In-situ Observed Pore Formation During Solidification of Aluminium

Hongbin YIN and Jean N. KOSTER

Department of Aerospace Engineering Science, University of Colorado at Boulder, Boulder, CO 80309-0429 USA.

(Received on September 13, 1999; accepted in final form on November 18, 1999)

Incidental porosity formation during pure aluminium solidification was visualized in real-time with an X-ray radioscopic facility. The dynamic growth process of a 10-mm pore is observed. Its growth is divided into two sequential stages. In the first stage, the radius of the pore increased very fast, with time to the power of 0.52. In the second stage, the growth slowed as the pore radius changed with time to the power of 0.25. Theoretical analysis of the pore growth based on the present observation shows that, in the initial stage, the growth is primarily controlled by a hydrogen diffusion mechanism; and in the second stage, growth is controlled primarily by volume shrinkage during solidification.

KEY WORDS: aluminium; hydrogen; porosity; solidification; X-ray radioscopy.

1. Introduction

Since the requirements for light metallic materials for high-performance applications become increasingly stringent, the porosity problem in aluminium alloys has attracted wide attention from materials scientists and engineers. Recently, Lee and Hunt argued that hydrogen diffusion is the inherent controlling mechanism in growth of porosity upon solidification based on their statistical results. However, this conclusion needs to be confirmed from dynamic observations on pore growth kinetics. The distribution and morphology of pores are additional important issues that may reflect the frequency and position of defects in an ingot of aluminium alloys. At least 3 kinds of pore morphologies were found in cast alloys: nearly globular, columnar and angular structures. Generally, when pores form at initial low fractions of solid, they are large and nearly globular, whereas at high fraction of solid they are more angular and adopt the shape of the interdendritic spaces. To better understand the mechanism of pore growth, in-situ real-time observation is essential.

In the present study, in-situ real-time observation with an X-ray radioscopic facility was carried out on pure aluminium solidification. The entire dynamic process of pore formation during solidification was observed in real-time. This visualization permitted to distinguish the comparative importance of two prime causes: hydrogen precipitation and solidification shrinkage.

2. Experimental

The X-ray radioscopic visualization technique used in this study was described in detail elsewhere. In principle, when an X-ray beam with initial intensity of $I_0$ passes through a target specimen of a substance, M, with thickness, $d$, the output intensity, $I$, is given by:

$$I = I_0 \exp(-\sigma \rho d)$$

where $\sigma$ is attenuation coefficient (cross section) and $\rho$ is the density of the substance. For a pure substance, a change of the thickness of the specimen, e.g., caused by a pore or shrinkage inside or outside of the specimen during solidification, results in a local change in the intensity of output X-ray beam. A variation of the density of the specimen, e.g., caused by liquid/solid phase transition, leads to the same effect. When the dynamic real-time X-ray image of the specimen is subtracted with a previously taken background image of the same specimen with uniform thickness and density, the local change in thickness and density of the specimen can be clearly detected with a CCD camera. Thus, pores, shrinkage, and solid/liquid interface of pure aluminium during solidification can be investigated in-situ and in real-time.

A precisely machined boron nitride (BN) crucible with a wall thickness of 2 mm was used as the container of the aluminium melt. Two pyrolytic BN heaters, as shown in Fig. 1, were used to heat the specimen. To ensure uniform heating of the specimen in horizontal direction, two Molybdenum (Mo) blocks were mounted at both sides of the crucible in-between the heaters and crucible walls. Two K-type thermocouples, one in each Mo block, monitored the temperatures of the heaters and provided the independent references for individual computer-controlled heating power input to the two heaters. Reticulated Vitreous Carbon foam material (RVC) was chosen as the insulation because of its low density, structure firmness, and high thermal resistance. The aluminium specimen sized as $32 \times 28 \times 8$ mm$^3$ was cut from a commercial pure aluminium ingot, whose

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composition is listed in Table 1. The surface-finished and cleaned specimen was introduced into the furnace that was covered with a BN cap as schematically illustrated in Fig. 1. Two more K-type thermocouples, each at a distance of 1 mm from both inner walls of the crucible, were inserted 3 mm deep into the specimen from the top surface. The entire system then was mounted into a vacuum chamber by placing the wide face of the specimen normal to the centerline of the X-ray source and CCD camera.

