ALUMINIUM PURIFICATION

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ABSTRACT

The paper presents an overview of aluminium recycling and more specific aluminium purification. Presently common techniques for purification are discussed and new development in this area, as taking place within the EEC framework of the Growth programme (G1RD-CT-2002-00728), are introduced and further elucidated.

INTRODUCTION

Aluminium is the second most used metal worldwide. The European aluminium industry has managed to grow with industries like automotive, aerospace and packaging. Aluminium also has a strong position within the building industry in windows, doors, facades and bathrooms, as well as a range of other daily life products. Current EU countries produce approximately 5.7m tonnes pa of aluminium, employing about 200,000 people related to 31 primary aluminium smelters, 200 secondary plants, 2500 foundries, 60 rolling mills, 200 extrusion plants and 85 foil mills plus converters. This production results in large amounts of run-around scrap, production scrap and consumer scrap. Together with primary aluminium, this run-around scrap forms the raw material input to the cast house. However, the cast house is producing high added value products with increasingly stringent demands on product specifications. Hence it becomes more and more difficult to match input quality with the demands of the output qualities.

One way of solving this problem is by applying good housekeeping, logistics and advanced sorting technologies. Good house keeping inside the production chain demands for careful separation of scrap produced during production. For this scrap, so called new scrap, the compositions are known and keeping the scrap separated during production is the only task. This will be relatively easy when the production takes place only at one plant, but becomes complicated when more plants are involved with the production of an end product. In the latter case good logistics is demanded.

For old scrap, which is material recycled from end products, recycling becomes more difficult. In most of the cases the aluminium is integrated into components existing out of different materials and different alloy. Separation techniques as magnetic separation, eddy current separators etc. allow to separate aluminium from the other materials. Still this recycled material is a mixture of different alloys. Remelting of this material results in a mixed composition and is more restricted in application possibilities. Hence the recycled material is regarded as a low value scrap, difficult to apply in production. Advance sorting techniques as laser sorting makes it possible to separate different alloys from each other. Although the potential of these techniques may be high, still a large volume technique is needed to cope with the problem of increasing amount of mixed scrap. In Europe, a stronger increase in mixed scrap compared to primary production can be expected. This becomes in contradiction with the evolution of producing high added value products with increasingly stringent demands on product specifications. Techniques to upgrade low valued scrap become more and more important in Europe.

ECONOMICAL DRIVERS FOR SUSTAINABLE PRODUCTION

Presently several developments run in parallel on the aluminium market. Of course, in the last decades the application of aluminium, especially in transport, has experienced a major growth and it is expected that this growth continues. Within the different markets for aluminium it is observed that the demand increases for high quality material, both for foundry as well as wrought alloy applications. Therefore, a strong demand exists for primary aluminium and quality recycled aluminium.

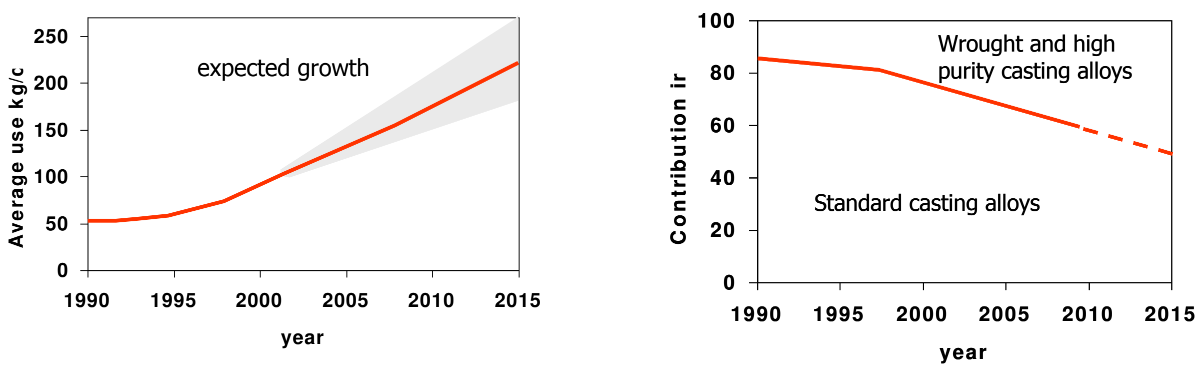

Figure 1, Development in the aluminium and recycling market. Right) The increased demands in aluminium forecasted for the coming decennia's, right) the change in quality demands

