Hydrogen-induced gas porosity formation in Al-4.5 wt% Cu-1.4 wt% Mg alloy

Prince N. Anyalebechi

Received: 21 November 2012/Accepted: 16 March 2013/Published online: 23 March 2013 © Springer Science+Business Media New York 2013

Abstract The effects of low $(0.067 \text{ cm}^3/100 \text{ g})$ and relatively high (0.19 and 0.27 cm³/100 g) initial melt hydrogen concentration, solidification processing conditions, and grain refining on the formation of hydrogen-induced gas porosity in Al-4.5 wt% Cu-1.4 wt% Mg alloy have been quantitatively investigated. The study was conducted with unidirectionally cooled laboratory-size ingots solidified at 0.2-37 K/s. An optical microscope-based image analyzer and precision density measurement based on the Archimedes' principle were used to quantify the characteristics of the hydrogen-induced porosity in the ingots. Predictably, increase in melt hydrogen concentration and decrease in solidification rate increased the amount of porosity and average pore size. However, the effect of solidification rate was greater at the very low melt hydrogen concentration $(0.067 \text{ cm}^3/100 \text{ g})$. These results are consistent with reported effects of solidification rate and melt hydrogen content on porosity formation in other aluminum alloys. Addition of grain refiner slightly increased the amount of porosity and the average pore size, especially at solidification rates above 1 K/s.

Introduction

Porosity formation in products of aluminum and its alloys compromises their tensile strength, fracture toughness, and fatigue properties [1-18]. It is therefore a serious concern not just in shaped castings but also in wrought products

P. N. Anyalebechi (🖂)

School of Engineering, Grand Valley State University, 347 Kennedy Hall of Engineering, Grand Rapids, MI 49504-6495, USA e-mail: anyalebp@gvsu.edu fabricated from ingots, billets, bars, or slabs of aluminum and its alloys. The pores are usually the crack initiation and propagation sites [6, 8, 9] and the largest pores tend to dictate the fatigue life of the aluminum products [9, 10, 14]. Porous regions within an aluminum product probably yield first due to the reduced tensile load bearing capacity, causing the concentration of the strain near the voids which subsequently results in premature fracture. In aluminum alloy ingots, billets, bars and slabs porosity formation is particularly problematic because of its persistence through fabrication and potential for reappearance or exacerbation during subsequent thermal treatment processes before and/ or after fabrication [19]. In fact, persistence of microporosity is a serious problem in large thick plates of wrought aluminum alloy products that must be rolled from correspondingly large direct-chill or electromagnetic cast ingots. Some of these thick plate products are machined into large aircraft components that are required in service to withstand multi-directional stresses and to possess high fatigue strength, fracture toughness, resistance to stress corrosion cracking, and strength in the short-transverse direction [1, 20].

In the past 60 years, porosity formation (gas and shrinkage) in cast aluminum and aluminum alloy products has been extensively investigated [20–42]. These experimental investigations have involved the study of the effects of casting process-related variables, namely, initial melt hydrogen content, cooling or solidification rate, grain refining, alloy composition, and modification in the case of the Al–Si alloys. Majority of the studies of porosity formation in aluminum alloys have been on casting aluminum alloys, especially A356. Published studies on the effects of solidification process variables on the formation of porosity in wrought aluminum alloys are limited in number [21–25, 31, 33, 35]. However, the scope of most of the studies is

limited. Many of them were conducted at unknown hydrogen levels or at relatively high hydrogen concentration, typically greater than $0.15 \text{ cm}^3/100 \text{ g}$ compared to less than $0.10 \text{ cm}^3/100 \text{ g}$ desired in aluminum products [25, 33]. In addition, in most of these studies, the range of solidification rate investigated is either limited or not very well known [23, 25], the amount of porosity is characterized by only density measurement, and the cast specimens contained both shrinkage and gas-induced porosity.

In this study, the effects of solidification rate, grain refining, and hydrogen concentration on porosity formation in Al–4.5 wt% Cu–1.4 wt% Mg alloy, a wrought aluminum alloy, are quantitatively investigated. Unlike in any previously reported study on porosity formation in wrought Al–Cu–Mg alloys, the focus of this study is on hydrogen-induced porosity, a wider range of melt hydrogen concentration (0.059–0.29 cm³/100 g), and the effect of grain refining. In addition to the measurement of porosity volume fraction by density measurement, a metallurgical microscope-based image analysis technique was also used to quantitatively determine the porosity volume fraction (area %) and pore size.

Experimental procedure

This study was conducted with laboratory-size rectangular plate ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy. The ingots, 290 mm long \times 95 mm wide \times 28 mm thick, were prepared with a bench-scale unidirectional cooling casting process. As shown in Table 1, the chemical composition of the ingot samples of the alloy is consistent with that of aluminum alloy (AA) 2024. It will henceforth be referred to as AA2024. The unidirectional cooling casting process involved the unidirectional cooling of about 3 kg of metal by extracting heat from only the bottom end of the solidifying melt column. The unidirectional cooling casting apparatus shown schematically in Fig. 1 consisted of rectangular insulating plaster mold with inside dimensions of 295 mm long \times 86–98 mm wide \times 30 mm wall thickness with a taper of about $1-2^{\circ}$ to allow easy removal of the solidified casting. The mold was wrapped in ceramic wool to ensure good thermal insulation. The whole assembly was mounted on a steel frame which allowed the mold to be tilted during pouring and precluded turbulence during the filling of the mold with molten metal. A fiberfrax gasket was installed between the mold and the steel frame to prevent any molten metal leakage during pouring. The bottom part of the mold consisted of a removable copper (or steel) plate. A controlled water spray at a rate of 0.0025 m³/s was directed upwards onto the removable copper chill plate. To obtain faster solidification rates the copper chill plate was withdrawn 25 s after pouring (i.e., after a solid shell was established), to expose the bottom of the solidifying casting to direct water impingement. The water flow rate was kept constant throughout the solidification of each casting.

