

Ultrasonic degassing of aluminium alloys: basic studies and practical implementation

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Ultrasonic processing is known to be an efficient means of aluminium melt degassing and structure modification with additional benefits of being economical and environment friendly. The present paper reports on the kinetics of ultrasonic degassing and regassing of foundry aluminium alloys and on pilot scale degassing trials. Efficiency of ultrasonic degassing is compared with conventional Ar rotary degassing. Direct measurements of hydrogen concentration in the melt by Foseco Alspek-H probe are used along with reduced pressure test. The effects of ultrasonic processing on porosity are studied using three-dimensional X-ray tomography.

Keywords: Ultrasound, Degassing, Aluminium, Hydrogen, Porosity, Melt treatment

Introduction

The quality of aluminium alloys is sensitive to melting conditions, temperature variations and humidity in the surrounding atmosphere.^{1,2} Hydrogen is the gas of most concern in aluminium as its solubility drops from 0.65 cm³/100 g in liquid aluminium just above the melting temperature to 0.034 cm³/100 g just below.¹ As a result, hydrogen recombines to molecules and precipitates between solid dendrites, forming porosity.¹ Gas porosity combined with shrinkage porosity is detrimental to the mechanical properties of final products, especially to the fracture toughness, fatigue endurance and ductility. In recent years, the role of oxide films in porosity development has been emphasised, e.g. Ref. 3. This approach considers the oxide bifilm as an initiator of porosity, while it treats dissolved gas as a contributor. The role of dissolved hydrogen, however, is still important even in this point of view.

The main source of hydrogen in liquid aluminium is water moisture or vapour in the atmosphere. This moisture reacts with liquid aluminium at the melt surface and produces alumina and hydrogen. The resultant atomic hydrogen is dissolved in liquid aluminium, and Al₂O₃ is deposited at the surface or dispersed in the liquid. Hydrogen that is not dissolved or hydrogen that precipitates during degassing or solidification forms molecular hydrogen.

It is important to understand that the concentration of hydrogen in liquid aluminium is not a constant or a fixed number. This concentration depends on the

conditions at the interface between the hydrogen containing medium (atmosphere or bubble) and the liquid metal (surface or interior). A quasi-equilibrium solubility exists for each combination of the hydrogen concentration in the atmosphere (humidity), in the melt (dissolved hydrogen) and the pressure (air pressure and partial pressure of hydrogen). In addition, the solubility is the function of temperature. There is, however, the limit equilibrium solubility of hydrogen that is a function of temperature and pressure only and is determined by the Al-H phase diagram.⁴

The melt can be saturated in hydrogen during melting, holding or transfer. In this case, the hydrogen concentration will lower to a quasi-equilibrium limit reflecting the actual humidity–pressure–temperature conditions. This process is called natural degassing. On the other hand, the melt with small concentration of hydrogen (e.g. just degassed), being brought under similar condition, will naturally regas. Eventually, both melts will have the same quasi-equilibrium concentration of hydrogen. The shift in the equilibrium due to the changed environmental conditions will result either in degassing or regassing. These ‘natural’ processes occur through diffusion of hydrogen across the gas/liquid interface and are rather slow, the degassing being faster than regassing.^{1,5}

Natural degassing takes considerable time, so different methods have been proposed for accelerating this process. Two types of degassing methods are currently used for aluminium alloys: gas purging (rotary and lance systems) and vacuum degassing. Chlorine containing gases, however efficient they are, have been replaced with inert gases, mostly Ar, due to environmental considerations.^{1,2,6} Bubbles formed by purged gas create numerous interfaces that promote recombination of hydrogen to molecular form and help to evacuate this gaseous hydrogen from the melt. The number and size of the bubbles along with the forced convection seem to be the main parameters of the process.² Gas purging also helps in cleaning the melt from oxide inclusions, further decreasing porosity and increasing metal soundness.^{1,2} Vacuum degassing is based on the decreased pressure

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above the melt surface that lowers the quasi-equilibrium hydrogen solubility and facilitates degassing. Additionally, the decreased pressure helps in evacuating the bubbles from the melt, accelerating the process of natural degassing. Ultrasonic degassing has been suggested quite some time ago as an environment friendly, robust and efficient means of melt degassing.^{7,8} Ultrasonic cavitation efficiently produces cavities in the liquid phase. Within the sound field, during alternating periods of compression and rarefaction (expansion), the cavity quickly turns into a bubble filled with hydrogen that diffused into it.^{5,8} Acoustic streaming and secondary convection flows distribute the bubbles inside the treated volume.⁸ Just as in the case of gas purging, the ultrasonic degassing also helps in cleaning the melt of oxide inclusions.⁸

