Continuous Casting

Proceedings of the International Conference on Continuous Casting of Non-Ferrous Metals

Edited by
H. R. Müller
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H. R. Müller
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Preface

In 1976 the Committee for Continuous Casting of the Deutsche Gesellschaft für Materialkunde (DGM) organised for the first time a continuous casting conference for non-ferrous metals. A periodical update every 5 years has in the meantime been proven to be useful. Following the very successful previous meeting in 2000 in Frankfurt, Germany, this year's conference reviews the complete range of the processing chain covering both melt treatment and casting technology as well as specific measures for micro-structural control. A focal point of the programme deals with modelling and simulation that has become an integral part of modern manufacturing. Current progress also includes spray forming as an increasingly important processing option. For the first time poster presentations are included.

Experts from the manufacturing industry, researchers and scientists from university and industry as well as suppliers of equipment and ancillary products present information on most recent technical and economical developments.

The organising committee thanks all authors for their contribution and last but not least the audience for their discussion and comments.

Dr. Hilmar R. Müller

Chairman of the Organising Committee
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Melt Treatment of Copper and Aluminium – The Complex Step
Before Casting

B. Friedrich, C. Kräutlein, K. Krone
IME Process Metallurgy and Metal Recycling RWTH Aachen

1 Introduction

Aluminium and Copper are second and third in metal production world wide after iron and steel. But in melt treatment technologies they are probably the number one. Although Copper is the metal that is longest used technological by mankind and Aluminium one of the shortest, in both industries a variety of melt treatments and sometimes similar technologies were investigated over time. But as for most industries a look into the technology of a non competing neighbour often is missing, because contact is lost due to a lack of connection points. This plenary paper tries to bridge this gap, here the most important melt treatment techniques are presented and compared between these two metals. It is accentuated what the industries can learn from each other. To see the differences for Aluminium and Copper the most important properties of Copper are summarised in Table 1.

Table 1: Properties of Copper and Aluminium [2]

<table>
<thead>
<tr>
<th>Property</th>
<th>Aluminium (high purity)</th>
<th>Copper (high purity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2698 kgm⁻³</td>
<td>8960 kgm⁻³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>660°C</td>
<td>1084°C</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>70.3 GPa</td>
<td>128 GPa</td>
</tr>
<tr>
<td>Ultimate yield strength (UYS)</td>
<td>90–100 MPa</td>
<td>210–230 MPa</td>
</tr>
<tr>
<td>Elect. conductivity</td>
<td>40 MS</td>
<td>64.5 MS</td>
</tr>
<tr>
<td>Heat Conductivity</td>
<td>237 Wm⁻¹K⁻¹</td>
<td>401 Wm⁻¹K⁻¹</td>
</tr>
<tr>
<td>Electr. Cond./density</td>
<td>14.8*10⁻³ MSm⁻¹kg⁻¹</td>
<td>7.2*10⁻³ MSm⁻¹kg⁻¹</td>
</tr>
<tr>
<td>Heat cond./density</td>
<td>87.8*10⁻³ Wm⁻¹K⁻¹m⁻¹kg⁻¹</td>
<td>44.7*10⁻³ Wm⁻¹K⁻¹m⁻¹kg⁻¹</td>
</tr>
</tbody>
</table>

The major difference of Aluminium and Copper is the affinity to oxygen. While Aluminium is a very un-noble element and its melt forms unsoluble oxides rapidly, Copper is considered a half noble metal but with a high solubility for oxygen in the liquid state. The major similarity is the outstanding heat and electrical conductivity of both metals. Although Copper has a 50 % better conductivity than Aluminium the conductivity to density ratio is in favour of Aluminium. This is especially in mobile applications of interest as for example heat exchangers in automobiles. In comparison Copper heat exchangers are preferably used in stationary and elevated temperature applications. For both metals partly similar melt treatment techniques were developed. Impurities like dissolved gases and solid inclusions are battled with the same principles, whereas dissolved metallic impurities have to treated differently. In this paper an overview on the melt treatment techniques of Aluminium and Copper melts are given and gas purging, slag treatment and filtration as examples are explained in more detail.
2 Applications of Aluminium and Copper

For increasing applications the Aluminium quality has to meet high performance specifications like foils, sheets for can bodies and offset plates as well as parts for the production of CDs. The requirements on the material in respect to cleanliness are very high, e.g. as the thickness of a can body sheet is nowadays only <300 μm. Therefore the number of defects caused by inclusions and gas pores has to be decreased drastically. More than 60 % of the Aluminium production is used for packaging from which a large part is Aluminium foils. Aluminium foils are used for the protection of food, e.g. in combination with plastic or paper for the production of juice containers. Inclusions of a size >10 μm lead to holes in the foil and cause spoiled products. Lithographic sheets for offset plates have to have a perfect surface.