The molds were preheated in a resistance furnace for more than 24 h at 1006 K (733 °C); that is about 42 K above the melt pouring temperature and 95 K above the liquidus temperature [911 K (638 °C)] of the alloy. This level of mold preheat was necessary because of the inevitable loss of heat, resulting in about 40 K mold temperature drop, during the transfer of the mold to the casting position. To obtain the desired directional solidification of the melt, the mold was preheated to above the liquidus temperature of the alloy.

A 45 kg melt of the alloy was prepared and held in an electric resistance heated crucible. The melt was heated to 50 K above the liquidus temperature of the alloy. For casting, about 3 kg of melt was transferred to a smaller crucible, and subsequently heated to the predetermined pouring temperature of 973 K (700 °C). In ingots A, B, C, and D an Al-5 wt% Ti-0.2 wt% B master alloy was added at the 0.02-0.025 wt% Ti level for grain refinement. The hydrogen content of the melt in the crucible was determined with an ALSCANTM instrument, a recirculating gas method. The AISCANTM instrument, jointly developed by Alcan and Bomem Inc. (Canada) operates on the principle of monitoring the hydrogen activity developed in a small quantity of inert gas or nitrogen continuously recirculated through the aluminum alloy melt until the gaseous hydrogen diffused into the nitrogen bubbles is in equilibrium with the solute hydrogen in the molten metal. After measuring the partial pressure of the hydrogen in the inert gas with a katharometer (a thermal conductivity cell), the concentration of the dissolved hydrogen in the molten metal is calculated through the Sievert's law [43]. In addition, Ransley (chill cast) samples of the melt were taken just before pouring and analyzed by the LECO RH-402 instrument, a nitrogen carrier fusion method [43]. This involved melting of solid cylindrical sample (about 7 g) machined from the Ransley samples in an outgassed graphite crucible housed in a quartz tube with a nitrogen gas stream flowing at atmospheric pressure. The hydrogen evolved from the sample is detected by a thermal conductivity cell (a katharometer wire) inserted in the gas train.

Samples were also taken with a vacuum sampler for chemical composition analysis 4 min after the grain refining master alloy was added and before pouring. In the cases where low hydrogen contents were required, the melt was degassed by bubbling pure argon into the melt in the smaller crucible for 3–10 min depending on the hydrogen level required. The rate of solidification at different locations in three of the solidifying castings was directly

Alloying elements Melt chemical composition, wt% Ingot A Ingot B Ingot C Ingot D Ingot E Si 0.02 0.02 0.02 0.02 0.02 Fe 0.04 0.04 0.04 0.03 0.03 4.49 Cu 4.48 4.51 4.45 4.60 0.01 0.00 0.00 0.02 0.02 Mn 1.37 1.35 1.25 1.42 1.46 Mg Cr 0.00 0.00 0.00 0.00 0.00 Ni 0.00 0.00 0.00 0.00 0.00 Zn 0.01 0.01 0.01 0.00 0.00 Ti 0.021 0.021 0.020 0.20 0.003 в 0.0008 0.0006 0.0002 0.0004 0.0011 A1 Bal. Bal. Bal. Bal Bal Grain refined Yes Yes Yes Yes No Initial melt H content ($cm^3/100$ g) 0.06 0.067 0.067 0.19 0.27

Table 1 Chemical compositions and the melt hydrogen content of the aluminum alloy 2024 ingots





Fig. 1 Schematic of the directional cooling casting apparatus used in the study

monitored with thermocouples mounted on a steel plate located through the top of the mold along the axis of the mold cavity at different distances from the copper chill (Fig. 1). The temperature data from different locations of the solidifying castings were recorded with a computercontrolled data acquisition unit, at the rate of five readings per second. The solidification rates were computed by dividing the freezing range of the alloy by the local solidification time; that is, the time interval between when the melt temperature reached the liquidus to the time it reached the eutectic temperature.

For characterization, the solidified rectangular plate ingots were sectioned longitudinally into three equal slices as shown in Fig. 2. Samples were taken at known distances from the chill copper plate for the different analyses, including alloy chemistry, optical metallography, hydrogen content determination, and precision density measurements. To avoid end effects and lack of directional heat extraction, the last 50 mm of the top and 15 mm of the bottom of each casting were discarded.

The amount of porosity (i.e., volume fraction of porosity or porosity volume fraction) was determined by the precision density measurement based on the Archimedes' principle. Each sample was weighed in air three times on a balance with a precision of 0.1 mg. The sample was then weighed in distilled water 3–5 times. The temperatures of air and water were measured just before the measurements. Atmospheric pressure was obtained from the local barometer. The sample density was determined with the following equation:

$$\rho = \frac{(W_{\rm air}\rho_{\rm water}) - (W_{\rm water}\rho_{\rm air})}{W_{\rm air} - W_{\rm water}} \tag{1}$$

where W_{air} and W_{water} are the sample mass in air and water, respectively, ρ_{water} and ρ_{air} are the densities of water and air, respectively, at the measured temperature and pressure.

