Melt-Treatment of Aluminium – Ways to a High Performance Metal

Friedrich, B.; Krone, K.; Kräutlein, C.

IME Process Metallurgy and Metal Recycling
Department and Chair of RWTH Aachen University, Intzestraße 3, 52056 Aachen, Germany

Key-note paper presented on the "Aluminium 2004 conference" in Essen

Introduction

Since the first technical production of aluminium in 1888/1889 (Heroult; Hall) the production, consumption and demand of aluminium products has continously increased. Today more than approx. 33 Mio t aluminium are produced and consumed worldwide each year. In the same time the requirements in respect to the quality of the produced aluminium products has increased continously, too. The high quality requirements which are needed for the production of thin foils and sheets for offset plates, cans and CD blanks can only be met with a high developed melt treatment technology. Today this treatment happens in-line by degassing, grain refinement and filtration before DC casting. A initial ladle treatment is carried out batchwise to remove too high contents of alkaline metals, occasionally. It is pertinent to note that the molten aluminium, which has to be cleaned by different melt treatment operations comes out of two different sources. It may be either primary pot-room or remelted/recycled metal.

This key-note paper introduces in the todays technology but focusses only on the two most important steps of melt cleaning: degassing and filtration. Additional melt treatment operations to be in use in secondary aluminium melters are not considered here.

Aluminium high-tech applications

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 CD´s. The requirements on the material in respect to cleanliness are very high, e.g. as the thickness of a <u>can body sheet</u> is nowadays only < 300 µm. Therefore the number of defects caused by inclusions and gas pores had to be decreased drastically. More than 60 % of the aluminium mill production are used for packaging from which a larger part are <u>aluminium foils</u>. 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 um lead to holes in the foil and cause spoiled products. <u>Lithographic sheets</u> for offset plates have to have a perfect surface.

Figure 1: High-tech application for aluminium

The highest demands in respect to cleanliness exist for material used for the production of computer discs. At CD´s 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.

Impurities in aluminium melts

Impurities in aluminium melts can be divided into "solid inclusions" and "dissolved impurities".

Solid inclusions: Solid impurities in aluminium have different sources. The *exogenous inclusions* may come from the melt environment as the 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- 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 coolin 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: 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 can not be 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 inacceptable gas pores in the produced material. Due to the rather small solubility of hydogen in aluminium melts its removing is a demanding task.

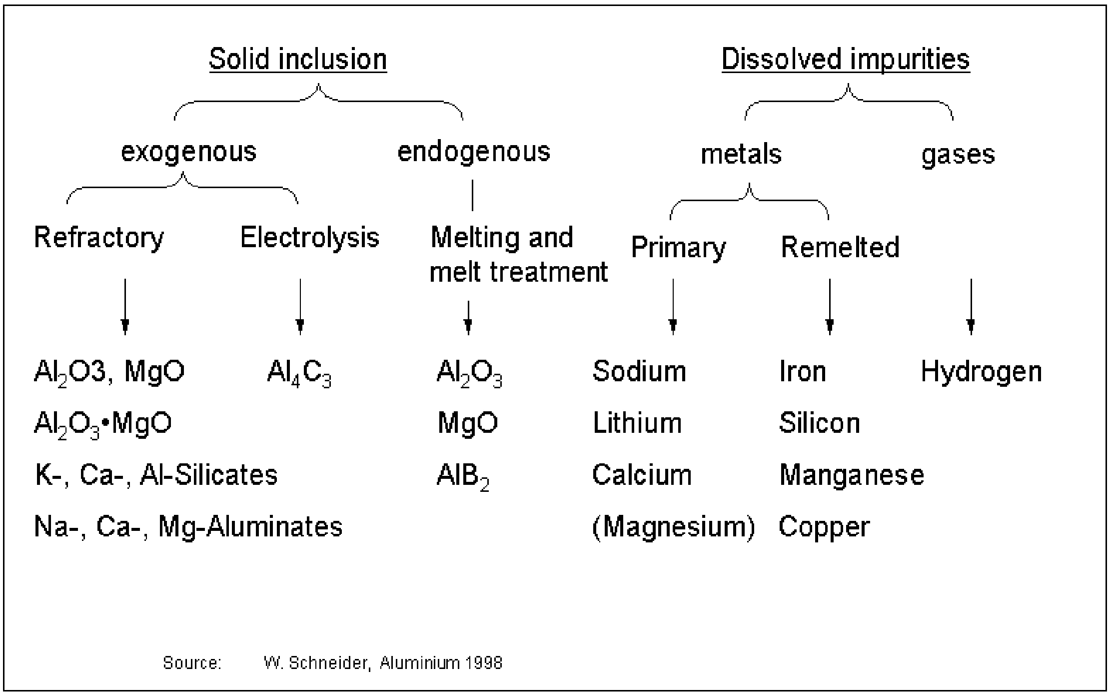

Figure 2: Impurities in aluminium melts

Requirements for clean aluminium melts

Potroom metal contains up to 0.3 ppm H, 150 ppm Na, 20 ppm Li, t 5 ppm Li and more than 1000 ppm of inclusions, mainly as Al_4C_3. The ppm-/ppb-/ppt-concentrations of inclusions are defined as the total volume of inclusions taken as Al_2O_3 related to the volume of 1 kg liquid aluminium. The impurity content of remelted materials sums up to max. 0.6 ppm H_2, to 40 ppm Ca, 10 ppm Na, and some 1000 ppms´s of inclusions mainly Al_2O_3, MgO, $MgO{\cdot}Al_2O_3$,Al_4C_3 and TiB_2.

