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Special feature

The latest molten metal refining processes in cast shop

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[Abstract]

As the demand for high quality Aluminum has been increased, the molten metal refining processes in cast shop has been more and more regarded as important. Furthermore, nowadays both molten metal quality and environmental issues are important and the demand from environmental aspect is increasing particularly in Europe and the USA. As regards to the behavior of Hydrogen in molten Aluminum and the mechanism of degassing, many reports and presentations have been made so far [1)~7).] Here this paper presents the recent foreign molten metal refining system to be applied in furnaces and in-line process.

[Refining process in furnace]

Even in the case where any in-line molten metal refining process (degassing and filtration) is used, the molten metal refining process in furnace is required to improve molten metal quality. Injection of gas mainly consisting Chlorine into molten metal has been common method as for molten metal refining process in furnace, which has been employed by refining and casting plants throughout the world. TAC[8)] system (Alcan) removes Sodium as dross (Na_3AlF_6-AlF_3-Al_2O_3) by converting Sodium in molten metal to Na_3AlF_6 using Fluoride.

On the other hand, MIXAL[9)] method (Pechiney) injects Ar-20%Cl gas using rotary injection device. The fundamental object of these methods is preliminary cleaning of molten metal before casting, i.e. removal of Hydrogen, non-metallic inclusions and alkaline metals. These methods have additional objects for maintenance such as reduction of deposit on hearth or furnace wall by making non-metallic inclusions such as oxide films, oxide particles, etc. generated in volume during melting process floated to molten metal surface and separated, and making Aluminum dross on molten metal surface dry. It is acknowledged that Chlorine has the effect of removing non-metallic inclusions because $AlCl_3$ bubbles generated by reaction with molten Aluminum absorbs suspended particles in molten metal, floats to molten metal surface and changes to dry dross which is not readily mixed with molten metal.

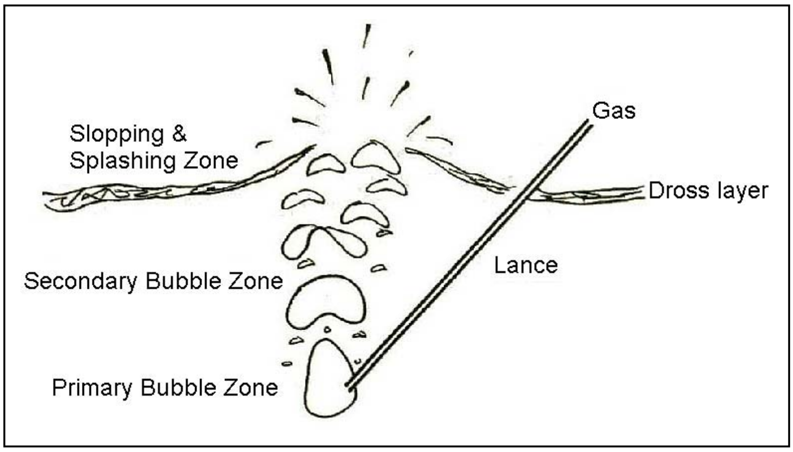

Figure 1：Gas injection with lance

In the case of injection with single opening lance pipe, oxide films on molten metal surface apt to be broken by splash due to floating large gas bubbles and to be mixed with molten metal, and furthermore as for alloys containing Magnesium, dross volume may increases because alloys react with atmospheric air depending on conditions[10).] As countermeasures against the above, graphite lance pipe having many small openings, porous plugs or porous plates set on the furnace bottom are used in actual Chlorine refining process. It is reported that, in the USA, simultaneous treatment of inclusion removal and metal circulation is conducted by generating fine gas bubbles with combination of a lance pipe and a metal pump. C. Celik and others[11)] reported that, treatment of pure aluminum with Chlorine was inefficient since large gas bubbles coming out from lace pipe was not retained in molten metal and floated to molten metal surface, whereby substantial

Hydrogen chloride gas and Aluminum oxides was generated.. On the other hand, as shown in Table 1, C. Celik and others demonstrated that treatment with Chlorine injected by rotary nozzle was very efficient and such backwash was less[11].