In air, mass of the samples from ingots A, B, and C varied between 7 and 12 g; samples from ingot D weighed 11–17 g and those from ingot E weighed 12–23 g. The average size of samples was increased to improve precision of the density measurement. The standard deviations of the mass of the samples were ± 0.4 and ± 1.0 mg in air and water, respectively. The deviation of the densities in ingots A, B, C, D, and E were ± 0.001 , ± 0.0005 , ± 0.0005 , ± 0.001 , and ± 0.0002 Mg/m³, respectively. The volume fraction of porosity (% porosity) was determined with the following equation:

$$f_{\rm p} = \frac{\rho_{\rm theoretical} - \rho_{\rm sample}}{\rho_{\rm theoretical}} \times \frac{100}{1} \tag{2}$$

Fig. 2 Sample locations



where $f_{\rm p}$ is percent porosity volume fraction in a given sample, $\rho_{\rm theoretical}$ is theoretical/maximum density of the aluminum alloy, and $\rho_{\rm sample}$ is sample density.

Due to lack of availability of theoretical density data for this given alloy composition, the highest density of 2.77 Mg/m³ obtained at the bottom of any one of the ingots where no pore was observed with the optical microscopy was adopted and used for the calculation of the % porosity. Image analysis was performed on some of the AA2024 alloy samples with an optical microscope based image analyzer. Each sample was evaluated at 50× magnification for the area percentage porosity and average pore size. More than forty fields of view and a total area of 121 mm² were scanned per sample.

Results

The average solidification rates obtained with the thermocouples located at known distances from the copper chill plate in three of the directionally solidified ingots are presented graphically in Fig. 3. With the possible exception of the location closest to the copper chill plate, the average solidification rates were comparable at given locations of the ingots. The consistency of the measured solidification rates in the three ingots implied that the average solidification rates in the five ingots used in the study were the same at comparable locations and that the castings were prepared under identical thermal conditions. The range of solidification rate of the ingots was between 0.25 K/s at 281 mm from the chill surface and 37.2 K/s (extrapolated) at the chill surface. Since the ingots were cast under the same thermal conditions, they have essentially the same solidification history as given in Fig. 3.



Fig. 3 Solidification rate as a function of the distance from the chill copper plate of the directionally cooled ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy

The photomicrographs in Figs. 4 and 5 show the effects of solidification rate and melt hydrogen content on porosity formation in the grain refined AA2024 ingots. As expected, the amount of porosity, the number and the average size of the hydrogen-induced pores increased with increase in initial melt hydrogen concentration from 0.067 to $0.19 \text{ cm}^3/100 \text{ g and decrease in solidification rate (Figs. 4, 5)}$. At 0.067 $\text{cm}^3/100$ g initial melt hydrogen content, porosity formation is not microstructurally evident at solidification rates greater than 1.5 K/s. Also, at this very low level of hydrogen concentration, the pores are present primarily at the dendrite cell and grain boundaries (Fig. 6). That is, the pores are not spherical in shape; they are primarily interdendritic in nature. At the higher initial melt hydrogen concentrations of 0.19 and 0.27 cm³/100 g, the hydrogeninduced pores are significantly larger in size and are present



Fig. 4 Photomicrographs showing the effects of solidification rate and hydrogen content on porosity formation in as-cast ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy

both at grain boundaries and within the grains (Figs. 4, 6). The smaller size pores in the ingot containing higher hydrogen content are also interdendritic in nature like the

pores observed in the ingot containing the very low hydrogen concentration. Also, for a given solidification rate, the number of pores in the ingot containing $0.19 \text{ cm}^3/100 \text{ g}$ is

Fig. 5 Photomicrographs showing the effect of melt hydrogen content on pore distribution in grain refined castings of Al–4.5 wt% Cu–1.4 wt% Mg alloy solidified at 0.5 K/s



(b) $0.19 \text{ cm}^3/100 \text{ g}$

600 µm

significantly greater than that in the ingots containing 0.067 cm³/100 g. This is particularly the case at solidification rates below 1 °C/s (Fig. 5).

The pore volume fraction calculated from the density measurements are shown in Fig. 7 as a function of solidification rate for ingots with different initial melt hydrogen levels. In general, for a given initial melt hydrogen content, pore volume fraction decreased with increase in solidification rate. The effect of solidification rate appeared to be greater on the pore volume fraction in the ingots containing low initial melt hydrogen concentration of 0.059 and 0.067 cm³/100 g. For example, at a hydrogen concentration of 0.067 cm³/100 g, an increase of solidification rate from 0.2 to 1 K/s decreased the volume fraction of porosity **Fig. 6** Typical morphologies of gas pores in grain-refined ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy with relatively (i) low and (ii) high initial melt hydrogen concentrations, solidified at 0.25 K/s



(i) 0.067 cm³/100 g

(ii) $0.19 \text{ cm}^3/100 \text{ g}$



(b) Average area percent porosity (Image analysis measurement)

