

# aluminium technologies 20.10.2015

#### Al-5Ti-1B / wrought vs foundry alloys before addition 2 min after addition



**AlSi7Mg** 



## Grain refinement in shape casting

Exact copy of the grain refinement practice in continuous casting!

Aluminium foundries use prealloyed stock with as much as wt% 0.1 Ti!

+ 0.2-0.4 wt% Al-5Ti-1B rod (2-4 kg/ton)

Al-5Ti-1B rod performance  $\downarrow$  cost  $\uparrow$ 

Foundries need better grain refiners that can offer superior performance in spite of the high Si content of foundry alloys! To counteract Si poisoning (Ti-Si compounds!)

#### Grain refinement in shape casting

Al-B alloys! Known to be effective for nearly 30 years.

B reacts with Ti to produce compounds! B reacts with Sr to impair modification process!

B-rich AlTiB grain refiners! : mixed Al(Ti,B)<sub>2</sub>!

Al-B alloys

have not been used commercially! instead they are used as alloying addition to improve electrical conductivity in conductor grade aluminium alloy!

Foundry alloys use prealloyed materials with Ti! B addition to Ti bearing alloy // addition of AlTiB!

#### Effect of Si on grain structure





#### Commercial purity aluminium (99.7)



AlB<sub>2</sub> is not stable in molten aluminium at B < 0.022 wt% !  $\alpha$ (Al) is the primary phase and AlB<sub>2</sub> is yet to form!



#### Grain refinement with B



at

16

#### Grain refinement 5 min after addition AlSi7Mg0.3

#### Before addition







#### AlSi7Mg0.3







#### AlSi11Cu2



# Grain refinement AlSi12CuFe 2 min after addition

#### Before addition

	<u>.500 um</u>



# Grain Refinement

Grain Refinement inoculation ↑ nucleation rate -Homogenous-heterogeneous nucleation

> Fragmentation / multiplication breakage of dendrites Mechanical/thermal/solutal disturbance ultrasonic-vibration

high solidification rate

Restrict grain growth  $\downarrow$  growth rate

#### Grain Refinement

#### low pouring temperatures

dendrites form and are broken up in the stream of flowing metal, fragments are swept into the bulk of the casting and if they do not re-melt, they can act as efficient nuclei.

mechanical, thermal or solutal disturbance during freezing will assist, such as surface shower multiplication, or grain refinement by vibration or stirring, such as electromagnetic stirring.

**Ultrasonic vibration** is also a well-known method of achieving grain refinement.

### Grain Refinement via restriction

#### **Effect of Alloying Elements**

- Finally, it is possible to restrict grain growth after nucleation.
- One way of achieving this is to use alloying elements with a low distribution coefficient, k, i.e. those solutes which segregate strongly ahead of the advancing front and so slow down diffusion and thus the rate of arrival of aluminium atoms to grow the primary aluminium dendrites.
- This is probably how Ti helps to grain refine Al alloys. In summary, there is widespread confusion between the concept of a grain and the concept of a dendrite.

#### Grain Refinement via restriction

#### **Effect of Alloying Elements**

Partioning of alloying elements at the solidificiation front (liquid-solid interface) restricts growth!: growth restriction (GRF)

elem.	Mn	Cu	Fe	Mg	Ni	Cr	Si	Ti
GRF	0.1	2.8	2.9	3.0	3.3	3.5	5.9	246

#### Grain refinement with Al-B

- Al-B is a perfect grain refiner for foundry alloys!
- Grain size is 3 times smaller with Al-B addition with respect to that obtained by Al-5Ti-1B!
- Average grain size as small as 200 µm is standard!
- For  $AlB_2$  particles to offer effective grain nucleation, the Ti level in the alloy must be controlled below <80 ppm); otherwise,  $AlB_2 \rightarrow TiB_2$
- The grain refinement of AlB<sub>2</sub> particles does not suffer fading since the nucleant in the case of grain refinement with Al-B form inside the melt shortly before the α-Al grains!
- Hence, Al-B is just as effective in remelt operations!

#### Microstructural features

- The composition of the alloy and the choice of casting process affect the microstructure of the aluminium alloy castings.
- Sand cast and gravity die cast alloys cool relatively slowly, resulting in a coarse lamellar eutectic structure which is detrimental to the strength of the castings.
- Pressure diecastings are rapidly solidified giving small grain size with a fine eutectic structure with small dendrites.
- The microstructure can also be changed by the addition of certain elements to aluminium-silicon alloys which improve castability, mechanical properties and machinability.

## Modification of aluminium alloys

- Si lamella transform into fine Si fibres upon modification.
- This fine structure improves elongation values. However, it increases porosity.
- Modification of the eutectic Si is critical for the ductility of the casting.
- modified alloys exhibit at least 3x higher ductility with respect to those not modified.
- Modification increases hot tear resistance and alloy feeding characteristics, decreasing shrinkage porosity.

## modification



### modification



# Modification of aluminium alloys

Modification of Si can be achived by different mechanisms.

#### Thermal modification:

Si phase is modified under rapid solidification conditions Si particles change during solution heat treatment.

#### Chemical modification:

Modification is executed via the addition of approximately 100-200 ppm Na, Sr, Sb, Ca, P

### thermal modification



Effect of solution heat treatment on eutectic Si particle characteristics observed in A356.2 alloy casting level 1 samples in a as cast condition and b after solution heat treatment at 540C for 80 h

### thermal modification



Effect of solution heat treatment on eutectic Si particle characteristics observed in Sr-modified A356?2 alloy SrM casting level 1 samples in a as cast condition and b after solution heat treatment at 540C for 80 h

### Thermal modification

#### Effect of solidification rate



Sand cast Al-12.5wt% Si alloy Chill Cast Al-11% Si alloy

## chemical modification

#### +100 ppm Sr



#### Modification of aluminium alloys

- The higher the silicon level in an alloy, the more modifying element is needed.
- The faster the freezing rate, the lower the amount of modifier required.
- Pressure diecastings are often not modified!
- Modification of pressure-diecast microstructures is also possible and the lamellar eutectic silicon will be changed to a fine fibre structure.