On the other hand, many products produced from aluminium have a lifetime of 10 years or even more. Therefore, the waste material of these products enters the recycling market in about 10 years from now. Taking into account that the need for high quality material still increases there will be an unbalance between the available low-value scrap and the need for high quality input material. Consequently, the margin between waste or recycled aluminium and the high quality aluminium increases. At this stage purification becomes a critical but also economical feasible route for production of high quality input material.

TACKLING THE PROBLEM

Purification, state of the art

Most of the contaminating elements are fully dissolved in the recycled material or entirely integrated (such as coatings, cast rotor windings, integrated parts). At this moment no technology is available which separates, in an economical interesting process, the contaminants from the material at room temperature. This leaves purification as only alternative. In strict sense purification implies upgrading (purifying) the melt by any kind of technique. Such a technique should force the element contaminants to segregate from the aluminium. This can be done by either focussing on the aluminium during its solidification process or by taking advantage of specific properties of the dissolved elements. In the former mentioned approach one makes advantage of the fact that in the first stage of aluminium solidification, the first formed crystals are almost pure aluminium crystals. Typical applications of this approach are

Partial solidification of aluminium

When aluminium solidifies pure crystals are formed. The impure melt can then be removed by filtration or flotation. Several Japanese and European firms have used such a process on pilot scale and possibly in full scale to produce pure aluminium from low alloyed materials (Ref. 1, 2, 3, 4). Australian firms have developed a method using a differentially heated column (Ref. 5, 6, 7). The process has been tried for low-alloyed material with success. A Chinese firm has developed a similar method for tin where the crystals are moved in the melt through a heat field (Ref. 8). This process is used in full scale for low-alloyed tin.

Partial remelting

When metal is heated, the phases with the lowest melting point start to remelt. This process has been used to remove lead and other elements on a laboratory scale. A variation of this method, zone refining, has been used to remove impurities on a small scale. It can be used to obtain very pure aluminium or other metals. The process has been considered to be too slow for aluminium alloys on full scale.

Other approaches focus more on eliminating the dissolved contaminants. By using their specific properties as solubility, electro/chemical response or thermodynamic stability when dissolved with other elements, specific elements can be removed. Typical techniques are:

Three layer electrolysis

This process is used industrially to produce very pure aluminium from commercial aluminium. Al 99.7 (Ref. 9, 10, 11). The method is expensive and not suitable for purification of scrap.

Evaporation and Distillation

This can be used for removal of volatile elements such as magnesium and zinc. The process has been used at laboratory scale with success and tried out on a pilot scale. The melt has to be stirred heavily and it takes place at low pressure (<1 bar) in the melt furnace (Ref. 12, 13). Årdal and Sunndal Verk (Ref. 14) used an analogous process, dynamic vacuum degassing, for removal of hydrogen and sodium in aluminium. If a lower pressure can be obtained, then this process may possibly remove magnesium and zinc.

Reaction

When aluminium is treated with specified fluorides or chlorides, elements like magnesium, calcium and/or sodium will react with the salt and particles are formed. These particles can be removed by flotation or by letting the melt move through a filter. This method is in industrial use for removal of sodium and calcium but not magnesium (Ref. 15, 16, 17, 17, 18).

Crystallisation

When elements like manganese or calcium are added to aluminium melts, inter-metallic particles can be formed and subsequently removed by filtration, centrifuging or flotation. The result can be a melt low in elements like Fe, Si and/or Cu. The process has been tried out with limited success (Ref. 19, 20, 21, 22, 23).

Boron treatment

When aluminium melts are alloyed with boron, borides are formed. Since the solubility boride is low in aluminium melts, elements like Ti, V and Zr can be removed. The method is used by the aluminium industry (Ref. 24; 25).