Fig. 7 Effect of solidification rate, initial melt hydrogen content, and grain refining on amount of porosity in grain refined as-cast ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy



Fig. 8 Comparison of pore volume fraction in ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy obtained by density and optical microscopebased image analysis measurements

from 0.83 to 0.05 vol%, a decrease of almost 94 %. In contrast, at a hydrogen concentration of 0.19 cm³/100 g, an increase of solidification rate from 0.2 to 1 K/s decreased the volume fraction of porosity from 2.3 to 0.7 vol%, a decrease of almost 70 %. It is noteworthy that results of the pore volume fraction calculated from the density measurements are quite reproducible. As apparent in Fig. 7, at comparable solidification rates, the pore volume fractions in the three ingots containing relatively low initial melt hydrogen content of 0.059 and 0.067 cm³/100 g are comparable. Furthermore, in all of the ingots, at slower solidification rates (typically less than 1 K/s, the dependence of the pore volume fraction on solidification rate increases markedly and the pore volume fraction becomes more sensitive to initial melt hydrogen content.



Fig. 9 Effect of solidification rate, initial melt hydrogen content, and grain refining on equivalent pore diameter in as-cast ingots of Al-4.5 wt% Cu-1.4 wt% Mg alloy

It is also interesting to note that for the same solidification rates and slightly higher concentration $(0.27 \text{ cm}^3/100 \text{ g} \text{ in the non-grain refined ingot compared to 0.19 cm}^3/100 \text{ g}$ in the grain refined ingot), non-grain refining decreases pore volume fraction (Fig. 7a). That is, addition of grain refiner to AA2024 appears to slightly increase pore volume fraction. This is particularly the case at solidification rates above 1 K/s.

The average area percent porosity values obtained by image analysis as a function of solidification rate in three of the five ingots are shown in Fig. 7b. Area percent porosity also increased with increase in initial melt hydrogen content and decrease in solidification rate (Fig. 7b). The observed trends in the dependence of area percent porosity on solidification rate and initial melt hydrogen content are consistent with those previously observed for the pore volume fraction (Fig. 7a).

The image analysis results also confirm the observed increase in the amount of porosity in the ingot caused by addition of a grain refiner to the ingot (Fig. 7a). It is noteworthy that the two measures of amount of porosity, the pore volume fraction and area percent porosity, compare fairly well with each other (Fig. 8). This is particularly the case at the higher porosity volume fraction level and at the lowest initial melt hydrogen level. The pore size was measured as the equivalent average pore diameter, defined as the diameter of a circle with an area equivalent to the measured average pore area. Average equivalent pore diameter as a function of average solidification rate for different initial melt hydrogen concentration is shown in Fig. 9. It is apparent that the equivalent pore diameter decreases as the solidification rate increases and as the initial melt hydrogen content decreases. Also, addition of grain refiner appears to increase the equivalent pore diameter. Like the pore volume fraction, the sensitivity of pore size to solidification rate, initial melt hydrogen content, and grain refining is greatest at slower solidification rates (typically less than 1 K/s).

Discussion

The results of this study clearly show that gas porosity formation in AA2024 ingots is sensitive to the rate of solidification of the ingot, initial melt hydrogen content, and addition of grain refiner. The results are reproducible even at very low hydrogen content $(0.059-0.067 \text{ cm}^3/100 \text{ g})$ and over a fairly wide range of solidification rate. The most pertinent findings are: (i) For a given initial melt hydrogen content, increase in solidification rate decreases pore volume fraction and size. (ii) The sensitivity of pore volume fraction and size to solidification rate and initial melt hydrogen content is greatest at slower rates of solidification (typically less than 1 K/s). (iii) Over the range of solidification rate investigated, increasing initial melt hydrogen concentration from 0.059 to 0.19 cm³/100 g in grain and non-grained AA2024 ingots increased the pore volume fraction and size (by more than 100 % at solidification rates below 1 K/s). (iv) Microstructurally, the hydrogen gas-induced pores in the ingot containing $0.067 \text{ cm}^3/100 \text{ g}$ were primarily interdendritic in nature. (v) Addition of grain refiner to AA2024 appears to slightly increase porosity volume fraction and average pore size. This is particularly the case at solidification rates above 1 K/s. Most of these results are consistent with reported effects of solidification conditions on porosity formation in other aluminum alloys [22-25, 33, 36, 38]. For comparable initial melt hydrogen concentration and solidification rate, the nominal volume fractions of porosity obtained in this study, with both the density and image analysis measurements, are comparable to those reported in other aluminum alloys.

There are two possible approaches to explaining these pertinent findings, namely: (a) the classical theory approach

that gas porosity formation in aluminum and its alloys is caused by the rejection of dissolved hydrogen from the solidifying phase into the liquid phase; and (b) the *bifilm* approach proposed by Campbell [44–53] which attributes gas porosity formation to the prevalence and opening (unfurling) of thin double oxide films (or bifilms) entrained in the aluminum alloy castings.