Although the application of ultrasound to degassing liquid metals has a long history and was successfully applied in industrial trials in the 1960–1970s,^{7,8} it was superseded by gas rotary degassing in the 1980s. The interest in ultrasonic degassing increased during the last decade due to its environment friendliness with no requirement for moving parts or expensive gases.^{9,10}

The efficiency of ultrasonic degassing depends on the same basic phenomena as in other degassing methods: transport of hydrogen from the melt to the bubbles present in the liquid, diffusion of hydrogen through the bubble/liquid interface and its recombination into molecular hydrogen and the removal of the bubbles with hydrogen through the melt surface.^{8,11} Melt convection induced by the cavitation zone and sound field assists in spreading the degassing effect over larger melt volumes and accelerates the degassing process. The controlling factors of ultrasonic degassing are, however, different from other methods such as rotary Ar assisted degassing. Degassing efficiency in rotary and lancing methods is given by the ability of the introduced bubbles to absorb hydrogen depending on the time, bubble sizes and number, inert gas flowrate and dissolved hydrogen characteristics. The creation of bubbles by cavitation from the dissolved gasses instead of introduced gasses gives ultrasonic treatment the edge in many industrial applications.

Experimental

Two commercial aluminium alloys were used for the experiments: A356 (Al–7Si–0.3Mg) and A380 (Al–9Si–3.5Cu–0.8Fe). The charges 2–60 kg in size were melted in graphite crucibles in an electric furnace with the melt temperature of $720 \pm 5^\circ\text{C}$. The ultrasonic equipment included a 5 kW generator and a 5 kW water cooled magnetostrictive transducer (Reltec, Russia). The sonotrode consisted of a Ti concentrator and Nb tip tuned to the frequency of the transducer (17.5 kHz). The sonication was performed by dipping the Nb tip (sonotrode) from the top of the melt to a depth of ~ 10 mm. The tip was preheated to 700°C , and the melt temperature was controlled during the process. There was no protective atmosphere. Ultrasonic treatment was applied to the molten metal for specific periods of time, e.g. 2 min, followed by periods without ultrasonic activity, e.g. 2, 5 or 10 min. The input power of the generator was kept at 4 kW with the corresponding amplitude at the Nb tip of $20 \mu\text{m}$. The null to peak amplitude was measured by a contactless vibrometer (BSUIR, Belorussia) in air. For measuring the degassing effect, the initial hydrogen

content was measured in the aluminium alloy charge at the given temperature. After treatment, the charge was kept stable in the furnace for up to 120 min, while hydrogen concentration measurements were taken at specific times. Two measuring techniques were used, i.e. an ALSPEK-H (Foseco) analyser for direct measurements and a reduced pressure test (RPT, 3VT MK GmbH) for a density index (DI). The accuracy of hydrogen measurement by ALSPEK-H was $\pm 0.02 \text{ cm}^3/100 \text{ g}$ or 3% of hydrogen concentration. The correlation between the measurements taken by these two methods was performed using regression analysis. Reduced pressure test gives as a result the DI, which is the ratio of the density difference of samples solidified in air and under vacuum to the density of the sample solidified in air. Although RPT results are affected by oxide inclusions,³ we assume that the contribution of those is similar in all degassing techniques so the correlation will still hold.

The information about relative humidity (RH) on the day of experiment was taken from weather reports and then converted to hydrogen concentration H ($\text{cm}^3/100\text{g}$) in the air using the following formula deduced from data in Ref. 2

$$H = 0.1772RH (\%) + 0.0394 \quad (1)$$

The limit solubility of hydrogen S ($\text{cm}^3/100 \text{ g}$) in a liquid alloy was calculated as follows¹²

