

TALAT Lecture 3202

The Liquid Metal

16 pages, 13 figures

Basic Level

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Objectives:

- To provide an introduction to factors affecting the quality of molten aluminium.

Prerequisites:

- Basic knowledge of foundry practice
- The student should be able to appreciate the differences between good and bad melting practices in a foundry.

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3202 The Liquid Metal

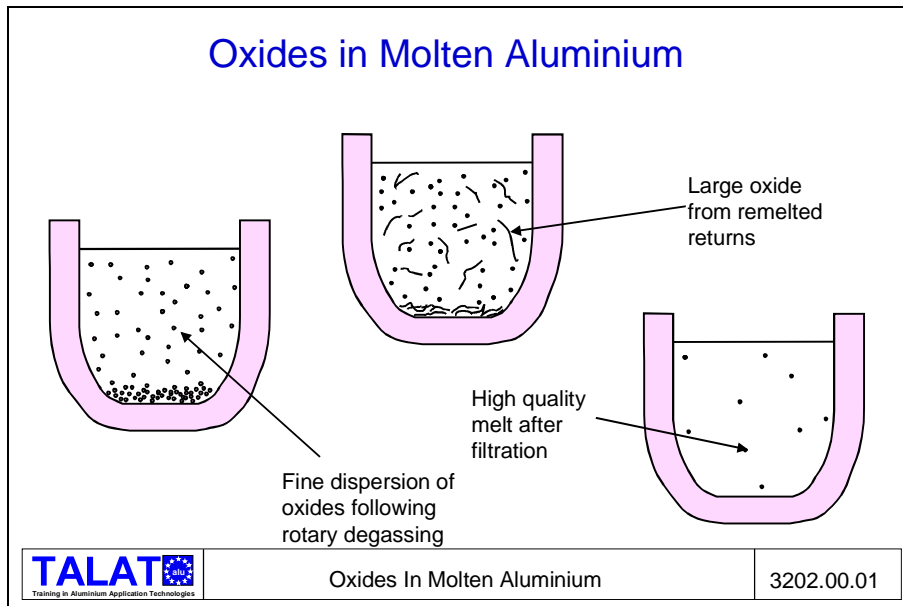
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Types of Impurities

Oxide pollution

When molten, and with its surface cleared of oxide, liquid aluminium looks like quicksilver. It is with regret, however, that we have to come to terms with the fact that the quality of the liquid underlying the silvery surface is likely to be anything but pure or clean metal (**Figure 3202.00.01**).



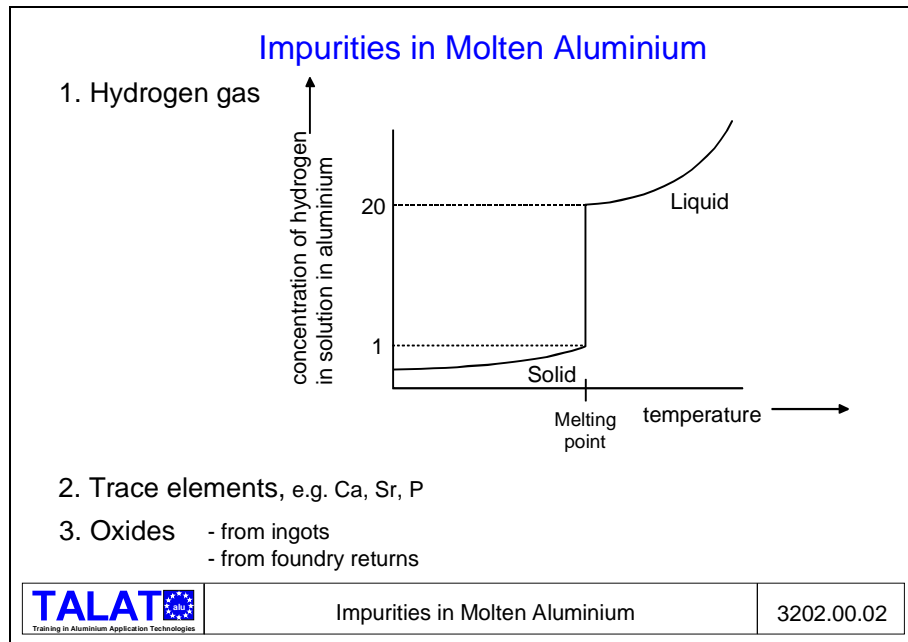
In fact, it is necessary to develop of view of the liquid as a slurry of sundry solid debris in suspension. It is only the size and quantity of solid debris which is changed from melt to melt and from one melting practice to another. In particular, we will see how the large oxide films which may be present from remelted returns can be substantially reduced by rotary degassing and filtration.