Average values	Injection type	Free Cl_2 (%)	Cl^- (%)	Fraction Emitted (%)	$MgCl_2$ Formed (%)
Pure Al	Lance	1	99	100	-
1% Mg	Lance	7	41	48	52
5% Mg	Lance	4	22	26	74
5% Mg	Rotor	1	5	3	95

Table 1.: Comparison of qualitative emission depending on alloy and injection type [11]

In the case of injecting inert gas, as the above effect can not be expected, fluxes (powder fluxes) containing active Fluoride or inorganic Chloride is injected with Nitrogen gas. However, both Chlorine and flux injected into molten metal readily float up and the residence time is short. Thus, these do not effectively react with molten metal and are apt to be emitted as non-reacted Hydrogen and hydrogen Fluoride. Consequently, injection of fluxes with inert gas is ineffective and has environmental issues.
Alcan developed the equipments (RGI, RFI) which inject gas and fluxes through the rotary nozzle. G. Beland and others reported that the rotary nozzle flux injection technique exhibited high efficiency for alloys 1000, 3000, 5000 and 6000[12]. M. A. Thibault and others reported that in comparison with the conventional Chlorine injection with lance pipe, Alcan Jet Stirrer could maximized utilization efficiency of Chlorine by injecting Chlorine under molten metal surface, by which Chlorine consumption could be cut by half[13].

Figure 2: Mobile type PHD-50

In view of the above, it can be acknowledged that the injection treatment using the rotary nozzle system is much more efficient owing to generation of fine bubbles and molten metal circulation and moreover leads to environmental improvement in terms of less emission of non-reacted gas. The SNIF technology (current Pyrotek Inc. SNIF Division) further evolved into SNIF PHD-50 (mobile type) and SNIF HD2000 (fixed type), which generate fine bubbles and stir molten metal by simultaneous injection of gas and flux and exhibit the maximized flux treatment efficiency.

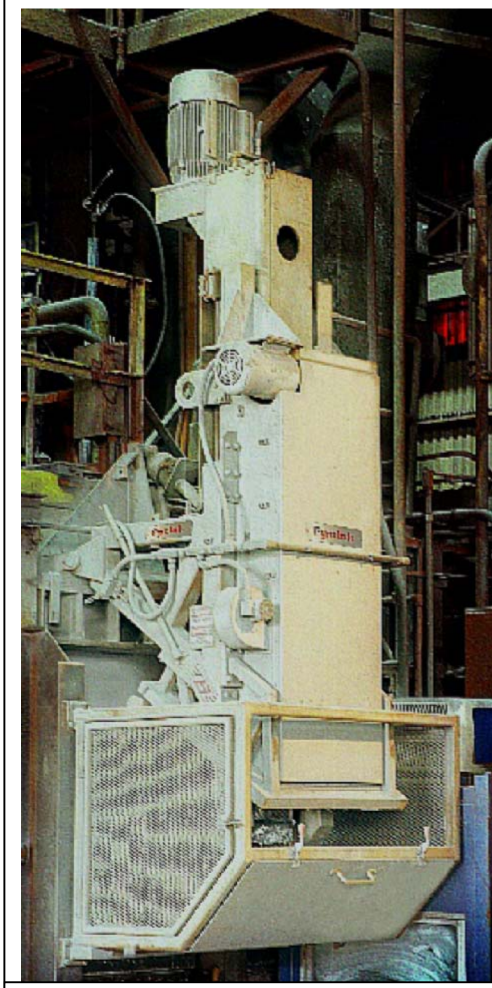

Figure 3: Fixed type HD2000

These equipments circulate molten metal. Accordingly, these are applicable to large sized furnaces and can be utilized as molten metal circulation system. It was confirmed that pre-fused granular formed refining flux, carnalite (PROMAG®) is optimum as refining flux for injection and was almost smokeless and odorless. It is also acknowledged that PROMAG® has the effect of removing alkaline earth/alkali metals such as Sodium, Calcium, etc. and non-metallic inclusions. Furthermore, $AlCl_3$ and molten salts generated in molten metal absorb inclusions, float up and form dry dross. Thus, it can be expected that PROMAG® also enables easy dross off operation in addition to inclusion removal effect. Melting point of carnalite type flux is 470C°. It changes to molten salt readily, that absorbs inclusions and contributes to reduction of Alkaline metals in molten metal and does not readily emit non-reacted hydrogen chloride. Table 2 refers to the result obtained by using PHD-50. Al-2.4%Mg-0.25%Mn-0.25%Si Alloy was produced from recycled Aluminum ingots and returned material using 37tons induction smelter.