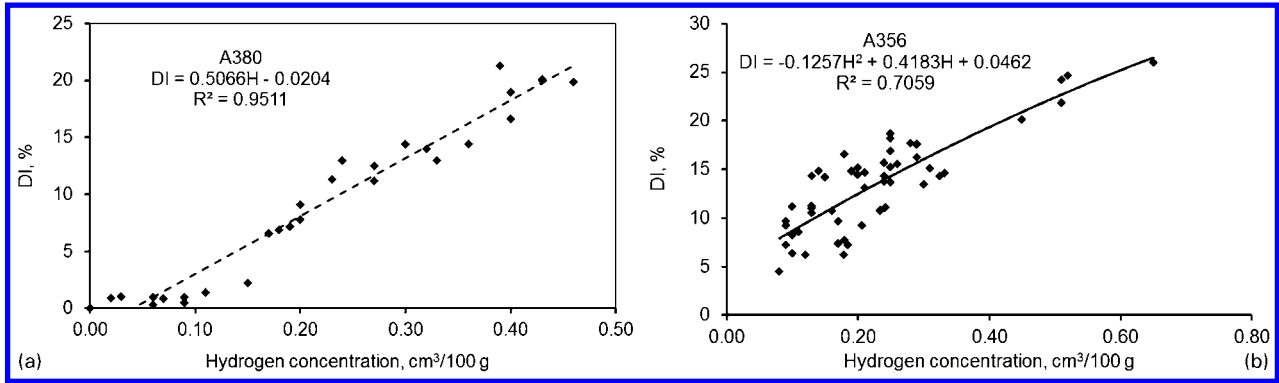
$$\lg S = -3050/T (\text{K}) + 2.94 \quad (2)$$

Selected samples were examined for microstructure (optical microscopy) and porosity (three-dimensional tomography; acceleration voltage, 165 kV; current, 250 μA ; filter, 2 mm Al; exposure time, 333 ms).

Pilot scale trials were performed with a 150 kg charge of an A356 alloy. The alloy was melted in an electric furnace with the crucible 500 mm in diameter and 500 mm in depth and kept at $725 \pm 5^\circ\text{C}$. In order to enhance the visibility of degassing performance, a tablet of Hydral [$\text{Al}(\text{OH})_3$] was added to the metal. Two methods of degassing were tested, i.e. ultrasonic degassing with a single ultrasonic source similar to that described above and Ar rotary (impeller) degassing using a commercially available Foseco degasser. Ultrasonic processing was performed at 17.5 kHz, 20 μm amplitude with the ultrasonic source slowly moving along the half-radius circumference of the melt surface, being submerged 40–70 mm below the melt surface. The Ar rotary degassing was performed with an Ar flow of 6 l min^{-1} . The hydrogen concentration was measured using a Foseco ALSPEK-H hydrogen analyser and RPT at different stages of processing. Probes were taken at ~ 150 mm below the melt surface along the centreline of the crucible. In both cases, the duration of degassing was limited to 15 min. The dross formed at the surface of the melt during degassing was collected after the end of processing and weighed. The melt was then transferred to a casting ladle, and the hydrogen measurements were taken again.

Results and discussion

A correlation formula between ALSPEK-H measurements and the RPT density indices makes possible to



1 Correlation graphs between direct hydrogen readings (ALSPEK-H) and density index (RPT) for a A380 and b A356 alloys

compare the readings obtained and present them in the same graph in $\text{cm}^3/100 \text{ g}$ (as unit).¹³ Figure 1 gives the correlation graph corresponding to the following regression relationships between DI (%) and H ($\text{cm}^3/100 \text{ g}$)

$$DI = -0.1257H^2 + 0.4183H + 0.0462, \\ R^2 = 0.7059 \text{ for A356} \quad (3)$$