Hydrogen pollution

Other undesirable impurities may also be present in solution (**Figure 3202.00.02**). Perhaps the most important of these is hydrogen. Hydrogen is especially unwelcome in aluminium alloys because it is highly soluble in the liquid, but hardly soluble at all in the solid. In fact, as the aluminium solidifies, only one twentieth of the hydrogen is retained in solution under equilibrium conditions. The other nineteen twentieths will be rejected and will form gas pores, providing nuclei are present. (If nuclei are not present, then the gas will be unable to precipitate as porosity in the casting, but will remain as a supersaturated solid solution. We shall consider this phenomenon in more detail later in this lecture).

Other pollutants

Other impurities may seriously affect certain alloys. For instance, the presence of traces of Ca, Sr or P in Al-Si alloys will lead to changes in the modification of the eutectic silicon. (This will be discussed in a later lecture). However, in this lecture we shall concern ourselves only with the solid materials in suspension and hydrogen in solution in the melt.



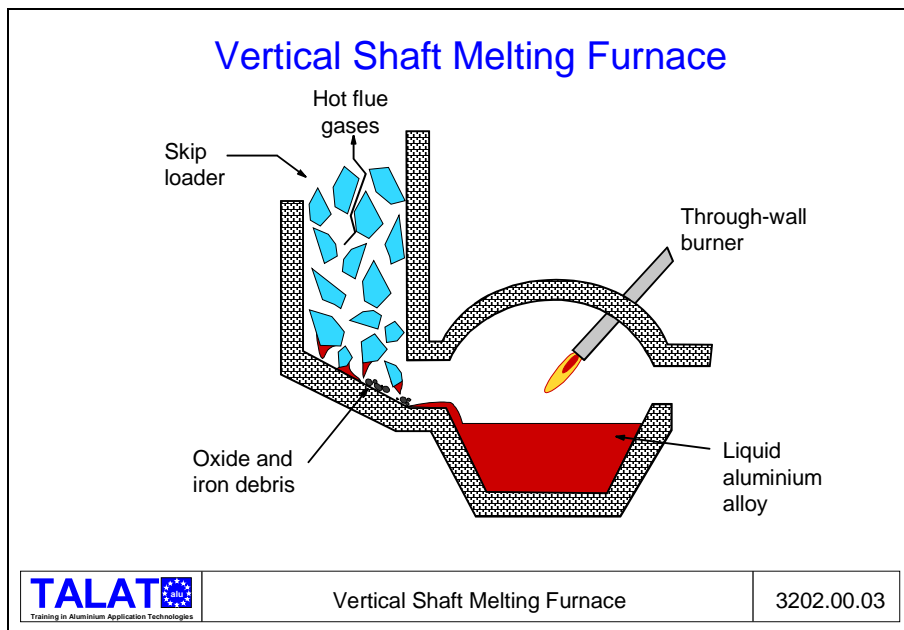
Origins of oxide inclusions

The solid materials arrive in the melt right from the start of melting. They arrive as oxide skins on the surface of the material to be melted. In the case of ingots (bars cast into cast iron pig moulds) the cooling rate of the ingots is rapid, and although carried out in air, the oxide skin which develops on the ingot during cooling is not especially thick. Thus when remelted in a crucible furnace, or other type of bath of molten metal, the oxide floats free and becomes dispersed in the melt.

In the case of a sand foundry remelting foundry returns, the oxide skin is especially thick and can remain intact during remelting and float into the area where metal is being ladled or pumped from the furnace. Such films can finish up as complete, massive, film-like or dross-like inclusions in finished castings.

This direct recycling of the oxide skins occurs in those situations where the material to be remelted is introduced directly into the melting bath. These include common types of melting furnace, such as crucible furnaces or reverberatory furnaces. Whatever is added to these kinds of furnace is automatically submerged and redistributed in suspension in the melt.