Copper is mainly used for electrical conductivity applications. Besides the day-to-day household uses there are some fields where extreme product cleanliness is necessary. One example is the use as a cladding material for superconductors as shown in Figure 2. In case of cooling failure (most super conductors still need very low temperatures) the Copper matrix takes over the

![Figure 1: High-tech application for Aluminium (Cans, CD, Lithography sheet, beverage containers)](image)

The highest demands in respect to cleanliness exist for material used for the production of computer discs. At CDs Aluminium is used as material which has to reflect the laser beam. The reflective material has to have constant reflective properties so that the information stored at the disc can be read out correctly. The spot where the laser reads the information is only ~ 0.5 μm wide, so the size of surface defects should be as small and their amount as low as possible.
conduction because of good deep temperature conductivity until the system is shut off. Contrariwise to the super conductors Copper does not reveal a sharp resistance step at a certain temperature.

Another example for Copper in the high-tech industry is the application in the micro electronics industry. The electronic industry boomed with the development of the so called printed circuit boards (PCBs) as shown in Figure 2: a Copper foil is applied onto a non conducting substrate; alternatively the Copper is deposited electrolytically on the substrate. Then the circuit lines are printed with a special colour, the excess Copper is etched away and the conductor lines remain. Nowadays layers of only 50 μm are applied. The boards with these thin Copper layers can also be made flexible. This is a great challenge for the material: it has to combine a high conductivity with good mechanical properties and elasticity.

One last example for a Copper high-tech application is the use in connector pins, an every day’s but often not recognised application. In modern automobiles numberless electronic helpers are connected to one central site. An example of connector pins is shown in Figure 3 Therefore tens of connectors are combined in one connector system. The pins need a high conductivity but also

**Figure 2:** Copper in printed circuit boards (left) and super conductors applications (right)

**Figure 3:** Copper strip and connectors (Bilder DKI, KME)
flexibility that allows to assemble and disassemble them often. At the same time they should be stiff enough to guarantee the electrical connection even at temperatures in an engine compartment and should have the same lifetime expectancy as the automobile.

These three fields of application are, of course, only a very small extract of the Copper world. Copper and its alloys are also used in vacuum switches, vacuum capacitors, electron beam tubes, welding electrodes, heat exchangers, as moulds for continuous casting of steel, Aluminium and Copper, in generators of power plants and wire.

Aluminium and Copper finished products are sometimes of comparable shape although their application fields are different as for example Aluminium foil for food containers and Copper foil for conducting purposes. Nevertheless both products require an extremely high amount of knowledge for their production and because of the effort that was put in their development they are called high-tech products

3 Impurities in Aluminium and Copper Melts

Impurities in Aluminium melts can be divided into “solid inclusions” and “dissolved impurities”.

Solid impurities in Aluminium have different sources. The\textit{exogenous inclusions} may come from the melt environment as the refractory linings of furnaces, ladles, reactors or launders etc. Mainly these are simple oxides as \(\text{Al}_2\text{O}_3\) and \(\text{MgO}\), \(\text{K-}\), \(\text{Ca-}\) and \(\text{Al-}\) silicates, \(\text{Na-}\), \(\text{Ca-}\) \(\text{Mg-}\) aluminates, spinels like \(\text{Al}_2\text{O}_3\text{MgO}\) or \(\text{TiB}_2\) cluster originating from grain refining. The\textit{endogenous inclusions} for e.g. \(\text{Al}_3\text{C}_4\), \(\text{AlN}\) or \(\text{AlB}_2\) are formed in the melt during production, e.g. in the electrolysis cell, at the melt treatment operations esp. during gas purging, or during storage and cooling down steps of the melts. Depending on the material produced the most important inclusions are \(\text{Al}_2\text{O}_3\), \(\text{MgO}\) and \(\text{Al}_4\text{C}_3\).

