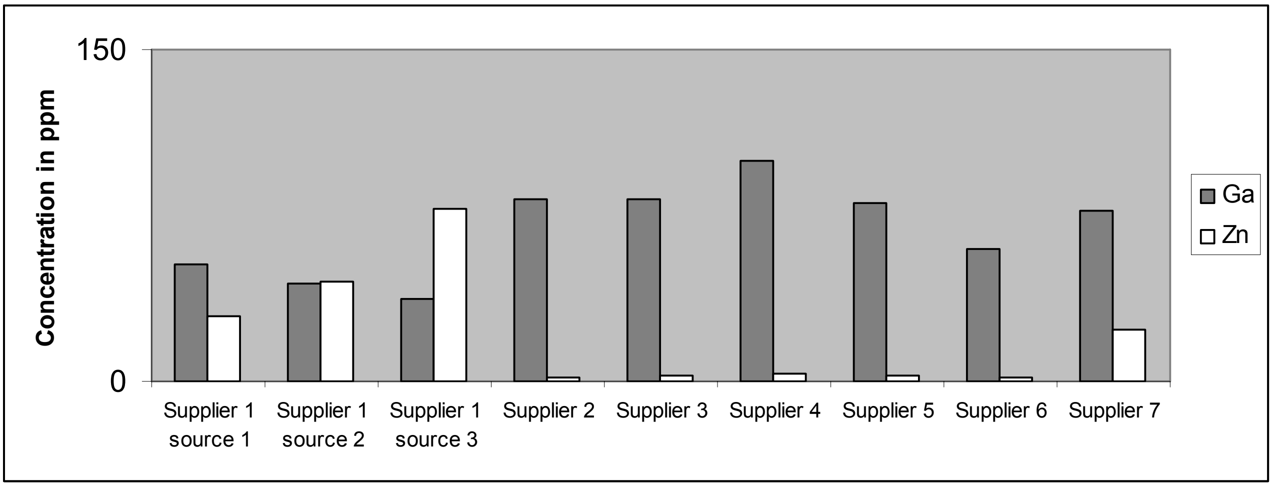
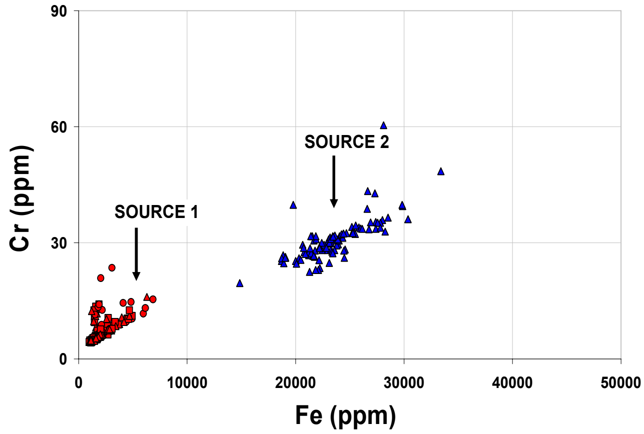


Figure 2: Average concentrations of Ga and Zn in alumina from different suppliers in a given time period.

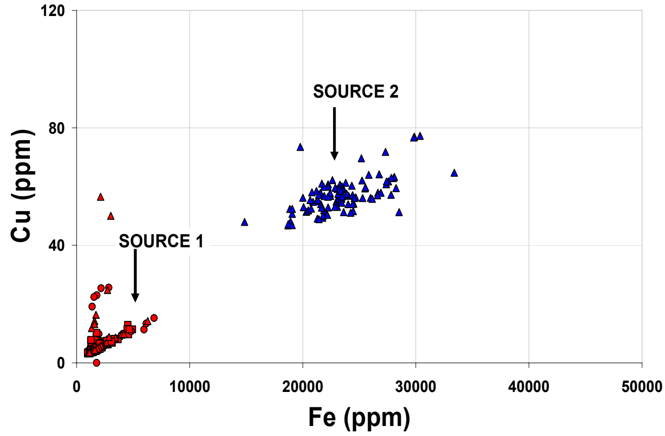
Process conditions in the cells like bath temperature, anode effect and acidity can also lead to the pick-up or rejection of certain trace elements into the liquid metal. In the casthouse other potential sources can be identified such as the cold metal for remelt, the alloying additions, scrap and the grain refiner. The process parameters and conditions in the electrolysis process as well as the processes in the casthouse are important factors and can influence the concentration of the trace elements released into the liquid metal.

