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IN-LINE TREATMENT OF MOLTEN ALUMINUM

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Abstract

Most commercial methods of fluxing aluminum alloys to produce low H_2, Na and inclusion content ingots rely upon furnace fluxing with gaseous mixtures that include chlorine or chloride salts resulting in copious fume generation. A considerable reduction in amount of chlorine required to achieve high quality metal was accomplished by use of a combination filter bed and argon gas scrubbing tower introduced eight years ago. The present paper describes a new, two step, in-line fluxing system which provides even greater reduction in air pollution while producing metal of the low H_2, Na and inclusion content required for high quality wrought products. First unit in the new process contains relatively large refractory particles through which Ar-Cl_2 gas is passed countercurrent to metal flow. The second unit contains a filter bed of finer refractory particles and also has a countercurrent flow of Ar-Cl_2 gas. Neither Cl_2 nor chloride fumes are detectable in the atmospheric samples from either fluxing unit. In first plant operation overall chlorine consumption was reduced 90%.

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Introduction

Commonly accepted methods of fluxing aluminum to remove sodium, hydrogen, and nonmetallics have been batch treatments with chlorine, mixtures of chlorine and inert gases, or a compound containing chlorides. Despite the potential hazards of using chlorine and chlorides for fluxing, the industry generally agreed that their use was essential to attaining the quality metal required. Substituting other fluxing methods generally fell short of capabilities obtained with the chlorine or chloride systems. Increased metal quality requirements, coupled with the demands to reduce furnace cycle, almost completely ruled out any method of metal treatment except batch treatment with chlorine or chlorides.

There have been many improvements made both in chlorine and chloride handling systems to minimize potential hazards and contain and treat fumes generated. However, the rising cost of pollution control has made fume elimination increasingly more desirable. Approximately 10 years ago, Alcoa began supplementing furnace fluxing with in-line filters for removal of inclusions and/or hydrogen (Ref. 1). The combination system provided a means to reduce fluxing time and the amount of chlorine required for a given metal quality. Increased production rates and some reduction in air pollution resulted while meeting critical metal quality requirements. However, total elimination of chlorine fluxing in a furnace was not possible using only these systems and development work continued.

Alcoa's commitment to flux metal without fume received a boost when the Federal Government passed the Air Quality Act of 1967 and the Clean Air Amendments of 1970. It quickly became apparent that regulations imposed on composition and visibility of stack effluent could not be met when fluxing an open hearth with chlorine or mixtures containing chlorine without fume collection and treating facilities.

Alcoa developed a fumeless, in-line fluxing system which will do the total job of metal treatment while eliminating the need for any fluxing in furnaces. Designated the Alcoa 469 Process, the system treats metal as it flows from the melting furnace to the casting pit, using refractory bed type filters and a fluxing gas mixture comprising essentially a nonreactive gas with small amounts of chlorine.

Process Description

The Alcoa 469 Process utilizes two types of filter beds, primary and secondary, with a mixture of chlorine and nonreactive gas flowing countercurrent to the metal passing through each unit (Figure 1). The most important part of the system is the unit with the packed filter bed which has been designated the primary unit. A roughing type filter, designated the secondary unit, is generally employed upstream of the primary unit to extend process life. Both units remove sodium, hydrogen, and inclusions, with the primary unit having the higher efficiency.

Packed refractory beds serve both to distribute the fluxing gas mixture and act as impingement type filters. Hence, the size of the nonmetallics removed from the molten metal is considerably smaller than the interstices of the bed. The filter bed may be of any refractory inert to molten aluminum, sufficiently hard to prevent fracturing or powdering during use, and of a specific gravity greater than molten aluminum. The material must also be inert to chlorine at the operating temperature of molten aluminum. Of the several materials which suit these requirements, tabular alumina is the preferred refractory, although any form of calcined alumina may be considered.

The primary filter bed is made up of 2 to 10 in. (5.08 to 25.40 cm) of 1/2 or 3/4 in. (1.27 or 1.90 cm) diameter balls covered with a 6 to 10 in. (15.24 to 25.40 cm) layer of -3+6 mesh (-6.35+3.37 mm) flake. The balls are used to: (1) assist in distribution of the fluxing gas, (2) support the -3+6 mesh flake above the baffle, thereby maintaining a uniform metal flow through the filter, and (3) retain the filter bed in a fixed position, preventing the washing of the bed granules into the ingot. The secondary filter bed consists of a 6 to 15 in. (15.24 to 38.10 cm) bed of 1/2 or 3/4 in. (1.27 or 1.90 cm) diameter refractory balls. The cross sectional area requirement of the refractory bed in each unit is determined on the basis of 10 to 60 lb of metal per hour per square inch (0.71 to 4.24 kg per hour per cm^2) of effective bed area depending on metal treatment required.