Dissolved impurities may be foreign metals and dissolved gas. \textit{Foreign metals} in potroom metal are \(\text{Na}, \text{Li},\) and \(\text{Ca}\) coming from the electrolyte. Remelted metal may contain \(\text{Fe, Si, and Cu}\) as impurities. These metals can not be removed industrially and must be diluted by the addition of pure Aluminium or corresponding alloys in the casting furnace. The only \textit{dissolved gas} in Aluminium melts is hydrogen, because it does not form compounds with Aluminium as other gases (e.g. nitrogen forms \(\text{AlN}\), oxygen forms \(\text{Al}_2\text{O}_3\)). Compared with iron and Copper Aluminium has a rather low solubility for hydrogen (at 660 °C liquid Aluminium dissolves 0.69 ppm H and solid Aluminium only 0.039 ppm H). Hydrogen has to be removed, because bubbles originating during solidification lead to unacceptable gas pores in the produced material. Due to the rather small solubility of hydrogen in Aluminium melts its removing is a demanding task. Elements and compounds typically occurring in Aluminium melts are summarised in Table 2.

The issue of impurities in Copper can be separated in two parts: impurities in primary Copper remaining or collected after refining electrolysis and impurities in secondary not electrorefined Copper scrap.

The refining electrolysis produces cathodes with min. 99.995 wt. % Cu, the major remaining impurities are silver, sulphur, nickel and iron. But the contents are usually so small that they are not detrimental to the properties of Copper. The more critical elements in this sense namely hydrogen and oxygen as well as inclusions enter the primary Copper usually during the remelting and casting process.
In secondary materials the impurity matter is more complicated. Remelting of Copper scrap makes ecological and economical sense because the material does not have to be lead back into the energy intensive primary electrolysis. There are two types of scrap, the sorted and mostly clean production scrap which is easily reusable and end of lifecycle scrap (="old scrap") consisting often of a mixture of different alloys or even compounds with other metals and materials. In the process of producing a clean and specified alloy the undesired elements either have to be removed or diluted. They can e.g. form intermetallic phases in the Copper matrix and as a result decrease the mechanical properties like the ultimate yield strength and the ductility. Due to the noble character of Copper, most elements like Silicon, Aluminium and iron can easily be removed from a Copper melt by selective oxidation up to a very low concentration (activity). Physically and chemically more similar elements like nickel, cobalt, tin and lead have to be treated with more attention. Elements and compounds typically occurring in Copper melts are summarised in Table 2. Dissolved metallic impurities in small amounts mostly are not detrimental to the properties of Copper, but some elements as for example Lead and Arsenic precipitate at the grain boundaries of the Copper materials and lead to embrittlement of the material.

Generally oxygen and hydrogen pick-up can lead to very negative effects. The two gases have a high solubility in liquid Copper that decreases sharply during solidification. This can lead to a bubble formation, i.e. porosity in the solid material. Oxygen can also form cuprous oxide (Cu₂O) above its solubility level that immediately reacts with the moisture of the air forming water vapour during annealing or welding, this phenomenon is called hydrogen illness. Dissolved hydrogen and oxygen (or Cu₂O) will react to water under extreme pressure in the lattice and will form cracks and lead to embrittlement.

Solid inclusions like intermetallics or oxides from alloying elements or the refractory material usually do not have a negative impact on Copper and Copper alloys. Because the density difference between the Copper melt and the particles is very high the particles tend to float to the surface (e.g. the density of Copper at 1100°C is 7.96 g/cm³ while iron oxide has a density of 5.25 g/cm³ [2]). However Stokes law predicts that even at high density differences very small particles tend to stay suspended (In case of FeO particles the diameter smaller than 10 μm rise with 0.59 m/h). This leads to problems where wires with a very small diameter are drawn, for thin Copper foils or where small connector pins are made from thin Copper strip, being etched or punched.

Generally impurities in metals can be distinguished in dissolved gases, dissolved metals and non metals as well as solid inclusions, Table 2 summarizes the typical impurity elements and compounds for Aluminium and Copper.