Inclusions: 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 dropped to less than 10 ppb. Alloyed material for extrusions can contain between a 10 - 100 ppb inclusions. The highest requirements ae exist in respect to melt cleanliness for materials used for computer disc production. They may contain only between approx. 100 - 1000 ppt inclusions.

Dissolved impurities: The alkaline content has to be lowered to a few ppm´s, while the hydrogen content has to be decreased to smaller than 50 ppb (0.05 ppm).

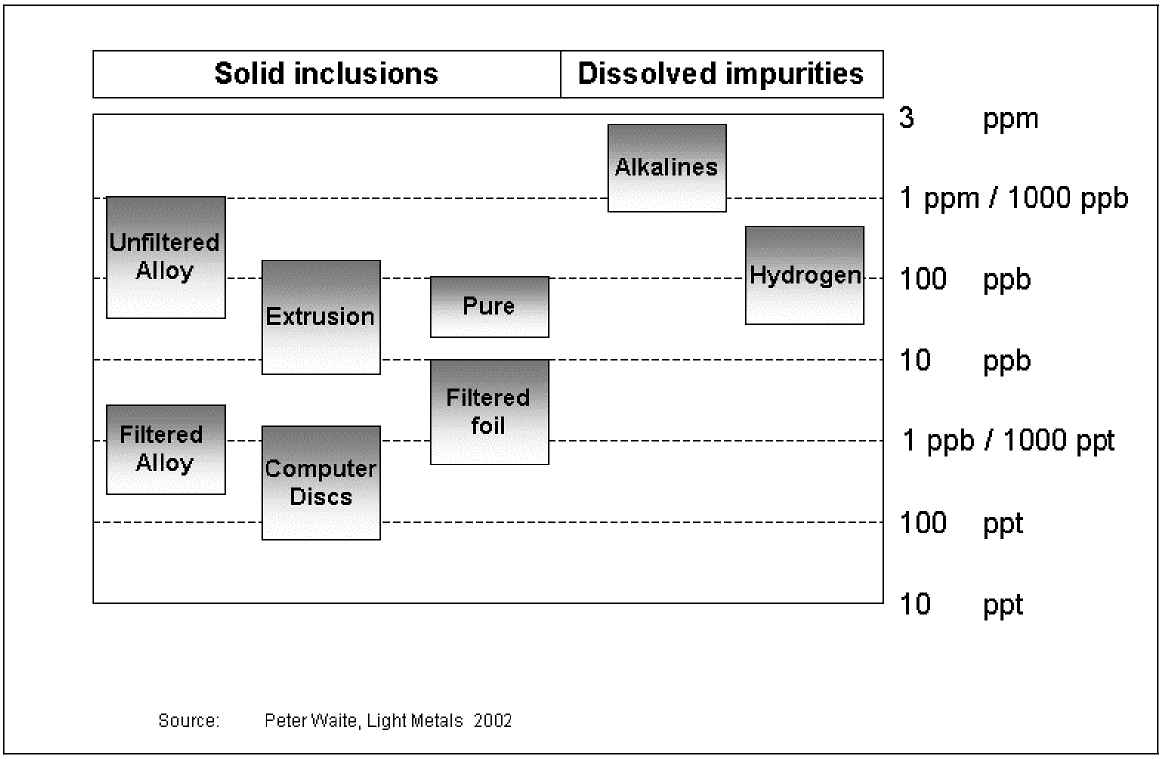

Figure 3: Requirements on metal cleanliness

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.

Possibilities of melt treatment

For the treatment of primary aluminium and secondary aluminium melts a variety of methods are in industrial use. A cheap and simple <u>settling</u> 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 ist only a small density difference between inclusions (e. g. Al_20_3) and liquid aluminium their settling is very slow. Small inclusions do not settle down 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. But a back reaction

$$3\ H_2O + 2\ Al \Leftrightarrow 6\ \underline{H}_{Al} + Al_2O_3 \qquad K_p = a_H / P^3_{H2O}$$

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.

Refining and Cleaning	Aim
Settling	Separation of H_2 and inclusions
Gas purging	Separation of H_2, Li, Na, Mg, Ca and inclusions
Chlorination	Separation of Mg
Filtration	Separation of inclusions
Vacuum distillation	Separation of Mg, Zn and Pb
Addition of primary aluminium	Dilution of metallic impurities as Fe, Si, Mn, Cu, etc.
Addition of aluminium alloys	Dilution of dissolved metallic impurities as Fe, Si, Mn, Cu, Zn, etc.

Figure 4: Possibilities of melt treatment

By a ladle treatment alkaline and earth alkaline metals can be removed by stirring in salts into the aluminium melt mechanically. 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).

By gas purging hydrogen is removed 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.

A 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.