Low temperature chemical reactions

Aluminium alloys can be selectively dissolved in several media. The remaining phases can be subsequently removed by filtration or flotation. Then the aluminium solution can be electrolysed at low temperature and aluminium can be precipitated. This process may be an effective way of splitting the metal into inter-metallic particles and relative pure metal. The process has never been tried out on larger scale and may be too slow.

Gas purging

Removal of hydrogen, alkali metals and non-metallic inclusions is done by various gas purging methods (Ref. 26, 27, 28, 29, 30) but the concentration of those impurities is mostly very low.

From the above mentioned only a few have been tested out in laboratory and pilot scale. A few have been used in full production for which it should be mentioned that these processes mainly focus on production of ultra clean aluminium. Within this market sectors, the amounts are relatively small. Therefore, one cannot speak about purification as process for recycling

PURIFICATION BY FORMATION OF INTERMETALLICS

Solidification back ground

As most of the aluminium products are made of an alloy rather than the pure aluminium, the solidification does not take place at a certain temperature but rather over a temperature interval. This process in elucidated in Figure 1 where the situation of a so-called hypoeutectic alloys is shown. In these systems the solidification starts with the formation of almost pure aluminium crystals. This particular behaviour is the base of some of the aforementioned purification processes as partial remelting, partial solidification and fractional crystallisation.

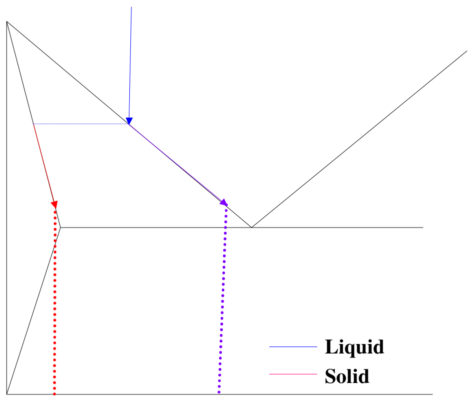

Figure 1, Simple phase diagram illustrating the solidification process

As the temperature drops during the process, more alloying elements can dissolve in the growing aluminium crystals. Still, the crystals contain far less alloying elements as the original melt. Therefore during the growth of the crystals the amounts of alloying elements in the remaining melt increases. This increase comes to an end as the concentration reaches a limit (eutectic composition) above which normally also other reaction products can form. These products are combinations of aluminium with the alloying elements. Typical reaction products are for example Al_6Mn, Al_3Fe, Mg_2Si. In most of the cases, these reaction products, called intermetallics, form in parallel with the formation of the aluminium crystals. This becomes evidently when looking at the aluminium structure after casting (Figure 2). Here, clearly the aluminium crystals can be seen (denoted with Al) which are formed in the earliest stage of the solidification process. During the second stage, also intermetallics form (dark particles) between the remaining aluminium resulting in a complex structure of small particles between the aluminium (denoted with Eutectic).

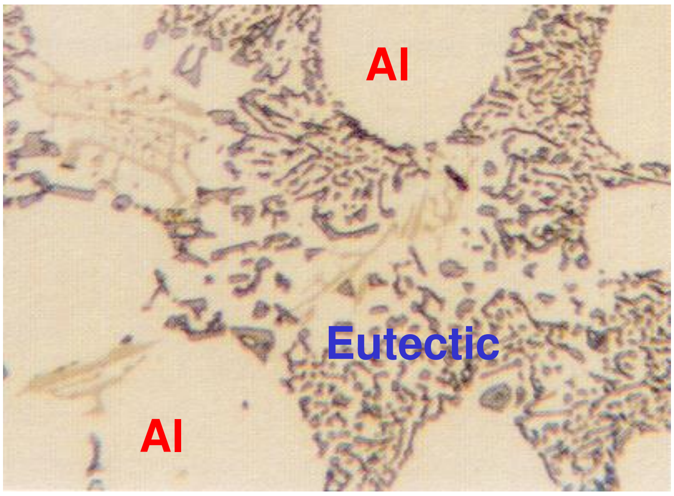

Figure 2, Typical Aluminium structure after casting clearly showing the aluminium crystals (earliest formed material) and the region where the combined formation of Intermetallics and aluminium took place (denoted with eutectic)

The process of purification by Intermetallics

The intermetallic is a compound existing out of different metallic elements. Therefore, the intermetallic carries a part of the aluminium contamination. Removal of the intermetallics from the melt during the solidification process therefore would purify the melt. For example a frequently found intermetallics in an aluminium iron alloy would be Al3Fe. By removing this intermetallic during the solidification process one can quite efficiently remove Fe from the melt with theoretical efficiencies of 90% or more.

