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Miniature Vacuum Degassing System

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Abstract

We report on the development and testing of a miniature vacuum degassing system designed for use in ladles, troughs, and furnaces. The system also generates an inert gas flow that can blanket the molten metal surface, thus degassing and preventing the reintroduction of hydrogen into the newly refined metal.

Keywords

Vacuum degassing • Aluminum • Hydrogen • Inerting

Introduction

Virtually all aluminum products go through at least one processing stage in which the metal is in a molten state. While aluminum is a very reactive metal with an affinity to oxidize, it can also absorb hydrogen gas. Hydrogen solubility is much higher in the molten state than in the solid phase (Fig. 1). Consequently, hydrogen is rejected during the cooling of the liquid phase. If the cooling occurs rapidly, which is most often the case in practical applications, the hydrogen can be trapped in the dendritic arms creating micropores or form larger pores if the interior of the aluminum solid is the last area to solidify. In most cases these discontinuities are detrimental to the physical properties of the final product and are to be avoided. Hydrogen can also be responsible for blisters or delaminations on rolled or extruded products. The most common way to reduce the formation of the pores is to reduce the hydrogen content of the molten metal just prior to casting.

The source of hydrogen in the molten aluminum is from the chemical decomposition of water by aluminum. The pertinent reaction is:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6\underline{H}_{diss.\,inAl}$$

The water can come from many sources, but the most common is the moisture found in air surrounding the molten aluminum, or from products of combustion in the furnace. Keeping the moisture away from molten aluminum through use of an inert gas blanket or "inerting" can be both a method to reduce dissolved hydrogen or to prevent the rapid reabsorption once the metal has been degassed. It has been observed by many practitioners that the amount of hydrogen present in the molten aluminum is higher when the surrounding air has more moisture and that it is more difficult to remove.

The mechanism of hydrogen removal involves mass transport from areas of high concentration (or partial pressure) to areas of low concentration (or partial pressure). It is typically a multistep process where diffusion of the dissolved hydrogen through the liquid aluminum is the rate determining step. Consider an inert gas bubble rising through a volume of molten aluminum with dissolved hydrogen. The dissolved hydrogen must migrate to the gas bubble first through the bulk metal by convective transport and then across a boundary layer surrounding the bubble by diffusion. At the bubble's surface the dissolved hydrogen must re-associate into a diatomic molecule and then diffuse into the gas bubble's interior. Using large swarms of small gas bubbles to increase total surface area and reduce the distance for bulk transport increases the rate of reaction.

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Fig. 1 Hydrogen solubility in aluminum [1]

Background

Degassing Methods

There are several methods [2] to degas aluminum and other molten metals:

- Wands or lances-typically used in furnaces,
- Porous plugs—used either in furnaces or in the trough system to the casting unit, and
- Rotary impeller degassers (RID)—used either in furnaces or in the trough system to the casting unit. RIDs in the trough system can either be in a sealed box or directly in-line with the troughing.

Effort continues [3] to improve the widely used [4] RID systems, which at minimum must have a vessel to contain the metal, the impeller, a motor to spin the impeller, gas and electrical connections, and a top structure. Depending upon the design, the units in the troughing system are often preheated before service or contain molten metal between casting cycles. There can be several units in line to improve efficiency and solid flux materials or reactive gases are often injected [5].

With its infrastructure the RID requires careful design if used for portable or mobile (e.g. moving ladle) vessels. The next option, a porous plug, must be installed in the holding vessel, sometimes clogs, and occasionally fails. They are more difficult to maintain when only used occasionally. The last option, a wand or lance, is portable, but its performance depends on insertion depth, bubble size, and gas flow rate. Typically, their rate of removal and efficiency is lower than the other systems due to larger bubble sizes. Vacuum degassing is widely practiced in the steel industry but is not common in non-ferrous production. There are two general types of vacuum degassing: one type puts the ladle in a vacuum tank; the other type lowers a vacuum apparatus on top of the vessel to pull a stream of liquid into the treatment zone. Vacuum methods usually agitate the liquid with a porous plug in the vessel bottom (tank type) or in the intake leg (stream type).

Tank vacuum degassing systems are usually stationary; while the movement of the stream unit is limited by its utility connection. Pumps or steam ejectors provide the vacuum.

Various groups are investigating ultrasonic degassing [6–9]. The initial removal is quite rapid and enhanced by blowing inert gas. However, the rapid hydrogen drops highlight the re-entry of atmospheric contaminants (hydrogen, nitrogen, oxygen) [10] if there is insufficient protection of the exposed surfaces.