2.2 Recycling of post consumed scrap

The use of post consumed Al-scrap is an increasing trend in the aluminium world. The use of recycled aluminium scrap enables a reduction in energy consumption. However, the disadvantage of introducing scrap into the aluminium value chain is that it makes it more difficult to control or avoid the introduction of a new stream of trace elements. These new stream of trace elements can come from surface treatments like anodizing, lacquering and painting and/or compounds that include other materials such as steel, composites, plastics, ceramics, organic materials. The critical levels for trace elements originating from Al-scrap sources are often not available and in some cases important to establish. In order to minimise the concentration of detrimental trace elements in recycled based metal sorting of scrap in solid state as well as purification of melts are very important process steps.



(a)



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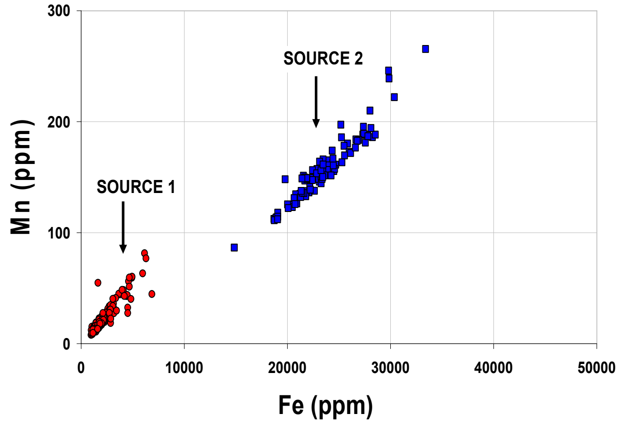


(c)

Figure 3: Trace element levels of (a) Cr, (b) Cu and (c) Mn in different primary based Al-sources represented by different Fe-levels.

3. Characterisation techniques of trace elements

A fundamental approach towards understanding the mechanisms that cause trace elements to influence process and product performance requires the use of best available experimental equipment with adequate sensitivity. There are several techniques that are used for characterization of trace elements (for details, see.Walmsley and Holme [1]):

(i) Scanning Electron Microscopy (SEM) which gives the overview of surface morphology,
(ii) Glow Discharge Optical Emission Spectroscopy (which is a technique that is rapid with good sensitivity and well suitable for depth profiling (but has a rather poor lateral resolution)
(iii) Glow Discharge Mass Spectroscopy (GDMS) with a high sensitivity and some depth profiling but with relatively poor lateral resolution
(iv) Secondary Ion Mass Spectrometry (SIMS) with a high sensitivity and depth profiling with ~1µm lateral resolution mapping
(v) X-ray Photoelectron Spectroscopy (XPS) which is a reliable quantification of chemistry at interfaces
(vi) Transmission Electron Microscopy (TEM) giving a detailed and direct observation of local microstructure and composition
(vii) Rutherford Backscattering (RBS) suitable for establishing segregation profiles

The use of these instruments is time consuming and quite expensive to apply. The standard way to analyse alloying and trace elements in the Al-industry is by Optical Emission Spectroscopy (OES). Important parameters that may influence the OES-results are (i) the spectrometer type, configuration and equipment (installed element lines), (ii) the performance of the measuring channels (stability, sensitivity, lowest limits), (iii) bare calibration, (iv) long term stability obtained by drift compensation (recalibration) and (v) inhomogeneity of the sample since most trace elements are concentrated at grain boundaries. The challenge in measuring the correct trace element values is even greater than measuring the main alloying elements due to lack of standards, the Detection Limits (DL) and the Background Equivalence Content (BEC).

4. The influence of processability on trace element segregations

The processing chains of rolled and extruded products are shown in Fig.1. The temperature in the different processing steps varies in the range from room temperature up to approximately 600ºC with different heating and cooling schedules. In addition thermo-mechanical processing involves hot and cold deformations with different strain rates and deformation ratios. During these processes dislocations and vacancies will be generated, which will have significant influence on the diffusion mechanisms of elements in aluminium alloys. The grain structure will also change during processing due to recrystallization. Structures with different grain sizes and different grain boundary misorientations will appear as a result of that. It is well accepted that the mobility of an atom along a grain boundary is higher than through the crystal volume. These interfaces have a more open structure and, hence less resistance to atom movement. In general, the smaller the grain size and the larger the grain boundary misorientation, the higher the diffusion rate. Another important interface is the surface of the products with a significantly higher diffusion coefficient than the grain boundaries. Consequently, bulk measurements of a product may indicate low levels of trace elements and can therefore be misleading. The diffusion mechanisms can result in relatively high concentrations in grain boundary areas and the surface regions leading to numerous and unpredictable changes in material behaviour.