As one can conclude from Figure 2, showing the strong coupling between the aluminium structure and the intermetallics after casting, removal of intermetallics will not be easy. During the solidification process they normally form, for standard alloys, quite late in the solidification process. At this stage, the aluminium crystals have become already quite large and separation of the intermetallics will be almost impossible. New routes and processes need to be developed in other to apply this process for purification of aluminium.

Creation of intermetallics

As intermetallics will form anyway in most of the solidification processes the challenge is the control over the formation process of intermetallics. Conditions, which should be full filled, are the separate formation of the intermetallics from the aluminium and the size of the intermetallics, which should be large enough to be removed. A part of the MAP project focuses on the process of generating intermetallics in a controllable way where several routes have been investigated.

The first route investigated was based on the assumption that small addition of trace elements could initiate the nucleation of ‘new’ intermetallics, which contain a high amount of the contaminating elements. A large-scale experimental procedure has been set-up (ref. 31) in order to find possible new intermetallics.

New routes are investigated which show that it might be feasible to create intermetallics in a 'divorced' way from the primary aluminium crystals.

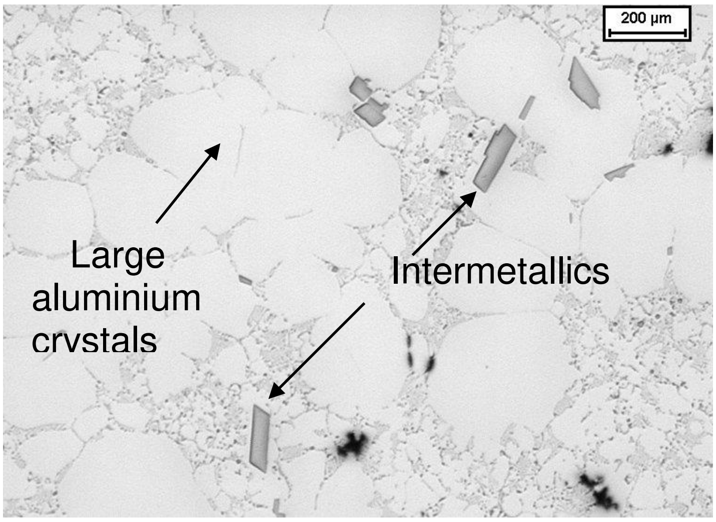

Figure 3, sample taken from a typical experiment in the MAP project showing the existence of intermetallics separated from the aluminium primary crystals

Removal of intermetallics

Once the intermetallics are formed, they need to be removed from the material to be purified. At this stage the material exists out of at least 3 different phases; the primary formed aluminium crystals, the formed intermetallics and the remaining melt. Techniques are needed to separate these phases from each other. This removal technology with precise temperature control should have very high yields and low losses. Different techniques to perform this separation are investigated and developed in side the MAP project. In each of these fields major advances have been made.

APPLICATION OF THE PROCESS

Application in Industry

The industrial application of the purification process, as developed within the MAP project, is applicable at smelter plants, cast houses or at the production of master alloys. Considering the application at a smelter plant (production of primary aluminium using electrolysis) the method can be applied parallel to the primary aluminium production. The method should be seen as a second production route to produce input material for the wrought alloy market where low grade recycled scrap material, used as input material, could be upgraded.

Economical even more interesting would be an inline implementation within a cast house production route (Figure 4). A simple device needs to be developed, including the intermetallics generation part as well as the removal unit, which can be added in the melt stream. In this way an effective application of the process is designed, reducing the cost for melting, operation (man power and facilities) and losses. Application in this way allows usage of low valued input material, obtained from the open scrap market, for production of high-end wrought alloy products as extrusion billets or rolling ingots.

