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MELT TREATMENT OF COPPER AND ALUMINIUM – THE COMPLEX STEP BEFORE CASTING

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INTRODUCTION

Aluminium and Copper are second and third most produced metal world wide after iron (steel). But in melt treatment technologies they are probably the number one. Although Copper is the metal that is longest used technologically 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]

Property	Aluminium (high purity)	Copper (high purity)
Density	2698 kgm^{-3}	8960 kgm^{-3}
Melting Point	660°C	1084°C
Elastic modulus	70.3 GPa	128 GPa
Ultimate yield strength	90 – 100 MPa	210 – 230 MPa
Elect. conductivity	40 MS	64.5 MS
Heat Conductivity	237 Wm^{-1}K^{-1}	401 Wm^{-1}K^{-1}
Electr. Cond. /density	14.8*10^{-3} MSm^{3}kg^{-1}	7.2*10^{-3} MSm^{3}kg^{-1}
Heat cond. /density	87,8*10^{-3} Wm^{-1}K^{-1}m^{3}kg^{-1}	44.7*10^{-3} Wm^{-1}K^{-1}m^{3}kg^{-1}

The major difference of Aluminium and Copper is the affinity to oxygen. While Aluminium is a very un-noble element and its melt forms insoluble 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 of interest in mobile applications 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.

APPLICATIONS OF ALUMINIUM AND COPPER

For increasing applications the Aluminium quality has to meet high performance specifications for 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 as the thickness of a can body sheet is nowadays only < 300 µm. Therefore the number of defects caused by inclusions and gas pores have to be decreased drastically. More than 60 % of the Aluminium production is used for packaging from which a large part is Aluminium foil. 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.

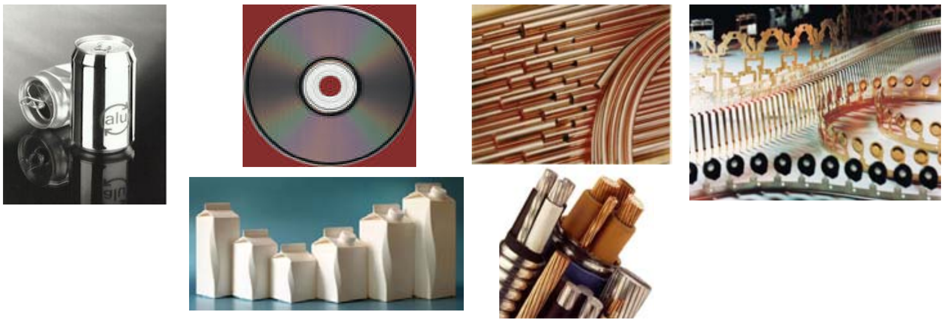

Figure 1. High-tech application for Aluminium and Copper (Cans, CD, Lithography sheet, beverage containers, tubes, contacts, wires)

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. In case of cooling failure (most super conductors still need very low temperatures) the Copper matrix takes over the conduction because of good deep temperature conductivity until the system is shut off. Contrarily 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). On the printed circuit boards 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 and smaller 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.

These 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

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 *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 Al_2O_3 and MgO, K-, Ca- and Al- silicates, Na-, Ca- and Mg- aluminates, spinels like $Al_2O_3{\cdot}MgO$ or TiB_2 cluster originating from grain refining. The *endogenous inclusions* for e.g. Al_3C_4, AlN or 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 Al_2O_3, MgO and Al_4C_3.

Dissolved impurities may be foreign metals and dissolved gas. *Foreign metals* in potroom metal are Na, Li, and Ca coming from the electrolyte. Remelted metal may contain Fe, Si, and Cu as impurities. These metals are not removed industrially and must be diluted by the addition of pure Aluminium or corresponding alloys in the casting furnace. The only *dissolved gas* in Aluminium melts is hydrogen, because it does not form compounds with Aluminium as other gases (e.g. nitrogen forms AlN, oxygen forms Al_2O_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.