# mechanism of modification



Twin Plane Reentrant Edge Mechanism Propagation of crystal due to reentrant corners

#### The effect of modification on the microstructures of aluminium alloys



LM6 before modification





LM27 after modification

after modification



LM25 after modification

LM 6: Al-12Si LM25: AlSi7Mg LM27: AlSi7Cu2Mn0.5



LM25 before modification

### chemical modification



# modification rating

AFS 1	unmodified	Large plates + acicular particles	A The second
AFS 2	Partially modified	Lamellar + acicular particles	
AFS 3	Partially modified	Lamella broken + acicular particles	

# modification rating

AFS 4	Under modified	More Lamella broken + fewer acicular particles		
AFS 5			· · ··································	
		fibers + no	State of	
	modified	acicular		
		particles		
			m Alter As	
			d Alexandre	
AFS 6	Super modified	Very fine fibers		

# modification with sodium

- The first hypoeutectic modifiers, based on sodium, are still widely used today although "fade", the gradual loss of sodium with time, can lead to problems of control.
- Sodium has a very large undercooling effect so that it is particularly useful in slowly cooled casting processes such as sand casting.
- Sodium can be added either as metallic sodium or as sodium salts.
- The modified structure is unstable and tends to fade, that is, to revert to the unmodified condition.

## Sodium metal method

- The rate of reversion depends on silicon content, temperature and size of the melt.
- Reversion is slow at temperatures below 750°C and does not occur to any considerable extent during a 10 min holding period as long as the metal is not agitated by stirring or degassing.
- Since some possibility of hydrogen pick-up is possible, it is preferable to degas after modification. The charge is melted under a layer of cover flux.
- The dross is pulled to one side and when the melt is around 750°C, the metallic sodium is plunged using a bell-shaped plunger which has been coated with refractory dressing.

## Sodium metal method

- When the reaction has subsided, the metal is stirred using the plunger, but without breaking the metal surface.
- The plunger is withdrawn and the Degassing Unit rotor immersed, degassing takes 3-5 minutes.
- The melt is then drossed off and poured without delay.
- The modified structure fades with time, and melts which are held for longer than 10 minutes should be partially or wholly remodified from time to time with further additions of sodium.
## Refinement effect

- When sodium is added to the alloy, the rate of advance of the dendritic front will only be 1/17th of the rate of the planar front.
- The eutectic spacing is coarse in the dendritic growth mode, whereas it is fine in the planar mode because it had rapidly solidified.
- This explains the action of sodium in refining the spacing of the eutectic silicon.
- castings which solidify rapidly, such as die castings (especially pressure die castings) have especially fine eutectic spacing, although additions of sodium will act to refine the spacing still further.

#### refinement effect

The refining of the eutectic spacing is generally carried out to enhance the strength and ductility of Al-Si alloys, particularly those alloys which contain more than about 50% eutectic phase such as Al-7Si-0.4Mg and higher Si alloys such as Al-11Si.

#### Al-12Si alloy modified with 0.005 wt% Na



## Sodium salt method

- The salts process, although slower in terms of sodium transfer, is less likely to introduce gas into the melt.
- Because of its reactivity, sodium is vacuum packed in aluminium containers for convenient addition.
- This minimises the possibility of gas pick-up.
- It also avoids the likelihood of undesirable crucible attack which may result from the use of modifying sodium salts.

## Sodium salt method

- When degassing with DEGASER tablets, it is advisable to degas before sodium modification, since degassing with hexachloroethane removes sodium from the melt.
- The Rotary Degasser removes much less sodium, but modification using flux is still best carried out after degassing.
- The charge should be melted under cover flux and heated to above 750°C then degassed for 3-5 minutes.
- The melt is skimmed before pouring.

#### **Problems of Sodium Modification**

- The addition of Na causes a lot of fume during addition when added as Na metal. The health and safety legislation make this aspect unpopular.
- When Na is added in salt form, then the residual chloride and/or fluoride salt has to be disposed of in some safe manner. Because of the danger of the pollution of ground water supplies, this procedure is also becoming less widely used.

#### Problems of Sodium Modification

- The temperature at which liquid aluminium is held is above the boiling point of Na, so that Na is lost from the melt by evaporation.
- The rate of loss of Na vapour means that most Na is lost within 15 or 20 minutes of an addition.
- It is therefore not easy to ensure that the level of Na in the melt is correct at all times.
- This poor chemical control is the main reason why Na is unpopular for control of eutectic modification.

Today, AlSr master alloys is almost exclusively used for the modification of Si phase.

#### composition

AlSr10 AlSr5

#### product form ingots

rod





- Strontium as a modifier has the advantage over sodium that it is less reactive and can be added in the form of master alloys so that precise control over additions is possible and fade only occurs over a period of several hours but it is less effective in heavy section castings.
- The ability of strontium to modify the structure of aluminium-silicon alloys without fading has made it popular for low pressure and gravity diecastings where it may be necessary to hold molten metal for relatively long periods.

- Strontium is added as a master alloy containing 10%
  Sr for use principally on hypoeutectic and eutectic
  Al-Si alloys (6-8% and 10-13% silicon) and is used
  mainly on alloys for gravity and low pressure
  diecasting.
- SrAl additions for eutectic modification (from Spooner S.J., Cook R., *Foundryman*, **90**, May 1997, p. 170)

Si of alloy (%)	Sr addition (%)	10SrAl Addition (kg/t)	
4-7	0.01-0.02	1-2	
8-10	0.03-0.04	3-4	
11-13	0.04-0.06	4-6	

- They are added to the melt at the Degassing Unit, allowing degassing and modification to take place at the same time.
- Addition of 200 g piglet to 100 kg of metal adds 0.02%
  Sr and, in good conditions, almost 100% yield is possible.
- Solution is usually complete within 3 min of plunging the piglets, which is within the treatment time when using the rotary degassing unit.
- The rate of loss of strontium from molten metal is slow and allows holding times of a few hours.
- Foundry returns from strontium-modified metal contain an uncertain amount of active strontium modifier.