Before heating was started, the vacuum chamber was pumped to $10^{-2}$ atm followed by a 20-min Argon gas flushing of the chamber in order to dilute the remaining air inside. Then, the chamber was pumped to $10^{-4}$ atm. After heating was started, the pressure inside the chamber reached $2 \times 10^{-2}$ atm and this pressure level was kept throughout all the experiment.

First, the specimen was molten entirely. An electronic background image was taken under isothermal conditions, i.e., the melt temperatures being at the same 677°C on both sides. Then, the cooling of the melt was started. The cooling ramps for both heaters are shown in Fig. 2. The digitally subtracted real-time images of the specimen from the background image were recorded and local changes in thickness/density of the specimen were visualized. Since solid aluminium has a higher density than its melt, the output X-ray intensity is lower after penetrating the solid phase, resulting in a darker area in the subtracted image. On the other hand, since a reduced thickness of the specimen leads to higher X-ray output intensity, pore or shrinkage of the specimen will be visualized as brighter areas in the image. However, if the brightness in a local area becomes over-saturated (exceeding 255 in gray-scale), the area will automatically switch to black. After completed solidification, remelting of the specimen was carried out following the reheating program shown in Fig. 2.

3. Observations

3.1. Pore Nucleation and Growth during Solidification

A sequence of the visualized pore formation during solidification is shown in Fig. 3. Since the cover was made of BN ceramic and pierced with many thermocouple holes, the heat loss at the top of the specimen was significant and consequently the solidification began along the top of the sample. The cooling curves for the vertical directional solidification of the specimen is illustrated in Fig. 2. Considering the observed initial appearance of the solid phase and the corresponding recorded temperature $T_B$, there was only ca. 1°C of undercooling. Figure 3(a) was taken at ca. 8 min after solidification began but shortly before the pore nucleated. The time and temperatures of the specimen corresponding to Fig. 3(a) are marked in Fig. 2. Since the temperature $T_A$ was high during the initial period of solidification, the solid phase at the top has not yet contacted the hot side of the specimen. Therefore, the melt was exposed to the vacuum environment through a small channel at the hot wall of the crucible, i.e., the pressure on the melt was the same as the pressure in the chamber. Because of the solidification shrinkage, the melt level fell and left a void area (whose shape is prescribed by the solid at the top) in the upper left corner of the specimen. This void connected to
the vacuum environment through the above-mentioned channel. The average vertical growth rate of solid was measured to be ca. 2.04×10^{-2} m/s in this initial period of solidification.

Five seconds after Fig. 3(a), a white spot appeared right in front of the solid/liquid interface, i.e., a pore nucleated there. The pore is shown in Fig. 3(b), taken three seconds after nucleation, at which time the solid fraction was evaluated as ca. 0.24. Here, the solid fraction is assessed from the entire dark area in this image. Note that the pore formed in a dome-shaped area. The growth of the globular pore was very fast, and 21 sec later, Fig. 3(c), the radius of the pore reached 2.9 mm (≈1.4×10^{-2} m/s). At the same time, the void in the upper left corner shrank, caused by the refilling with melt that was displaced by the growing pore. Obviously, hydrogen could diffuse out of the melt through the above-mentioned small channel that connected the melt and the vacuum environment. Because of the small channel size, most of the hydrogen remained inside the melt and led to the observed pore nucleation. It is interesting to note that the top of the pore did not move significantly downward, suggesting that the pore was not pushed by the advancing S/L interface. While the pore grew further, the void at the upper left corner filled completely with melt and half of the pore was enclosed by solid [Fig. 3(d)]. At about 200 sec after nucleation of the pore, the growth of the pore in horizontal direction stopped due to the entrapment by surrounding solid, whereas the growth in vertical direction continued, making the pore elongated as shown in Figs. 3(e) to 3(i). At the same time, a decrease in transversal size of the pore (a thinner pore) is clearly visible.