	Before treatment	After treatment	Removal ratio
Na	13.3	2.9	78%
Ca	13.0	6.0	54%

1) Alloy: Al2.4%Mg-0.25%Mn0.25%Si
2) Treatment temperature, time: 710C° 20mimutes
3) Promag addition rate: 0.5kg/ton

Table 2: Actual result withPHD-50 / Promag

Figure 4: Treatment with PHD-50

As mentioned above, the introduction of fine bubbdle injection system using spinning nozzle/rotary nozzle in place of lance pipe injection has been promoted mainly in the USA and also in order to clear way for hazardous property of chlorine treatment drastically, Carnalite type liqui flux injection system using spinning nozzle/rotary nozzle has become widely used in Europe and the USA. In practice, Chlorine and mixed gas was reduced to half for a start by injection and was phased out fully while confirming performance.

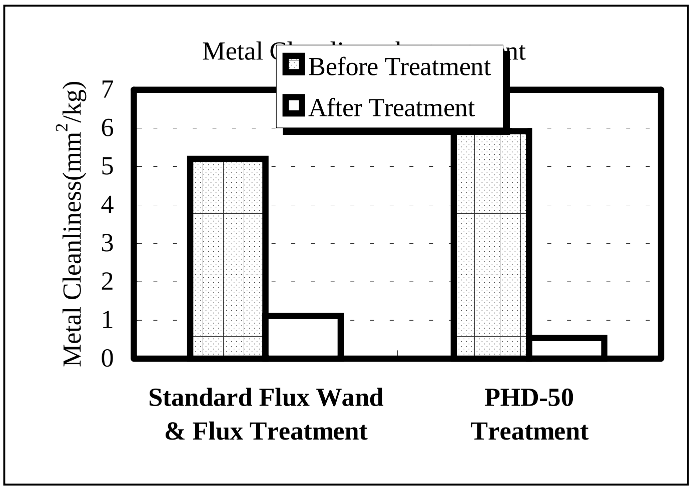

Figure 5: Inclusion removal efficiency

Figure 5 shows inclusion removal effect of the conventional flux injection and PHD-50 in PoDFA value. During this test, in-furnace treatment was carried out injecting argon only for 20 minutes using PHD-50 and inclusion removal efficiency was compared with the conventional method of 30 minutes flux injection. It is acknowledged that PHD-50 has molten metal cleaning effect owing to fine bubbles. It was reported that actual operation of fixed type HD2000 unit for 80tons furnace demonstrated reduction of Chlorine consumption to half, shortening of treating time from four hours to one hour and cut-down of dross to one third. Major manufacturers mainly in the USA have started to introduce such type equipments. The effects are summarized to the following five points. Finally, abolishment of chlorine will proceed.

- Efficient molten metal treatment owing to fine bubbles generated by rotary nozzle.
- Reduction of Chlorine and flux consumption, and shortening of treating time.
- Control of non-reacted gas emission owing to fine bubbles and environmental improvement.
- Treatment throughout furnace area by rotary nozzle.
- Improvement of metal loss by diminishing turbulence on metal surface.

[In-line degassing equipment]

A number of in-line degassing equipments had been on the market and had been presented by many persons. The basic technical trend started with porous plug to generate fine bubbles at the initial stage, continued with method to release fine bubbles from small openings of fixed nozzle, then rotary nozzle system. In these days, the rotary nozzle system dispersing fine inert gas bubbles prevails practically and SNIF[14) 15)], GBF[16) 17)], Alpur[18) 19)], Hycast[20)], ACD[21)] and 622 process[22) 23) 24)] are in operation.