- Its great advantages are that it is effectively, easily and fumelessly added to the melt.
- Strontium is less reactive and can be added in the form of master alloys so that precise control over additions is possible and fade only occurs over a period of several hours but it is less effective in heavy section castings.
- It is lost slowly by oxidation. However, this is similar to the rate at which other oxidisable elements such as Mg are lost, and so can be effectively kept under good control.

disadvantages to the use of Strontium:

- The melt seems sensitised to the pickup of hydrogen gas, so that castings often display dispersed gas porosity.
- When the melt is allowed to remain in contact with moisture in the air, the strontium reacts with the water, forming strontium oxide on the melt surface and releasing hydrogen gas to go into the melt.

- This seems to happen less in low pressure die casting where holding the melt inside an enclosed pressure vessel keeps the it out of contact with air.
- The action of strontium on straightening the freezing front of the eutectic is not quite the same as that of sodium.

#### ADVANTAGES

Almost complete absence of fade, hence chemical control is good.
 No fume or other environmental problems.

#### PROBLEMS

- 1. Hydrogen adsorption from water in the environment.
- 2. Solidification front is cellular, not planar as in the case of Na.





#### microstructure of Al-Sr



## modification with antimony

- Antimony (Sb) is another permanent alloying addition which has a modest effect on the refinement of the Al-Si eutectic.
- However, it is not usual to use Sb in foundry applications.
- There is a danger of formation of toxic stibnine gas (SbH<sub>4</sub>).
- there is a danger of overmodification when scrap is recycled.

#### modification with antimony

- Sb addition can seriously impair the performance of Na and Sr additions.
- Its effect on sand castings is sufficiently insignificant that it is usually not used for such applications.
- It is claimed to be reasonably useful for die castings of various sorts, and is used particularly in gravity die foundries.

#### Refinement of hypereutectic alloys

- Al-Si alloys containing over 12% Si are used for their wear resistance and it is important for consistent casting properties that primary silicon is evenly dispersed throughout the casting.
- growth and flotation of primary silicon particles may occur with long solidification ranges.
- Large silicon particles are detrimental to castability, machinability and mechanical properties.
- Refinement of the structure is therefore desirable.

#### **Al-Si Hypereutectic Solidification**

- In the hypereutectic Al-Si alloys, primary silicon is the first phase to separate on solidification. This solidifies as chunky crystals of pure silicon.
- If there are few nuclei on which the silicon can form, then the silicon will form as large separated particles which will float out rapidly, segregating to the top of the casting.
- To avoid this problem, and to obtain a fine and nicely dispersed form of the primary silicon, it is necessary to make a prolific addition of suitable nuclei.

#### **Al-Si Hypereutectic Solidification**

- Hypereutectic alloys are refined with phosphorus additions of 0.003-0.015%.
- The aluminium phosphide , AlP<sub>3</sub>, forms and provides nucleation sites for primary silicon ensuring a fine dispersal of silicon in the eutectic matrix.
- Care needs to be taken to ensure that sodium or strontium are not present when P is added.
- These two groups of elements are antagonistic in aluminium alloys and effectively neutralise each other. Thus if one is present, the other has to be added in sufficient amounts first to react and negate the effect of the first before any beneficial action can be gained.

#### **Al-Si Hypereutectic Solidification**

Hypereutectic alloys may be modified with phosphorus



• in hypereutectic alloys, large crystals of Si form first and float!

- This is overcome by the addition of P to form AlP<sub>3</sub> nuclei.
- Note that Na and Sr neutralize P and vice versa!

## alloying additions

element	M.P. (°C)	
Al	660	
Fe	1535	
Mn	1245	
Cu	1083	
Si	1410	
Ti	1660	
В	2300	
Sr	769	
Mg	650	

High melting point alloying additions (Fe, Mn) must not be made in elemental form. It takes long times for such elements to dissolve in the aluminium melt and the OES analysis over time may be very misleading! Low melting point alloying additions (Mg) must be made as close to casting as possible!

# commercial master alloys

alloy	% alloying element	alloy	% alloying element
Al-Mn	%10/%15/%20/%25/%30/%60/%80	Al-Mo	%10
Al-Mg	%20/%25/%50/%65/%75	Al-Ni	%20/%50
Al-Bi	%10	Al-Sc	%2
Al-B	%3/%4/%5/%6/%8	Al-Si	%20/%25/%30/%50
Al-Ca	%5/%6/%10	Al-Ag	%10
Al-Ce	%10	Al-Sr	%3.5/%5/%10/%15
Al-Cr	%5/%10/%20/%80	Al-Ti	%5/%6/%10/%80
Al-Co	%5/%10	Al-Ti-B	5/1, 3/1, 5/0.2
Al-Cu	%33/%50/%80	Al-Ti-C	3/0.15, 3/0.2
Al-Fe	%10/%20/%25/%30/%45/%80	Al-Li	%2/%5
Al-Sb	%8/%10/%15	Al-Be	%2.5/%5

# Alloying-Master alloys

Master alloys with a high fraction of the alloying element are in the form of tablets pressed from a mixture of element powder and flux!



#### Raw materials

- Foundries usually purchase pre-alloyed ingots from specialist suppliers who convert miscellaneous scrap into high quality, accurately specified material subject to national standards.
- Scrap metal is carefully sorted by the supplier using spectroscopic analysis and melted in large induction or gas-fired furnaces.
- There is always a danger of contamination by impurities, particularly iron, and by alloying additions such as magnesium and silicon.
- Ingots are usually about 5 kg in weight and may be colour coded to avoid danger of mixing.

# Melting procedures for commonly used aluminium alloys

#### Medium silicon alloys, 4-7% Si

- The alloys should be melted under a covering/ drossing flux and degassed.
- Grain refinement is advantageous and can assist response to heat treatment.
- Modification is not essential.