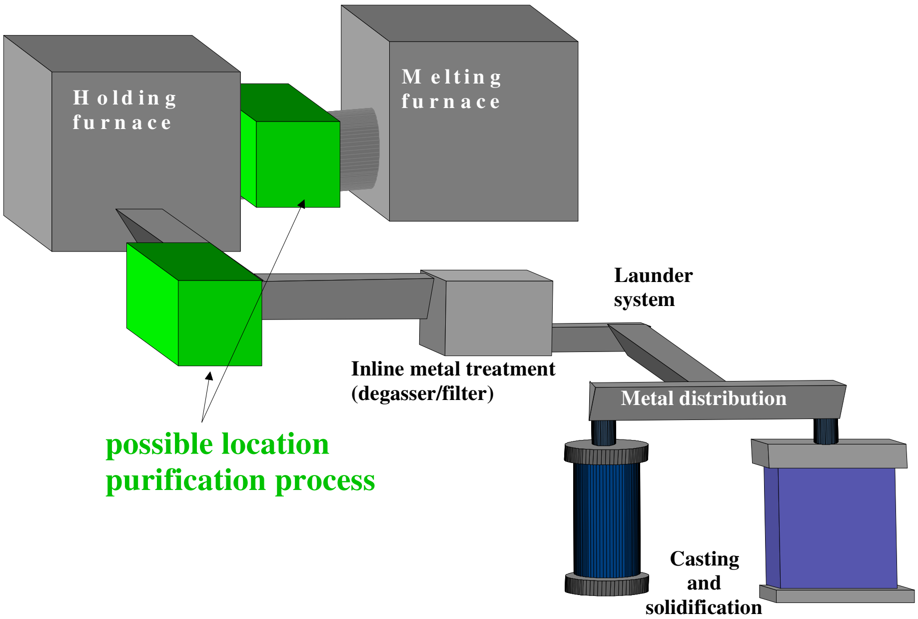

Figure 4, Schematic representation of the application of the MAP process inside the existing production process of ingot and billet casting

CONCLUSIONS

From an economical and environmental perspective new techniques are needed for recycling of aluminium. At this stage, development of an advanced purification techniques seems a viable route to go. The present article outlines the development as presently in progress within the MAP project. Several steps have been made to develop an economical interesting process, which allows producing, within existing production routes, purified aluminium starting with low-grade scrap.

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REFERENCES

1. R. K. Dawless, R. E. Graziano and A. A. Bonarett: "Fractional Crystallization Process", US-patent 4,221,590 (September 9, 1980)
2. French patent no 1.594.154 [1970],
3. Japanese patents no A-56-55530 (1981) and A-57-82437 (1982) to Showa Aluminium K.K