A solid cone formed at the center of the specimen bottom in Fig. 3(e) and grew upwardly as seen in Fig. 3(f). Then, the cone united with the solid freezing downwards and the melt was split and enclosed in two bottom corner areas as seen in Fig. 3(g). The upward growing solid cone, together with the downward growing solid did not engulf the pore, but left the pore, until the end of the solidification, with a small opening that connects to the remaining melt. At the same time, the lower cone forced the pore to turn its growth direction to the right, pointing to the lower right corner of the crucible. In the entire process of the solidification after the elongation of the pore began, the tip of the pore adopted the same moving velocity as the downward advancing S/L interface. The distances from the triple point at pore/melt/solid three-phase junction, and from the pore bottom to the specimen bottom are shown in Fig. 4. The vertical position of the triple point changed almost linearly with time after pore nucleation, at an average velocity of 3.2×10^{-2} m/s. Because of the interfacial energy between the melt and pore, the tip of the pore adopted a hemispherical shape that extended into the remaining melt at all times.

Thus, the distance between the triple point and the pore bottom remained almost constant, except for the initial and final growth stages of the pore. During the initial stage, i.e. the first 50 sec, the globular pore grew very fast. Then the growth rate suddenly slowed down, even before the pore elongation process began. Therefore, a dramatic change in the distance between the triple point and the pore bottom is revealed within the first 200 sec of pore growth (Fig. 4).
The thinning of the pore starting from Fig. 3(e) demonstrates the obvious reduction of the pore growth rate.

In Fig. 5, the radius of the pore, \( r_p \), is plotted against time, \( t \), together with the evolution of the solid volume fraction, \( f_s \). After the pore commences its elongation, i.e., 200 sec from pore nucleation, the pore radius is taken as the area-equivalent-radius of the elongated pore. The solid fraction changed almost linearly with time (noting the curve in Fig. 5 in log–log coordinates), giving the following regressed relationship:

\[
f_s = 7.83 \times 10^{-2} t + 0.234 \quad \text{...............(1)}
\]

with regression coefficient, \( R^2 \), of 0.996. However, the change of the pore radius is more complex; it can be divided into two periods. In the first 50 sec after pore nucleation, the regressed relationship with regression coefficient, \( R^2 \), of 0.996. However, the difference between the two stages is more significant. Note that the transition between the growth mechanisms occurred long before the pore became elongated, implying that the transition has nothing to do with the elongation process. It is expected that there were metal films in between the crucible walls and the pore after the short axis of the pore reached the maximum value, i.e., the pore did not touch the wall during the entire process.

### 3.2. Solidification Shrinkage

Solidification shrinkage was observed at the hot side of the specimen as solidification lasting after the residual melt was enclosed by solid. Visualized in Fig. 3(g), a shrinkage void formed close to the left crucible wall and grew downward along the wall until the end of solidification shown in Fig. 3(i). Unlike the state of the pore that had a clear white boundary with the metal phase, now a gray area surrounded the shrinkage void in Fig. 3(i). The reason is that the solidification shrinkage occurred directionally and led to a continuously reduced thickness of the solid phase towards the sidewall, in contrast to a sharp transition. From the investigation of other specimen with similar shrinkage behavior, the horizontal section here is shown schematically in Fig. 6. With the step function applied during image processing to the X-ray output intensity, the X-ray radioscopic image of Fig. 3(i) shows the gray and black area of the void.

By measuring the area of the black region including the white boundary, which represents the shrinkage volume, the change of the area-equivalent-radius, \( r_p \), with \( t \) is shown in Fig. 7. The change of the melt volume fraction, \( f_L \), in the residual melt portion relates linearly to \( t \) as

\[
f_L = -7.71 \times 10^{-4} t + 0.179 \quad \text{...............(4)}
\]

The absolute value of the slope in Eq. (4) is very close to that in Eq. (1) and the two can be treated as equivalent given the measurement accuracy. The regressed relationship between and \( t \) is

\[
r_p = 6.76 \times 10^{-4} t^{0.25} \quad \text{...............(5)}
\]

The power index of time in Eq. (5) is very close to the index in Eq. (3) but far from the one in Eq. (2). This sug-
suggests that the growth mechanism of the shrinkage void may be the same as the mechanism of the pore growth during its second stage. This will be discussed below in further detail.