## Medium silicon alloys, 4-7% Si

#### **Bulk melting**

- Melt under granular cover flux using about 0.5 kg/m<sup>2</sup> of melt area, forming a complete cover adding half early and the rest when the charge is molten.
- Transfer the required amount of metal to the transfer ladle, grain refine.
- Degas.
- Grain refinement can be carried out simultaneously with degassing by using TiB 5/1 rod.
- Suggested pouring temperatures for sand castings: Light castings, under 15mm 730°C
   Medium castings, 15-40mm 710°C
   Heavy castings, over 40mm 690°C

## Medium silicon alloys, 4-7% Si

#### **Crucible melting**

- Melt under cover flux, raising the temperature to 750-760°C.
- Grain refinement can be done.
- Skim off the flux.
- degas for 3-5 minutes.
- grain refinement can be carried out simultaneously with degassing by using TiB 5/1 grain refiner.
- 6-10 kg/tonne addition. Grain refinement and degassing take place simultaneously. Skim the metal clean before casting.

## Eutectic silicon alloys, 12% Si

- The alloys should be melted under a cover flux.
- Grain refinement benefits heavy section castings and the eutectic alloys benefit greatly from modification.

#### **Bulk melting**

- Melt under granular cover flux using about 0.5 kg/m<sup>2</sup> of melt area, forming a complete cover adding half early and the rest when the charge is molten.
- Transfer the required amount of metal to the transfer ladle.
- Modify the alloy by plunging metallic sodium.

#### Eutectic silicon alloys, 12% Si

#### Bulk melting

- If strontium modification is preferred, which may be the case if the metal is to be transferred to a holding furnace, 10SrAl master alloy can be plunged adding 200 g to 50 kg of metal (0.04%).
- Degas for 3-5 minutes.
- If grain refinement is needed as well, add TiB 5/1 rod before degassing.
- Skim the metal clean before use.
- Suggested pouring temperatures for sand castings: Light castings, under 15mm 730°C
   Medium castings, 15-40mm 710°C
   Heavy castings, over 40mm 690°C

# Eutectic silicon alloys, 12% Si

#### Crucible melting

- Melt under cover flux, increase T to 750°C.
- Modify the alloy by drawing the dross to one side and plunging metallic sodium.
- When the reaction has subsided, raise and lower the plunger a few times to stir the metal gently, allow the metal to stand for a few minutes, then skim off the dross.
- degas for 3-5minutes.
- If grain refinement is required, grain refiner may be plunged before degassing. Alternatively TiB 5/1 rod can be added before degassing.
- Skim clean before casting.

# assesment of melt quality

#### Assesment of melt quality

Analysis (OES) of molten alloy conformance to alloy specs / homogeneity alkaline and alkaline earth metals Ti/B/Sr

#### cleanliness

measurement of H<sub>2</sub> gas measurement of inclusions castability fluidity hot tearing tendency Die soldering

## measurement of hydrogen

Measuring dissolved hydrogen in molten aluminum alloys is vital in meeting quality requirements in aluminium foundries.

- Hydrogen **must be lower than 0.18ml/100 g** for a high quality casting!
- Over the years several techniques have been developed for performing this task.
- Qualitative and semi-quantitative cast shop techniques
- Quantitative laboratory analysis techniques
- Closed Loop Recirculation techniques
# Qualitative and semi-quantitative cast shop techniques

- The Straube-Pfeiffer test (also called the Reduced Pressure Test) in which the gas content can be estimated from the density of a metal sample solidified under reduced pressure, or from a comparison of a polished cross-section of the solidified metal with known "standards".
- One of the most widely used methods of assessing the quality of molten Al alloys.
- The test is quick, and the required apparatus is inexpensive, durable, and simple to use.

# Quantitative laboratory analysis techniques

These include the vacuum subfusion and the nitrogen carrier gas techniques, known respectively as the **Ransley or hot extraction method, and the LECO method.** 

**Closed Loop Recirculation techniques** These are in-situ methods that are based on the recirculation gas principle and include the **AISCAN and Telegas methods.** 



- This test simply comprises taking a small spoon sample from the melt,
- pouring this carefully into a small stainless steel crucible of the size of an eggcup, and
- placing this under a bell jar from which the air is evacuated by a vacuum pump,
- reducing the air pressure to typically one tenth (or possibly as low as one thirtieth) of one atmosphere while the sample solidifies.

- The reason for carrying out the test under reduced pressure is simply for the convenience of the magnification of the volume of gas by a factor of ten (or more if carried out at lower pressure; a factor of 30 is rarely exceeded).
- The pores are much more easily seen as they emerge at the surface, and are easily visible when the sample is cut up for subsequent examination.

- The observation of the sample during solidification is important.
- The emergence of many bubbles indicates the presence of gas.
- Similarly, the final density of the sample may be low (although this is not an unambiguous result, since the precipitating gas may have entirely escaped from the free surface of the sample; hence the need to observe it during freezing).

- As the sample solidifies, it rejects hydrogen due to the decrease in the solubility of hydrogen in aluminium alloys with decreasing temperature.
- The reduced pressure over the sample during its solidification enhances nucleation and growth of hydrogen bubbles, thus exaggerating their appearance for easy detection.
- The results that are produced are easily repeatable and correlate well with casting quality.
- These results may be interpreted either qualitatively, or semi-quantitatively.

#### Qualitative Interpretation of RPT Results

- The main objective of the qualitative assessment is to rapidly gauge the effect of dissolved hydrogen in an aluminium melt.
- It relies on observing the extent of formation of porosity in an aluminium alloy sample under controlled reduced pressure conditions.
- The result is an indication of the amount of hydrogen in the melt.

Semi-quantitative Interpretation of RPT Results -

- The specific gravity of a sample is measured and the result is correlated with the hydrogen dissolved in the melt.
- The results are only semi-quantitative because they are confounded by factors such as the impurity level of the melt (hydrogen bubbles tend to nucleate on oxides and inclusions), and alloy modification.
- Nevertheless, the RPT can be an effective quality control tool if the confounding variables are controlled and understood.

