# KINETICS OF ULTRASONIC DEGASSING OF ALUMINUM ALLOYS

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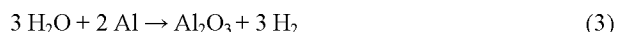[2]Universidad Autónoma de Ciudad Juárez, Juárez, 32310, MX

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## Abstract

Ultrasonic processing was shown to be an efficient means of aluminum melt degassing with benefits of being economical and environment friendly. The fundamental reason for ultrasonic degassing is known to be diffusion of dissolved hydrogen to cavitation bubbles assisted by their pulsation, and their subsequent evacuation from the melt. This paper reports on the kinetics of ultrasonic degassing of an Al–Si casting alloy. The kinetics is studied through interplay of cavitation bubble generation, melt agitation through acoustic streaming, and flotation of gas bubbles to the surface of the melt. Direct measurements of hydrogen concentration in the melt by Foseco ALSPEK-H probe are used along with a reduced-pressure test. The possibility of using short sonication times is discussed.

## Introduction

The quality of aluminum alloys is sensitive to melting conditions, temperature variations and humidity in the surrounding atmosphere [1–3]. Special attention is given to hydrogen as a contaminating gas dissolved in molten aluminum. This is because dissolved hydrogen can be measured up to 0.65 cc/100g in liquid aluminum just above the melting temperature and just below, the solubility drops down to 0.034 cc/100g [1]. During solidification, this difference makes the excess hydrogen to precipitate and, being trapped between the solid dendrites, form porosity [1]. Gas porosity combined with shrinkage porosity is detrimental to the mechanical properties of the final products, especially to the fracture toughness, fatigue endurance and ductility. Moreover, hydrogen that have not had time to precipitate and formed supersaturated solid solution with aluminum will precipitate during downstream processing, e.g. homogenization, extrusion or hot rolling, forming delaminations and secondary porosity, especially detrimental in thin gauge products or surface critical applications [4]. This is why hydrogen measurement and control is of industrial interest, and hence the need for controlling the hydrogen levels for production of ingots, billets and castings [3–5].

$$3\,H_2O + 2\,Al \rightarrow 6\,H + Al_2O_3 \qquad (1)$$

$$H + H \rightarrow H_2 \qquad (2)$$

$$3\,H_2O + 2\,Al \rightarrow Al_2O_3 + 3\,H_2 \qquad (3)$$

The main sources of hydrogen are: the molecular hydrogen in air and water moisture or vapor in the atmosphere. The latter reacts with liquid aluminum at the surface of the melt and produces alumina and hydrogen through reaction (1). The resultant atomic hydrogen is dissolved in the aluminum and $Al_2O_3$ 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 (reaction 2). Water vapor can react with liquid Al producing molecular hydrogen as well; this will dissolve in the air (reaction 3).

It is important to understand that the solubility of hydrogen in liquid aluminum is not a constant or a fixed number. The solubility depends on the conditions at the interface between the hydrogen-containing medium (atmosphere or bubble) and the liquid metal (surface or interior). The 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).

The high hydrogen concentration in the melt, resulting from the previous processing conditions, will decreased to the quasi-equilibrium concentration reflecting the actual humidity–pressure–temperature conditions. This would appear as natural degassing. On the other hand, the melt with small concentration of hydrogen, being brought under similar condition, will naturally re-gas. Eventually both melts will have the same quasi-equilibrium concentration of hydrogen. The shift in the equilibrium will result either in degassing or re-gassing. These "natural" processes occur through diffusion of hydrogen across the gas/liquid interface and are rather slow, the degassing being faster than re-gassing [1, 6].

Alloying elements may influence of hydrogen concentration in the aluminum melt in three ways [5]. Firstly, some elements change the solubility of hydrogen in the liquid aluminum, e.g. Mg and Li increase solubility while Cu, Si and Fe decrease it [7]. Also the solubility of hydrogen in the solid Al can be affected. Secondly, some elements change the nature of the oxide layer on top of the melt, affecting the oxide layer permeability. For example, Mg changes the composition of the surface layer from alumina to spinel, which increases the permeability as spinel film is much less continuous and strong than alumina. As a result the processes of degassing and re-gassing are both accelerated. Beryllium on the contrary strengthens the oxide film and prevents re-gassing of the melt. Thirdly, an alloying element can act a surfactant and change the interfacial energy at the surface of a bubble forming in the melt during degassing. Magnesium thus assists in forming larger bubbles that more easily float to the surface, therefore accelerating degassing.