Processing of molten aluminium

The cleaning processing of aluminium melts may start with a ladle treatment esp. of potroom metal for the removal of alkaline metals, before the melt is tranfered into the the casting furnace. There the alloying is carried out and a settling operation may be takes 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 [1, 2].

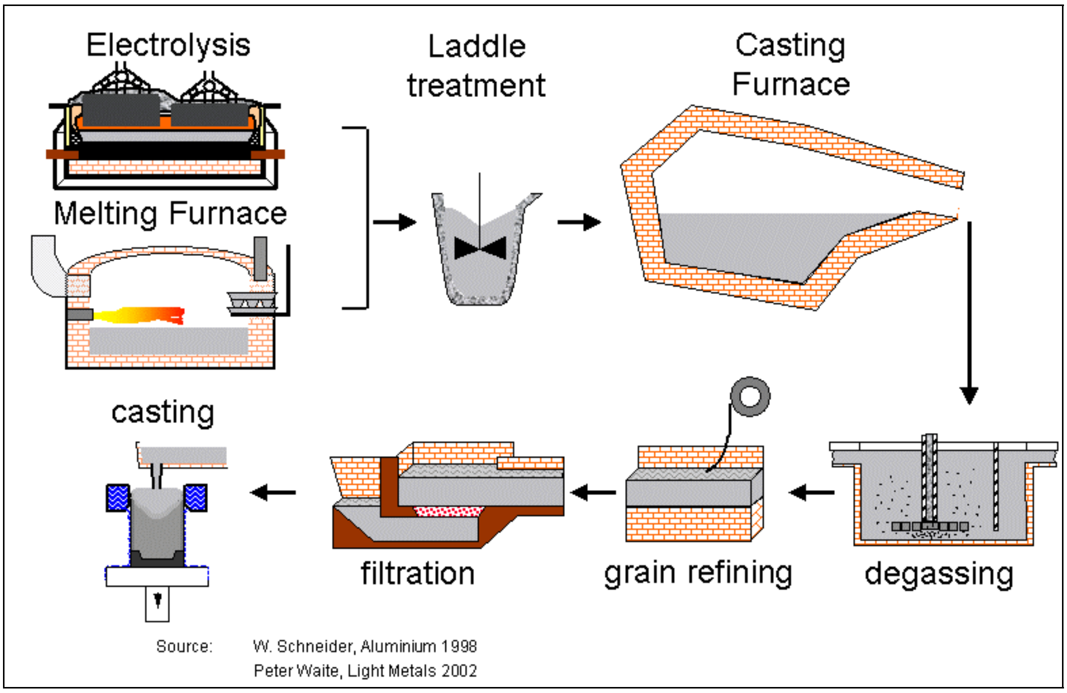

Figure 5: Processing of molten aluminium

Gas purging of aluminium melts

Development of gas purging

First mentioning of gas purging of metallic melts goes back to 1856 for steel [3]. 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 [4]. Based on the basic work of Röntgen and Haas the chlorine/nitrogen converter was deloped and set in operation in 1948 [5]. A couple of those units have been used up to the early 1960ties in Europe. In 1964 the trigas mixture was developed. Carbon-monoxide was added to the chlorine-inertgas 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 focussed 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 alumium industry. At the beginning of the 1990ies 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 desintegrated into very small bubbles by shearing forces. A couple of different in–line systems were developed as the SNIF-,HY/HYCAST-, RDU/RFU-, ALPUR- and the ALCOA-system, which differ mainly in the design of the rotor [6]. 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.

Principles of gas purging

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:

$$\underline{H}_{Al} \Leftrightarrow \tfrac{1}{2} H_2 \qquad K_P = a_H / P_H^{1/2}$$

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 not long enough to reach equilibrium conditions.