### 3.3. Pore Behavior during Directional Melting

Following the solidification, a melting experiment of the solidified specimen was carried out to observe the pore behavior during these conditions. As shown in Fig. 2, what was the cold side during the solidification experiment was set to be the hot side in the remelting experiment. During melting, the dynamic behavior of the pore is quantified as shown in Fig. 8(a). In Fig. 8(a), the solidified specimen began to melt directionally at the side next to the pore and the melt soon reached the pore. At 72 sec from Fig. 8(a), the pore extended slightly into the melt, Fig. 8(b). As the melt flowed continuously into the pore, the bottom of the pore was filled and, at the same time, the gas inside the pore was displaced upward, making the pore extrusion more pronounced as seen in Fig. 8(c). Since the volume of the specimen expanded during melting and some of the gas inside the pore re-dissolved into the melt, the total area of the pore in these images shrunk with time. It is most interesting to note that, 6 sec later than Fig. 8(c), most parts of the pore shifted into the melt and became a bubble, seen in Fig. 8(d). Then, within a second, the bubble floated up and created a channel with opening to the environment at the crucible wall, Fig. 8(e). It is believed that the gas remaining in the bubble that did not dissolve into the melt exited the specimen into the vacuum environment. After the gas inside the bubble was out, a remaining void volume along the wall, seen in Fig. 8(f), shrunk gradually while the melting continued and finally disappeared close to the end of the remelting process.

### 4. Discussions

#### 4.1. Nucleation Site of the Observed Pore

Since the X-ray image is in two-dimensional shadow projection, the nucleation site of the observed pore in Fig. 3 may have two possibilities of origination: on the crucible wall or inside the Al specimen. This origination must be clarified before any discussion on the growth process of the pore can be done, because the volume of the pore will be quite different for these two cases. If the pore nucleated on the wall, the pore would be a spherical cap whose volume depends on the contact angle at the triple line of gas/crucible-wall/melt. There are two reasons that the pore in Fig. 3 is believed to nucleate inside the melt. Firstly, in view of the interfacial properties, the BN crucible wall is not wetted by Al melt, and hence, nucleation of a pore at the crucible wall is unlikely. Secondly, the shrinkage during solidification is in three dimensions and there must be a thin gas-filled gap between the crucible wall and the solidified Al. Thus, if the pore nucleated on the wall, the pore would be a spherical cap whose volume depends on the contact angle at the triple line of gas/crucible-wall/melt.

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Almost all of the gas inside the pore in Al alloy casts is
hydrogen, hence attention will be paid exclusively to hydrogen. As the observed pore in the present experiment nucleated at \( f_s = 0.24 \), the Al melt at this time must be super-saturated with \( H_2 \). The degree of super-saturation, \( S \), is defined as

\[
S = \frac{H_L - H_s}{H_L} - 1 \quad \text{(6)}
\]

where \( H_L \) is the hydrogen content in the melt during solidification, and \( H^*_L \) is the equilibrium hydrogen content in the melt. From the equilibrium lever rule, we have

\[
H_i = f_s H_s + f_L H_L \quad \text{(7)}
\]

where, \( H_i \) is the initial hydrogen content in the specimen and \( H_s \) is the hydrogen content in solid. Thus, by combining Eqs. (7) and (6), the value of \( S \) can be given as:

\[
S = \frac{H_i - f_s H_s}{1 - f_s} - 1 \quad \text{(8)}
\]

Assuming that the experiment is run in equilibrium state at 660°C under a certain partial pressure of \( H_2 \) in the vacuumed atmosphere, \( P_{H_2} \), the Eq. (8) will be:

\[
S^* = \frac{H^*_L - f_s H^*_s}{1 - f_s} - 1 = \frac{1 - f_s K}{1 - f_s} - 1 \quad \text{(9)}
\]

where \( K (=H^*_s/H^*_L) \) is the distribution ratio of hydrogen between solid and liquid at equilibrium, which is independent of \( P_{H_2} \). Since the value of \( f_s \) is 0.24 when the pore nucleated in this experiment and \( K \) is 0.0522, \( S^* \) the value of \( S \) is calculated as ca. 0.3.