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 electro refined 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 at least down to a very low concentration (activity). Physical and chemical more similar elements like nickel, cobalt, tin and lead have to be treated with more attention. 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 an oxygen and hydrogen pick-up can lead to very negative effects on mechanical and physical properties. The two gases have a high solubility in liquid Copper that decreases sharply during solidification. This can lead to bubble formation, i.e. porosity in the solid material. Oxygen can also form cuprous oxide (Cu_2O) 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 Cu_2O) will react with 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

Impurity type		Aluminium	Copper
Gas		H_2	H_2, O_2
Metals	Less noble	Li, Na, Mg, K	Pb, Sn, Ni, Zn, Fe, Si, Cr, etc.
	More noble	Fe, Mn, Si, Cu, Ni	Au, Ag, PGM
Inclusions	Exogenic	Al_3C_4, Al_2O_3, MgO, Silicates, Aluminides	SiO_2, Al_2O_3, SiC etc.
	Endogenic	Al_2O_3, MgO, AlB_3	Cu_2O, Me_xO_y

For both metals Hydrogen is a major problem as dissolved gas, whereas oxygen is insoluble 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/CO_2. 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 are required. 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.

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 conducted 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 use industrially. 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 there is only a small density difference between inclusions (e.g. Al_2O_3) 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 vapour within the atmosphere hydrogen can be removed. 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 brought in by remelted metal in to high 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 or oxygen 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 the earliest 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 CO_2 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.

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 treatment 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.

Table 3. Comparison of melt treatment principles

Melt Treatment	Aluminium		Copper	
	Reactant	Removal of	Reactant	Removal of
Gas purging	Cl_2, Ar, N_2	H_2, alkalines and floatation of inclusions	Ar, CH_4, CO, O_2	H_2, O_2, less noble metals (Fe, Pb, etc.)
Chlorination	Cl_2	Alkalines , Mg	-	-
Vacuum treatment	-	Mg, Zn, Pb, H_2	-	Zn, As, Sb, H_2, O_2
Filtration	Ceramic Foam (Al_2O_3)	Inclusions	Ceramic foam (SiC)	Inclusions
Settling	"Time"	Inclusions (Al_2O_3, MgO etc.)	"Time"	Inclusions (Cu_2O, Me_xO_y)
Slag treatment	NaCl, KCl	Inclusions (Al_2O_3, MgO etc.)	SiO_2 etc.	Pb, Ni, Mn, Fe

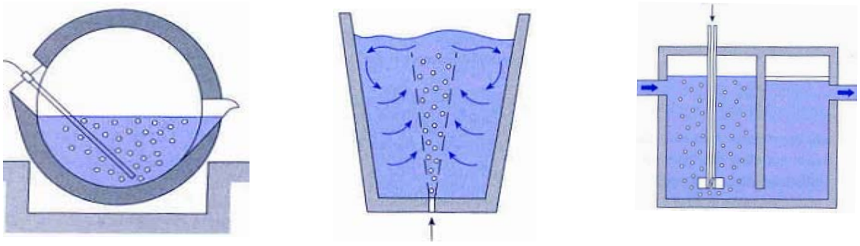

Figure 2: Different gas purging technologies (lances, porous plugs, rotary degasser

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 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 implemented 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 easily into the melt treatment line. They are in use in foundries 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 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 pressure decreases and hydrogen is taken up; theoretically until the thermochemical equilibrium is reached. Normally the retention time of the gas bubbles in the melt is in the area of seconds so that the equilibrium is mostly not reached.

The effectiveness of gas purging operations depends 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:

$$\frac{d_{c_H}}{dt} = \frac{-\beta \cdot x \cdot A}{V} \qquad \textit{Eq.1}$$

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 β,
- 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.

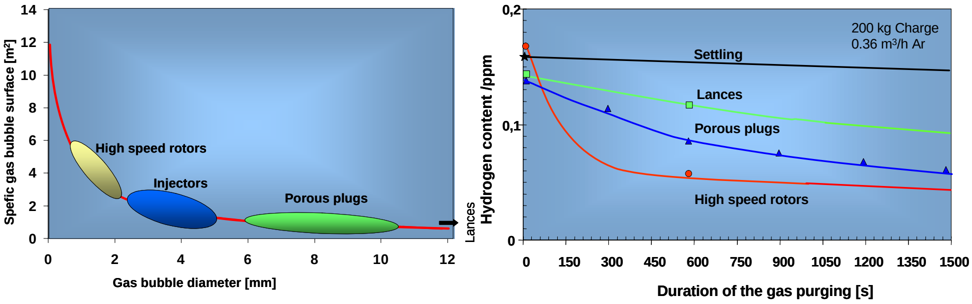

Figure 3. Specific Gas bubble surface versus bubble diameter (left), efficiencies of different gas purging devices (right)

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.