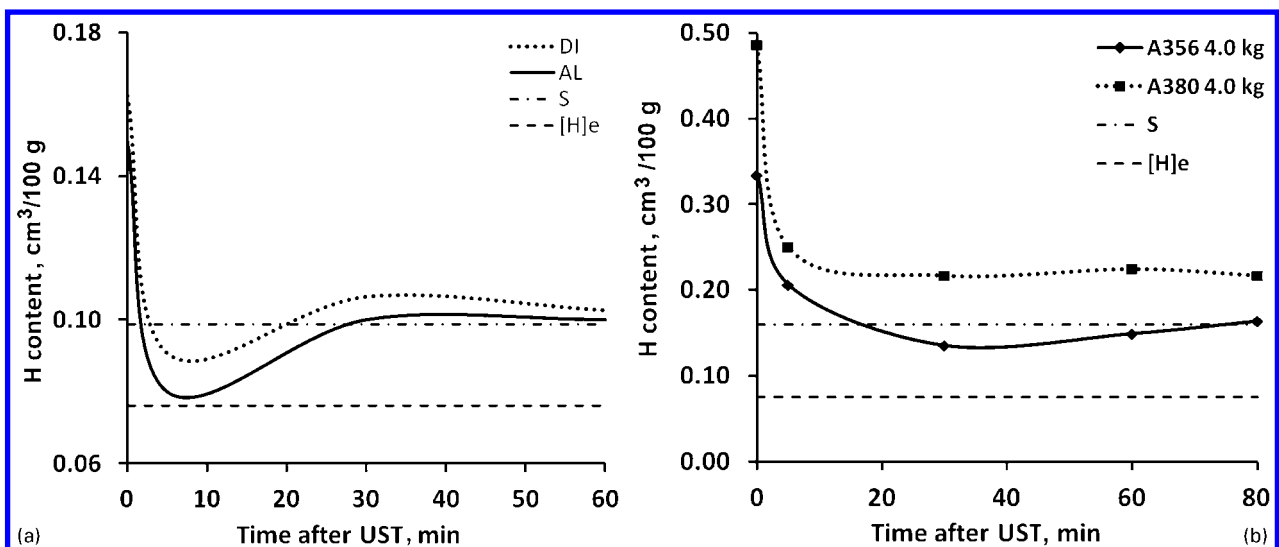
$$DI = 0.5066H - 0.0204, R^2 = 0.951 \text{ for A380} \quad (4)$$

where R^2 is the regression coefficient.

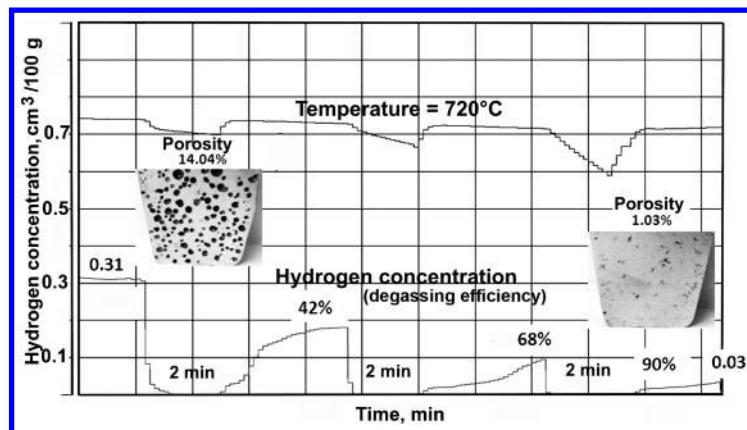
Figure 2a shows curves for data obtained with ALSPEK-H (identified as AL) and RPT (DI line) from the same charge: 4 kg, A380 alloy. The ultrasonic degassing was performed for 2 min. Both readings were taken at the same time, but from different positions in the crucible. Reduced pressure test samples were obtained from the liquid close to the surface, while the ALSPEK-H measurements were taken 150 mm deeper. As can be seen, hydrogen measurements by both techniques show the same kinetics. The shift in the readings can be attributed to the changes in hydrogen levels due to the positioning of readings, with upper surfaces of the melt demonstrating more substantial degassing. In the same figure, the dashed line gives the hydrogen equilibrium

solubility level ($0.079 \text{ cm}^3/100\text{g}$) and the chain line, the stabilisation (quasi-equilibrium) level due to humidity in the air ($0.098 \text{ cm}^3/100\text{g}$) on the day of experiment. One can easily see that the ultrasonic degassing can decrease the hydrogen concentration toward the equilibrium solubility level ($[H]_e$), but, after 30 min, degassing takes the hydrogen level closer to the quasi-equilibrium limit under ambient conditions S . It is important to note that the results produced from different charges on different days cannot be directly compared; the starting concentration of hydrogen and the quasi-equilibrium limit are different and should be taken into account.