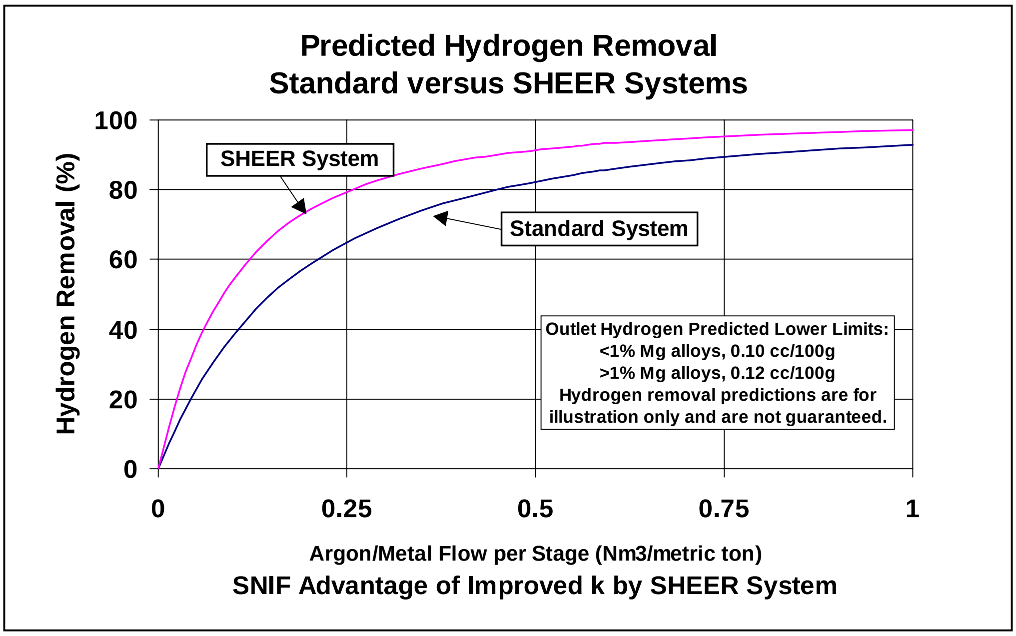

Figure 6: Degassing efficiency with SNIF SHEER technology

As for in-line metal treating equipments, design technique of treatment vessel in addition to rotary nozzle design greatly affects on the metal refining performance of the system, but this point is discounted contrary to expectation. Vessel design is important for not only residence time of molten metal in vessel, but also for controlling flow pattern of molten metal and fine bubbles, by which gas-liquid reaction is enhanced and also inclusion trapping efficiency is improved owing to collision of inclusions and bubbles. Scholars and experienced technical experts in Europe and the USA have made comments on respective rotors, but only few reports gave consideration from vessel design point of view. Needless to say, combined technique of rotary nozzle and vessel design brings out high molten metal refining effect.

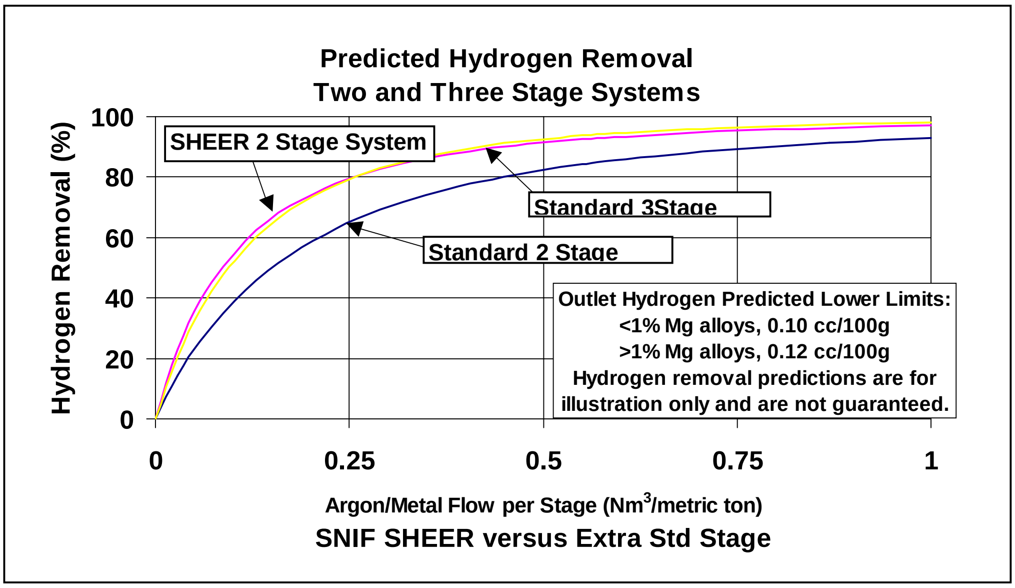

Figure 7: Degassing efficiency comparison between SHEER and none SHEER

SNIF makes much of high-density fine bubbles and bubble residence flow pattern and GBF, in addition to high-dense fine bubbles, focuses on mixing efficiency of bubbles and molten metal to enhance gas-liquid reaction. Both systems focus on increasing volume and density of fine bubbles to trap inclusions. That is to say, great emphasis is placed on not only gas miniaturizing technology but also how to generate fine bubbles in molten metal as much as possible. SNIF technology pursues stable bubble flow pattern (maximizing residence time of fine bubble) in molten metal to enhance gas-liquid reaction between bubbles and molten Aluminum. For this purpose, SHEER rib is installed on hearth of treatment vessel to extend residence time of bubbles and downward bubble flow is controlled with unique SHEER nozzle design. On the other hand, GBF aims at enhancing gas-liquid reaction by stirring plenty of bubbles inside molten metal with high speed nozzle (600-900RPM) and baffle plates preventing molten metal turbulence. As for SNIF, ribs are arranged on hearth of vessel and rotary nozzles corresponding to ribs are employed. Thus SHEER technology was established, which enhanced gas-liquid reaction between fine bubbles and molten metal as demonstrated by the report[14)]. Figure 6 shows comparison between SHEER technology and standard SNIF on Hydrogen removal effect. Figure 7 shows that SHEER system equipped two rotors demonstrated Hydrogen removal effect comparable to that of standard system equipped with three rotors. So far, substantial standard SNIF systems were replaced with SHEER systems.