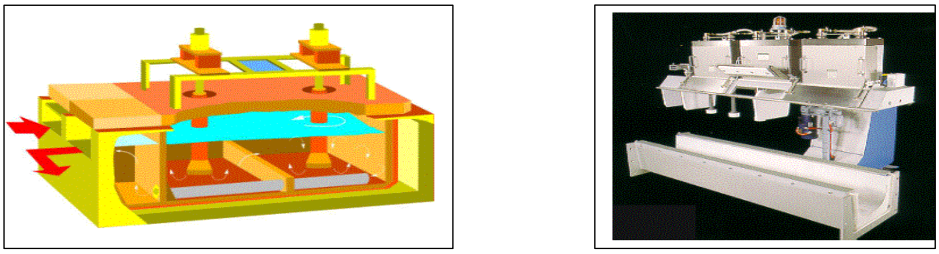

Figure 4. In line Aluminium gas purging: SNIF Box (left) and Alcan compact degasser (right)

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.
- 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 first was mentioned in writing 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 1970s. Also oil or coal dust were used as reducing agents, the problem of these substances was their impurity content, especially sulphur that enriches in the Copper melt.

Natural gas as a reducing agent was tested by Klein [13] but the process was found to be very ineffective and slow. In comparison a reformed, partially oxidised natural gas where the carbon hydrates are reacted to carbon monoxide and hydrogen leads to a fast deoxidation of the Copper melt. This process was implemented at the Phelps Dodge refining works in the 1960s according to US-patent 2,989,397. An intensive investigation on the kinetics of the Copper deoxidation by carbon monoxide was carried out by Andreini et al. in 1977 [14]. The chemical gross equation of deoxidation with carbon monoxide is:

$$2\underline{O}_{Cu} + CO \Leftrightarrow CO_2 \qquad \textit{Eq.2}$$

It was found that the oxygen diffusion in liquid Copper to the gas bubbles is the reaction rate controlling step, valid in a concentration interval of 50 ppm to 1000 ppm. Below 50 ppm the kinetics of the oxygen removal decreases sharply. This can not be explained by the equilibrium, it is possibly due to interactions with sulphur in the melt. This study agrees fairly well with an older study from Nanda et al [15] who also found a sharp decrease of the deoxidation speed below a concentration of 50 ppm oxygen. The lowest oxygen concentration in liquid Copper that could be achieved by this process was

10 ppm. As an alternative to carbon hydrates ammonia was investigated as a possible reducing agent by Henych et al.[12]. The gross equation of this reaction is:

$$3\underline{O}_2 + 4NH_3 = 2N_2 + 6H_2O \qquad \textit{Eq.3}$$

The reducing element in this case is the hydrogen. The developing nitrogen is an inert gas and does not dissolve in the Copper melt. The lowest oxygen concentration in liquid Copper that could be achieved by this process was 200 ppm. This technique never reached industrial scale.

Up till now the favoured gas injection technology in the Copper industry are tuyeres/injectors and top blowing lances even though in other industries different gas supplying techniques are used as rotary vaned dispersers and porous plugs

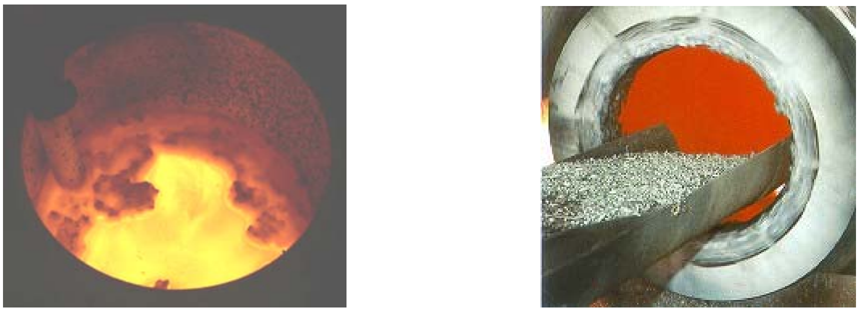

Figure 5. Copper slag cover in induction furnace (left), Al-chip melting in rotary furnace with salt slag (right)