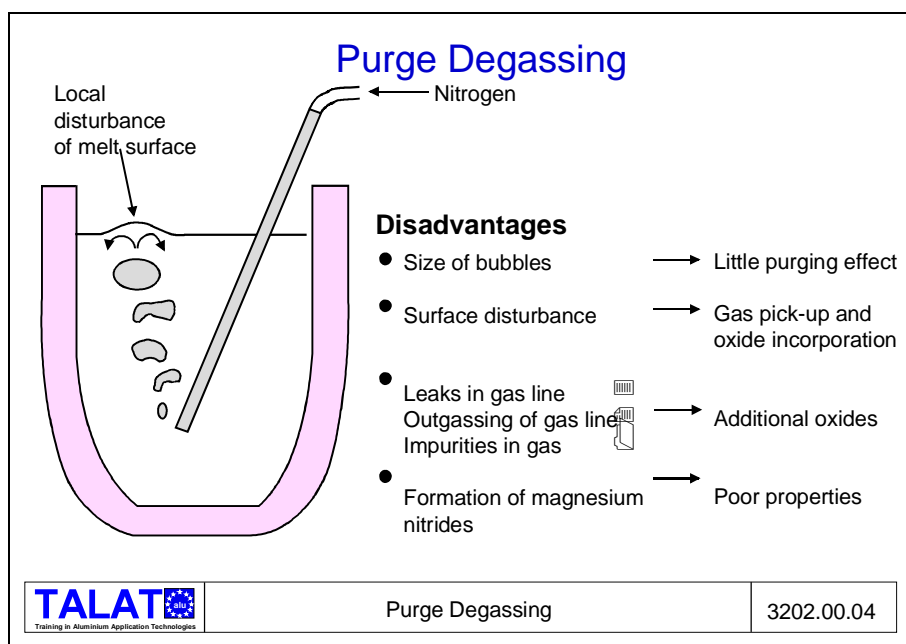
The action of the tower, or vertical shaft, type melting furnaces is quite different (**Figure 3202.00.03**). The material to be melted is loaded into the vertical shaft where it is preheated with the flue gases from the melting and holding region of the furnace. The shaft is offset from the bath so that unmelted debris does not enter the liquid metal directly - metal enters the bath by first melting and then running over a supporting platform, and so joining the bulk of the melt. The oxide skins are left behind at the base of the shaft, together with other unwanted debris such as iron inserts in scrapped castings. The sloping hearth of the furnace can be scraped clean of such accumulations from time to time as melting progresses.



Having started with a reasonable quality of liquid metal, it is necessary to try to keep it in good condition. However, it is again with regret that it has to be reported that most aluminium foundries do not achieve this. (It is achieved in casting houses designed for the continuous casting of wrought quality aluminium alloy, especially that to be used for such discriminating applications as foil or can stock.)

Various treatments are notorious for the introduction of much additional oxide debris into the melt.

Effect of Purge degassing



Disadvantages

- Size of bubbles → Little purging effect
- Surface disturbance → Gas pick-up and oxide incorporation
- Leaks in gas line
Outgassing of gas line
Impurities in gas → Additional oxides
- Formation of magnesium nitrides → Poor properties

One such treatment is degassing (see **Figure 3202.00.04**). This is often carried out badly, using an open-ended lance to introduce a purge gas into the melt.

The size of bubbles from such a lance and the disturbance of the melt surface ensure that:

1. little gas is purged from the liquid, and
2. that the melt comes into equilibrium with the surrounding environment because the freshly presented surface is ideal for re-introducing fresh hydrogen into the melt. In addition, the rolling action of the surface creates extra oxide and may stir this into the melt. Furthermore, the impurities in the purge gas will generate additional oxide in the liquid. These impurities arise from leaks in the gas line, or the out-gassing of the gas line, especially if it contains long lengths of rubber or plastic. The extended time for such low efficiency degassing methods means that much additional oxide is introduced.

Where degassing with nitrogen is carried out continuously, as in some large holding furnaces, and where the alloy contains some Mg (which is most often the case), there is an additional danger from the build-up of nitrides in the liquid. This can become so prolific that the melt takes on the appearance of a slurry such as porridge or cement. The mechanical properties of the resulting castings are lamentably low because of the embrittling effect of the large concentration of nitrides. The only way to avoid such disasters when attempting to degas continuously is to use a truly inert gas such as argon. In addition, of course, the gas lines should be soundly plumbed in metal throughout.

Effect of flux degassing

A treatment which purports to clean the melt and simultaneously degas is flux degassing (**Figure 3202.00.05**). This process blows in a powdered chloride and/or fluoride flux into the melt on a carrier gas, usually nitrogen.

Flux Degassing

- ❑ Powered chloride and/or fluoride flux introduced using nitrogen carrier gas.
- ❑ However ... oxides and gas are not totally eliminated.
- ❑ Environmental disposal problems.

For example:

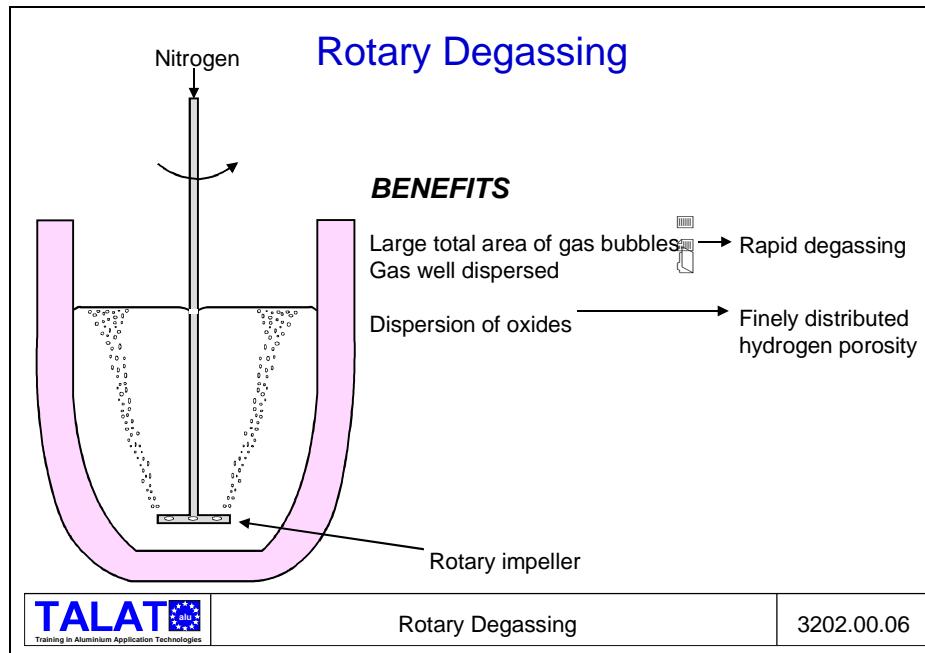
If oxide content reduced by 95%
and if gas content reduced by 75%