Figure 2b compares the degassing kinetics for two alloys treated under same conditions. The degassing efficiency for both alloys was more than 50%. However, the A380 alloy did not show degassing, while the A356 alloys demonstrated hydrogen readsorption. For simplicity, we consider that the quasi-equilibrium level is given mainly by the hydrogen–aluminium–water vapour equilibrium, and then the S value is the same for different alloys under the same conditions. In this set of experiments, the A380 charge did not reach the quasi-equilibrium limit and, hence, did not show degassing, while the A356 charge was degassed to the level below the quasi-equilibrium limit and clearly showed degassing. This difference in



2 Ultrasonic degassing kinetics: a 2 min degassing of 4 kg A380 charge, values converted from density indices using RPT (DI) and measured using ALSPEK-H (AL); for reference, graph shows lines of stabilisation or quasi-equilibrium level S and hydrogen equilibrium ($[H]_e$) and b degassing of 4 kg charges of A356 and A380 after same degassing and ambient conditions



3 Kinetics of degassing for 2 kg A380 melt showing efficiency of 2 min intermittent treatment as measured by ALSPEK-H

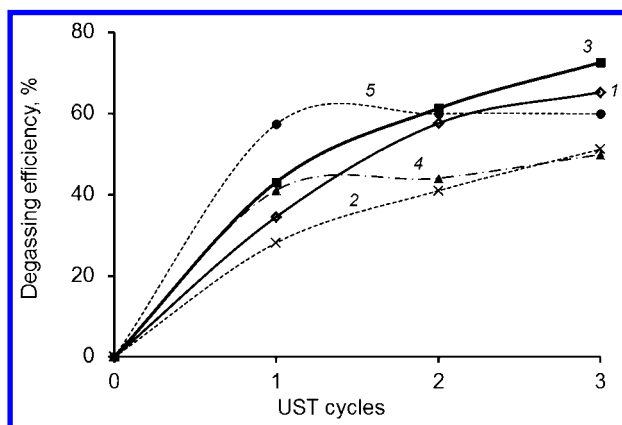
behaviour can be further related to increased hydrogen solubility in the Mg containing A356 alloy.¹⁴

It is worth noting here that ultrasonic degassing due to specific conditions of solubility under the cavitation is capable of decreasing the concentration of hydrogen in liquid aluminium to levels 50% lower than the quasi-equilibrium solubility.⁸ This would mean more stimulus for regassing after the end of degassing.

We can summarise that the regassing behaviour would depend on the degree of degassing below the quasi-equilibrium level and on the environmental conditions that define this limit.¹³

Experimental work carried out earlier on ultrasonic degassing of liquid aluminium typically puts focus on the duration of continuous processing, demonstrating that the degree of ultrasonic degassing increases with the processing time.^{8–10} An intermittent short treatment was suggested as a beneficial alternative for degassing schedule as well.⁷ Our results confirm that 1–2 min ultrasonic processing with 5–10 min intervals can gradually decrease the hydrogen concentration to levels well below the quasi-equilibrium level. This is illustrated in Fig. 3. For relatively small volumes of liquid metal, shorter ultrasonic degassing could be as efficient as a longer one as demonstrated in Fig. 4.

The ultrasonic degassing of a larger melt volume shows similar trends. Figure 5a illustrates the degassing



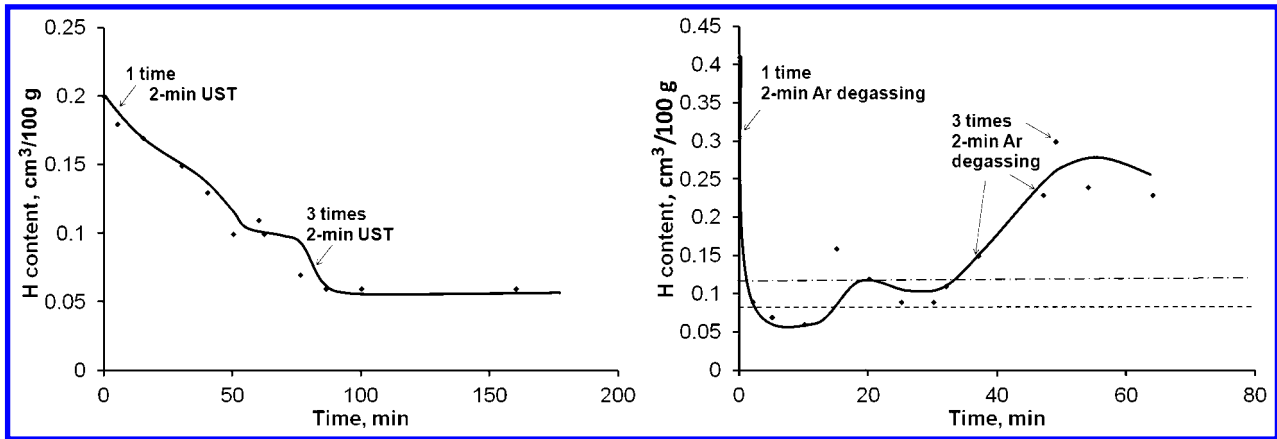
4 Efficiency of degassing (decrease in hydrogen concentration from initial one) for 2 kg charges of A380 alloy treated with ultrasound for 30 s (1), 1 min (2), 2 min (3), 3 min (4) and 5 min (5) with 5 min idle intervals between degassing sessions; three cycles are shown