Aluminum alloys have different typical levels of hydrogen content: commercially pure Al will have between 0.2 and 0.3 cc/100g, Al–Si and Al–Cu alloys will retain and pick-up more hydrogen than pure aluminum, from 0.4 to 0.5 cc/100g. In the case of Al–Mg alloys the hydrogen levels are 0.4 to 0.6 cc/100g; these alloys may pick-up more hydrogen, but at the same time release more hydrogen. For a given charge of liquid aluminum,

hydrogen content can be naturally reduced to 0.1–0.2 cc/100g (degassing) giving time (up to 1 h) and typical conditions (750 °C, 30% humidity) [1, 5].

Natural degassing is impractical for industrial applications, so different methods have been proposed for accelerating this process. Two types of degassing methods are currently used for aluminum 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, 3, 5, 8]. Bubbles formed by purged gas create numerous interfaces that promote recombination of hydrogen to molecular form and evacuate this gaseous hydrogen from the melt. The number and size of the particles along with the forced convection seems to be the main parameters of the process [2, 3]. Vacuum degassing is based on the decreased pressure above the melt surface that should result in the decrease in the quasi-equilibrium hydrogen solubility and facilitate 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 [9, 10].

Ultrasonic Degassing
Metallurgical applications of ultrasound can be traced back to 1930s and substantial work was reported during the 1950-70s [9, 11, 12, and references within]. The interest to ultrasonic technology has been invigorated during the last decade [8, 13–15]. The versatility of ultrasonic applications includes different treatments and processing of liquid metal such as grain refinement, segregation control and degassing.

Ultrasonic treatment can be used for degassing and for complementing other melt degassing methods. There are various viewpoints on the mechanism of ultrasonic degassing. Kapustina [6] considers that the oscillation of the bubble is the most important driving force behind the degassing. In the expansion stage the reduced pressure inside the bubble forces the dissolved hydrogen to diffuse and recombine to molecules inside the bubble. During the contraction phase part of this hydrogen is forced to go back. However the surface/volume ratio is such that the continuously oscillating bubble acts as a pump taking overall more hydrogen in then letting out. In this mechanism the bubble oscillation produced by ultrasound is more important than cavitation. Note that Kapustina [6] developed and experimentally validated her models using water where microscopic bubbles are quite usual natural occurrence. Kapustina admits that cavitation, producing much more bubbles and with much smaller size, dramatically accelerates the degassing process. However, the amount of naturally occurring bubbles in the metallic melt is rather negligible so the cavitation is an essential part of degassing in metallic melts. G.I. Eskin reports that hydrogen can be most efficiently removed from Al-based alloys only when ultrasonic treatment is accompanied by developed cavitation [9, 10, 16]. The developed cavitation increases the efficiency of ultrasonic degassing by 30 to 60% as compared to non-developed-cavitation ultrasonic treatment, and much more as compared with pre-cavitation regime [16]. In ultrasonic melt treatment, the cavitation can be initiated in the liquid by introducing certain level of energy into the melt. The energy is related to the frequency and amplitude of ultrasonic vibrations. The cavitation threshold in typical aluminum melts is between 0.55 and 0.85 MPa [10] and corresponds to the acoustic power of about 10 W and the vibration amplitudes above 5 µm, or to the intensities about 10 W/cm$^2$ [10]. Ultrasonic cavitation efficiently produced cavities in the liquid phase. During alternating periods of compression and rarefaction (expansion) the cavity quickly turns into a bubble filled with hydrogen that diffused into it [9, 10].