Recent in-line degassing systems have been considerably improved in terms of mechanical technology and most of systems are equipped with tilting device and various heating devices. However, these systems have good and bad points in a practical sense. Mechanical technologies introduced in these years are airlock for improving air tightness, electrical immersion heater, hydraulic lifting device for furnace cover and P cartridge based on integration of treatment vessel, P60/4 system which allows to select exit based on employment of four ports, four rotor system (P240UHB). etc.. Requests from users are downsizing and improving inclusion removal performance. As a matter of course, key points are design of treatment vessel and densifying fine bubbles.

As mentioned above, technological progress of degassing has been made in these years. On the other hand, filtration technology has not changed in its principal process for many years, and bed filter, ceramic foam filter and tube filter (RMF) are being used in accordance with product quality required. In this paper, filtration technology is not referred to because of space limitation here in this paper.

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References

1) A. Sieverts: Z. Metalkde., 21(1929), 37
2) L. W. Eastwood: American Society for Metals, (1953)
3) Nishi, Shinada, Kurobuchi, Japan/Soviet news agency, Japan Institute of Light Metals 24(1974),89.
4) Ushioda: Japan Institute of Light Metals 34(1985), 242
5) Aluminum material and its basic industrial technology: Japan Institute of Light Metals (1985)12-16
6) Tadakazu Ohnishi: Japan Institute of Light Metals, 39(1989), 235
7) Ryotatu Otsuka:Japan Institute of Light Metals, 44(1994), 461
8) Ghyslain Dube, V. J. Newberry "TAC-C Novel Process for the removal of Lithium" Light Metals 1983 P991
9) F. Achard, Ch. Leory "PRETREATMENT IN POTLINES CRUCIBLES" light Metals 1990 P765
10) M. Nilmani: Aluminum Melt Refining And Alloying, Theory and Practice, M. Nilmani, ed., University of Melbourne, Australia, (1989), F1.
11) C. Celik and D. Doutre: Light Metals, (1989) 793.
12) G. Beland, C. Depuis and G. Riverin, "Rotary flux injection: Chlorine-free technique for furnace preparation", Light Metals, 1998, 843-847
13) M. A. Thibault, F. Tremblay, and J. C. Pomerleau, "Molten metal stirring: The Alcan Jet Stirrer" Light Metals 1992, 1005-1011
14) J. E. Buehler and R. A. Frank, *Start Up and Evaluation of the SNIF SHEER System at Kaiser Aluminum, Trentwood Works* (Paper presented at the 122nd TMS Annual Meeting, Denver, Colorado, 21-25 February 1993)
15) Light Metals 1991 Ward C. Eister, Willam R. Krumme.
16) R. Otsuka, S. Tanimoto, K. Toyoda, M. Sakaguchi: Japan Institute of Light Metals, 40 (1990), 290
17) Yoshikazu Ohno, Duanne T. Hampton, Andy Moores Light Metals, 1993, 915-921
18) JH. H. Hicter: Light Metals, TMS., 13B(1986), 31
19) J. Bildstein and I. Ventre, "Alpur Technology - Present and Future" Light Metals 1990, p755-763
20) Bodil Hop, Frede Frisvold, Bjorn Rasch and Stein Tore Johansen, "The Fluid Mechanics in the H110 Hycast reactor", Light Metals 1997, p837-841
21) Peter D. Waite Light Metals 1998, P791
22) 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 Metals 1986, p837-845.
23) J. G. Stevens and H. Yu, "Mechanisms of Sodium, Calcium, and Hydrogen Removal from an Aluminum Melt in a Stirred Tank Reactor – The Alcoa 622 Process," Light Metals 1988, p437-443.
24) D. C. Chesonis, H. Yu, and M. Scherbak, "In-line Fluxing with High Speed Multiple Rotor Dispenses, "Light Metals 1997. pp. 843-846.