Slag treatment. A slag treatment of Aluminium and its alloys is only necessary when very fine particles like chips are molten. The natural Aluminium oxide skin prevents the burning of Aluminium melts up to 700°C. In Aluminium recycling where fine fractions are molten usually salts on the basis of sodium chloride and potassium chloride are used. The mixture depends on the local deposits and suppliers. This system is selected, because the melting temperature is close to the melting temperature of Aluminium but at the same time the system has a rather high evaporation point. This mixture has a better wetting behaviour for oxides that for Aluminium metal and therefore takes up oxides during a melt treatment and last but not least it is readily available and cheap. Usually to the salts on chlorine base fluoridic compounds like AlF_3 or CaF_2 etc. are added. The fluorides accelerate the cracking of the Aluminium oxide layer and therefore improve the coalescence [15]. Oxidic slags are not used in the Aluminium industry because of their high melting point and also because Aluminium is very un-noble and tends to reduce most of the slag oxides as for example Silicon oxide.

Slags in Copper refining have the task to take up the impurity oxides, formed during the oxidation procedure. Their properties should be:

- High solubility for impurity oxides
- Low solubility for Copper and Copper oxide
- Melting temperature close to the melting temperature of Copper
- High thermal stabil\ity
- Low interaction with the refractory material

Before or during a slag treatment the Copper melt has to be oxidised for example by top blowing of air. A slag that is industrially used is the so called “Fayalite” slag, which is also applied in the primary Copper metallurgy. It is based on the system $FeO – Fe_2O_3 – SiO_2$ and effective for the gross removal of Cd, Fe, Pb, Sn and Zn especially for elements with the valence of two that can be trapped as silicates. This slag can be used in furnaces with silica refractory [17]. This is the slag mainly used today.

On laboratory scale other slag types were investigated as well, for example Calcium-ferrite slags which are based on the ternary system $FeO – Fe_2O_3 – CaO$. They remove the elements Al, As, Fe, Sb and Sn, especially elements which exhibit an acidic character in a slag at their highest oxidation levels [17]. This slag can be used with base refractory. Another system is based on $CaF_2 – CaO – MgO – SiO_2$ this slag shows the same behaviour as the “Calcium-ferrite” slag but with a lower solubility for Copper oxide.

Also investigated by researchers were salt slags that are mainly based on Sodium carbonate (Na_2CO_3) but also on other alkaline carbonates like Lithium carbonate (Li_2CO_3) and Potassium carbonate (K_2CO_3). They are very effective refining slags, but they all attack “usual” refractory of the Copper industry. It was found that by fluxing with a Sodium carbonate slag the amount of arsenic and antimony could be lowered below 0.1 ppm. The problem that occurred was, that the binary solution of Sodium carbonate and Antimony oxide let to an increase of solubility of Copper oxide in the slag and therefore to high Copper losses [18]. For fluxes on other salt base mainly fluorides can be suitable because their melting and evaporation point is very high. Here especially systems based on Calcium fluoride (CaF_2) mixed with Aluminium fluoride (AlF_3) or Sodium fluoride (NaF) are possible candidates.

All fluxes operate in the best way when the reaction surface between metal and slag is increased for example by solid flux injection in the metal melt [19] instead of an addition to the surface.