The fluxing gas mixture for both units consists of a nonreactive gas containing small amounts of a chlorine-containing gas, usually chlorine. Inert gases such as helium, neon, argon, krypton, and xenon are also suitable, although argon is preferred because of its effectiveness, availability, and modest cost. Nitrogen and carbon dioxide are not used to avoid the possibility of forming nitrides, oxides, carbides, and their complexes within the units. The amount of nonreactive gas through each unit is related to the cross sectional area of the filter bed. Nonreactive gas flow per unit of bed area is set as high as possible to achieve maximum hydrogen removal with a minimum of molten metal surface turbulence at the top of the units. Typical rates range from 0.05 to 0.2 scfh per square inch (2.3 x 10^{-4} to 9.2 x 10^{-4} standard m^3 per hour per cm^3) of filter bed.

The chlorine portion of the fluxing gas may be any type of chlorine-containing product which reacts with impurities in molten aluminum. Examples are chlorine, aluminum chloride, and certain chlorinated hydrocarbons such as hexachloroethane. However, chlorine is preferred as it is readily available at reasonable cost, is effective and relatively easy to handle.

The chlorine gas is introduced to provide 1 to 10 parts chlorine to 100 parts of the nonreactive fluxing gas on a volume basis. The actual amount used depends on the trace elements which are to be removed from the molten aluminum during processing. The amount may range from the stoichiometric quantity up to ten times stoichiometry. Even for the higher concentrations, the amount of chlorine gas involved is so small that any excess readily reacts with a miniscule amount of magnesium or aluminum in the alloy being processed. As shown in Table I, fluxing 20,000 lb (9,100 kg) of metal with a chlorine flow of ten times that required to remove Na and Ca results in only 0.017 percent reduction in magnesium content.

Although fluxing gases can be introduced to the refractory bed separately using a separate diffuser for each gas, it is preferred that the gases be mixed to provide a homogeneous mixture which is continuously introduced through a common dispersing system. The fluxing gas mixture must be dispersed uniformly across the entire cross section of the filter bed. This can be accomplished with any number of porous materials which are relatively inert to molten aluminum and chlorine at elevated temperatures. Porous alumina, porous graphite, and porous carbon are three commonly used materials.

Results

The Alcoa 469 Process has been evaluated extensively both in the laboratory and in a number of plants. Typical efficiency of the basic process is tabulated in Table II for most common alloy systems. In all cases, the Alcoa 469 Process was employed as the only means of metal treatment, and furnace fluxing was totally eliminated.

Process efficiency was monitored by measuring the hydrogen contents in all cases, and the sodium concentrations in most cases. The inclusion content has not been quantified as no good test exists to measure oxide content in aluminum.

Fast neutron activation analysis (FNAA) has been employed and generally shows treated metal to contain less than 4 ppm total oxygen. However, FNAA has not yet demonstrated a degree of reproducibility at the levels required for adequate confidence in the figures. Of commercial value, the Alcoa 469 Process has consistently reduced inclusion content to a level comparable with previously employed fluxing systems on the most critical applications.

The first and last examples in Table II demonstrate fluxing with only primary type filters to produce metal with a very low hydrogen and inclusion content. Alloy 1145 was fluxed to 0.08 ml H_2/100 gm and the ingot produced was satisfactorily rolled to 0.00035 in. (8.85×10^{-4} cm) foil with a normal pinhole count of less than 15 per square foot (160 per m^2). Alloy 7175 was fluxed to 0.11 ml H_2/100 gm and the forging ingot had an absolute minimum of ultrasonic indications. Mechanical properties of the forgings produced from this metal were excellent. Foil, memory disc, and forging stock are about the only applications where it has been desirable to use two primary type filter beds rather than a secondary and a primary. As expected, two primary filter beds are more efficient filters than the normal arrangement, but they have less process life.