5. Product properties of extruded, rolled and cast products

5.1 Surface properties

In several papers (see overview by Nisanciouglu [2]) it has been reported that trace elements may alter the surface properties of aluminium products. It has been shown that their negative impact may be compensated for by a carefully designed thermomechanical process route. In particular, the effect of surface activating Pb, In, and Sn in medium strength 1000, 3000 and 6000 alloys has been studied extensively, as well as the role of small Cu content in relation to the alloying element Si in grain boundary corrosion of 6000-series alloys. The effect of Zn on grainy/surface appearance in extruded profiles is an actual topic in the building and interior design sector where the visual aspects of products have to be taken into consideration. As shown by Chandia et al. [3] the Zn-concentration in the profile up to 0.10wt% does not have any influence on the surface appearance of the profile. However, the Zn level in the etching bath becomes critical for the occurrence of a grainy appearance when this concentration exceeds 5-6ppm. The Zn level in the bath reflects the Zn-concentration in the profiles and the operational conditions at the anodizer. This depends also on how often the bath is cleaned and/or the use of additives. To make the products and processes more consistent and robust it is important to create an even closer collaboration between suppliers and customers. This allows an understanding of the basic mechanisms and how the different parameters can be controlled/ and optimised.

5.2 Mechanical properties

Ca may be introduced into an Al-product through different sources such as raw materials, contaminated scrap during recycling, bone ash, refractory from the launder and the concrete during casthouse operations. A trial was carried out to investigate the effect of relatively small amounts of

Ca on mechanical properties in an extruded 6060 alloy. The alloy (Al-0.40Mg-0.40Si-0.20Fe) with different Ca-levels between 0-1000 ppm was DC-cast to 95 mm billets and homogenised following industrial practise. The billets were extruded to flat profiles on the SINTEF laboratory press. The billet temperature was 460ºC, the ram speed 2mm/s and extrusion ratio of 44. The profiles were air cooled after extrusion. The profiles were stored for 24 hours and subsequently artificially aged at 185ºC for 6 hours. As shown in Fig. 4 the strength and ductility are rather independent of the Ca level for concentrations less than approximately 100 ppm. However, the strength and ductility are reduced significantly with Ca-levels of 485ppm and above. The drop in mechanical properties is explained by the tendency of the Ca to form particles containing Si and sometimes Mg containing particles [4]. Less Si and Mg are then available to form age hardening precipitates which reduces the age hardening potential of the alloy.

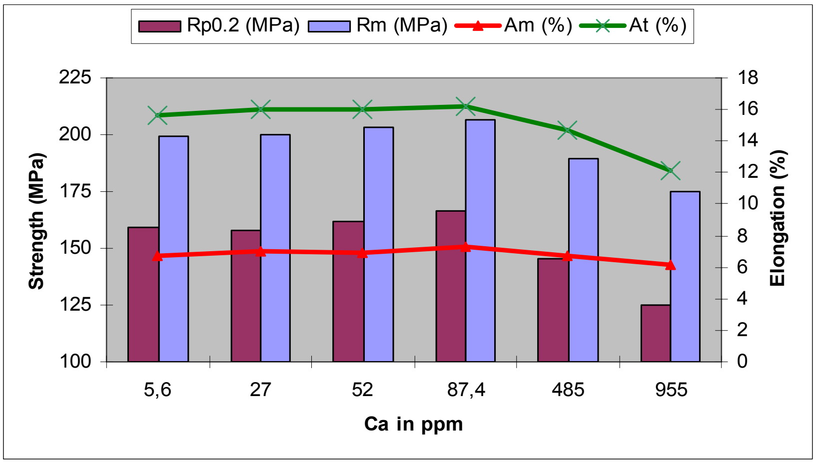


Figure 4: Mechanical properties in a 6060 alloy with different Ca contents.