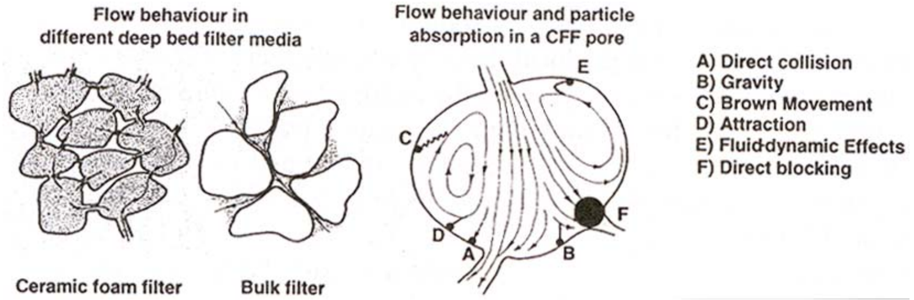

Figure 6. Filtration mechanisms in ceramic foam filters

Filtration. In 1935 a procedure was proposed for the filtration of light metal melts by DEGUSSA, which was transferred to Aluminium melts very soon. The bed filtration (BF) was developed using bulk petrol coke and/or ceramic particles by ALCAN in the 1940´s. The development of ceramic foam filters (CFF) started in the beginning of the 1970´s by SELEE. First rigid media filters (RMF), which are called also bonded particle tube filters (BPF), appeared on the market in the 1980ies, but were initially not accepted by the Aluminium industry. In the 1990ies two stage filter systems were developed having much better particle removal efficiency. The latest advances in filtration technology are the development of surface active filter systems starting in the mid 1990s.

By the formation of active surfaces inside the filter itself the effectiveness for the separation of small inclusions was significantly improved.

For the filtration of molten metals the same laws apply as for aqueous suspensions. Two different kinds of filtration have to be distinguished: cake and bed filtration. Usually both filtration types occur combined and happen successively. In the case of cake filtration the filtration process itself happens at least at the beginning by sieve effects. First inclusions larger in size as the pore diameter of the filter settle on the filter surface form a thin layer. The thickness of the cake increases as more melt flows through and more inclusions are separated. For Aluminium melt treatment cake filtration is rather unusual and limited to melts with high inclusions contents (> 200 ppm) and larger inclusions.

Bed filtration is the common mechanism used for Aluminium melts. In this case the separation of inclusions from the melt is rather complex. It happens mainly by direct collision or adhesion of particles to/at the filter surface, sedimentation by gravity as well as by inertia forces, collision of particles by Brown’s movement or/and fluid dynamic effects. Up to now no closed theory exist of the filtration of Aluminium melts [20]. So a mathematical modelling, which would allow calculating filtration efficiencies, filtration times, filter sizes etc. is not yet possible.

The filter materials are generally refractory material, preferentially Al_2O_3.

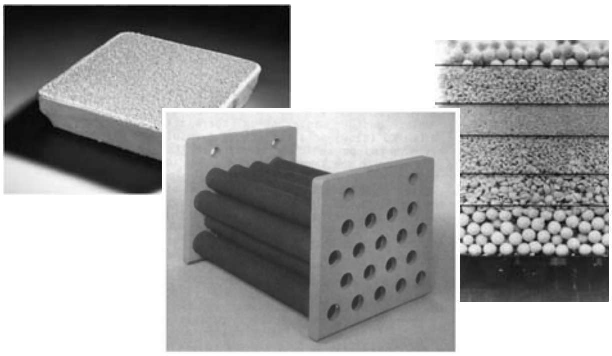

Figure 7. Filter devices for Aluminium melt filtration (from left to right: CFF, RMTF, BF)

Bed filters (BF) are bulks built of Al_2O_3-balls or chips with a size of 2 – 8 mm. Bulks of carbon or coke are not used anymore. BF´s are separate in-line units, which need rather much space. They are built in externally heated boxes and are suited for the throughput of large amounts of melts up to 1000 t. Particle form and size, layer thickness, and the sequence of different layers are varied to improve the filtration effectiveness. BP filters are suited for the separation of small inclusions < 20 µm from melts with low inclusion concentrations.

Ceramic foam filters (CFF) consist of a labyrintic structured ceramic material in which a very effective cleaning of the Aluminium melt happens by deep bed filtration effects. They are produced by the infiltration of a ceramic sludge into porous polyurethane foam. During firing the plastics decomposes and the porous ceramic remains. CFF are also built in separate boxes, which must not be heated externally. Filter plates are commercial available in different sizes, thicknesses (normally 50 mm) and pore sizes between 10 ppi to 80 ppi (pores per inch). They are one-way products and rather cheep so that the operational costs are low. This filter type is used most often in Aluminium metallurgy [21].