The second example demonstrates the ability of the process to flux 3004 alloy to an excellent purity level using a minimum of chlorine. Metal was treated at the rate of 10,000 lb per hour (4,555 kg per hour) using a total of 50 scfh (1.5 sm^3 per hour) argon and 2 scfh (0.06 sm^3 per hour) chlorine. Sheet produced from this ingot was comparable to that produced by normal furnace fluxing.

The third and fourth examples illustrate the minor effect of metal flow rate on process efficiency. Alloy 5182 is consistently fluxed to 0.0001 percent Na and less than 0.15 ml H_2/100 gm, a very satisfactory purity level. Fluxing gas flow rates ranged from 3.5 scfh (0.1 sm^3 per hour) chlorine and 50 scfh (1.5 sm^3 per hour) argon at a metal flow of 10,000 lb per hour (4,555 kg per hour) to 11 scfh (0.33 sm^3 per hour) chlorine and 189 scfh (5.67 sm^3 per hour) argon at a metal flow of 18,000 lb per hour (8,200 kg per hour). These examples also demonstrate the fume free nature of the process even when chlorine flow rate greatly exceeds the stoichiometric requirement for removal of sodium and calcium.

The fifth example demonstrates typical results when fluxing extrusion alloys with the conventional Alcoa 469 Process. The critical parameters of sodium, hydrogen, and inclusion content are readily held at levels which maximize production rates in both the ingot and fabricating plants. Virtually all small diameter extrusion ingots produced by Alcoa are treated with this new process.

A unique feature of the Alcoa 469 Process is the excellent life of the refractory filter bed. The fluxing gas mixture de-wets inclusions and back flushes the filter bed continuously. Chloride reaction products are simultaneously swept to the metal surface by the same purging action. Thus, the effective filter bed life is extended appreciably beyond that of the same type of filter operated with only nonreactive gas. In one instance the processing life of a filter bed was increased from 3,000,000 lb (1,360,000 kg) with only argon gas flow to over 7,000,000 lb (3,180,000 kg) by using argon with a very small amount of chlorine. In another plant, adding a small amount of chlorine to the nonreactive gas flow provided a 50 percent increase in filter bed life while allowing the elimination of furnace fluxing.

Both filter beds employed in the Alcoa 469 Process may be rejuvenated in place during idle periods in the casting process. The task is relatively easy to accomplish in terms of manpower and time, and the rejuvenated filters have a life almost as long as a new filter bed. Four rejuvenations are not uncommon before the units must be replaced. It is not uncommon to treat 10,000,000 lb (4,550,000 kg) of metal with the Alcoa 469 Process before replacing the fluxing units.

Figure 2 shows that refractory bed particles removed from a used filter bed of the type described in Ref. 1 are normally a cohesive mass bound together by oxides and aluminum. Particles removed from an Alcoa 469 filter bed after a comparable period of time are quite clean and relatively free flowing.

The gas mixture also produces a dry skim which is easily handled. The skim is low in aluminum content and contains oxides and chlorine reaction products. Normally there is no evidence of molten $MgCl_2$ or other salt on the surface of the metal in the fluxing unit. Evidence of any molten salt would be an indication of improper chlorine gas flow.

The result of using these small amounts of chlorine is reduction of undesired trace elements to very low levels with an absence of detectable fume. Chlorine and chloride measurements made with Mine Safety Appliances Co. detectors indicate zero parts per million chlorine and chloride in the atmosphere immediately above the fluxing units.

Summary

The Alcoa 469 Process simultaneously reduces hydrogen, inclusions, and undesirable trace elements to very low levels without fume. The process eliminates need of prior furnace fluxing with chlorine or compounds containing chlorides. A nonreactive-reactive fluxing gas mixture is bubbled countercurrent to metal flow through two types of packed refractory particle bed filters, the primary and secondary units. Normally, the nonreactive portion of the fluxing gas mixture is controlled at 90-99 percent argon; balance of the mixture is chlorine. Proportions are dependent on quality requirements of the aluminum alloys being treated. Chlorine flow is carefully balanced to react with the undesirable trace elements in a nearly stoichiometric manner so the process is free of chlorine or chloride fume.