of a 60 kg charge of an AA 380 alloy. The flotation of gas bubbles to the surface in the larger volume takes more time so the degassing is slower than in smaller volumes and may be accelerated by additional short cavitation treatments and by additional stirring. Note that the regassing was not observed in this case, probably due to the smaller ratio of the melt surface (interface for natural hydrogen intake) to the melt volume and to the quiet state of the melt surface with no disturbance.

Conventional rotary degassing with Ar demonstrates the regassing as shown in Fig. 5b. In this particular case, the regassing happened after some period of holding of the melt after initial degassing and, more substantially, after the additional short degassing sessions. Similar additional ultrasonic degassing session (three times 2 min degassing followed by 5 min resting time) shown in Fig. 5a led then to additional degassing. The reason for such a significant regassing in the case of Ar rotary processing is not only the significant disturbance of the surface that facilitates the access of moisture from the ambient air to the hydrogen depleted melt but also an accumulation of dross layer on top of the processed melt. This dross formation is typical of rotary degassing and results from high turbulence and constant surface disruption as well as from oxides extracted from the melt volume by the bubbles, while the amount of dross formed during ultrasonic degassing of the similar volume is ~5 times less (as measured in the present work, see Table 1). The dross acts as a natural accumulator of hydrogen through adsorption of molecular hydrogen and water (in the form of hydroxide) that can be substantial at temperatures above 600°C.^{6,15} The accumulated hydrogen can be drawn back to the melt by the repeated 'degassing'.

The ultrasonic degassing has some obvious consequences for the structure. The degassing results in considerably lower porosity as demonstrated in Fig. 6 with three- and two-dimensional tomographic images of A356 samples taken after RPT before and after 2 min ultrasonic degassing. The actual amount of porosity in samples solidified under normal pressure conditions decreases five times, from 1.6 to 0.3 vol.%. The microstructure of the as cast alloys does not change much with ultrasonic processing as it is performed at a rather high temperature and cannot directly affect solidification conditions.¹⁶

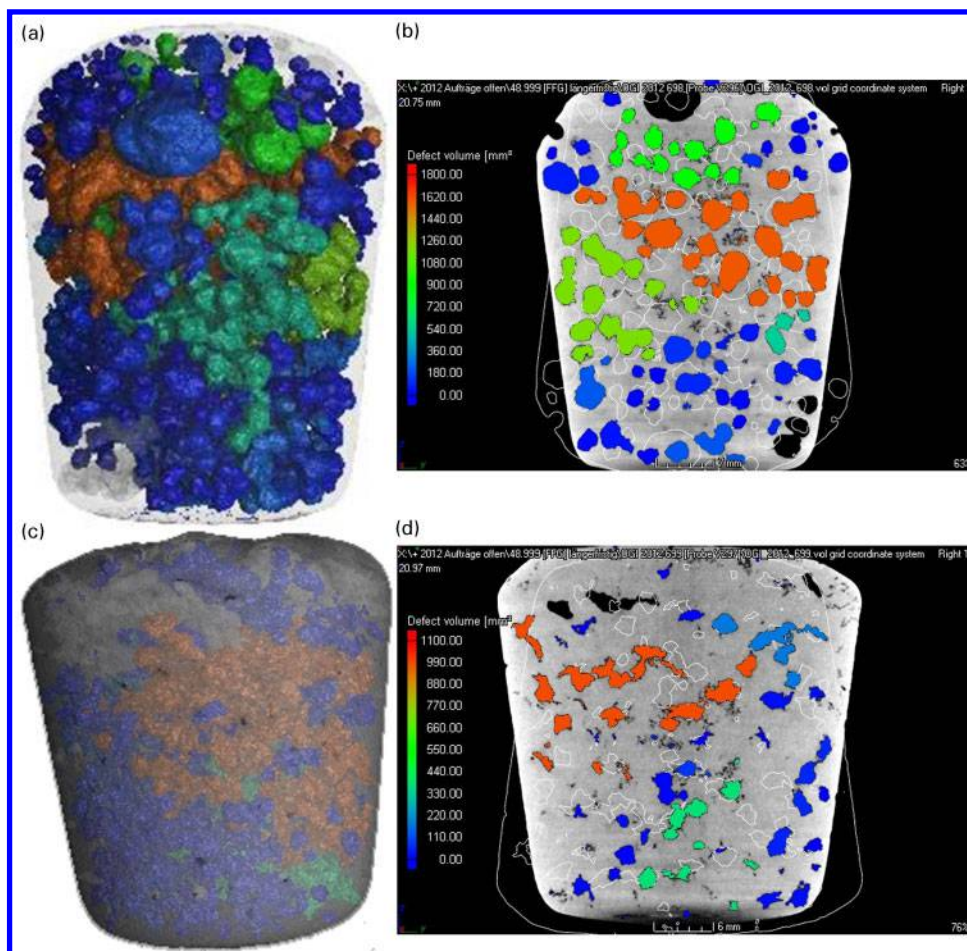
Pilot scale trials performed on 150 kg charge of A356 alloy included either ultrasonic degassing or Ar rotary