- ▷ 25% of remaining gas precipitates on 5% of remaining nucleation sites
- ▷ General porosity in the casting is reduced, but is 5x worse in more scattered areas

By this means both the oxide content and gas content of the melt are reduced. However, the oxide content and gas content are not, of course, eliminated. A problem arises, therefore, that if the oxide content is reduced by perhaps 95 % and the gas content reduced by 75 %, then we have the situation where 25 % of the gas now tends to precipitate on only 5 % nucleation sites. Thus the porosity in these more widely scattered regions is now 5 times worse than before. Whereas in the original material, the porosity might have been acceptable in a finely dispersed form (which might actually have been invisible on a radiograph), the casting is now rejected for occasional concentrated severe pores.

Effect of rotary degassing

An alternative degassing treatment is rotary degassing (**Figure 3202.00.06**). In this treatment a central hollow rotor introduces a purge gas (usually nitrogen) into the centre of a melt, where the emerging bubbles are fragmented and dispersed by the rapid rotation of the rotor. The large total area of the bubbles and their wide dispersion throughout the melt give a rapid degassing action. Whereas the hollow lance might give only poor degassing in an hour or so, the rotary technique typically reduces hydrogen to very low levels in only 10 minutes.



Because rotary degassing is a relatively new technique, little investigative work has been carried out on it so far. There seems to be evidence that the system causes large oxide films to float out, and maintains them at the surface so that they can be skimmed clear after degassing.

In addition, however, it may be that the system actually introduces a new dispersion of fine oxides, possibly by fragmenting the large films which were originally in suspension, or possibly by reaction with the oxide or moisture contamination of the purge gas, which can arise either from trace impurities in the original gas or impurities introduced from sources in the local plumbing. An additional dispersion of nitrides is to be expected if nitrogen is used for degassing melts which contain some Mg.

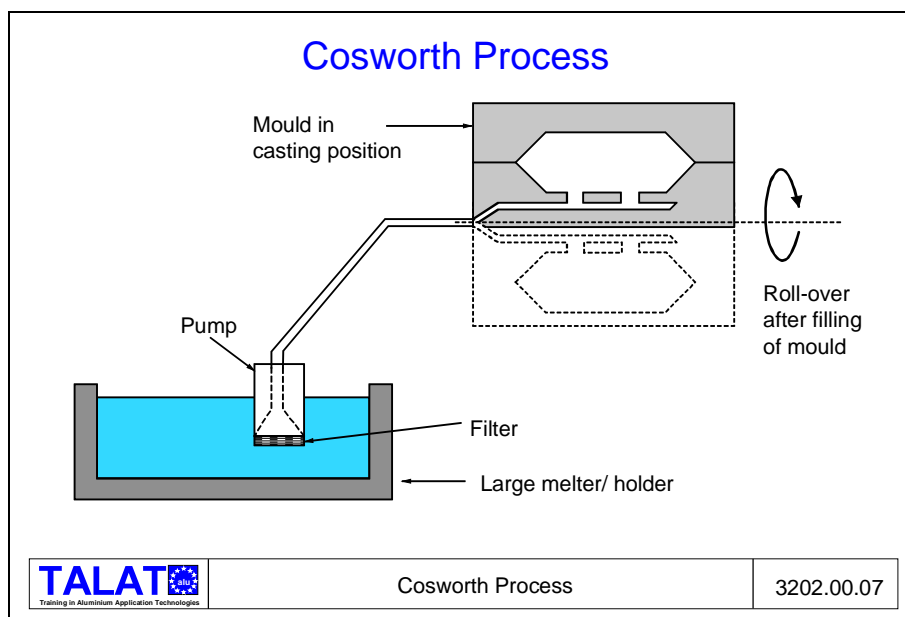
This fine dispersion of solids may have some benefits to melts intended for the production of shaped castings (provided that very high mechanical properties are not required). The low hydrogen content, together with the high density of nuclei on which the hydrogen can precipitate, will probably ensure that the residual hydrogen porosity, if present at all, is extremely fine and well dispersed. Thus the quality of the melt will be expected to be quite different from that produced by flux degassing.