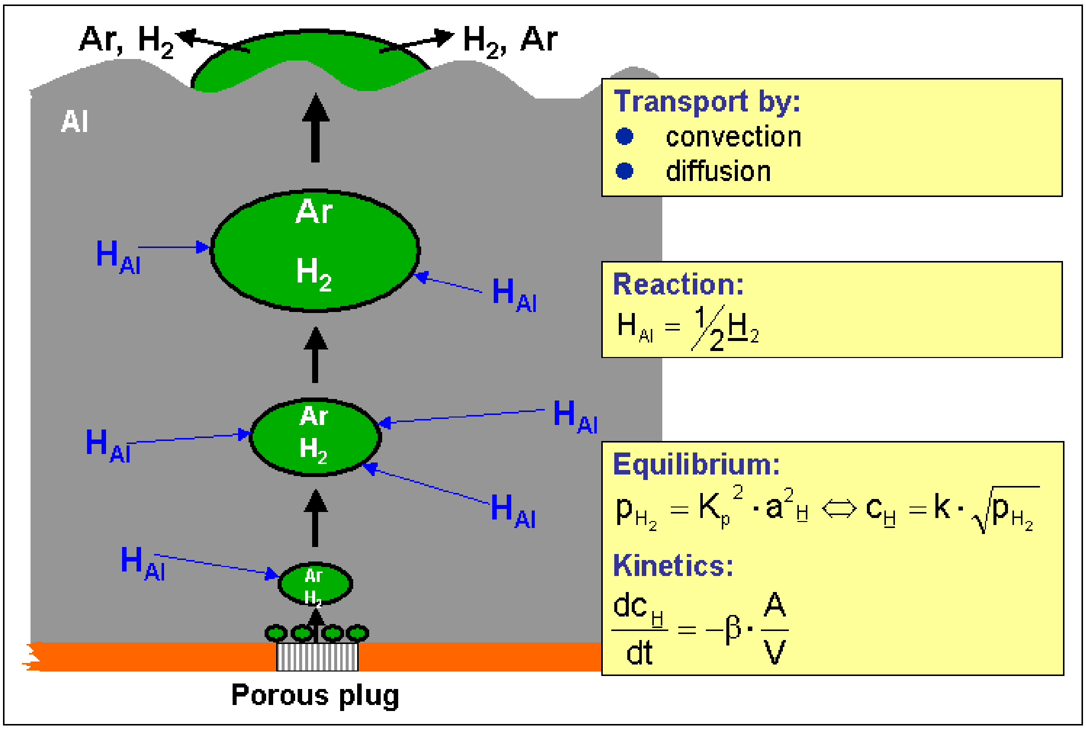

Figure 6: Principle of gas purging

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 rougly by the equation:

$$dc_H/dt = - \beta \cdot x \cdot A/V$$

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-tranfer 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.

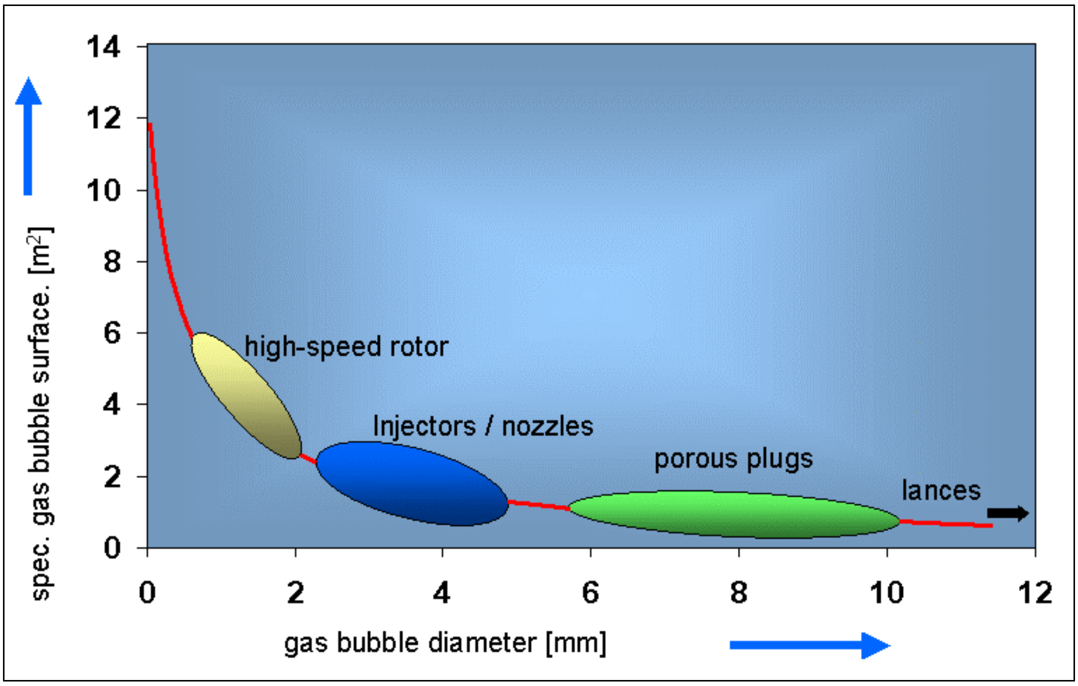

Figure 7: Gas bubble surface versus bubble diameter

While using porous plugs a carefull 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 an bubble source (so called "flooding"). The smallest bubbles can be procuced by the application of high-speed rotor systems like HY/HYCAST, SNIF etc. Lances are almost ineffective for gas purging operations.