5 Kinetics of degassing of 60 kg charge of *a* A380 alloy (ultrasonic degassing) and *b* A356 alloy (Ar rotary degassing); notations are same as in Fig. 2

(impeller) degassing with the same temperature and time parameters. A photo of ultrasonic transducer with sonotrode inside the furnace is shown in Fig. 7. The

short ultrasonic sessions that were shown to be efficient for ultrasonic degassing of small volumes were implemented for a larger volume through the slow movement



6 Computer tomography of RPT samples of A356 alloys *a, b* before and *c, d* after 2 min ultrasonic degassing

Table 1 Results of pilot scale degassing trials for 150 kg of A356 alloy: comparison of ultrasonic degassing (US) and Ar rotary degassing

Degassing type	Initial hydrogen/cm ³ /100 g	Hydrogen after hydral addition/cm ³ /100 g	Hydrogen after 15 min degassing/cm ³ /100 g	Hydrogen after melt transfer to casting ladle/cm ³ /100 g	Dross/g
Ar rotary	0.26	0.59	0.31	0.48	1800
US	0.28	0.61	0.41	0.45	340



7 Photograph of ultrasonic transducer and sonotrode inside 150 kg crucible during degassing trials

of sonotrode along the melt surface. In this case, the 'unit volume' is treated for a relatively short time, while the processing is translated to the larger volume through the sonotrode movement. The main results are shown in Table 1.

Ultrasonic degassing (which is still instrumentally under development) performs rather well as compared with optimised and commercially produced impeller system. The differences in performance become negligible after the melt is transferred to the casting ladle. The increase in hydrogen concentration after the transfer maybe due to the contact with air and some residual moisture in the ladle lining. The amount of dross is significantly reduced in the case of ultrasonic degassing. This is due to the much lesser turbulence and downward direction of forced convection in the case of ultrasonic processing. These results give us confidence in proceeding in further practical implementation of ultrasonic degassing in industrial application. Mechanical properties of the produced samples have been tested and discussed elsewhere.¹⁷ Here, we just mention that the mechanical properties after either of degassing procedures were quite close with somewhat better ductility demonstrated by ultrasonically degassed metal. This confirms that the ultrasonic degassing acts in similar manner as Ar rotary degassing, decreasing not only hydrogen concentration in the melt but also oxide inclusions that may deteriorate mechanical performance of the as cast metal.

Conclusions

Ultrasonic processing is an efficient means of degassing liquid aluminium alloys that can be applied to relatively large volumes of melt with reasonable processing time and efficiency comparable to currently widely used Ar rotary degassing.

Short processing times separated by gas release idle periods can be used in ultrasonic degassing practice. For

large volumes, this intermittent regime can be substituted for sonotrode movement.

Melt degassing is followed by regassing stage with the magnitude of regassing being dependent on the extent of degassing below the quasi-equilibrium hydrogen concentration under given environmental conditions.

Ultrasonic degassing is accompanied by significant decrease in dross formation as compared to Ar rotary degassing, which stipulates lesser regassing during repeated degassing sessions and also leads to lesser metal loss during degassing.

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