During the compression–rarefaction cycle, pulsating bubbles keep absorbing hydrogen making the bubbles to grow more. Part of bubbles will collapse (in compression periods) producing more fine bubbles. The important part of the degassing mechanisms suggested by G.I. Eskin (1998) is the role of solid inclusions, e.g. alumina in the melt. The surfaces of small alumina inclusions contain some molecular hydrogen (0.002–0.003 cc/100 g) [5]. Therefore, these numerous inclusions act as very efficient nuclei for cavitation, effectively multiplying bubbles by orders of magnitudes. This can only be achieved under cavitation conditions. Collapsing bubbles will further multiply the number. In the next stage, the bubbles will grow and float to the surface, degassing the melt. The degassing then will continue until the quasi-equilibrium condition is achieved. The quasi-equilibrium concentration of hydrogen in aluminum melt is reported to be about 50% of the solubility reflecting the environmental conditions [10].

The efficiency in ultrasonic degassing depends on the same basic phenomena as in other degassing methods: 1) transport of hydrogen from the melt to the bubbles present in the liquid, 2) diffusion of such hydrogen through the bubble/liquid interface and its recombination into molecular hydrogen, and 3) the removal of the bubbles with hydrogen through the melt surface [17]. The kinetics of ultrasonic degassing is, however, different from other methods such as rotary Ar-assisted degassing. Degassing efficiency in rotary methods is given by the ability of the introduced bubbles to drag hydrogen depending on the time, bubble sizes and number, inert gas flow rate, 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.

Re-gassing
In most experiments and in industrial practice the degassing process is performed until the desirable concentration of hydrogen (usually about 0.1 cc/100 g) is achieved. After that the melt is cast. It is known that in degassing large volumes, some time is required to finalize the process of degassing by allowing the bubbles to float to the surface. What is much less studied is the process of re-gassing, or what could happen to the degassed melt after the end of the degassing process. The re-gassing is seldom reported but there are some data that it is not an unusual phenomenon. First of all, general considerations of gas/ liquid equilibrium attest for the both processes, i.e. degassing and re-gassing, occurring simultaneously with eventually re-establishing a metastable equilibrium that reflects the environmental and process conditions. Experimentally re-gassing was observed after the end of rotary Ar-assisted degassing, with ambient humidity being reported responsible for that [3, 18]. The re-gassing phenomenon has been apparently observed also after ultrasonic degassing but is usually neglected, with the results being either truncated or approximated by a line.

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This paper reports results on ultrasonic degassing by short-time processing as well as the re-gassing upon melt holding after the end of degassing.

## Experimental Procedure

Two commercial aluminum alloys were used for this series of experiments: A356 (Al–7% Si–0.3% Mg) and A380 (Al–9% Si–3.5% Cu–0.8% Fe). The charges of 4 and 6 kg were melted in graphite crucibles in an electric furnace with the melt temperature 720 ± 5 °C. The ultrasonic equipment consisted of 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 approximately 10 mm. The tip was preheated and the melt temperature was controlled during the process. There was no controlled atmosphere. Ultrasonic treatment was applied in the molten metal for specific periods of time, i.e. 0.25, 0.5, 1, and 2 min. The input power of the generator was kept at 4 kW with the corresponding amplitude at the Nb tip of 20 μm. The null-top-peak amplitude was measured by a contactless vibrometer (BSUIR, Belorussia) in air. The principle diagram of experiments is shown in Figure 1. For measuring the degassing effect, the initial hydrogen content was measured from the aluminum alloy charge at the given temperature. After treatment, the charge was kept stable in the furnace for up to 80 minutes while hydrogen concentration measurements were taken at specific times. Two measuring techniques were used, i.e. an ALSPEK-H (Foseco) analyzer for direct measurements and a reduced pressure test (RPT, 3VT MK Gmbh) for a density index. The accuracy of hydrogen measurement was ±0.02 cc/100 g or 3% of hydrogen concentration [19].
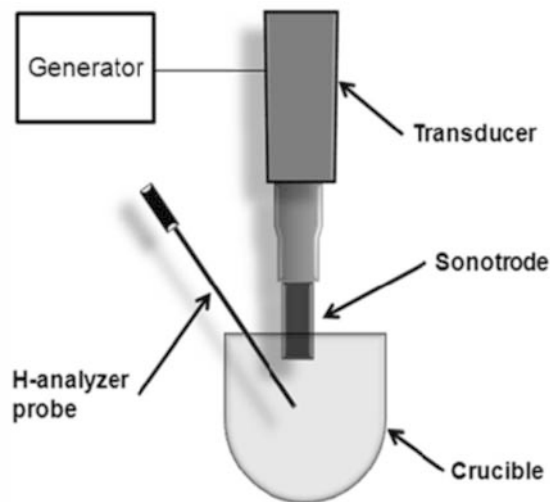


Figure 1. Experimental scheme showing the set-up arrangement and components.