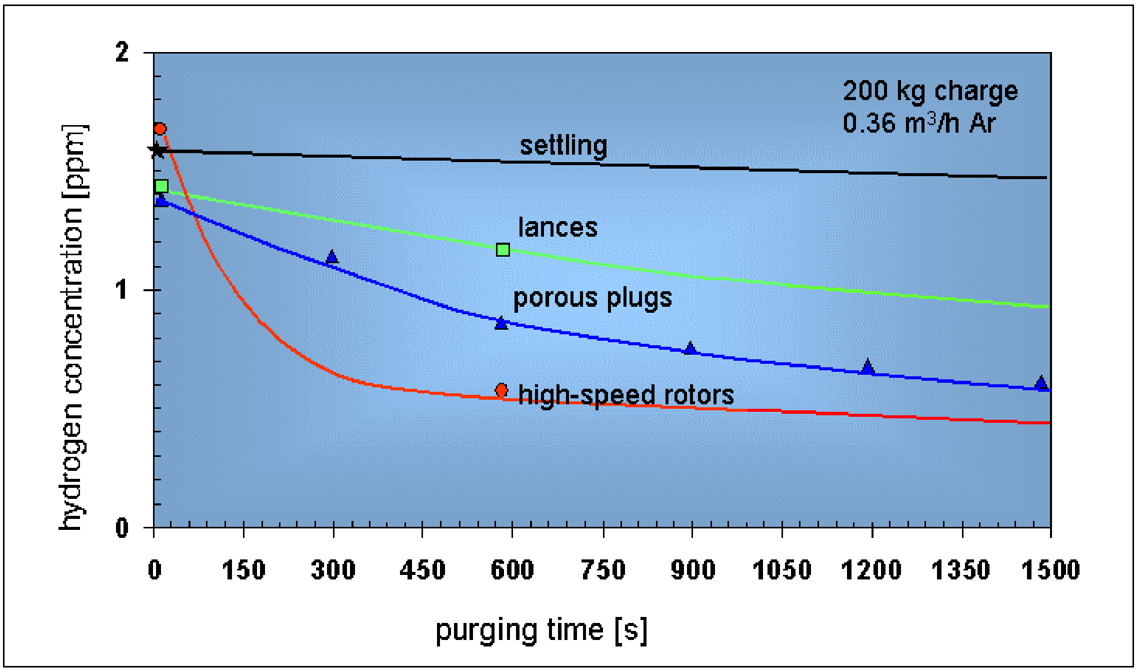

Figure 8: Efficiency of gas purging methods

Gas purging of aluminium melts – State of the art and future challenges

State of the art in aluminium melt treatment is the application of degassing boxes as e. g. the SNIF- or HY/HYCAST-box which are used worldwide. They are installed in-line between casing furnace and grain refing unit. Further developments of the RGI technology are the launder resp. through degassing units using also rotor systems, e. g. the ALCAN Compact Degasser or the HYCAST Ir-60 SIR–system.

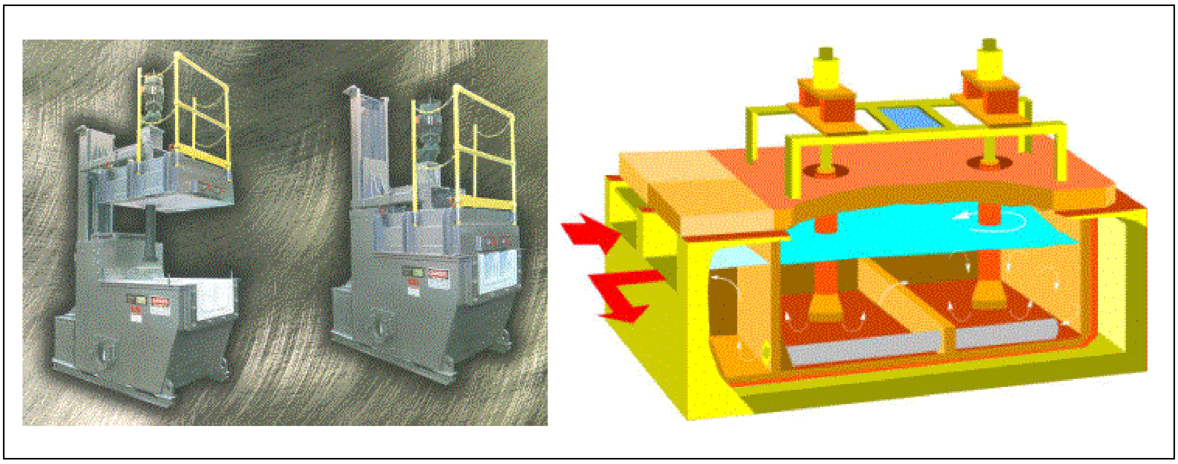

Figure 9: In line aluminium gas purging: SNIF Box

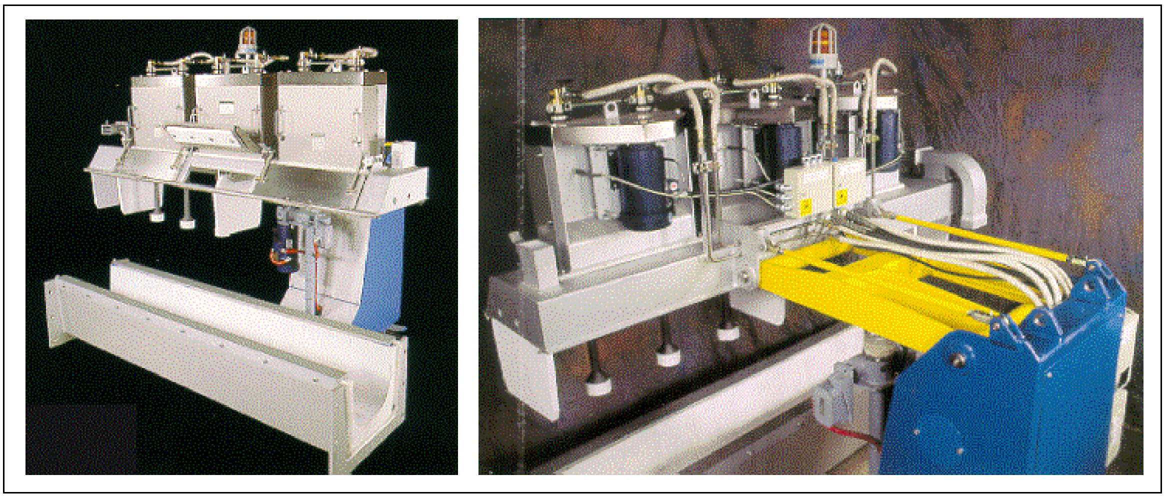

Figure 10: In line aluminium gas purging: Alcan Compact Degasser

Compared to the earlier used degassing boxes like e.g. the SNIF- or the HY/HYCAST-box the launder (compact) degassing technology has following advantages:

- Reduced production costs by
  - diminuished 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 emmissions.
- Reduced space consumption.

All further developments must have have the following targets:

- Increasing the effectiveness of hydrogen (and inclusion) removal by
  - diminuishing 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.

<u>Filtration of aluminium melts</u>

Development of the aluminium melt filtration

In 1935 a procedure was proposed for the filtration of light metal melts by DEGUSSA, which was transfered 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 flters (CFF) started in the beginning of the 1970´s by

SELEE. First rigid media filters (RMF), which are called also bonded particle tube filter´s (BPF), appeared on the market in the 1980ies, but were initially not accepted by the alumium industry. In the 1990ies two stage filter systems were developed having a much better particle removal efficiency. The last advances in filtration technology is the developement of surface active filter systems starting in the mid 1990ies. By the formation of active surfaces inside the filter itself the effectiveness for the separation of small inclusions was significantly improved.

Principles of filtration

For the filtration of molten metals the same laws apply as for aqueous dispersions. Two different kinds of filtration have to be distinguished: cake and bed filtration. Usually both filtration types occur combined and happen succesively. 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 forming 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.

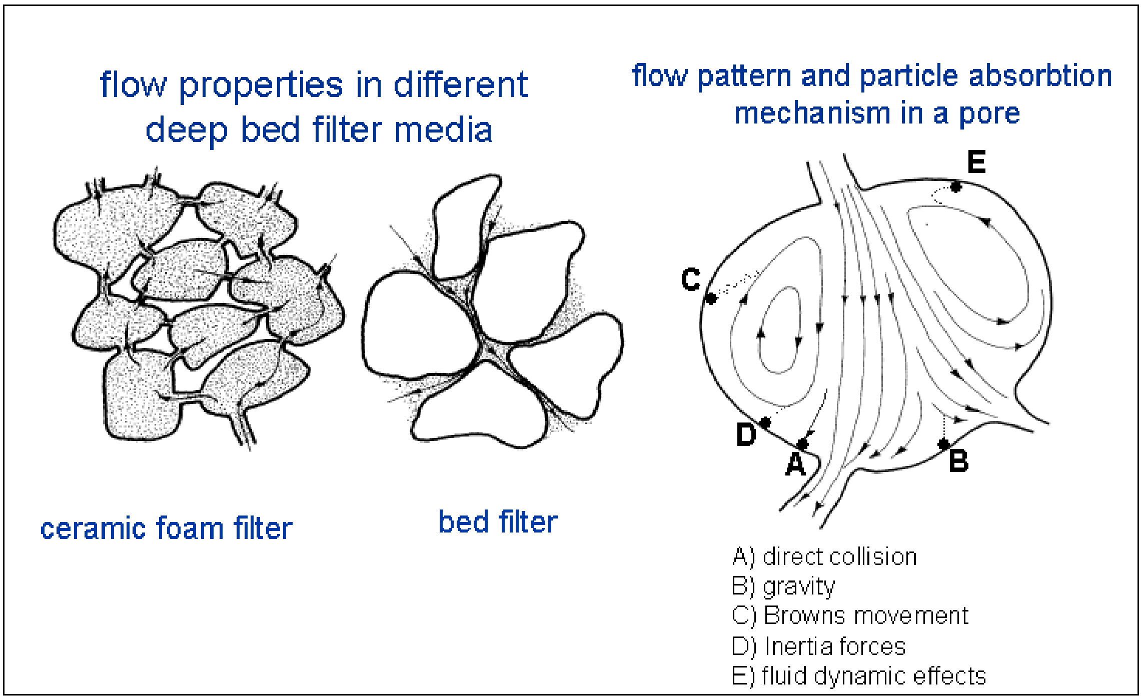

Figure 11: Principles of melt filtration

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 [7]. So a mathematical modelling, which would allow to calculate filtration efficencies, filtration times, filter sizes etc. is not yet possible.

Filter types and systems

The filter materials are generally refractory material, preferentially Al_2O_3. They can be distinguished between

- bed filters (BF),
- ceramic foam filters (CFF) and
- rigid media resp. bonded particle tube filters (RMF resp. BPF).