So far the melt has sat in its furnace, but has had to suffer a number of treatments, most of which will have increased its oxide content. Measurements of oxide contents of liquid aluminium in a major low pressure die casting plant have shown that the quality of alloy sitting in the well is good at the beginning of the Monday morning shift. However, as the shift progresses, the slopping of the metal up and down the riser tube, and the consequent disturbance of the sediment on the furnace bottom, results in a considerable increase in oxide level. A further major increase occurs when the furnace is topped up. The churning and surging of the melt and the thorough mixing-in of floor sediments greatly impair the melt quality further. During the day, the melt continues to deteriorate, finally becoming unrecognisably bad by the last shift on a Friday.

Low inclusions casting processes

Cosworth Casting Process

Such degrading of melt quality by turbulent transfer operations and by the general dipping and slopping which accompanies the casting operation itself is typical of many casting operations. This underlines the importance of those processes which are designed to handle the melt without unnecessary disturbance, such as the well-established Cosworth Casting Process (**Figure 3202.00.07**). In this process, the metal is melted and held in a large furnace. The furnace holds enough metal for several hours production so that there is some time for oxide films to sink or float. It can be noted that there is only a small density difference between molten aluminium and its oxide, and air is often entrained in folds of the film. Thus the separation takes place only slowly, and may be downwards or upwards. A significant proportion of films have, by chance, almost neutral buoyancy and so never sink. It is essential, therefore, to ensure the removal of residual films by filtration.



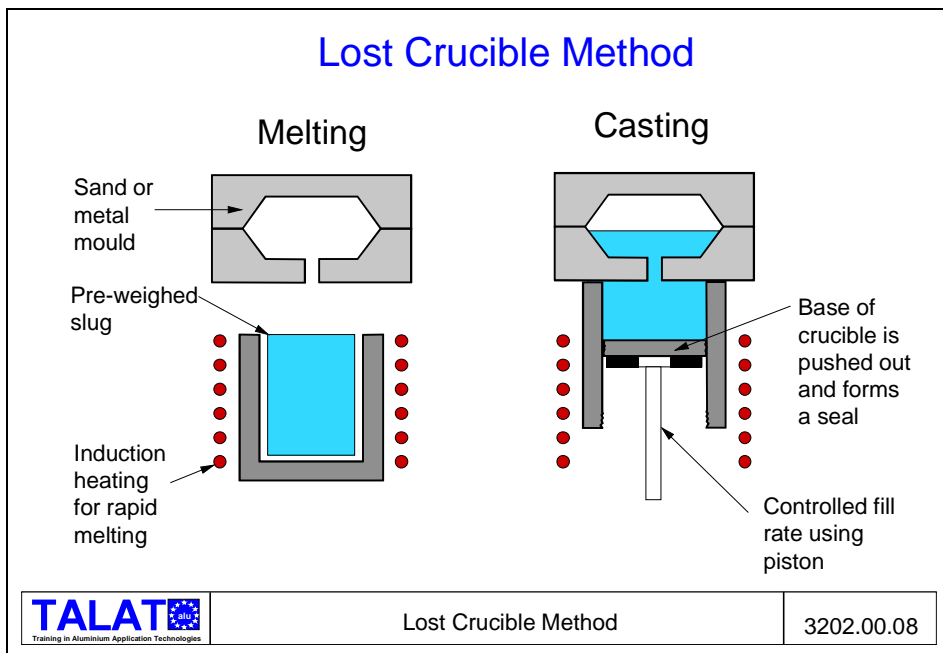
An electromagnetic pump is used to remove the molten metal which is taken from mid-depth in the furnace to minimise the risk of transferring oxides. Furthermore, a filter, integral with the base of the pump, is used to trap any oxides. Thereafter, the molten metal travels only uphill. The metal is pumped at a controlled rate through vertical gates into the casting. This approach ensures that the metal rises through the system in a non-turbulent manner, thereby minimising the formation of excessive oxide films and their incorporation into the casting.

In its original form, the Cosworth Process had two main disadvantages. Firstly, the mould had to remain attached to the pump until the casting had solidified, which resulted in a slow production rate. Secondly, this method of mould filling resulted in the

coldest metal being at the top of the casting which (as we will see in **TALAT Lecture 3206**) is not conducive to producing sound castings (i.e. free from shrinkage). Both of these problems can be overcome by the latest variant of the process in which the mould is filled from the side and is rolled over after casting. This means that the mould can be removed from the filling station (and replaced by an empty mould), increasing the production rate from about 1 casting every 4 minutes to better than 1 casting per minute. Furthermore, after inverting the mould the hottest metal is at the top of the casting and, in effect, the preheated runner bar now acts as the feeder.