The information about relative humidity (RH) on the day of experiment was taken from weather reports [20] and then converted to hydrogen concentration (H) in the air using the following formula deducted from data in Ref [3]:

$$H \ (cc/100g) = 0.1772RH \ (\%) + 0.0394. \tag{4}$$

The limit solubility of hydrogen (S, cc/100 g) in a liquid alloy was calculated as follows [21]

$$\lg S = -3050/T \ (K) + 2.94. \tag{5}$$

## Results and Discussion

A correlation formula between ALSPEK-H measurements and the RPT density indices makes possible to compare the readings obtained and present them in the same graph in cc/100g (as unit). Figure 2 shows curves for data obtained with ALSPEK-H (identified as AL) and RPT (DI line) from the same charge. Both readings were taken at same time, but from different positions in the crucible. RPT samples were obtained from the liquid close to the surface, while the ALSPEK-H measurements were taken 150 mm deeper. Figure 2 also illustrates degassing results in a stable charge of 4 kg (A380 alloy), after UST for 2 min using 4 kW and 20 μm amplitude at 720 °C. As can be seen in the Figure 2, 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 re-gassing. In the same Figure the dashed line gives the hydrogen equilibrium level (0.079 cc/100g) and the chain line – the stabilization (quasi-equilibrium) level due to humidity in the air (0.098 cc/100g) on the day of experimenting [20]. One can easily see that the ultrasonic degassing can decrease the hydrogen concentration toward the equilibrium solubility level ([H]e) but, after 60 minutes re-gassing 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 as well as the quasi-equilibrium limit are different and should be taken into account.
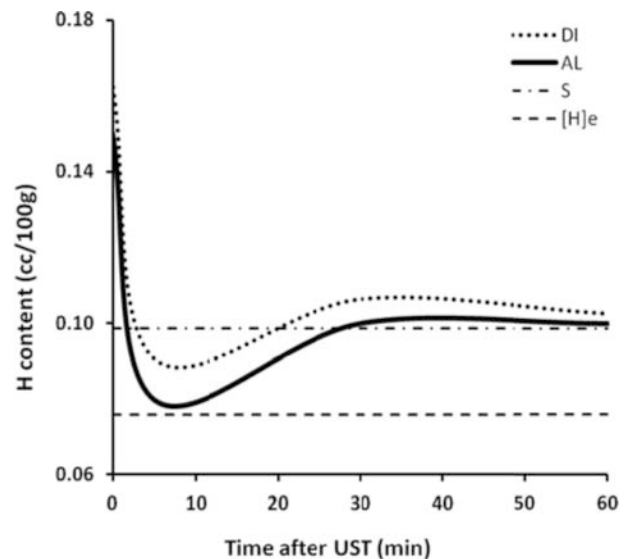


Figure 2. Hydrogen level measurements after 2-min degassing (ultrasonic processing stops after 2 min), values converted from the density indices using RPT (DI) and measured using ALSPEK-H (AL). For reference, the graph shows lines of the stabilization level (S) and hydrogen equilibrium ([H]e).

Results after different short times of degassing treatment (times below 1 minute) in 4-kg charges of an A380 alloys are given in Figure 3. There is a notable difference in the recovery behavior. The resulting hydrogen values were measured close to the stabilization level (see Figure 3). In the case of 1-min degassing, obvious re-gassing occurs with approaching the quasi-equilibrium limit (0.11 cc/100g @ 16 °C 82% RH [20]) after 20–30 min exposure. In the case of the shorter degassing times, the efficiency of degassing was less and the resultant hydrogen level did not reach the quasi-equilibrium values, hence there was no re-gassing.
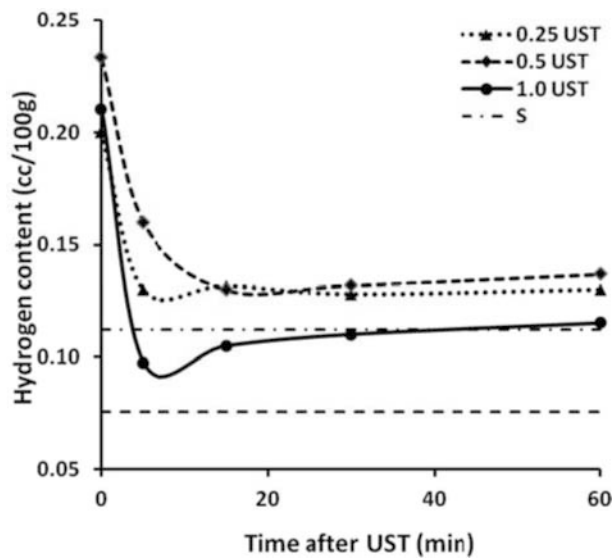