4. Japanese patent no A-57-171640 [1982] to Sumitomo Aluminium and Sumitomo Chem. Ind. K.K.
5. J. D. Esdaile, G. W. Walters and J. M. Floyd: Australian-patent 48570/72 (1972)
6. J. D. Esdaile and G. W. Walters: "Continuous reflux refining of metals", US-patent 4 043 802 (1975)
7. J. D. Esdaile, A. B. Whitehead, G. W. Walters and W. T. Denholm: "Method and apparatus for promoting solid-liquid flow", US-patent 4 138 247 (1977)
8. M. G. Li et al.: ”Verfahren und Anlage zur Raffination von Rohzinn bzw. Entfernung von Blei und Wismut aus Rohzinn (in chinese), CN 85107356A dated 3.9. 1986
9. Hopper og Hoopes: U.S. Patent 673,374 (1901)
10. Yazawa A., S. Nakazawa and T. Kurosawa: "Vacuum Refining of Aluminium and its alloys", Proc. Fourth Int. Conf. on Vacuum Metallurgy, Tokio (1974) pp180-184
11. W. T. Denholm og M. Rossiter: "Production of Super-Purity Aluminium", "Aluminium melt treatment and casting" 7:1-7:10; Red.: N. Madhu, University of Melbourne (1991)
12. M. Ohtaki and H. Kudou: ”Application of some vacuum distillation process to refine Zn from aluminium scrap,” Japan Institute of Light Metals, Tsukamoto Sozan Bldg., 6F, 4-2-15 Ginza, Chuo-ku, Tokyo, 104-0061, Japan, 1998, Aluminium Alloys: Their Physical and Mechanical Properties, s. 357-362 Conference: ICAA-6: 6th International Conference on Aluminium Alloys, Toyohashi, Japan, 5-10 July 1998, Publ: The Japan Institute of Light Metals
13. Aarflot and F. Patak: “Dynamic vacuum treatment of molten aluminium and its alloys”, Light Metals 1976, volume 2, pp 389-402, Ed.: S. R. Leavitt, Met.Soc AIME, New York
14. G. Dubé and V. J. Newberry: “TAC – A novel process for the removal of Lithium and other alkalis in primary Aluminium”, Light Metals 1983, pp. 991-1003
15. B. Gariépy, G. Dubé, C. Simoneau, and G. Leblanc. "The TAC Process: A Proven Technology" Journal of Metals Vol. 36 No. 11 November 1984 pp. 40-43
16. Bornand,J-D; Buxmann, K.. DUFI: a Concept of Metal Filtration. Swiss Aluminium Ltd.,The Metallurgical Society/AIME
17. Rasch B.,Myrbostad E., Hafsås K., Proc. Of Ligth Metals, TMS, Ed. Welch B., San Antonio, pp. 851-854, (1998)
18. Wærnes Aud N., Hansen Søren G., Tuset J. Kr, Rasch Bjørn, Ligth Metals,TMS, Ed. Eckert C. E., San Diego, pp. 861-867, (1999)
19. M. Nagao, K. Oosumi og T. Nakamura: ”Removal of impurity silicon from molten aluminium alloy with compound method”, J. Japan Institute of Light Metals 46 (11) 588-591 (1996)
20. M. Nagao and S. Nishi: ”Equilibrium between Silicon and Calcium in molten Aluminium”, Aluminium alloys 1 (1998) 242-248
21. Flores A., J. Escobedo, J. Méndez and M. Méndez: ”Kinetic mechanisms of iron segregation from Al-Si-Cu-Fe-Mn melts”, Light Metals 1992, s.845-850, Red.: E. R. Cutchall, TMS., USA

22. Hwa-Soo Kim, S.-C. Kang, K.-J. Kang og M.-H. Dzo: ”A study on the Fe Removal in the Aluminium and Aluminium-Silicon Alloy”, J. of the Korean Inst. of Met. & Mater. 34 (1996) 1040-1049

23. T. Takeshi: ”Method for removing iron from aluminium alloy material”, Japansk patent JP 08035021 (1996)

24. P. S. Cooper and M. A. Kearns: ”Removal of Transition Metal Impurities in Aluminium melts by boron additives”, Materials Science Forum, 217-222 (1996) 141-146

25. G. Dube: "Removal of impurities from molten aluminium", US-patent 4507150 (1982)

26. K. Krone. Aluminium-recycling, vom Vorstoff bis zur fertigen Legierung. Vereinigung Deutscher Schmelzhütten e.V. Düsseldorf BRD 2000

27. L. Butterwick and G.D.W. Smith. "Aluminium Recovery from Consumer Waste - I. Technology Review" Conservation and Recycling Vol. 9, No. 3, pp. 281 - 292, 1986

28. D.V. Neff. "The Use of Gas Injection Pumps in Secondary Aluminium Metal Refining" Recycle and Secondary Recovery of Metals Proc. Int. Symposium pp. 73-95. Fort Lauderdale FL USA 1 – 4 December 1985. Eds. : P.R. Taylor, H.Y. Sohn, and N. Jarrett

29. D.V. Neff and B.P. Cochran. "Chlorination Technology in Aluminium Recycling". Light Metals 1993 pp. 1053-1060

30. J.G. Stevens and H. Yu. "A Computer Model of a Stirred Tank reactor in Trace Alkaline Elements Removal from Aluminum Melt - the Alcoa 622 Process". Light Metal 1986 pp. 837-845

31. Alexander Pisch, Christoph Kräutlein, Pierre Le Brun, Georg Rombach, Paul de Vries, Marc Ryckeboer, Christian J Simensen, Submitted to Light Metals 2005, Conference proceeding of the TMS annual conference, San Francisco