Table 2: Comparison of impurities in Aluminium and Copper

<table>
<thead>
<tr>
<th>Impurity type</th>
<th>Aluminium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>H₂, Li, Na, Mg, K</td>
<td>H₂, O₂, Pb, Sn, Ni, Zn, Fe, Si, Cr, etc.</td>
</tr>
<tr>
<td>Dissolved metals</td>
<td>Less noble</td>
<td>Fe, Mn, Si, Cu, Ni</td>
</tr>
<tr>
<td></td>
<td>More noble</td>
<td></td>
</tr>
<tr>
<td>Inclusions</td>
<td>Al₂C₄, Al₂O₃, MgO, Silicates, Aluminides</td>
<td>SiO₂, Al₂O₃, SiC etc.</td>
</tr>
<tr>
<td></td>
<td>Exogenic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Endogenic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃, MgO, AlB₃</td>
<td>Cu₂O, Me₂O₂</td>
</tr>
</tbody>
</table>
For both metals Hydrogen is a major problem as a dissolved gas, whereas oxygen is unsoluble in Aluminium and forms immediately solid compounds. In Copper melts the oxygen concentration can exceed 1 wt.% and is the second major problem due to the reaction with hydrogen to water vapour or with carbon to CO/CO₂. Dissolved metallic impurities are generally not a problem as long as they are less noble than the target metal. But as Aluminium is one of the least noble elements the variety and amount of more noble metals is much greater than in Copper and Aluminium is difficult to clean. In Copper mainly noble metals like Silver, Gold and PGMs can not be removed from the melt, but also metals with low activities at low concentrations like lead or nickel, if very high purities have to be obtained. The high oxygen affinity of Aluminium leads to a vast formation of oxides that can harm the products. In Copper ceramic impurities are mainly from the refractory and from less noble alloying elements not being transferred to the slag.

4 Purity Requirements for High Performance Materials

Potroom Aluminium contains up to 0.3 ppm H, 150 ppm Na, 20 ppm Li, up to 5 ppm Li and more than 1000 ppm of inclusions, mainly as Al₄C₃. The ppm-/ppb-/ppt-concentrations of inclusions are defined as the total volume of inclusions taken as Al₂O₃ related to the volume of 1 kg liquid Aluminium. The impurity content of remelted materials sums up to max. 0.6 ppm H, to 40 ppm Ca, 10 ppm Na, and some 1000 ppms of inclusions mainly Al₂O₃, MgO, MgO/Al₂O₃, Al₄C₃ and TiB₂.

Alloyed Aluminium melts supplied to the casthouse shall contain not more than 1 ppm inclusions, pure Aluminium melts up to 100 ppb inclusions. After filtration this content can be reduced to less than 10 ppb. Alloyed material for extrusions can contain between a 10–100 ppb inclusions. The highest requirements exist in respect to melt cleanliness for materials used for computer disc production. They may contain only between approx. 100–1000 ppt of inclusions.

The alkali-metal content has to be lowered to a few ppms, while the hydrogen content has to be decreased to smaller than 50 ppb (0.05 ppm). The requirements of different Aluminium applications is shown in Figure 4.

Examples for the increased quality requirements of Aluminium melts are can body sheets and foils. In the early 1960’s at the beginning of the production of Aluminium can bodies the thickness was approx. 0.5 mm, today it is thinner than 0.3 mm. This means a decrease of 40 % in thickness with a corresponding reduction in weight. Today Aluminium foil is rolled out to a thickness of only 6 μm, which is in the magnitude of order of typical inclusions. Without an effective melt cleaning by gas purging and filtration the requirements for the production of these materials can not be met.

The most frequent impurity in refined Copper is oxygen. If the alloy is not molten under oxygen free atmosphere, Copper melts will always pick up oxygen. Copper melts hyper saturated with oxygen lead to the so called hydrogen illness during casting and welding in case hydrogen is present in the material or the atmosphere. Dissolved oxygen can also oxidise less noble elements which leads to the formation of brittle oxides in the material. In technically alloys, an oxygen content of a few hundred ppm is accepted whereas in special grade materials the content has to be lowered below one ppm, some grades and their respective tolerated oxygen content are shown in Figure 5.
In technical alloys the DIN limit for specified metallic impurities mainly varies between 0.1 wt. % and 0.5 wt. %. The sum of all not specified remaining elements should not exceed 0.5 wt. %. However some elements are more detrimental as for example Aluminium, arsenic and lead, their content must be kept below 0.01–0.05 wt % [3]. For high quality products limits of < 90 ppm Pb, < 50 ppm Sn and < 150 ppm Ni are required. Solid inclusions are especially a problem in thin wire drawing and thin sheets rolling. Equation 1 describes the critical inclusion size, any particle bigger will initiate wire breaks:

\[ d_{\text{critical}} \geq \frac{D \cdot K}{T^n} \]  

(1)
with $d_{\text{critical}}$: inclusion size that leads to a break, $D$: wire diameter, $K$ is a material constant, $T$: applied pulling tension, $n$: reduction ratio.