Typical purity of metal treated by the Alcoa 469 Process is 0.12 ml H_2/100 gm, 0.0001 percent sodium and an acceptable inclusion level. This level of purity is normally achieved using a total of 4-40 scf (0.12 to 1.2 sm^3) nonreactive and 0.4-4.0 scf (0.01 to 0.12 sm^3) reactive chlorine gas per 1000 lb (455 kg) of metal treated. Metal flow rates in excess of 50,000 lb per hour (22,700 kg) have been treated successfully in production.

Commercial use of the Alcoa 469 Process has established a capability of metal purification that meets all known government pollution standards without requiring fume handling equipment. Capital expenditures to install the Process are much less than that needed to install chlorine fluxing on a furnace and treat the fume generated. Contrary to normal anticipation when considering consequences of anti-pollution laws, operational benefits can result from the process through lower operating costs when compared to conventional furnace fluxing. Plant tests indicate total treatment can be accomplished for 0.05 to 0.10 cents per pound.

Reference

1. K. J. Brondyke, P. D. Hess, Transactions, AIME, 1964, p. 1553.

TABLE I

MAGNESIUM REDUCTION AT 10 TIMES STOICHIOMETRIC Cl_2 FLOW

Data:

Metal flow - 20,000 lb/hr (9,100 kg/hr)
Sodium reduction - 0.0015 to 0.0001%
Calcium reduction - 0.0020 to 0.0001%

Calculation:

Na and Ca reduction requires 1.106 lb (0.5 kg) Cl_2/hr
10X the quantity = 11.06 lb (5 kg) Cl_2/hr)
Excess chlorine = 11.06-1.11 = 9.95 lb (4.52 kg) Cl_2/hr
9.95 lb Cl_2/hr reacts with 3.41 lb (1.55 kg) Mg/hr

Result:

For metal flow of 20,000 lb/hr (9,100 kg/hr) Mg loss at flow of 11.06 lb (5 kg) Cl_2/hr = 0.017%

TABLE II

TYPICAL EFFICIENCY OF ALCOA 469 PROCESS

Example No.	Alloy	Metal Flow lb/hr	Unit Size[1] (lb/hr/sq in. inlet area) Unit 1	Unit 2	Gas Flow (scfh)[2] Unit 1 Cl_2	Unit 1 Ar	Unit 2 Cl_2	Unit 2 Ar	Wt. % Na Fce	After Unit 1	After Unit 2	H_2 Level (ml/100 gm) Fce	After Unit 1	After Unit 2
1*	1145	17,500	26	26	5	50	5	50	--	--	--	.24	.14	.08
2	3004	10,000	40	40	1	25	1	25	.0011	.0003	.0001	.25	.18	.10
3	5182	18,000	12	12	8	92	3	97	.0014	.0002	.0001	>.45	.25	.15
4	5182	10,000	40	40	2.5	25	1	25	.0012	.0002	.0001	.40	.25	.12
5	6XXX	8,000	14	14	1	40	1	50	.0015	.0005	.0001	.35	.23	.10
6*	7175	15,000	21	11	2	100	2	100	--	--	--	.30	.22	.11

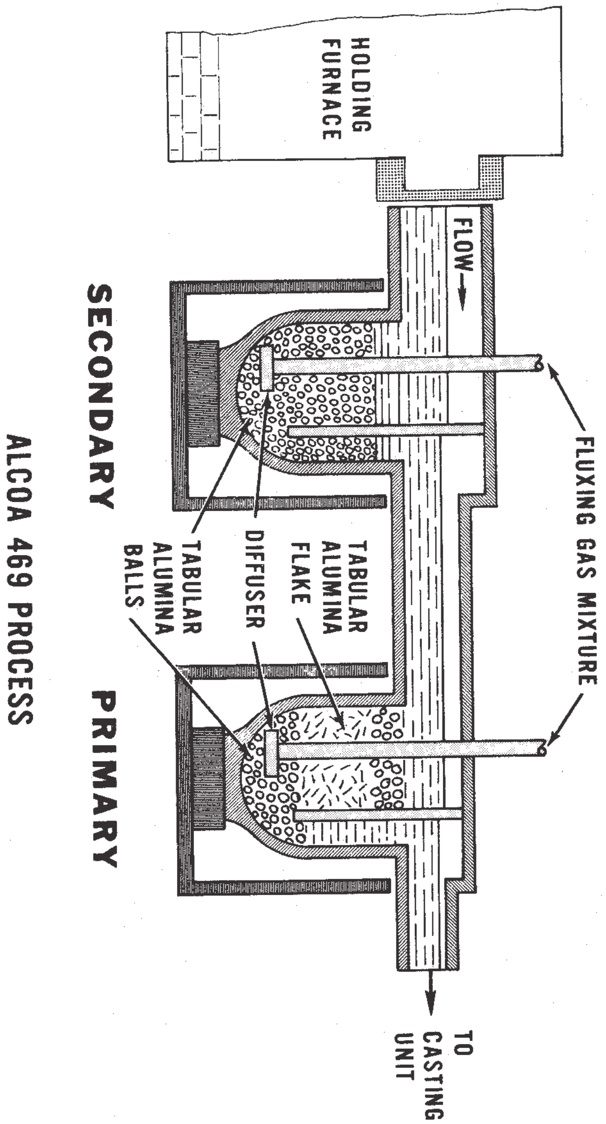
Note: A - Alcoa 469 Process consists of primary and secondary units unless otherwise noted.