Lost Crucible Process

Alcan have recently invented another means of preventing poor transfer of metal, known as the *Lost Crucible Process* (**Figure 3202.00.08**). In this, a pre-weighed slug of material is rapidly melted in an induction furnace. However, instead of the normal refractory crucible, a disposable fibre-ceramic crucible is used. Once the charge is molten and at the required temperature, the base of the crucible is pushed out by a vertically moving piston. As the piston continues to move upwards, the base of the crucible acts as a seal and the molten metal is introduced through the bottom of the mould at a controlled rate. This new Alcan Lost Crucible Process, if fully developed for production in due course, will conserve the quality of the alloy as produced by the primary producer.

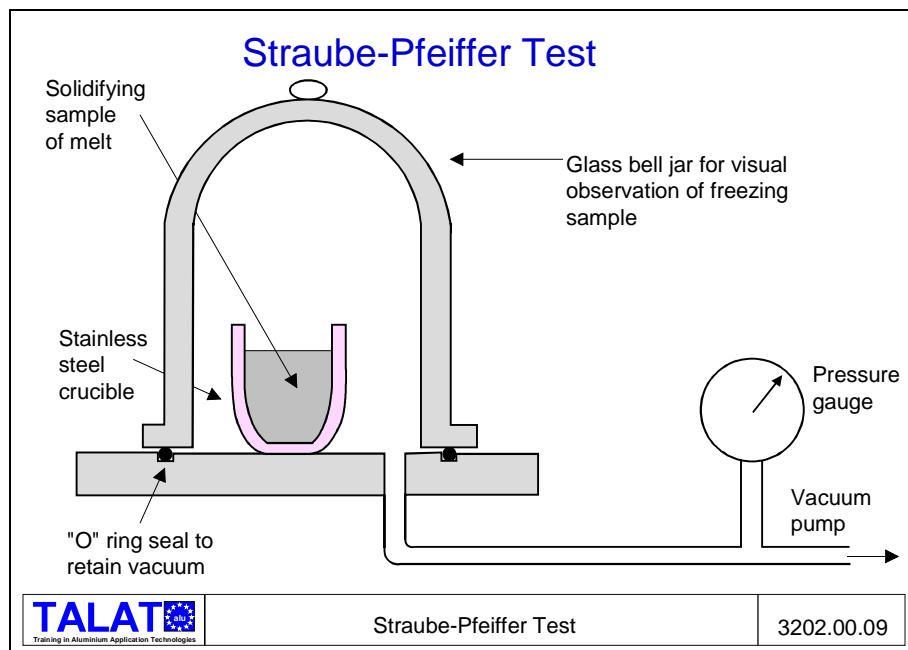


However, for all other processes, where the metal has to be melted in a furnace and then transferred for casting, the problem exists of how to test the quality of the metal.

Melt quality Assessment

Reduced Pressure Test

One of the simplest and oldest tests is the Straube-Pfeiffer Test, or Reduced Pressure Test (**Figure 3202.00.09**). 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 egg-cup, 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 observation of the sample during this time 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).



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.

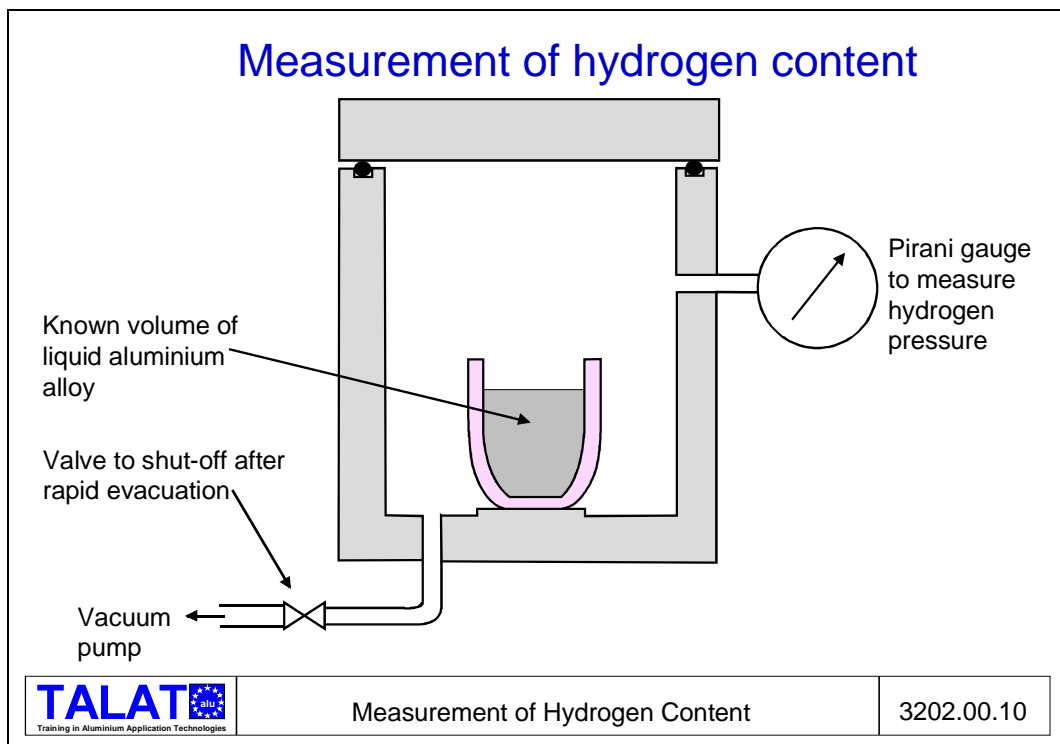
However, the test is interesting, since if no bubbles are observed one cannot conclude that the sample contained no hydrogen in solution. In fact, the hydrogen level may have been high, but the sample has retained its gas in supersaturated solution. This is because the gas cannot precipitate without the presence of nuclei which are usually non-wetted interfaces such as oxides. (It should be noted that TiAl_3 , TiB_2 , 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 non-wetted, 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 quality of the castings.