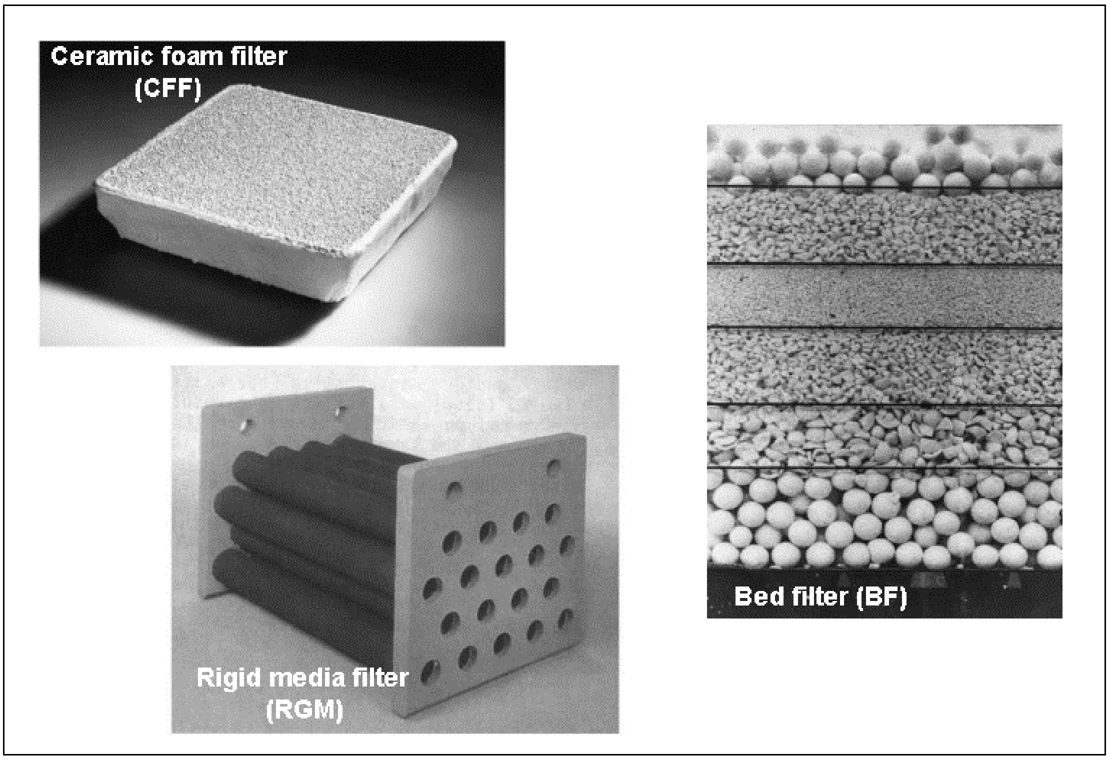

Figure 12: Filter devices for aluminium melt filtration

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 more used. BF´s are separate in-line units, which need rather much space. They are built in externally heatet boxes and are suited for the through-put 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 the aluminium melt happens by deep bed filtration effects. They are produced by the infiltration of a ceramic sludge into a porous polyurethan 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 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 [8].

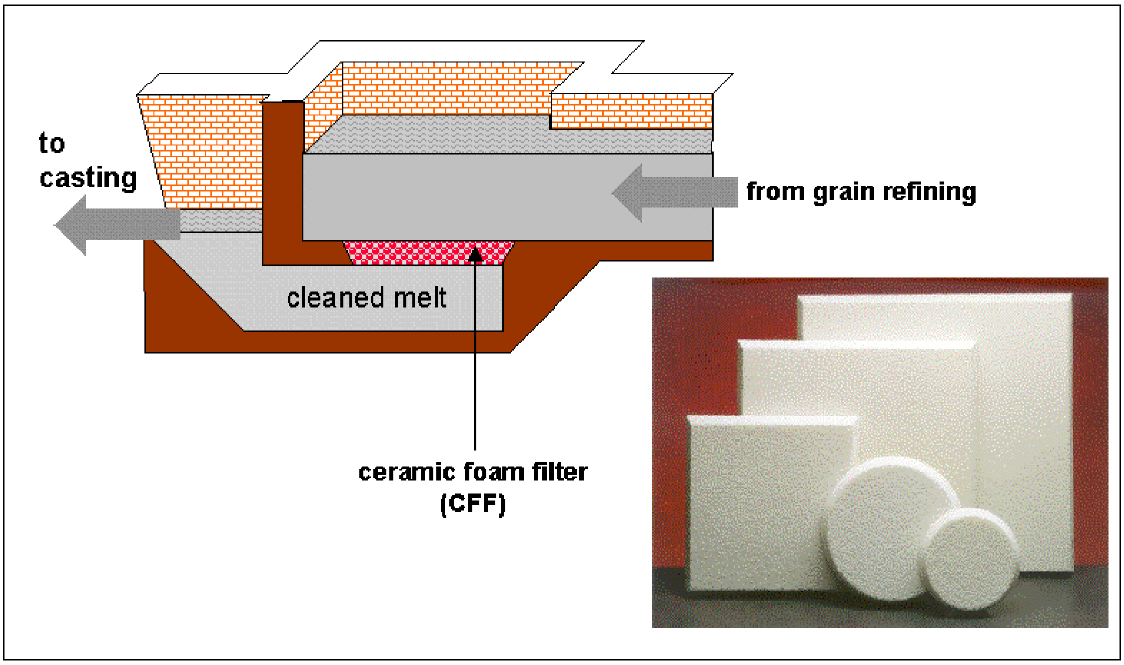

Figure 13: Technology of aluminium melt filtration

Rigid media filters (RMF) consist of porous ceramic tubes, which are built in, as 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 higher pressure drop and they have a shorter lifetime. RMF´s are rather expensive in respect to investment and operation costs, therefore their application is limited to special applications.