Degassing Kinetics

Many researchers have observed that the rate of removal for hydrogen during degassing follows first order removal kinetics, i.e. the rate of removal is proportional to the concentration. Expressed mathematically, with "%H" representing the hydrogen concentration:

$$rac{d\%~\mathrm{H}}{dt} = -etaig(\%~\mathrm{H} - \%~H_{eq}ig)$$

Under normal circumstances $\%H_{eq}$ will be dependent upon the moisture concentration of the atmosphere surrounding the molten aluminum. In a vacuum, the partial pressure of hydrogen is very close to zero, and $\%H_{eq}$ approaches zero leaving

$$\frac{d\% \text{ H}}{dt} = -\beta(\%H)$$

$$\ln \frac{\%H}{\%H_0} = -\beta t$$

$$H = H_0 e^{-\beta t}$$

ŀ

This classic exponential decay generates curves like this (Fig. 2).

To maximize degassing, using a vacuum for $\% H_{eq} = 0$ maximizes the driving force and allows for the potential of lower overall final hydrogen concentration in the metal.

Parameter β relates the mass transfer coefficient k, the area involved A, and the volume of the melt V:

$$\beta = \frac{kA}{V} [=] \frac{\frac{kg.m}{minute}m^2}{m^3} [=] \frac{kg}{minute}$$



Fig. 2 Theoretical hydrogen contents at different degassing parameters

A larger value for the parameter β means more rapid removal of the dissolved hydrogen. In practice we seek to increase both the area term (small and numerous bubbles) and the mass transfer term (high stirring energy). We lump both in β since there is no direct way to measure either the area or mass transfer term. We can use β to roughly evaluate different degassing methods, studies, gas-liquid systems, and degassing method to get an indication of performance. We should be careful that direct comparisons are valid only in the same gas-liquid system and geometry. β values for a few studies are summarized in Table 1; the column "Half time" is the time in minutes required to reduce the concentration to one half of the initial content.

Table 2 is a table of average and standard deviations for the data in Table 1; Table 3 shows results of 2-sample T-tests for statistical significance for selected systems.

While the differences between methods might not be statistically significant, to estimate how the kinetics in water scales to a value in aluminum, we shall divide the average β for RID in aluminum by the value in water, a 0.7 ratio.

Table 2 Average and standard deviations

| Method-system | Number | Avg. β | Standard deviation |
|------------------------------|--------|--------|--------------------|
| Ultrasonic-Al-H ₂ | 3 | 0.271 | 0.0301 |
| RID-water-O ₂ | 3 | 0.229 | 0.0451 |
| RID-Al-H ₂ | 4 | 0.161 | 0.0998 |
| Plug-Al-H ₂ | 2 | 0.110 | 0.1287 |
| Vacuum-steel-H ₂ | 4 | 0.058 | 0.0236 |

 Table 3
 2-sample T-tests

| Method-system 1 | Method-system 2 | <i>P</i> -value | T-value | DF |
|-----------------------|------------------------------|-----------------|---------|----|
| RID-Al-H ₂ | RID-water-O ₂ | 0.29 | -1.22 | 4 |
| RID-Al-H ₂ | Ultrasonic-Al-H ₂ | 0.127 | -2.09 | 3 |