Semi-quantitative Interpretation of RPT Results

- A constant vacuum level, of course, is a prequisite for the most consistent results.
- Frequent calibration of the vacuum gauge and maintenance of the vacuum pump and regulator and the bell jar seal are important because constant use of the test system in the foundry environment can affect the results over time.

- if no bubbles are observed, one cannot conclude that the sample is free of hydrogen.
- In fact, the hydrogen level may have been high, but the sample has retained its gas in solution.
- This is because the gas cannot precipitate without the presence of nuclei which are usually nonwetted interfaces such as oxides. (It should be noted that TiAl<sub>3</sub>, TiB<sub>2</sub>, Al solid, and other interfaces on which the solid is thought to nucleate are well-wetted and thus probably good nuclei for solid aluminium, but of no use as nuclei for pores. Nuclei for pores will require to be nonwetted, such as oxide films.)

- The reduced pressure test is therefore a good test for the combined effects of hydrogen and nuclei.
- As such, it is really a "pore forming potential" test, in other words, a porosity test (i.e. it is definitely not a gas test, as is commonly supposed, and unjustly criticised when the test fails to agree with other fundamental techniques for the measurement of gas content).
- It is therefore a good test for the practical foundryman since it will reflect the likely overall quality of the castings.





Test results are only qualitative since oxides and and other insoluble particles encourage the formation of bubbles (i.e. Porosity).

However, sound conclusions can be drawn from this test if the solidification of the melt sample under partial vacuum is observed during the entire test.

No bubbling at the surface: $\downarrow$  inclusions $\downarrow$  gasVery few bubbles: $\uparrow$  inclusions $\downarrow$  gasBubbles only at the end of test: $\downarrow$  inclusions $\uparrow$  gasBubbling from the very start: $\uparrow$  inclusions $\uparrow$  gas

Section of samples taken from the same point solidified under different vacuum levels.



#### Gas Content Measurement

Other tests for hydrogen content in the melt are based on sampling, and measuring the volume of hydrogen gas that emerges under vacuum during the freezing of the sample. Clearly this test relies on most of the hydrogen escaping, and

will thus probably give an underestimation of the hydrogen content of the metal where the ve metal is lig particularly value

![](_page_87_Figure_3.jpeg)

## First bubble prensible

![](_page_88_Picture_1.jpeg)

## The Ransley Method

- The device works on the recirculating gas principle.
- The porous ceramic probe is immersed in the melt and an inert carrier gas, typically nitrogen, is circulated through. The carrier gas contacts the molten metal at the probe-melt interface, and since the initial partial pressure of hydrogen in the carrier gas is negligible, hydrogen diffuses from the liquid alloy into the carrier gas.
- The recirculation process is continued until the hydrogen in the carrier gas comes into equilibrium with the hydrogen dissolved in the liquid metal.
- The partial pressure of hydrogen in the carrier gas is then measured through a thermal conductivity sensor.

## The Ransley Method

The probe can be left in place indefinitely, continuing to sample on a continuous basis.

![](_page_90_Figure_2.jpeg)

#### Gas Content Measurement

- these tests assess the gas content in situ in the melt, and have the advantage of the possibility of continuous operation.
- These devices, now much improved by further sophistication from Alcoa and Alcan, repeatedly cycle a small amount (about 3 ml) of an inert gas such as argon (or nitrogen) through the melt, where it picks up hydrogen.
- The hydrogen content of the carrier gas gradually increases, reaching a condition of equilibration between the hydrogen gas in solution in the melt and the partial pressure of hydrogen gas in the carrier gas.
- This takes about 5 minutes.

## **AlSCAN Method**

The AlSCAN analyzer allows a direct, User Interface quantitative measurement of hydrogen in **Re-Circulating** Pump Microprocessor aluminium melts on the foundry floor. Detector It consists of a porous ceramic block Nitrogen Gas Bottle  $(24 \times 24 \times 6mm)$ to which two capillary stainless Temperature steel tubes are connected. Probe

## **AlSCAN Method**

- The porosity of the ceramic probe is such that penetration of the metal into the ceramic is avoided, and a good exchange between the hydrogen and the carrier gas is ensured.
- Movement of the probe in the melt is required to keep its interface free of oxides and other contaminants that can slow down the diffusion of hydrogen into the recirculation gas.
- This movement is accomplished through a cam and a small electric motor.
- The AlSCAN analyzer has a built-in microprocessor, which controls its operation and processes data.

## **AlSCAN Method**

As the temperature of the melt is also simultaneously measured, the concentration of hydrogen dissolved in the melt, [H], can be calculated from Sieverts' law:

$$[H] = S_o P_i C_A C_T$$

- $S_o$ : the solubility of hydrogen in pure aluminum at 973K ( $S_o = 0.92$  ml/100g of melt),
- P<sub>i</sub>: the partial pressure of hydrogen in the carrier gas
- C<sub>A</sub>: a correction factor for alloy composition (1.0 for pure aluminum)
- $C_T$ : a correction factor for melt temperature (1.0 at 973K-660°C).

#### Hydrogen measurement-ALSCAN

#### continuous monitoring of residual hydrogen concentration

![](_page_95_Picture_2.jpeg)

![](_page_95_Picture_3.jpeg)

## Telegas method

- The TELEGAS analyzer is based on the same principle as the AlSCAN analyzer, but
- the design of the TELEGAS probe is different from that of the AlSCAN analyzer.
- Unlike with the AlSCAN analyzer, the depth of immersion of the TELEGAS probe in the liquid metal is critical and gas bubbles  $(N_2 + H_2)$  are collected in the probe's head for analysis.

## **Telegas method**

- Measures the hydrogen gas content of the molten aluminium in a continuous fashion.
- When equipped with an alarm system, works very efficiently for the gas control in continous casting processes.
- A small amount (~3ml) of inert gas (argon or nitrogen) is continuously purged through the aluminium melt.

## Telegas method

The amount of hydrogen inside the circulating inert gas (to achieve equilibrium) is measured precisely with a catherometre (an instrument that measures the temperature of a thin wire inside the circulating inert +  $H_2$  gas).