The classical approach to explaining gas porosity formation

Porosity is usually caused by two concomitant mechanisms, namely, volumetric shrinkage (or contraction of the alloy) and the change in the solubility and associated precipitation of hydrogen during solidification. The liquid that must flow towards the root of the dendrites to compensate for the volumetric shrinkage induces a pressure drop across the mushy zone and the liquid. The magnitude of the pressure drop depends on the local solidification conditions, but it can be as low as -200 kPa near the end of solidification [41]. According to the classical theory, gas porosity formation in aluminum and its alloys is attributed to the enrichment in dissolved hydrogen in the interdendritic liquid during solidification engendered by the large difference in the solubility of hydrogen in liquid and solid states. As the metal solidifies, hydrogen is rejected from the solidifying phase at the solid/liquid interface into the liquid phase which becomes increasingly enriched in hydrogen. The dissolved hydrogen exerts a pressure as given by Sievert's law, and a pore is formed when the hydrogeninduced pressure in the melt is equal to the sum of the atmospheric, metallostatic, and surface tension pressures, in accordance with the well-known Laplace equation:

$$P_{\rm H_2} = P_{\rm ext} + P_{\rm m} + P_{\rm s} + \frac{2\gamma_{\rm l/g}}{\rm r}$$
⁽³⁾

where $P_{\rm H_2}$ is the pressure of the gaseous hydrogen inside of the pore due to hydrogen segregation, $P_{\rm ext}$ is external or atmospheric pressure, $P_{\rm m}$ is metallostatic pressure, $\gamma_{\rm l/g}$ is interfacial tension at the liquid/gas interface (i.e., surface tension of the melt), and *r* is radius of the pore.

The precise mechanism for nucleation of gas porosity is still not well understood. The above analysis does not take into consideration the difficulties associated with the nucleation of a gas pore. The energy requirements and the required internal pressure within the pore make homogeneous nucleation very unlikely to occur. The initiation pressure for homogeneous nucleation of gas pores in aluminum is estimated to be about 3×10^4 atmospheres [44]. However, one of the proposed and accepted mechanisms for gas pore nucleation is heterogeneous nucleation on non-wetted surfaces such as oxide films and inclusions, refractories, mold walls, and possibly grain boundaries.

At all of the initial melt hydrogen levels investigated. the amount of porosity formed during solidification in the ingots decreased with increase in solidification rate. This is shown by the decrease in the measured volume and area fractions of porosity obtained in the density and image analysis measurements, respectively. At a given initial melt hydrogen concentration, the effect of solidification rate on porosity formation can be explained in terms of the effects of solidification rate on the pore nucleation and subsequent growth of the nucleated pores during solidification. However, the effects of solidification rate on the volume fraction and size of the pores are easier to explain than its effect on pore nucleation. The observed decrease in porosity volume fraction and size with increase in solidification rate can be attributed to its effect on: (i) the distance through which hydrogen can diffuse during the period of pore nucleation and growth, (ii) time available for pore growth, and (iii) availability of hydrogen for pore growth. The growth of nucleated pores is a diffusion-controlled process; so the volume fraction and sizes of pores is dependent on the time the pores have to grow (i.e., the time between nucleation and end of solidification). It requires time for the diffusion of hydrogen from the bulk liquid and solid to the nucleated pore sites for growth [33, 35, 36, 42] and for coalescence of growing pores.

Faster rates of solidification retard growth by reducing the time available for hydrogen diffusion to the nucleated pore site. Faster rates of solidification also engender greater retention of hydrogen in a supersaturated solid solution in the solidified solid and thus deprives the nucleated pores the hydrogen they require for growth. The final size and shape of the gas pores also depend on the ability of the growing pores to resist the pressure from the surrounding solidifying solid phase. At faster rate of solidification, the growing pores probably do not have enough internal partial hydrogen pressure to resist the fast growing solid aluminum around them. As a result, gas pores that formed in the faster solidified ingot specimens are typically less spherical, in shape [38]. The effect of solidification rate on porosity formation is greater at the lowest hydrogen levels investigated (Fig. 7). Similar observations have been made on other aluminum alloys [38, 39]. This is not entirely surprising, since at higher hydrogen concentration, the early nucleation and subsequent faster growth of the hydrogen-induced pores tend to overcome or reduce the suppressing effect of solidification rate on pore growth.

The observed trend of increase in pore density with increase in solidification rate could be attributed to the effect of solidification rate on pore nucleation. Increase in solidification rate increases degree of undercooling. According to the nucleation theory, the number of potential nucleation sites increases with increase in undercooling. Consequently, as solidification rate increases, pore nucleation is expected to increase. This in turn results in greater number of pores in the faster solidified ingots and is compounded by the fact that at fast solidification rates, the pores do not have sufficient time to grow and coalesce into less number of pores. However, Atwood et al. [42] have shown that the relationship between pore nucleation and undercooling (hence, solidification rate) does not quantitatively follow the behavior predicted by the heterogeneous nucleation theory. They attributed this to the fact that nucleation of a few gas pores causes a decrease in available hydrogen due to diffusion into the growing pores. This reduction in available hydrogen causes a decrease in the rate of pore nucleation as time progresses and the existing pores grow. This suggests that the magnitude of the effect of solidification rate on pore nucleation and possibly pore density may be a function of the aluminum alloy composition and the solidification processing conditions. This is compounded by the complexity and lack of our complete understanding of pore nucleation mechanism.