| Study | Data source | Degasser | β | Liquid—degas | Half time, min |
|-----------------------------|-------------|-----------------------|-------|-------------------------|----------------|
| Abreu-Lopez et al. [3] | Impeller C | RID | 0.278 | Water-O2 | 3 |
| | Impeller B | RID | 0.221 | Water-O ₂ | 3 |
| | Impeller A | RID | 0.189 | Water-O2 | 4 |
| Friedrich and Kräutlein [2] | Fig. 3 | RID | 0.112 | Aluminum—H ₂ | 7 |
| | Fig. 3 | Porous Plug | 0.034 | Aluminum—H ₂ | 21 |
| | Fig. 3 | Lance | 0.020 | Aluminum—H ₂ | 35 |
| | Fig. 3 | None | 0.003 | Aluminum—H ₂ | 231 |
| Gobinath et al. [11] | Table 1 | Vacuum tank | 0.092 | Steel—H ₂ | 8 |
| Warke [12] | Fig. 4 | RID | 0.060 | Aluminum—H ₂ | 12 |
| Nunis et al. [13] | Table 2 | Vacuum tank | 0.052 | Steel—H ₂ | 14 |
| | Table 2 | Vacuum tank | 0.038 | Steel—H ₂ | 19 |
| Karouni et al. [14] | Table 3 | Vacuum tank | 0.049 | Steel—H ₂ | 14 |
| Zeng et al. [15] | Fig. 4 | Porous absorber | 0.019 | Aluminum—H ₂ | 35 |
| Puga et al. [7] | Fig. 3 | RID (Ar) | 0.18 | Aluminum—H ₂ | 4 |
| | Fig. 3 | RID (N ₂) | 0.29 | Aluminum—H ₂ | 3 |
| | Fig. 3 | Ultrasonic | 0.3 | Aluminum—H ₂ | 2 |
| Rundquist and Gill [9] | Fig. 7 | Ultrasonic | 0.24 | Aluminum—H ₂ | 3 |
| | Fig. 7 | Ultrasonic | 0.274 | Aluminum—H ₂ | 2 |
| | Fig. 7 | Plug—gas only | 0.201 | Aluminum—H ₂ | 3 |

Table 1 Collection of studies

Inerting Background

An effective inert blanket system limits atmospheric contact with the metal, decreasing the concentration of atmospheric gases (oxygen, nitrogen, and hydrogen via water vapor), thus decreasing the driving force of absorption. The key to inerting is to control jet entrainment and turbulence.

Hot metal surfaces heat the adjacent gas, decreasing the gas's density and making it buoyant relative to the colder ambient gases. The hot gases rise; cold atmospheric gases fill in the volume—a "chimney" effect. Effective inerting limits the chimney effect.

Laminar jets [16] delay the mixing. Distributing the blanket gas becomes unwieldy as the exposed surface area increases. Blanket gas consumption, which scales with surface area, can be large.

Gases blown tangentially [17] in a distribution box make a vortex, which delays atmospheric entrainment.

Dropping liquid argon or liquid nitrogen onto the metal surface [18] causes the volume to fill with inert gas, creating a shield.

Increasing the distance between the hot metal surface and the vessel opening to the atmosphere does much to improve performance of the blanket.

The Miniature Vacuum Degassing System

Can we address the need for high quality metal with a device that can degas, inert, be portable, and be inexpensive so it can be used on an as needed basis?

Praxair designed and tested a series of actual size plastic prototypes (Fig. 3) to establish operating parameters for a

Fig. 3 Water models

system. One gas connection drives: (1) a small jet pump to generate a vacuum and (2) a small wand. The pump's exhaust flows across the surface of the molten metal.

Water Model Experiments

We measured the dissolved oxygen content of water as a function of time and these factors (Table 4).

| Table 4 Water model test para | meters |
|---------------------------------------|--------|
|---------------------------------------|--------|

| Start oxygen content, ppm | >14 | 8-14 | <8 |
|-----------------------------|------|-------|-------|
| Bubbler flow, L/min | 1.3 | 2.6 | 4.2 |
| Pressure, Torr | 760 | 757.2 | 754.4 |
| Vacuum chamber diameter, cm | 10.2 | 15.2 | |



Fig. 4 Regressed values versus actual





Fig. 5 Vacuum versus supply pressure



Fig. 6 Theoretical height of metal column

The dissolved oxygen content measurement was taken near the wall of the container; β ranged from 0.01 to 0.05. Linear regression of the data produces this result (R² = 88%). Figure 4 plots the regression versus observed values.

 $\beta = 1.455 + 0.000655 dia vacuum cm - 0.001927 + 0.008113 bubbler L/min$

Figure 5 shows the vacuum generated by the jet pump as a function of operating pressure; Fig. 6 shows the equivalent molten metal column for aluminum, iron, and copper.

Tests in Aluminum

Data from molten aluminum testing was not available at the time of submission for this paper. Our test plan starts with these conditions:

- molten aluminum—100 kg
- device diameter—15 cm
- bubbler flow—2 L/min
- pressure—745 Torr.

For water under these conditions, the regression equation gives $\beta = 0.065$ (half time 10.7 min). Extrapolating to aluminum with a 0.7 scaling factor, has $\beta = 0.046$ (half time 15 min). These values are in the performance range expected for a wand degasser. Using the maximum vacuum (approximately 670 Torr, 43 cm aluminum column) would increase β to 0.092 (half time 7.5 min), which is approaching RID type performance. However, the high column of liquid could decrease mass transfer by retarding the mixing of refined liquid with the bulk.