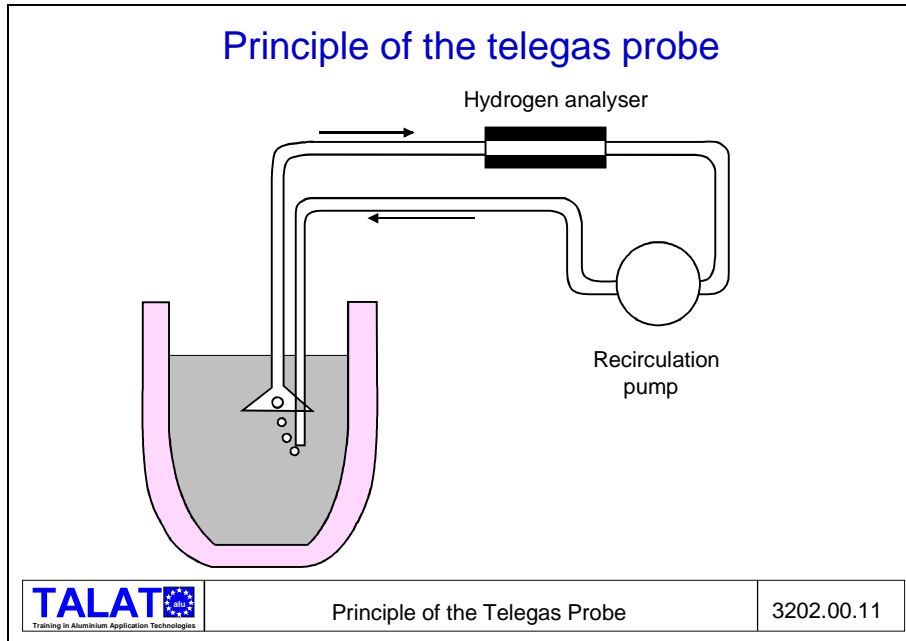
Gas Content Measurement

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 (**Figure 3202.00.10**). 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 metal is particularly clean.