Filtration of aluminium melts – State of the art and future challenges

State of the art is the application of deep bed filtration in casthouses, 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 CMF plates or combination of CMF´swith different pore sizes are built in in separate boxes which must not be heated externally. They are are positioned in-line directly before the DC unit. The melt is allowed to run through the filter plate, mostly downwards. CMF´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 come into the melt after filtration. Targets for the filter delopment in future are filters that can remove even finer particles with high efficency at a reasonable pressure drop and with minimized metal losses.

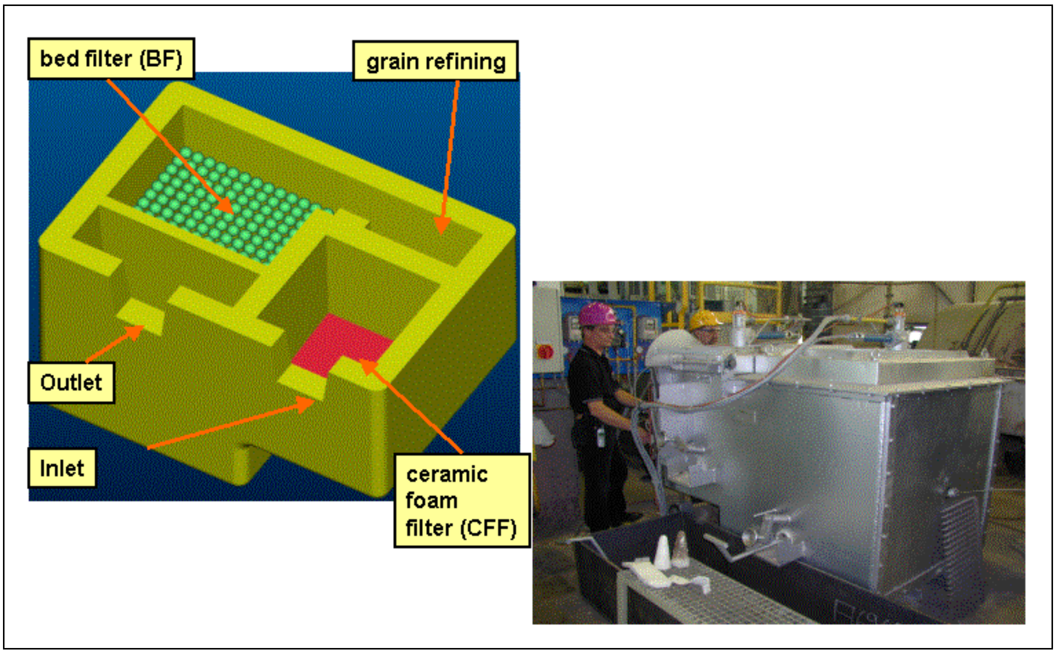

Figure 14: In line aluminium melt treatment: Hydro (VAW)-Filter

Summary

High-tech aluminium products need carefully cleaned, pure aluminium melts for their production. The allocation of those melts can happen only, if a high-tech melt cleaning technology is used. In this presentation selected high-tech applications for aluminium were presented. The basis are the requirements in respect to the metal quality to achieve the necessary melt quality. The types and origins of the different impurities occuring in aluminium melts are described. In more detail the very important process steps in aluminium melt cleaning, the treatment of melts by gas purging and filtration are discussed in respect to process development, cleaning principles, state of the art and future developments.

[1] P. Waite: „ A technical perspective on molten aluminium processing“; Light metals 2002 Ed. W. Schneider; TMS; Warrendale Pa. 2002; pp. 841 ff

[2] W. Schneider, H.-P. Krug, N. Keegan: „ Untersuchung der Wirksamkeit verschiedner Filtertypen für die Filtration von Aluminiumschmelzen, Teil 1“; Aluminium 43 (1998) Nr.10, S. 40 ff

[3] US Patent 23123 (1859): Steward, Christopher and Forward „Refining iron and steel“

[4] W. Koch; „Behandlung von Handelsaluminium und Aluminiumlegierungen mit Chlor und Stickstoff“; Zeitschrift für Metallkunde 34 (1931) Nr. 10, S.. 95 ff

[5] Dautzenberg.W. Die Chlor-Stickstoff- Raffination von NE-, insbesondere Leichtmetallen Metall 4 (1950) Nr. 7/8 ; S.125 ff

[6] K. Krone; Aluminium Recycling; Hrsg. VDS Düsseldorf; Aluminium Verlag Düsseldorf 2000

[7] B. Hübschen; Grundlagenuntersuchungen zur Tiefenfitration von Metallen; Shaker Verlag Aachen 2004

[8] W. Schneider; Gießen von Aluminium-Werkstoffen; VAW Aluminium AG