That means that the possibility for a wire break increases sharply with the size reduction ratio and the pulling tension. In foils production inclusions lead in the worst case to a foil break. Smaller inclusions lead to surface defects and elongated holes in the material.

5 Processing of Molten Aluminium and Copper

The cleaning of Aluminium melts starts with a simple ladle treatment esp. of potroom metal for the removal of alkaline metals, before the melt is transferred into the casting furnace. There the alloying is carried out and a further settling operation may take place. From the casting furnace the molten metal is fed via a launder to the degassing unit for the removal of hydrogen. Grain refining is carried out by wire injection between the gas purging unit and the filtration station. Sometimes gas purging is combined with a filter in one unit. After the melt treatment the liquid metal is cast in a DC casting unit to billets, cakes or slugs [5, 6].

The processing of primary Copper usually starts with the melting of Copper cathodes in a shaft furnace. For melting of Copper scrap in general induction furnaces or drum furnaces are applied. After the preliminary melting furnace the melt is either casted directly or subjected to a casting furnace where the melt is stored, (alloyed) and heated to casting temperature. For Copper the continuous wire casting by casting wheels or Hazelett casters is especially important. Besides this also vertical and horizontal slab casting is applied as well as mould casting.

For treatment of Aluminium melts a variety of methods are in industrial use. A cheap and simple settling procedure in the casting furnace is an easy but ineffective method to clean an Aluminium melt. Solid inclusions settle down depending on size, form and density. Because

![Figure 6: Processing of molten Aluminium](image-url)
there is only a small density difference between inclusions (e.g. Al₂O₃) and liquid Aluminium their settling is very slow. Small inclusions do not settle at all. According to the difference in partial pressure between hydrogen dissolved in the melt and hydrogen resp. water vapor within the atmosphere hydrogen can be removed. The return reaction:

$$H₂O + 2Al \leftrightarrow 6H₂ \text{Al} + Al₂O₃$$

leads to a new hydrogen pick up and oxide formation. Hydrogen and solid inclusions can be removed only partially using this method. So settling is only rarely used as a preliminary step to treat Aluminium melts.

By a ladle treatment alkaline and earth alkaline metals can be removed by mechanically stirring in salts into the Aluminium melt. Different technical solutions are in industrial application (e.g. the TAC-process). Today ladle treatment is replaced by the development of the RFI processes (see below). Gas purging removes hydrogen as well as solid inclusions, latter only partially by flotation. Also alkaline and alkaline earth metals are removed if chlorine is added to the purging gas. Melt filtration is used extensively for the separation of solid particles. Elements like Fe, Si, Mn and Cu, which may be contained in remelted metal in forbidden concentrations, cannot be removed at all and have to be diluted by the addition of pure Aluminium or corresponding alloys in the casting furnace.

The “classical” melt treatment of Copper is the oxidation by air through oxygen injection or top blowing. With this technique elements that are less noble than Copper can be removed from
the melt. Today this technique is often combined with a specific slag that can take up the impurity oxides and supplies a certain oxygen potential to improve the impurity separation.

To remove dissolved gases especially hydrogen and oxygen the oldest method is first of all the right melt handling. Hydrogen can be removed by an excess of oxygen in the melt, oxygen is usually added by blowing air on the melt surface. After the removal of hydrogen by oxidising conditions, the melt has to be treated under reducing conditions to remove the oxygen. For the reduction since former times the so called poling by tree trunks especially birch is used [4]. This technique is still used today in some places. A new pick-up of hydrogen has to be avoided by shielding of the melt. An advantage of the tree trunks is that they have a CO₂ emission of zero, as plants are considered to be regenerative. Alternatively to this classical procedure, modern techniques reduce the partial pressure in the surrounding atmosphere; this led to vacuum and gas purging technologies like for Aluminium.