We can examine increasing the device diameter and/or the bubbler flow once the device has demonstrated its effectiveness. It is unlikely that the device will replace rotary degassers; but it could prove useful in pre and/or post processing metal to decrease the load on the existing degasser. It could also provide degassing in situations and conditions where standard degassing is impractical.

Summary

Hydrogen is detrimental to producing high quality aluminum and effort continues to develop and improve degassing technology. In this paper, we review degassing kinetics, existing methods, and document studies of a device that combines bubbling, vacuum, and inerting with no moving parts.

References

- 1. "Aluminum and Aluminum Alloys," in ASM Handbook, J. R. Davis, ed., ASM, 1993, p. 200.
- B. Friedrich and C. Kräutlein, "Melt Treatment of Copper and Aluminum – The Complex Step Before Casting," *Metallurgia – Journal of Metallurgy, Association of Metallurgical Engineers of Serbia*, pp. 251–266, 2006.
- D. Abreu-Lopez, A. Amaro-Villeda, F. Acosta-Gonzalez, C. Gonzalez-Rivera and M. Ramirez-Argaez, "Effect of the Impeller Design on Degasification Kinetics Using the Impeller Injector Technique Assisted by Mathematical Modeling," *Metals*, pp. 132– 146, 2017.
- AFS, "Aluminum Degassing: Methods and Measurements," Modern Casting, pp. 30–34, 2015.
- R. Brindi, J. Prebble and V. Ivo, "Promag Improvements in Casthouse Processing Using In-Furnace and In-Line Systems," in *International Congress and Exhibition: Non-Ferrous Metals 2011*, Krasnoyarsk, 2011.
- Q. Han, H. Xu and T. T. Meek, "Degassing of Molten Alloys with the Assistance of Ultrasonic Vibration". US Patent 7,682,556 B2, 2010.
- H. Puga, J. Barbosa, E. Seabra, S. Ribeiro and M. Prokie, "New Trends in Aluminum Degassing - A Comparative Study," in Fourth International Conference on Advances and Trends in Engineering Materials and Their Applications, Hamburg, 2009.

- G. Eskin, "Prospects of Ultrasonic (Cavitational) Treatment of the Melt in the Manufacture of Aluminum Alloy Products," *Metallurgist*, vol. 42, no. 8, pp. 284–291, 1998.
- 9. V. F. Rundquist and K. S. Gill, "Ultrasonic Device with Integrated Gas Delivery System". US Patent 8,652,397 B2, 2014.
- N. Alba-Baena and D. Eskin, "Kinetics of Ultrasonic Degassing or Aluminum Alloys," in *Light Metals 2013*, The Minerals, Metals & Materials Society, 2013, pp. 957–962.
- 11. R. Gobinath, N. Viswanathan and N. Ballal, "Dehydrogenation Model for Vacuum Tank Degasser," in *Scanmet V*, Lulea, 2016.
- V. S. Warke, "Removal of Hydrogen and Solid Particles from Molten Aluminum Alloys i the Rotating Impeller Degasser: Mathematical Models and Computer Simulations," Worchester Polytechnic Institute, 2003.
- A. L. Nunis, T. R. Ribiero, J. B. Ferreira Neto, M. B. Leite, R. C. Badaraco and C. R. Serantoni, "Model for Dehydrogenation

During Secondary Steelmaking," in AISTech 2015 Proceedings, 2015.

- F. Karouni, B. P. Wynne and J. Talamantes-Silva, "Mathematical Modeling and Optimization of Hydrogen Degassing in an Argon-Stirred Ladle," in *AISTech 2017 Proceedings*, 2017.
- J. Zeng, B. Wu, Z. Hu, L. Wang and D. Cao, "A New Vacuum Degassing Process for Molten Aluminum," in *Light Metals* 2014, 2014.
- 16. M. Nowotarski, "Wide Laminar Fluid Doors". US Patent 4,823,680, 1989.
- Z. Zurecki, J. L. Green, R. C. Best and D. J. Lach, "Method and Apparatus for Inert Gas Blanketing of a Reactor or Vessel Used to Process Materials at Elevated Temperatures such as an Induction Furnace used to Remelt Metals for Casting". US Patent 5,518,221, 1996.
- S. H. Anderson and N. F. Lutgen, "Process for the Production of a Bath of Molten Metals or Alloys". US Patent 4,806,156, 1989.