Another important finding in this study is that over the range of solidification rate investigated, increasing initial melt hydrogen concentration from 0.059 to 0.19 cm³/100 g in grain-refined AA2024 ingots increased the porosity volume fraction and pore size (by more than 100 % at solidification rates below 1 K/s). These results are consistent with published results of studies of gas porosity formation in Al-Cu and other aluminum alloys [20-39]. The observed effects of initial melt hydrogen content can be explained in terms of the effect of the following: (i) extent of hydrogen segregation and associated hydrogen partial pressure in the melt, (ii) fraction of solid and/or temperature at which pore nucleation occurs and the time left for pore growth prior to completion of solidification; and (iii) availability of hydrogen for diffusion to and growth of the nucleated pores. At high initial melt hydrogen concentration, early saturation of the melt with hydrogen causes early nucleation of pores at higher temperature and results in faster rate of pore growth [42]. At high hydrogen concentration, pores nucleate early, become stable and grow to a point where they would compel the solidifying solid to take their shape. In fact, simple Scheil-type estimates of hydrogen segregation during solidification indicates that at the high melt hydrogen contents $(0.19-0.27 \text{ cm}^3/100 \text{ g})$, the concentration of the solidifying melt exceeds the solubility of hydrogen in AA2024 at between 0.4 and 0.5 solid fraction. Also, at higher initial melt hydrogen concentration there is enough hydrogen even at faster solidification rates for diffusion to and growth of the nucleated pores. All of these result in larger pore size, higher porosity volume fraction, and lower pore density. At the lowest initial melt hydrogen content of $0.059 \text{ cm}^3/100 \text{ g}$, saturation of the melt with hydrogen occurs very late toward the end of the solidification, 0.85 solid fraction. This explains why microstructurally, the hydrogen gas-induced pores in the ingot containing $0.067 \text{ cm}^3/100 \text{ g}$ were primarily interdendritic in nature; probably because they nucleated at late stages of solidification of the alloy (Fig. 6).

Addition of grain refiner to AA2024 appears to slightly increase pore volume fraction and size (Figs. 7, 9). It is important to note that the increase in the amount of porosity by grain refining was obtained in both the density and image analysis measurements. Interestingly, the non-grain-refined ingot contained higher initial melt hydrogen content $(0.27 \text{ cm}^3/00 \text{ g in the non-grain-refined ingot compared to})$ $0.19 \text{ cm}^3/100 \text{ g}$ in the grain refined ingot). The observed increase in volume fraction of porosity and pore size by grain refinement is not consistent with the reported effects of grain refinement on porosity formation in aluminum alloys A356 and Al-4.7 wt% Mg [26, 27]. In Al-4.7 wt% Mg and A356 alloys, grain refining decreased porosity volume fraction and average pore size [26, 27]. Atwood et al. [36] suggest that decrease of porosity volume fraction and pore size by grain refinement can be attributed to two influences of grain refinement on pore growth. The first effect is that the increase in the number of nucleated grains increased the overall fraction solid. This affects the rate at which hydrogen is rejected from the growing solid, increasing the ambient hydrogen concentration in the surrounding melt, whilst decreasing the effective diffusion coefficient of hydrogen. This is expected to impede pore growth. The second effect is the impingement of the pores with grains which determines the extent of uninhibited spherical growth of the pore [36]. Both of these effects could impede pore growth and result in smaller pore size and less porosity volume fraction. Another (and simpler) explanation proposed for the reduction of porosity volume fraction and pore size is that grain refined aluminum alloy melts contain more sites for pore nucleation. This results in greater number of nucleated and consequently smaller pores. However, in this study, the observed increase in porosity volume fraction and pore size may possibly be due to combined effects of earlier and increased pore nucleation at grain refiner-related oxide nucleation sites. Another possible but unlikely reason is that, because of the greater affinity of titanium for hydrogen, addition of grain refiner increases the amount of hydrogen in the melt and thus exacerbates porosity formation.

The bifilm approach to explaining gas porosity formation

The commonly accepted ideas of heterogeneous pore nucleation and growth have been challenged by Campbell [44–50]. He proposed a nucleation-free mechanism for hydrogen-induced porosity formation based on the concept of *double oxide films or bifilms*. He contends that *double oxide films or bifilms* are the primary initiation sites for the formation of hydrogen porosity in aluminum alloy castings

[44–50]. Double oxide films (bifilms) are oxide defects in aluminum (and some other metal castings) that form during turbulent pouring of the molten metal in a casting operation. Bifilms consist of two oxide layers and a layer of air trapped between the unbonded internal surfaces of the oxide film. They can be produced when the turbulent pouring condition causes the oxide film on the surface of an aluminum alloy melt to fold upon itself and then becomes entrained or submerged into the bulk molten metal. After entrainment, the turbulence causes the bifilms to convolute and contract [46, 47]. They resemble and act as cracks in the molten metal. The bifilms with their air pockets are then apparently the natural seeds or beginnings of gas pores in the molten metal. According to Campbell, these cracklike bifilm oxide defects in the molten aluminum act as the preferred initiation sites for hydrogen porosity formation in aluminum alloy castings. He contends that their presence would eliminate the need for the nucleation stage to occur during the formation of a hydrogen bubble and hence exacerbate gas porosity formation. The bifilms are apparently the preferred sites for formation of gas pores because [47]: (i) the required pressure conditions for homogeneous and heterogeneous nucleation of a hydrogen gas bubble or pore (in the absence of bifilms) are so difficult that internal initiation of gas porosity in castings is almost impossible and thus cannot explain the abundance and persistent prevalence of gas porosity in aluminum alloy castings; (ii) the oxide films are not readily or well wetted, unlike dendrites (since they are wetted by the melt they are formed from), borides, carbides, and nitrides; and (iii) unlike in other types of heterogeneous nucleation, the opposing effects of surface tension is negligible. Campbell's hypothesis has gained significant attention and results of several studies [48-53] have clearly confirmed the formation of double oxide films in aluminum alloy castings and some have shown close association between the oxides and gas porosity. It is, however, noteworthy that the effect of oxide inclusions on gas porosity formation in aluminum and its alloys have long been recognized in the aluminum industry. Oxide films and inclusions have long been known to exacerbate the prevalence of gas porosity in cast and wrought aluminum products [54–56].