Figure 3. Rapid degassing graphs for different processing times of 4 kg of A380 melt. Metastable behavior for 0.5 and 0.25 and re-gassing effect for 1 min processing (under given conditions)

A comparison of the effect of ultrasonic degassing on different volumes is shown in Figure 4(a). UST was applied for 2 minutes to 4 and 6 kg charges of an A356 alloy under the same environmental conditions. The quasi-equilibrium limit was estimated as 0.17 cc/100g on the day of the experiments (for 76% RH @ 20 °C [20]). Degassing of 4 kg was more efficient and values significantly lower than the estimated quasi-equilibrium level were achieved, followed by re-gassing after aprox. 40 min. For the 6-kg charge the degassing was less efficient and the re-gassing less significant. We have not considered in this analysis the surface area/volume effect, which is important for de- and re-gassing kinetics [17]. Figure 4(b) 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 re-gassing while the A356 alloys demonstrated hydrogen re-adsorption. This difference is probably due to the effect of Mg on hydrogen solubility as has been discussed in Introduction. For simplicity, however, we consider that the quasi-equilibrium level is given mainly by the hydrogen–aluminum–water vapor 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 re-gassing. While the A356 charge was degassed to the level below the quasi-equilibrium limit and clearly showed re-gassing.
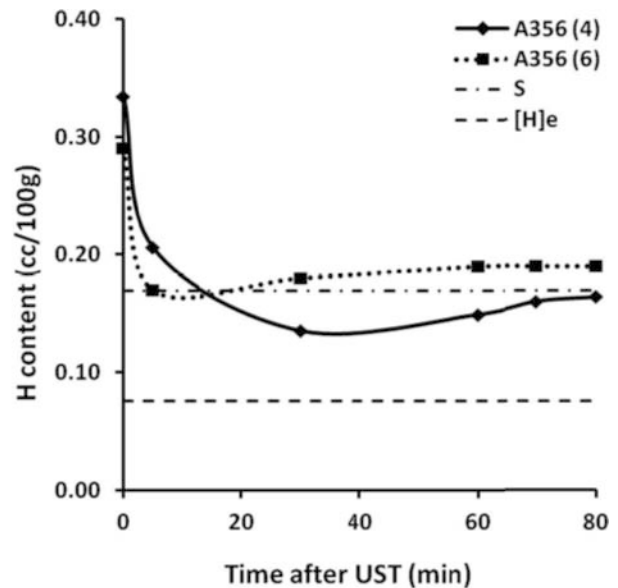


a)
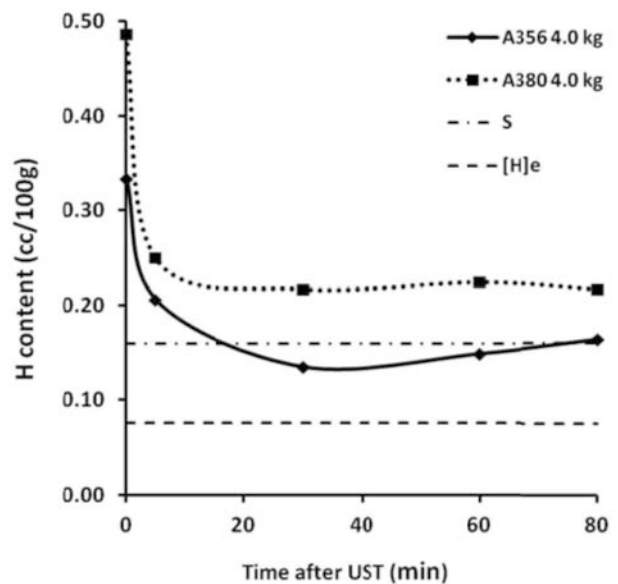


b)

Figure 4. Hydrogen levels of a) ultrasonic degassing of A356 charges but changing the volume and b) charges of A356 and A380 after the same ultrasonic degassing and ambient conditions.