The influence of Mg, Cu and Mn in trace levels on strength in 1xxx series alloys: The alloys, with compositions as shown in Table 1, were DC cast in the laboratory facilities at Hydro Bonn to ingots with a dimension of 125 mmX350 mmx500 mm. The ingots were scalped, homogenised and pre-heated for hot rolling from 100mm to a final hot rolling gauge of 4mm. The sheets were cold rolled from 4 mm to a final gauge of 0.3 mm without any intermediate annealing.

The ultimate tensile strength of the different alloys after cold rolling is presented in Fig. 5. The results show that relatively small amounts of Mg, Cu and Mn have a significant influence on strength due to strain hardening. Adding approximately 70ppm of Mg to the base alloy increases the strength as much as 22MPa, while similar amounts of copper increases the strength with 17MPa. The effect of Mn on strength is seen to be somewhat less as compared to Mg and Cu.

Table 1: Chemical composition of the 1xxx-series alloy variants

	Alloying elements (wt%)			Trace elements (ppm)		
	Fe	Si	Zn	Cu	Mg	Mn
Reference	0,36	0,08	0,012	1,2	1,9	0,4
Low Mg	0,36	0,09	0,012	1,1	**69**	0,3
High Mg	0,35	0,09	0,012	1,3	**198**	0,4
Low Cu	0,36	0,09	0,011	**33**	1,3	0,2
High Cu	0,36	0,09	0,012	**72**	1,0	0,3
Low Mn	0,36	0,09	0,012	2,4	0,8	**94**
High Mn	0,35	0,09	0,010	2,2	3,4	**194**
Low Mg + Low Mn	0,35	0,09	0,011	7,1	**18**	**34**

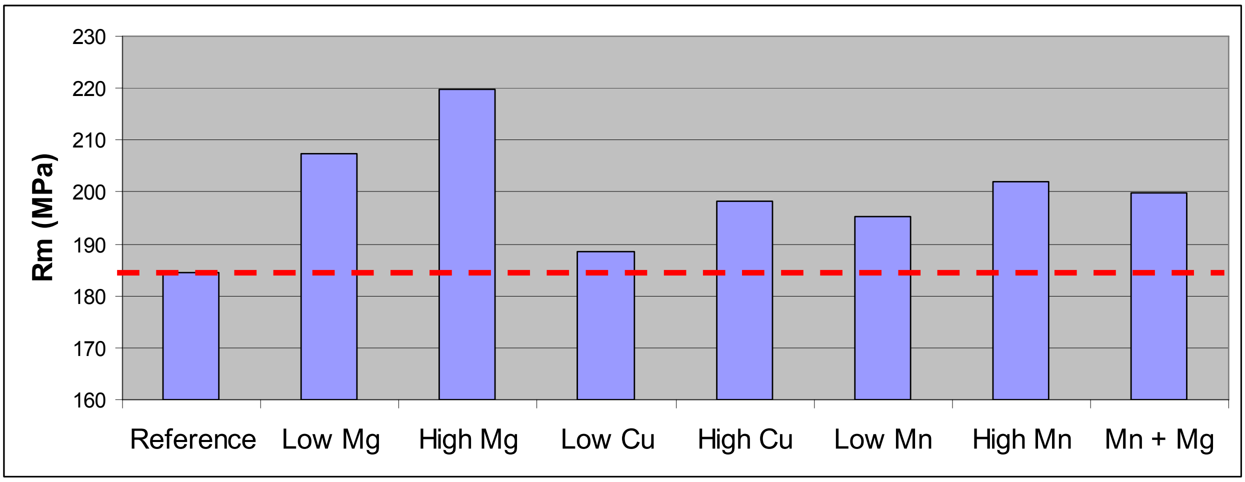
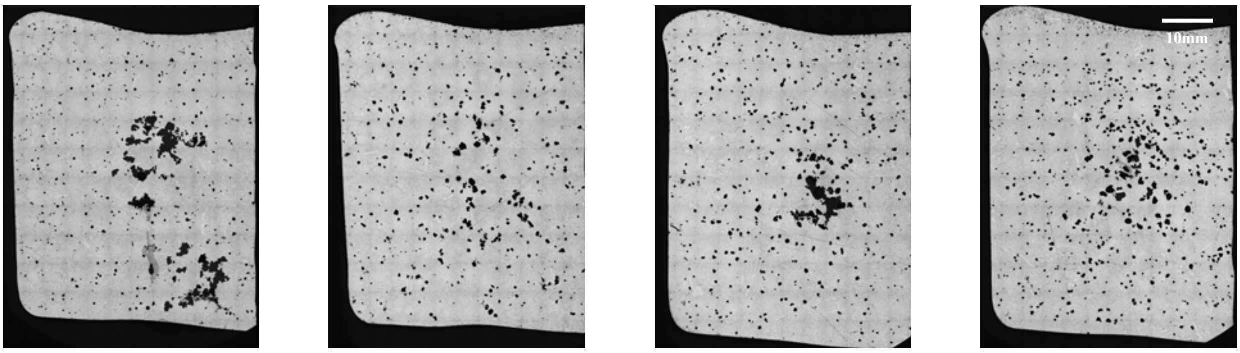