The removal of dissolved metals in Copper is an upcoming problem because of the increasing recycling material volume not being treated by refining electrolysis. Metals like Zinc, Arsenic and Antimony can be evaporated by a vacuum treatment, for others like Nickel, Cobalt, Tin and lead a special slag treatment is more economic. Nevertheless very often the high specifications of high tech applications cannot be met using only one refining technique. To remove solid particles from Copper melts a simple settling is usually enough for standard qualities. But the increasing requirements, e.g. for wire production, led to the development of filtration and flotation techniques.

All the melt treatment techniques are actually batch processes. They have to be implemented in the existing process routes in a way that their effect is not lost before casting and solidification of the metal. That means that after deoxidation, a pick up of oxygen has to be avoided by proper casting gutters protected by a coal or coke cover or a shielding gas. After filtration a laminar flow of the melt through the launder has to be assured to avoid turbulences that promote abrasion of the refractory and formation of oxides.

Although the impurities in Aluminium and Copper are different, the applicable melt treatment principles are almost the same in general gas purging, vacuum treatment, filtration and settling can be applied. The reactants of the different melt treatment technologies are shown in Table 3.

<table>
<thead>
<tr>
<th>Melt Treatment</th>
<th>Aluminium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant</td>
<td>Rem. of</td>
<td>Reactant</td>
</tr>
<tr>
<td>Gas purging</td>
<td>Cl₂, Ar, N₂</td>
<td>H₂, alkalines and floatation of inclusions</td>
</tr>
<tr>
<td>Chlorination</td>
<td>Cl₂</td>
<td>Alkalines, Mg</td>
</tr>
<tr>
<td>Vacuum treatment</td>
<td>–</td>
<td>Mg, Zn, Pb, H₂</td>
</tr>
<tr>
<td>Filtration</td>
<td>Ceramic Foam Inclusions</td>
<td>Ceramic foam Inclusions</td>
</tr>
<tr>
<td>Settling</td>
<td>“Time”</td>
<td>“Time”</td>
</tr>
<tr>
<td>Slag treatment</td>
<td>NaCl, KCl</td>
<td>Inclusions (Al₂O₃, MgO etc.)</td>
</tr>
</tbody>
</table>

From both metals dissolved gases can be removed by inert gas purging, where the principles are actually the same. Most dissolved impurity metals are removed from Aluminium by a treat-
ment with Chlorine while in Copper melts an oxidising procedure is favoured. With a vacuum treatment dissolved gases as well as highly volatile elements like Zinc, Arsenic etc. can be removed. The filtration removes solid inclusions in both metals only the type of filter material is different reflecting the different properties of the metals. Settling is a simple but standard technique to avoid solid inclusions in the melt.

5.1 Gas Purging

First mentioning of gas purging of metallic melts goes back to 1856 for steel [7]. The gas purging of Aluminium melts was mentioned first by D.R. Tullis in 1928, who used pure chlorine. Mixtures of chlorine with inert gases esp. nitrogen were developed very soon. In 1931 Koch proposed the use of a mixture of chlorine and nitrogen for the removal of Fe and Si from commercial Aluminium alloys [8]. Based on the basic work of Röntgen and Haas the chlorine/nitrogen converter was developed and set in operation in 1948 [9]. A couple of those units have been used up to the early 1960s in Europe. In 1964 the trigas mixture was developed. Carbon-monoxide was added to the chlorine-inert gas mixture to lower the Aluminium-oxide formation at the inner surface of the bubble. This enhanced the transport of hydrogen through the gas-melt interface. After the development of the gas mixtures the research was focused on the technology of gas purging.

In the early times of Aluminium melt treatment simple tube lances were used to introduce the purging gas into the melt. Jet injection technology was developed already in the 1970ies where using a high-speed jet of gas is injected into the melt via nozzles. The gas is dispersed into fine bubbles and distributed in the reactor. Porous plugs were introduced in the Aluminium metallurgy in 1973. Porous plugs are mounted into the furnace technology, so their application is limited. But, they are widely spread in the Aluminium industry. At the beginning of the 1990s porous plugs were placed in launders.

In the middle of the 1970ies the rotary gas injection (RGI) technology was developed by different companies nearly at the same time. The principle of this technology is the fact, that a gas stream introduced into a melt via a high speed rotor is disintegrated into very small bubbles by shearing forces. A couple of different in–line systems were developed which differ mainly in the design of the rotor [10]. These units are built in form of boxes, which can be fitted into the melt treatment line easily. They are in use in casthouses worldwide.