Rigid media filters (RMF) consist of porous ceramic tubes, which are built in like BF´s in external heated boxes in form of pipe bundles. The melt flows from the outside to the inside of the pipes. The filtration processes are very similar to the CFF´s. Because they have a smaller pore size there is a greater pressure drop and they have a shorter lifetime. RMF´s are rather expensive in respect to investment and operation cost, therefore their application is limited to special applications.

State of the art is the application of deep bed filtration in foundries, where large amounts of the same alloy have to be cleaned. For general purposes CFF´s are used. Only for special applications RMF´s are in operation because they are most efficient for the removal of very small particles. In normal filter systems single CFF plates or combination of CFF´s with different pore sizes are built in in separate boxes which must not be heated externally. They are positioned in-line directly before the DC unit. The melt is allowed to run through the filter plate, mostly downwards. CFF´s are used in combination with BF´s and with degassing units, too. Additional ceramic filter clothes may be used at the DC casting unit to retain coarse impurities which can enter the melt after filtration. Targets for the filter development in the future are filters that can remove even finer particles with high efficiency at a reasonable pressure drop and with minimized metal losses.

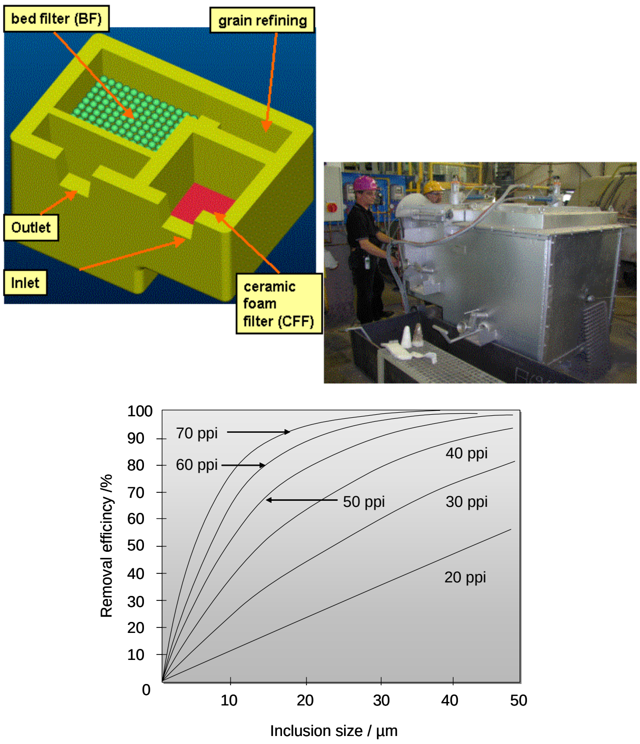

Figure 8. In line Aluminium melt treatment: Hydro (VAW)-Filter (left), removal efficiency of for different particles sizes in different filters (right.

Filtration of Copper is not very common, because the density difference between the Copper melt and the characteristic solid inclusions is big enough that they settle in the casting furnace. But because of the increasing demands on the semi finished products as for example Copper strip with 50 µm the amount of very small particles < 10 µm that do not settle easily has to be reduced. In 1981 the filtration of Copper melts was first mentioned by Chia et. al. Today filtration of Copper melts is mainly applied for material that is drawn into wire [23]. The filtration of Copper melts will increase with a further demand on wire and strip thinness.

SUMMARY

In this paper the today melt treatment techniques for Aluminium and Copper are presented. Emphasis was laid on gas purging, slag treatment and filtration because these techniques are widely spread in both industries. Until now the development of melt treatment techniques always was in step with the demands of the semi finished product producers and also with the demands for environmental safety. But the future holds more challenges. Because of size reduction foils and wire diameters will further decrease. For the Aluminium industry the avoidance of Chlorine is a major point that needs to be solved. For Copper the removal from dissolved elements from scrap charges has priority to avoid the energy intensive refining electrolysis.

The principles of melt treatment give both industries guidelines in which direction to proceed and to produce the optimum metal quality.

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