This method can be successfully employed in continuous casting lines.

Modern probes can work for hours in fact for days.

![](_page_98_Figure_4.jpeg)

![](_page_99_Figure_0.jpeg)

## CHAPEL test

Continuous Hydrogen Analysis by Pressure Evaluation in Liquids

a porous graphite probe connected to a pressure transducer is dipped into the melt and quickly evacuated. Hydrogen in the melt diffuses into the disc until the pressure in the probe and the hydrogen partial pressure in the melt have equalised. (About 30-60 min is required to establish equilibrium) Since hydrogen is the only gas which dissolves in molten aluminium, the total pressure measured in the probe is equal to the hydrogen partial pressure. By simultaneously measuring the temperature, Sievert's Law then allows the hydrogen concentration CH to be derived from the hydrogen partial pressure pH2.

#### Chapel Test-direct measurement

![](_page_101_Figure_1.jpeg)

## **LECO** Method

- The LECO method employs the inert gas fusion principle.
- A weighed solid sample taken from the melt is placed in a high-purity graphite crucible and fused under a flowing helium gas stream at temperatures sufficient to release hydrogen in the form of a gas.
- The gas is passed through heated copper oxide, which converts it to  $H_2O$ .
- An H<sub>2</sub>O detector determines the total hydrogen content in the test sample.

## **LECO** method-fusion method

Aluminium sampled from the melt is melted in a graphite crucible under argon. The Hydrogen gas liberated during melting is transferred with carrier gas. The thermal conductivity of the carrier gas with hydrogen is measured and compared with calibration data to estimate the  $H_2$ 

content in ml/100g.

![](_page_103_Picture_3.jpeg)

#### Hydrogen gas measurements

- equipment used for quantitative measurements includes: aluminium melt tester (first-bubble method)
- **HYCON tester**
- HYSCAN (measurement of the partial pressure of hydrogen) ALSCAN (continuous measurement in the melt)
- **TELEGAS** (introduction of inert gas until equalisation of the partial pressure)
- **ANDION** (new, low-priced measuring system) measurement of the apparent density (density measurement
- using Archimedes' principle)

Methods for providing a qualitative statement: reduced-pressure test (Straube-Pfeiffer test) pour or cup sample (solidification of a small amount of metal in fireclay)

## **Oxidation-oxides**

- oxidation
  - meltingfurnace atmosphere / burner flamemelt treatmentsfoundry atmosphere / moisture!melt transferturbulence
  - Melt temperature +10°C  $\Rightarrow$  oxidation rate x2 Mg > 2%; T > 760°C  $\Rightarrow$  oxidation  $\uparrow$ !
- Temperature control critical!

T of melting furnace < 760°C; holding furnace < 730°C

- Alloying additives / practice : 40 ppm during Mg addition
- Scrap charge (upto 35 ppm).
- ingot/ (alumina based from the electrolysis cell!)

#### Oxide inclusions

Frequent oxides and inclusions

 $\begin{array}{rcl} \mathsf{Mg} \downarrow \downarrow & \Rightarrow & \mathsf{Al}_2\mathsf{O}_3 \text{ films / particles} \\ \mathsf{Mg} \uparrow \uparrow & \Rightarrow & \mathsf{MgAl}_2\mathsf{O}_4 \text{ and } \mathsf{MgO} \text{ based} \end{array}$ 

 $\rho_{oksit} \sim \rho_{Al}$  settlement and floatation very slow  $\uparrow$  Spesific surface area they remain in suspension!

Selection of flux and drossing practice critical!

When the heel is too low, the risk of inclusions at the bottom of the bath increases  $\uparrow$ !

When the refractory lining erodes and reacts with molten aluminium:

 $2SiO_2 + 2 Al (s) + Mg (s) = MgAl_2O_4 + 2 Si$ 

## inclusions

#### **Indigenous impurities**:

inclusions that form during melt treatment operations such as degassing and that come from the electrolysis cell, namely  $Al_3C_4$ , AIN and/or  $AIB_2$ .

Most critical: Al<sub>2</sub>O<sub>3</sub>, MgO and A<sub>4</sub>C<sub>3</sub>.
# inclusions

#### extogenous impurities:

Furnace refractories, transfer systems, transfer crucibles and the tools used during melt treatments are all source of extogenous impurities such as simple and complex oxides

Al<sub>2</sub>O<sub>3</sub>, MgO and Al<sub>2</sub>O, MgO spinels K-, Ca- and Al- silicates Na-, Ca- and Mg- aluminates

TiB<sub>2</sub> clusters that come from the grain refiners.

### Measurements of inclusions

- Common practice to measure the inclusion content of aluminium melts relies on filtering of the melt through a thin ceramic foam filter.
- The inclusions inside the melt are retained on top of the filter. The residue that builds up on the filter is analyised with standard metallographic methods. Inclusion are counted, statistically evaluated, identified with SEM-EDS.
- This is a laboratory practice; takes time and requires expertise.
- There are other methods where inclusions are seperated from the melt by centrifuge.

- Independent measurements of the inclusion contents of melts is rarely carried out outside of continuous casting operations.
- However, this would undoubtedly be of considerable advantage to foundries attempting to produce very high quality parts.
- Two main types of continuous devices are currently used:

Ultrasonic reflection from particles Conductivity measurements

### continuous inclusion content measurements

<u>inspection of the melt by ultrasonics</u>. An ultrasonic beam directed into the liquid metal, and is reflected from floating particles. The density and intensity of reflections is monitored electronically and processed to give information on the quality of the melt.

#### A conductivity probe measures the electrical current

Flowing through a small hole through which a sample of the melt is continuously being passed.

As inclusions pass through the hole the electrical resistivity of the current path changes in proportion to the size of the inclusion.

The signals are processed electronically to monitor the size and number of inclusions.