The question arises as to whether the bifilm concept, like the classical theory, can be used to explain the effects of solidification rate, melt hydrogen content, and grain refining addition on porosity volume fraction and size observed in this study. For example, can the bifilm concept be used to explain why decrease in solidification rate decreased porosity volume fraction and size (Figs. 7, 9)? According to Campbell [47], the first stage of gas porosity simply involves the opening (or unfurling) of the double oxide films (that contain a thin layer of gas) by separation of their unbonded halves. This implies that the gas cavity formed by the bifilms by entrapping air within the folded film can be considered preexisting gas pores in the molten metal. These pores apparently grow by the unfurling of the oxide bifilms with a pressure drop caused by insufficient liquid feeding and/or the diffusion of hydrogen into the cavity. This suggests that the effects of solidification rate on porosity formation can be explained by its effects on: (i) the rate and extent of unfurling of the oxide bifilms, (ii) the rate of diffusion of hydrogen into the bifilm cavity and the extent of the resulting inflation of the bifilms, and (iii) the amount and rate of growth of the oxide bifilms. It is conceivable that slow solidification rates (i.e., longer solidification times) will result in sufficient time for hydrogen diffusion into the bifilm cavities and consequently sufficient inflation of the bifilms [47, 51] resulting in the opening of the oxide folds. The longer solidification time will allow more time for hydrogen diffusion to and opening of more bifilms. All of these effects could explain the observed increase in porosity volume fraction and size at slower solidification rates. However, there is no documented established relationship between solidification rate and the formation and evolution of the double oxide films (bifilms) during solidification of aluminum alloys.

Results of the study by Raiszadeh and Griffiths [51] suggest that dissolved hydrogen in an aluminum melt diffuses into the trapped air bubble between the oxide bifilms and causes their expansion, extending the time it takes to reduce their volume. This occurs if the initial melt hydrogen concentration is higher than the equilibrium amount in the ambient environment. The fact that diffusion of hydrogen into the double oxide film defect may extend the time that the defects contain an atmosphere (and remain a pore during the solidification process) may partly explain the observed increase in porosity volume fraction by increase in hydrogen concentration in the molten metal. Furthermore, the rate of unfurling of the oxide bifilms may be sensitive to the concentration of hydrogen in the solidifying molten aluminum [47]. Higher melt hydrogen concentration results in higher driving force for hydrogen diffusion into the bifilm and consequently a higher internal pressure. This also suggests that even with the prevalence of bifilms, the nature and extent of gas porosity formation in aluminum alloys are still subject to the effects of alloy composition and their effects on the equilibrium partition coefficient and the diffusion of hydrogen in aluminum.

Conclusions

1. Over the range of solidification rate investigated, increasing initial melt hydrogen concentration from 0.059 to $0.19 \text{ cm}^3/100 \text{ g}$ in grain refined AA2024

ingots increased the porosity volume fraction and pore size.

- 2. For a given initial melt hydrogen content, increase in solidification rate decreased porosity volume fraction and pore size.
- 3. The sensitivity of porosity volume fraction and pore size to solidification rate and initial melt hydrogen content is greatest at the slower rates of solidification (typically at below 1 K/s).
- Addition of grain refiner to AA2024 appears to slightly increase porosity volume fraction and pore size. This is particularly the case at solidification rates above 1 K/s.
- 5. Microstructurally, the hydrogen gas-induced pores in the ingot containing $0.067 \text{ cm}^3/100 \text{ g}$ were primarily interdendritic in nature; probably because they nucleated at the late stages of solidification of the alloy.