Figure 5: Effect of Cu, Mg and Mn in trace levels on ultimate tensile strength in a commercial pure Al-alloy. Strength levels above dotted red line are due to strain hardening.

5.3 Castability

For users of foundry alloys, the most important property is "castability". This is a general term used to describe the ability of an alloy to fill the mould and produce a defect free casting. The main defect of concern is porosity and in particular how the porosity is distributed throughout the casting. Many variables such as; grain size/morphology, eutectic growth mode, permeability of the mush, freezing range of the alloy, hydrogen concentration and level of inclusions/oxides significantly influence porosity [5]. Clearly, some of the afore mentioned variables will be more dominant than others and in the case of Al-Si foundry alloys, the eutectic solidification mode will be extremely influential on the final porosity distribution.

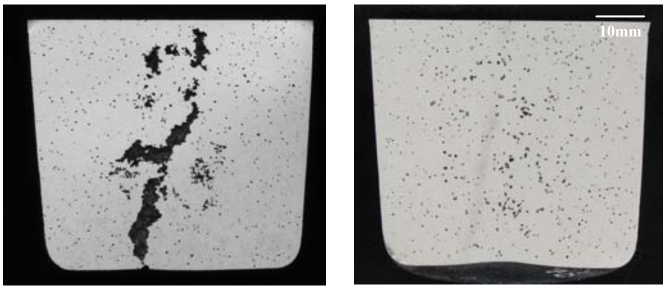
It is well documented that in an unmodified Al-Si melt the eutectic Si nucleates on AlP particles [6]. However, most casthouses add Sr to the melt prior to casting to modify the eutectic morphology thus improving the mechanical properties. Sr poisons the AlP particles causing an increase in the eutectic grain size [7] and the final porosity distribution will be strongly influenced by the size and number of eutectic grains. Therefore the ratio of P to Sr will influence the eutectic solidification and thus the feeding behaviour and porosity distribution. This is illustrated in Fig. 6 for gravity die cast cylindrical samples, alloy AlSi11MgSr.



0ppm P | 10ppm P | 20ppm P | 40ppm P

Figure 6: The effect of different P levels on porosity distribution in AlSi11Mg alloy, gravity die cast cylindrical samples.

Another investigation revealed that Ca also can significantly influence the porosity distribution. The addition of 50ppm Ca to an AlSi11Mg (the AlSi11Mg alloy also contained 350ppm Sr, 0.01wt% Ti and TiB_2 grain refiner at 0.001 wt% B) changed the pore distribution, see Fig. 7.



AlSi11Mg AlSi11Mg + 50ppm Ca

Figure 7: The effect of adding 50ppm Ca on pore distribution.

These two examples serve to illustrate that a difference in concentration of several ppm can significantly influence the eutectic solidification and thus castability of a foundry alloy. The resulting effect will be a combination of elements influencing the solidification characteristics and the casting method and parameters, i.e. the parameters influencing the feeding behaviour during solidification.

6. Summary

The present paper has highlighted the challenge related to future raw materials sources for aluminium products (alumina, anode quality, scrap metal), their role to variations in trace element levels and their subsequent impact on processability and product quality. Some elements may give detrimental effects even in very small concentrations while other elements may improve the product quality. The most important request for customers is to have products with consistent and predictable quality. To fulfil this requirement more knowledge about the impact of trace elements is needed. Masking the effects from trace elements by changing the process parameters and/or conditions along the whole value chain must also be considered in the quest for more robust processability and consistent product qualities.

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