# melt cleanliness measurement via ultrasonics



# conductivity probe

Liquid Metal Cleanliness Analyzer for Continuous Monitoring-LIMCA can characterize the cleanliness of a melt at time intervals in the order of one minute. It can therefore monitor, in real-time, the evolution of cleanliness along a cast as a function of process parameters and melt-handling practices. The impact of furnace preparation, alloying practice, feedstock mix, settling time, and similar parameters on melt cleanliness is easily determined.



A standard technique is the passing of a known volume of melt through a fine filter. The inclusions are caught on the filter and are subsequently identified and counted on a polished cross section under the optical

microscope. This sampling method is of course rather laborious, but has been used to calibrate the continuous measurement techniques.





Weigth of the filtered melt SEM-EDS analysis of the inclusions withheld at the filter











### Analysis of inclusions



## sludge

High melting point intermetallics- from low quality furnace charge-alloying additions etc. and improper melting practice! quality is seriously impaired when they end up in the casting! They must be cleaned when they remain in the furnace/ crucible



#### "sludge" factor = %Fe + 2x%Mn + 3x%Cr

# impurities in primary/recycled aluminium

	ingot	recycled
alloy	>% <b>99.7</b> Al	
hydrogen	0.1-0.3 ppm	0.2-0.6 ppm
Na	30-150 ppm	<10 ppm
Ca	2-5 ppm	5-40 ppm
Li	0-20 ppm	≤1 ppm
residues	$\geq 1$ mm <sup>2</sup> /kg Al <sub>4</sub> C <sub>3</sub>	$\begin{array}{l} 0.5 \leq mm^2/kg \leq 5.0 \\ \text{Al}_2\text{O}_3, \ \text{MgO}, \ \text{MgAlO}_4, \\ \text{Al}_4\text{C}_3, \ \text{TiB}_2 \end{array}$

# Chemical analysis

fast and reliable measurement is required for industrial production.

#### **Optical Emission Spectrometer:**

- equipment that measures the composition of the alloy with an accuracy of %1-3
- very popular and widely used in aluminium foundries.

# Chemical analysis

- For sound analysis of the composition, the sample itself must be uniform and must also represent the molten bath it is taken from.
- This condition is largely met with disc samples solidified rapidly on a chilled surface to avoid segregation.
- The chilled surface of the disc sample is made smooth on a lath machine before the analysis.



A spark is ignited on the sample surface. The light emitted by the sample is collected by detectors adjusted for different wave lengths.





The composition of the sample is measured by comparing the light intensities emitted with known standards with precise compoisitons.



| E1-initial energy level

E2-energy level after ignition-electron excited

back to the initial energy level after releasing a photon with a wavelength of  $\lambda$ !



- New generation spectrometers not only provide a chemical analysis but also give you an estimate of the inclusion content.
- It is essential that the spectometer be equipped with each detector for each and every element you want to measure.

#### Ex:

Aluminium foundries; Sr, Ti, B Foil manufacturers: Ca, Na, K

### recycling contamination

# Fe, Si and Cu contamination arising from the melting of scrap!

Since these elements cannot be reduced under normal condition, they can be controlled only diluted by mixing with pure Al.

### Thermal analysis

As the atoms are increasingly close packed during solidification, heat is evolved and the entropy increases (solidification is an exothermic process). The opposite takes place when the atoms become further apart during melting.

insulation

insulation

Ceramic

crucible

The structural transformations can be traced during cooling of the melts by measuring the change in temperature of the melt with time, owing to the heat exchange that accompanies such transformations.

The change in slope and inflection points on cooling curves represent structural transformations.

### Thermal analysis

The extent of undercooling below the T<sub>liqiudus</sub> during solidification is a measure of the effectiveness of the grain refinement. If the grain refinement is effective, the undercooling will be limited.



### Thermal analysis

The extent of modification can also be estimated from the analysis of cooling curves.



# K-mold test







### K-mold test

a simple robust shoop floor test to evaluate the quality of the charge and the cleanliness of the melt.

The melt is poured in a stepped mould and is then fractured along the steps. Finally the fractured sections are examined visually for control of the presence of inclusions on the fracture surface.

The fracture surfaces with inclusions are rated against those that are clean.

#### advantages:

Fast evaluation Practical Simple sampling Portable Sensitive to oxides and inclusions cheap

# castability

Castability of an alloy is identified on the basis of 3 criteria:

fluidity hot tearing tendency die soldering

- Hot tearing is a consequence of stresses developing during feeding until the casting tears itself apart.
- Hot tearing is not found in alloys used in HPDC.
- Die soldering is important because, in improperly designed castings, soldering can be a significant problem that can severely inhibit productivity.

# Fluidity

- Fluidity is the distance to which a metal, when cast at a given temperature, will flow in a given test mould before it is stopped by solidification.
- Fluidity is therefore a length, usually measured in millimetres or metres.
- fluidity depends on heat flow during solidification.

# Fluidity

#### **Measurements of Fluidity**

Traditionally fluidity has been measured in a spiral mould. The rationale behind this is clearly the desire to compress the fluidity test into as small a mould as possible, and that the flow distance is sensitive to levelling errors, and that these are minimised by the spiral path of the liquid.

# Spiral fluidity test

Molten alloy is poured into a sand mould at a specified temperature. The length the melt has travelled is measured once the sand mould is broken.

#### Factors that affect fluidity

Mould coatings Alloying additions Molten metal head-feeding Melt superheat Solidification range (fluidity decreases with increasing range.) Cleanliness of the melt (fluidity increases with decreasing cleanliness)

# fluidity

Vacuum fluidity testing allows for the evaluation of various alloys and process modifications in a laboratory setting under rapid solidification conditions, but suffers from a poor reputation and, as a consequence, has principally been used for qualitative experimentation.

La	boratory Test	
N	Maximum fluidity length	+
		To Vacuum

### Fluidity vs phase diagram

#### increasing solidification range $\rightarrow$ decreasing fluidity

Hence, Fluidity is maximum at or near the eutectic point! However, in Al-Si system, the peak in fluidity is not at the equilibrium eutectic, but is nearer 15% Si.