References

- 1. Turner AN, Bryant AJ (1967) J Inst Metals 95:353
- 2. Eady JA, Smith DM (1986) Mater Forum 9:217
- 3. Surappa MK, Blank E, Jacquet JC (1986) Scr Metall 20:1281
- Kobayashi M, Dorce Y, Toda H, Horikawa H (2010) Mater Sci Technol 26:962
- Ohsasa K, Ohshima T, Takahashi T (1989) J Jpn Inst Light Metals 39:109
- 6. Ca'Ceres CH (1995) Scr Metall Mater 32:1851
- Kobayashi T (1998) In: Sato T et al (eds) Proceedings of a conference on aluminum alloys—their physical and mechanical properties, The Japan Institute of Light Metals, p 127
- 8. Shneider GL et al (1982) Mekhanika Materialov 18:93
- 9. Zhang Y, Xu J, Zhai T (2010) Mater Sci Eng A 527:3544
- Couper MJ, Neeson AE, Griffiths JR (1990) Fatigue Fract Eng Mater Struct 13:213
- 11. Skallerud B, Iveland T, Harkegard G (1993) Eng Fract Mech 44:857
- Odegard JA, Pedersen K (1994) SAE Technical Paper No. 940811, International Congress & Exposition, Detroit, Michigan, p 25
- 13. Ikuno H, Iwanaga S, Awano Y (1995) Keikinzoku 45:671
- Zhang B, Poirier DR, Chen W (1999) Metall Mater Trans A 30A:2659
- 15. Wang QG, Apelian D, Lados DA (2001) J Light Metals 1:73-84
- Jang Y, Jeong Y, Yoon C, Kim S (2009) Metall Mater Trans A 40A:1090
- 17. Ammar HR, Samuel AM, Samuel FH (2008) Int J Fatigue 30:1024
- Elsner JH, Kvam EP, Grandt AF Jr (1997) Metall Mater Trans A 24A:1157
- 19. Anyalebechi PN, Hogarth J (1994) Metall Mater Trans B 25B:111
- 20. Jordan MF, Denyer GD, Turner AN (1962) J Inst Metals 91(63):48

- 21. Ransley CE, Talbot DA (1955) Z Metallkunde 46:328
- 22. Thomas PM, Gruzleski JE (1978) Metall Trans B 9B:139
- 23. Gruzleski JE, Thomas PM, Entwistle RA (1978) Br Foundrym 71:69
- Entwistle RA, Gruzleski JE, Thomas PM (1979) Proceedings of a conference on solidification and casting of metals, The Metals Society, p 345
- 25. Weinberg F, Hirschfeld HA (1979) Metal Sci 6:335
- Fang QT, Anyalebechi PN Granger DA (1988) In: Boxall LG (ed) Light metals 1988, The Metallurgical Society, Phoenix, p 477
- 27. Fang QT, Granger DA (1989) AFS Trans 209:989
- 28. Gupta AK et al (1991) In: Proceedings of INCAL-91, p 521
- Shivkumar S, Wang L, Lavigne R (1992) In: Das SK (ed) Light metals 1993, The Metals, Minerals, and Materials Society, Warrendale, p 829
- 30. Tynelius K, Major JF, Apelian D (1993) AFS Trans 101:401
- 31. Kao ST, Chang E, Lee YW (1995) Mater Technol 11:933
- Roy N, Samuel AM, Samuel FH (1996) Metall Mater Trans A 27A:415
- 33. Lee PD, Hunt JD (1997) Acta Mater 45:4155
- Nagaumi H, Komatsu K, Hagisawa N (1998) In: Sato T et al (eds) Aluminum alloys—their physical and mechanical properties, vol 1. The Japan Institute of Light Metals, Pasadena, p 231
- 35. Yin H, Koster JN (2000) ISIJ Int 40:364
- 36. Atwood RC, Sridhar S, Zhang W, Lee PD (2000) Acta Mater 48:405
- 37. Knuutinen A et al (2001) J Light Metals 1:241
- Anyalebechi PN (2003) In: Crepeau PN (ed) Light metals 2003, The Minerals, Metals, and Materials Society, Warrendale, p 971
- 39. Emadi D (1995) Ph.D. Thesis, McGill University, Montreal
- 40. Lee PD, Hunt JD (1997) Scr Mater 36:399
- Felberbaum M (2010) Ph.D. Thesis, Ecole Polytechnique Federale De Lasaunne, Switzerland
- 42. Atwood RC, Sridhar S, Lee PD (1999) Scr Mater 41:1255
- 43. Anyalebechi PN (1991) Cast Metals 3:182
- 44. Campbell J (2003) In: Castings, Butterworth Heinemann, London
- 45. Bangyikhan K (2005) Effects of oxide film, Fe-rich phase, porosity and their interactions on tensile properties of cast Al–Si– Mg alloys, Ph.D. Thesis, University of Birmingham, Birmingham
- 46. Campbell J (2006) Metall Mater Trans B 37B:857
- 47. Campbell J (2011) In: Complete casting handbook—metal casting processes, metallurgy, techniques and design, Butterworth Heinemann, London
- 48. Gopalan R, Prabhu NK (2011) Mater Sci Technol 27:1757
- Dispinar D, Campbell J (2005) In: Tiryakioglu M, Crepeau PN (eds) Proceedings on shape casting: the John Campbell symposium, The Minerals, Metals, & Materials Society, p 23
- Raiszadeh R, Griffiths WD (2005) In: Tiryakioglu M, Crepeau PN (eds) Proceedings on shape casting: the John Campbell symposium, The Minerals, Metals, & Materials Society, p 13
- 51. Raiszadeh R, Griffiths WD (2006) Metall Mater Trans B 37B:865
- 52. Nateghian M, Raiszadeh R, Doostmohammadi H (2012) Metall Mater Trans B 43B:1540
- Yao L, Cockcroft S, Reilly C, Zhu J (2012) Metall Mater Trans A 43A:1004
- 54. Brondyke KJ, Hess PD (1964) Trans AIME 230:1542
- 55. Hess PD (1973) J Metals 10:46
- 56. Liu L, Samuel M, Samuel FH, Doty HW, Valtierra S (2003) J Mater Sci 38:1355. doi:10.1023/A:10228700067215