B - Hydrogen determinations were made on molten aluminum by a Telegas instrument.

[1] Multiply by 0.07 to get kg/hr/cm^2

[2] Multiply by 0.03 to get standard m^3 per hour

*Both units primary



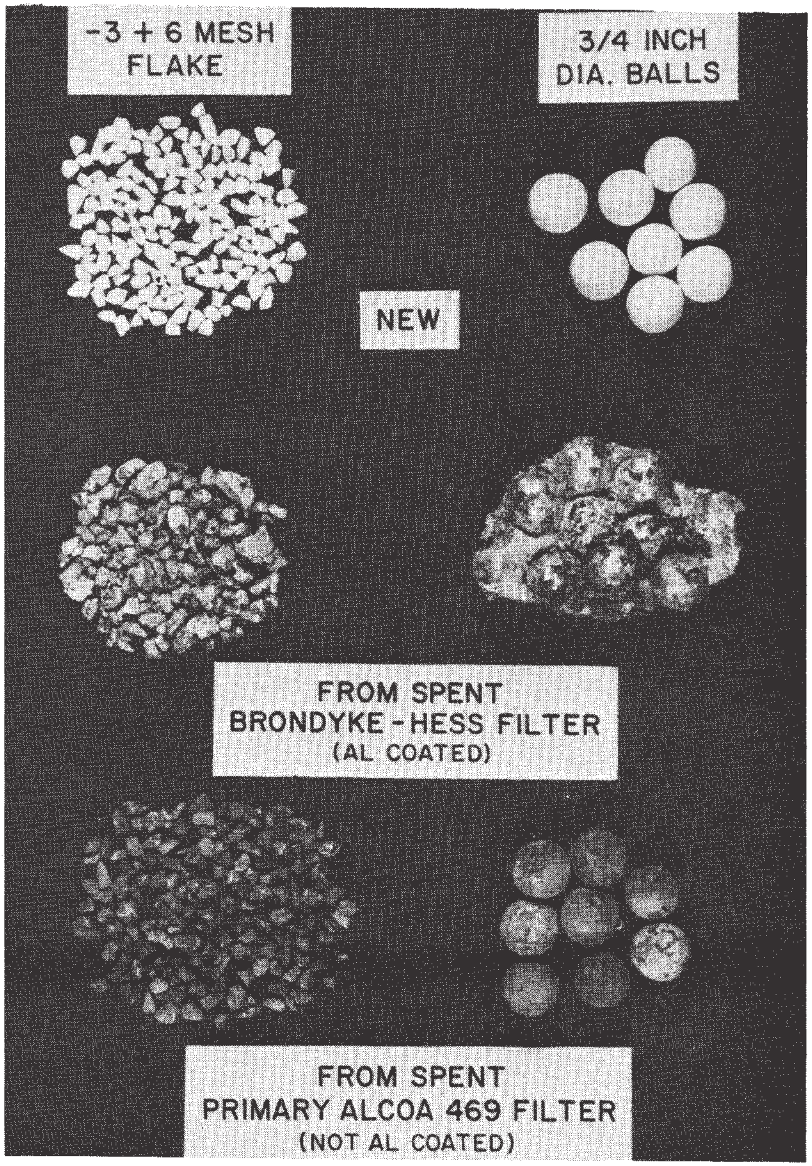


FIGURE 2 - Condition of Tabular Alumina Filter Bed Media