The results obtained as well as degassing mechanisms suggested in literature (see Introduction) allow us to suggest the following interpretation on the re-gassing phenomenon after the end of ultrasonic degassing. There are several hydrogen levels that can be achieved in the aluminum melt as illustrated in Figure 5. For a stationary melt exposed for a sufficient time to the ambient conditions, there is always a quasi-equilibrium hydrogen level that

reflects the balance between hydrogen flows out (degassing) and in (re-gassing) the melt. This level is related to the environmental conditions (humidity, temperature, dew point, pressures, etc). If the degassing level achieved is above this quasi-equilibrium level, the hydrogen concentration will remain stable for a period of time, or may even decrease towards the quasi-equilibrium limit. This is shown as partial degassing in Figure 5. When the degassing level reaches below this quasi-equilibrium concentration and given enough time after the end of the degassing, a re-gassing effect will occur (quasi-equilibrium in Figure 5)
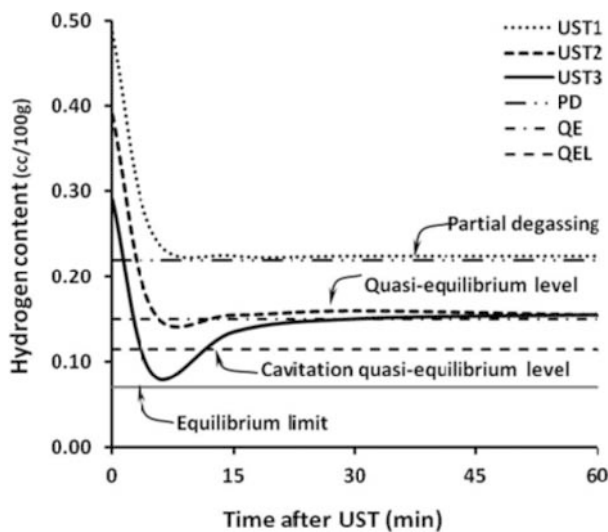


Figure 5. Illustration of quasi-equilibrium and equilibrium levels that control the degassing of aluminum alloys.

The reason for decreasing the hydrogen concentration below the quasi-equilibrium level is in the nature of cavitation degassing, when the pulsating bubbles have very low pressure inside during the rarefaction phase of oscillations, dramatically changing the local equilibrium and forcing hydrogen from the liquid solution. In this case the degassing can proceed to the "cavitation quasi-equilibrium". The theoretical limit for that is the hydrogen limit solubility in liquid aluminum ([H]e) under normal atmospheric pressure and zero humidity (shown as equilibrium limit in Figure 5). When the degassing stops and all bubbles either float to the surface or dissolve in the melt, re-gassing up to the level of quasi-equilibrium occurs. The rate of this re-gassing will be a function of the difference between the achieved hydrogen concentration and the quasi-equilibrium value, surface area/volume ratio and the amount of oxide inclusions inside the melt. The first parameter gives the stimulus for the process. The second determines the interface through which hydrogen accesses the melt. The third factor assists in retaining the hydrogen in the melt by its adsorption to oxide particles surface [10]. The re-gassing process takes longer time than the degassing, which is in good agreement with the reported studies [1, 6].

## Conclusions

The kinetics of ultrasonic cavitation degassing and re-gassing of the melt after the end of the degassing process has been studied using two typical casting alloys. It is shown that the degassing

with about 50% efficiency can be achieved within 1-2 min of processing. For the first time the re-gassing of the aluminum melt after ultrasonic degassing was experimentally demonstrated and analyzed. The re-gassing occurs only in the case when the hydrogen concentration achieved during ultrasonic degassing decreases below the quasi-equilibrium limit that reflects the ambient conditions. Further investigations of this phenomenon are required with varying the intensity of ultrasound, melt temperature, and pressure above the melt.

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