This corresponds of course to the non-equilibrium eutectic composition.

It is expected that the presence of Na or Sr as promoters of the eutectic phase, and suppressers of the primary Si, might influence the position and height of the fluidity peak.



# Fluidity of Al-Si alloys

The general increase in fluidity with increasing silicon content in this particular alloy is the result of the powerful effect of Si. Its latent heat of solidification is among the highest of all natural elements, and is nearly 5 times greater than that of Al. Thus  $t_s$  is significantly increased as Si levels are raised.



# fluidity



### hot tearing

- a casting phenomenon that occurs in sand castings where the solidification rate is slower than in diecastings.
- It can occur also in high integrity castings depending on stress distribution.
- solidification behavior is critical.
- hot tear is a uniaxial tensile failure, which results in cracks on the surface or inside the casting.
- Alloys having a wide freezing range have a higher tendency to hot tear.
- Variables that influence hot tearing include alloy composition and processing variables.
## Hot tearing

solidification behavior in the mushy zone is critical! Solidification can be divided into four stages:

Mass feeding where the liquid and solid are free to move; Interdendritic feeding when the dendrites begin to contact each other, and a coherent solid network forms;

Interdendritic separation. With increasing fraction solid, the liquid network becomes fragmented. If liquid feeding is not adequate, a cavity may form. As thermal contraction occurs, strains are developed and if the strain imposed on the network is greater than a critical value, a hot tear will form. Interdendritic bridging or solid feeding occurs. Simply stated, hot tearing occurs if the solidification shrinkage and thermal deformation of the solid cannot be compensated by liquid flow.

# Short freezing range alloys

The solidification front is planar.

Solidification is from the outside walls in towards the centre as the metal proceeds along the mould. The flow of metal stops when the two freezing fronts meet



#### long freezing range alloys

- solidification front is no longer planar but dendritic, and because freezing is occurring in a moving liquid, the bulk turbulence in the liquid carries pockets of hot liquid into the cooler regions, and thus remelting dendrite arms and other fragments, to build up a slurry of dendrite debris.
- As heat is lost from the slurry, the slurry thickens, gradually becoming so thick that it is too viscous to flow. This occurs at different fractions of solid in different alloys, and also seems to be influenced by the metallostatic head driving the flow.
- In general, however, the flow of liquid is arrested when the volume fraction of solid is somewhere between 25 and 50 %.

### long freezing range alloys



Flow stops when solid fraction reaches %25-50



## **Die Soldering**

- occurs when the cast aluminum alloy comes into contact with die steel.
- Due to the natural affinity of iron and aluminum, a reaction occurs at the surface, which results in the formation of Al-Fe intermetallic phases.
- Over a series of shots, a significant amount of aluminum becomes stuck to these phases at the die surface, and the resulting cast part can begin to miss critical tolerances or to lose integrity.
- At this point, the die must be shut down and cleaned, which is an expensive process when it occurs too frequently.

# **Die Soldering**

- It is estimated that 1 to 1.5% of variable overhead is directly attributed to die soldering in casting plants.
- With such a large economic effect on the casting process, it is clear why die soldering needs to be controlled.
- There are several ways in which this can be achieved:

melt chemistry, process conditions and the die surface condition.

### Die Soldering-melt chemistry

- Fe has the greatest effect of any alloying element in the study on reducing die soldering.
- Fe has long been added to die casting alloys in order to reduce the die soldering tendency of alloys.
- It is well known that alloys with insufficient iron content (< 0.8-0.9%) will solder readily to the die.</li>
- The solubility of Fe in aluminum with 10% Si at typical casting temperatures is quite low, around 2-3%. At temperatures where the melt is likely to be in contact with the die, this solubility drops even lower.
- The presence of Fe in the melt reduces the chemical potential gradient of Fe from the steel to the melt and slows the reactions that occur at the surface.

### Die Soldering-melt chemistry

- Sr also has the potential to help control die soldering, in addition to its common use as a eutectic modifier.
- In industrial trials a small Sr addition was shown to reduce die soldering by more than 20%.
- The mechanism behind this reduction has to do with the effect Sr has on the viscosity and surface tension of the alloy.
- The addition of Sr changes the apparent viscosity and subsequently the surface energy of the alloy.
- This causes a reduction in the ability of the alloy to wet the die surface and reduces the contact area and the reaction between the two.

#### Die Soldering-process conditions

- High temperatures and high melt velocity lead to soldering.
- high temperatures are more critical and must be avoided through careful design of the die.
- By configuring the part and optimizing the design of the die cooling system, the potential for soldering can be greatly reduced.
- It is very important to consider this during the design phase of a die because once a die is manufactured it is very difficult to reduce any hot spots.

#### Die Solderingsurface/process conditions

- Other potential solutions include using additional spray in the high solder areas for cooling or the use of inserts with high conduction coefficients.
- Impingement velocity is important to control as well.
- The die surface should be coated with lubricants and is likely oxidized from prior treatment.
- A high impingement velocity can wash these protective coatings off of the die surface, exposing the die steel to the aluminum alloy and begin erosion of the die surface.
- Both of these effects will promote the beginning of die soldering.

#### Die Solderingsurface/process conditions

- SSM processing can help to reduce both the temperature and velocities apparent in the casting system, and should help reduce die soldering.
- Die coatings can be useful as a diffusion barrier between the steel in the die and the aluminum in the cast alloy.
- An effective coating must be able to withstand the harsh conditions at the surface of the die.
- Coatings which are sometimes used include CrN+W, CrN, (TiAl)N and CrC.

#### Die Solderingsurface/process conditions

- surface treatments such as nitriding and nitro-carburizing can help to strengthen the surface and prevent erosion, which accelerates the soldering process by roughening the surface and creating local temperature excursions at the peaks of the die surface, which solder very quickly.
- Accurate modeling of the casting process during the design phase is very important to an effective control against die soldering.
- All of the mentioned controls require additional cost during the design and manufacturing of the die, and it must be understood how badly soldering will affect the process before the costs of any of those controls can be justified.