The latest development in the middle of the 1990ies was the rotary flux injection (RFI) technology, in which salts, replacing chlorine in metallurgy, are added to the inert purging gas and are injected via a rotor into the Aluminium melt. The main target of this development is a decrease of chlorine consumption and emission. In the course of the development of gas treatment systems the chlorine consumption decreased from up to 0.7 kg Cl/t Al using lances, over 0.1–0.2 kg/t with the RGI-system down to 0.05 kg/t in the RFI-systems.

Gas purging is based on the difference in the partial pressures of hydrogen dissolved in the melt and within the bubbles of the purging gas. The purging gas, usually nitrogen or argon, is introduced into the melt by lances, nozzles, porous plugs or high–speed rotors. A bubble formed e.g. at a pore of a porous plug has a hydrogen partial pressure of nearly zero. Hydrogen atoms dissolved in molten Aluminium are transported to the bubble by convection and via diffusion through the melt-gas boundary layer. There the dissolved hydrogen atoms combine to gaseous hydrogen by chemical reaction. The ascending bubble becomes larger because the metallostatic
The effectiveness of gas purging operations depend on the kinetics of the reactions during the degassing process. The speed of the hydrogen removal can be described by a first order reaction and roughly by the equation:

\[
\frac{dc_H}{dt} = -\beta \cdot \frac{x \cdot A}{V}
\]  

(3)

Therefore the decrease of the hydrogen concentration in the melt \( c \) depends on

- the retention time \( t \) of the bubble in the melt,
- the mass-transfer coefficient \( \beta \),
- the melt volume \( V \), and
- the mass-transfer area \( A \) (most important).

The mass-transfer area \( A \) is the total surface of the bubbles in the melt during gas purging. Consequently the formation of as many and small bubbles as possible in units is essential. Furthermore the depth of the melt is important, because the retention time of the bubbles in the melt is determining too.

While using porous plugs a careful adjustment of the gas-throughput is necessary. Only at slow gas velocities small bubbles are formed; at high velocities rather large bubbles are produced because the whole plug surface acts as a bubble source (so called "flooding"). The smallest bubbles can be produced by the application of high-speed rotor systems. Lances are almost ineffective for gas purging operations.
State of the art in Aluminium melt treatment is the application of degassing boxes which are used worldwide. They are installed in-line between casing furnace and grain refining unit. Further developments of the RGI technology are the launder resp. through degassing units using also rotor systems.

Compared to the earlier used degassing boxes the launder (compact) degassing technology has following advantages:

- Reduced production costs by
  - diminished metal losses,
  - decreased process gas consumption and
  - decreased depreciation due to less expensive equipment.

**Figure 9:** Gas bubble surface versus bubble diameter

**Figure 10:** Efficiency of gas purging methods
Increased cleanliness of the melts by
– decreased hydrogen content to below 0.05 ppm and
– improved inclusion content of lower than 20 ppb.

• Reduced chlorine emissions.
• Reduced space consumption.

All further developments must have the following targets:

• Increasing the effectiveness of hydrogen (and inclusion) removal by
  – lowering the bubble size,
  – increasing the bubble residence time and
  – improving the bubble distribution in the reactor
• Further decreasing of operation costs
• Decreasing the chlorine emissions to zero, which is the main challenge for the future.

The purging technologies of Copper alloys can be divided in those with inert gases and those with reactive gases. Purging with inert gases is based on a low partial pressure of the gas that needs to be removed. This process is diffusion controlled, i.e. the speed depends on the diffusion constant and the specific surface area of the melt-bubble interface. A diffusion controlled mass transfer can be influenced by rising temperatures (technically not feasible) and a decrease in the thickness of the Nernst layer. Such the process can significantly be intensified by an increase of the surface of the gas bubbles by appropriate gas supplying technique. The principles for the gas purging was described above. Argon and nitrogen are appropriate inert gases for purging Copper, especially for hydrogen removal. Their solubility in liquid Copper is negligible.

Also gas purging methods for Copper deoxidation were developed to replace the poling with tree trunks that goes back at least to the year 1200 AD when it was mentioned in ”De Re Metallica”. In the 1960s extensive research was conducted on reactive gases with different gaseous and solid reducing agents. Reducing gases were tested like different carbon-hydrates [11], carbon monoxide as well as hydrogen. Ammonia [12] for gas purging was investigated in the