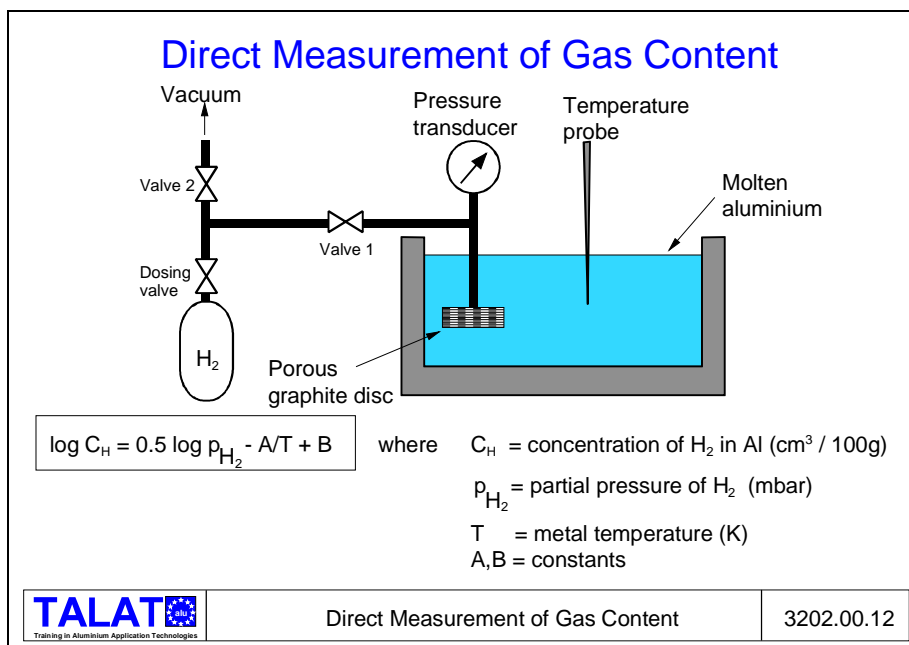


Other tests attempt to assess the gas content in situ in the melt, and have the advantage of the possibility of continuous operation. Such devices include the Telegas type instruments originally invented by Ransley (**Figure 3202.00.11**). These devices, now much improved by further sophistication from 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. The hydrogen in the carrier gas is measured by a catheterometer, an instrument for comparing the temperature of a hot wire in the flowing gas with the temperature of a similar hot wire in a stream of pure argon gas. The probe can then be left in place indefinitely, continuing to sample on a continuous basis. Modern probes appear to last for many hours, if not days, when used continuously or semi-continuously.



A recent variation of the Ransley test is the CHAPEL test (Continuous Hydrogen Analysis by Pressure Evaluation in Liquids), see **Figure 3202.00.12**.



In this, 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 minutes is required to establish equilibrium but this can be reduced by dosing the probe with hydrogen using the valve arrangement shown here.) 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 C_H to be derived from the hydrogen partial pressure p_{H_2} ,

$$\log C_H = 0.5 \cdot \log p_{H_2} - A / T + B$$

where A and B are Sievert's constants (dependent on alloy composition) and T is metal temperature (K).

This elegantly direct and simple approach has yet to be developed for regular industrial use.

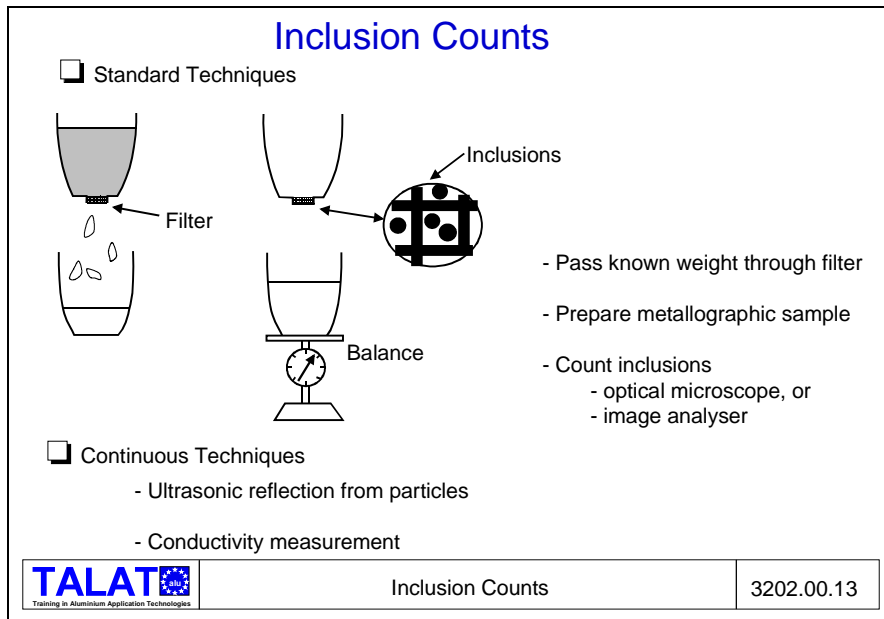
Some attempts have been made to develop hydrogen sensors based on solid electrolyte cells immersed in the melt. However, these are at an early stage of development, and their lifetime and cost have yet to be established.

Clearly, an independent measurement of hydrogen content, especially if carried out by a fundamental technique such as a Telegas type probe or direct reading pressure probe, when combined with the results of the Reduced Pressure Test would give an indication of both the gas and inclusion contents of the liquid metal.

Inclusion content measurements

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.

A standard technique is the passing of a known volume of melt through a fine filter (see **Figure 3202.00.13**). 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 which I will now describe.



Two main types of continuous devices are currently used:

1. An inspection of the melt by ultrasonics. 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.
2. 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. Again, the signals are processed electronically to monitor the size and number of inclusions.

Conclusions

In this lecture, I have tried to alert you to the potential problems of melting aluminium prior to introducing it into a mould. Melting inevitably leads to the formation of oxides and often to the absorption of hydrogen, but the effects of these on castings can be minimised by careful handling of the molten metal. The success of the Cosworth Process has underlined the improvements that can be achieved when full attention is paid to controlling the quality of the molten metal and points the way forwards to future foundry techniques. Finally, it can be commented that although this lecture has concentrated on aluminium, the general principles are widely applicable to other metals.

Literature/References

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Blackburn, R. B.: Sampling molten aluminium for non-metallic inclusions. Aluminium, 1980, Vol. 56, No. 9, 585-587.

Chen, Xiao-Guang and Engler, S.: Measuring hydrogen content in molten aluminium alloys using the CHAPEL technique. Cast Metals, 1993, Vol. 6, No. 2, 99 - 108.

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