In fact, the present solidification experiment was not in equilibrium state, therefore, the quantification analysis of the \( S \) is tentative because the values of \( H_i \) and \( H_s \) in Eq. (8) are hardly known during the experiment. To estimate the real value of \( S \), an approximation is done here by assuming:

1. \( H_i = 0.1 \cdot H_0 \) (H_0: the original hydrogen content in the specimen). The solidification in Fig. 3 started only 10 min after the total melting of the specimen and there was no stirring of the melt. At the same time, the free surface of the melt exposed in the low-level vacuum (10⁻² atm) was small (8 × 32 mm²) and quickly covered by the solid phase after solidification started. Therefore, the hydrogen removed from the melt was limited before solidification started.

2. The level of \( P_{H_2} \) changes in a large range from 10⁻⁵ to 10⁻¹¹ atm since the real \( P_{H_2} \) was unknown. It is expected, however, the level of \( P_{H_2} \) should not exceed this range during the experiment.

3. \( H_s = 10 H^*_s \) at various levels of the presumed \( P_{H_2} \). Since the solidification was not in equilibrium, some extra amount of hydrogen would be frozen in the solid phase. However, the solidification in the present experiment was rather slow (2.04 × 10⁻³ m/s), and the extra amount can not be very high. Here, the factor 10 that is taken arbitrarily may be greater than the actual value.

Under these assumptions, the analysis results of \( S \) are shown in Fig. 9 after Eq. (8). Here, the solubility data of hydrogen in solid aluminium at 660°C under atmospheric pressure is taken from Ref. 12. It can be seen that the actual \( S \)-value may be orders of magnitude higher than the...
value of $S^*$ (=0.3). Under such circumstances, the homogeneous nucleation of the hydrogen pore inside the melt is possible although the interfacial energy for $H_2/Al$ melt system is high. Furthermore, by considering the hydrogen distribution inside the melt caused by diffusion, the melt adjacent to the S/L interface contains the highest hydrogen concentration, i.e., has the highest super-saturation. Thus, it can be stated that the observed pore in Fig. 3 nucleated and grew inside the melt ahead of the interface. The following discussion will be done based on this conclusion.

4.2. Growth Mechanism of Pore in the Initial Growing Stage

As mentioned above, there are two mechanisms controlling the growth of the observed pore: the hydrogen diffusion and the volume shrinkage. In the initial stage of the observed pore growth, shown in Fig. 3, the shrinkage void in the upper left corner of the specimen was refilled with melt previously displaced by the growing pore. Therefore, it cannot be said that the volume shrinkage during solidification contributes substantially to the initial growth of the pore. In view of the diffusion growth mechanism for a spherical pore, the rate of $H_2$ mass increase inside the pore equals to the mass being transferred by diffusion of hydrogen in the melt through a boundary layer of thickness $\delta$, i.e.,

$$
4\pi r^2 \frac{d(r\rho^h_r)}{dt} = 4\pi r^2 \frac{D_{H_2}}{\delta} (\rho^h_r - \rho^*_{H_2})
$$

or

$$
\frac{d(r\rho^h_r)}{dt} = D_{H_2} (\rho^h_r - \rho^*_{H_2}) / \delta 
$$

where $\rho^h_r$ is the density of $H_2$ inside the pore, $D_{H_2}$ is the diffusion coefficient of hydrogen in Al melt, $\rho^*_{H_2}$ is the hydrogen density in bulk melt and $\rho^*_{H_2}$ is the hydrogen density at the pore/melt interface. According to the ideal gas law,

$$
\rho^h_r = \frac{M_{H_2} p^h}{RT}
$$

with $M_{H_2}$ the molar weight of $H_2$ and $R$ the gas constant. Since temperature $T$ during the faster growth of the pore can be treated as constant, the pressure of the pore, $P^h_r$, relates to $\rho^h_r$ as

$$
\rho^h_r = \frac{2\times10^{-3}}{8.314\times(660+273)} \times \rho^*_{H_2} = 2.58 \times 10^{-7} \rho^*_{H_2} \text{ (kg/m}^3\text{)}
$$

The gas pressure in the pore is given by

$$
P^h_r = P^0 + \rho_L gh
$$

where, $P^0$ is the ambient pressure, $\rho_L$ is the density of Al melt, and $h$ is the static pressure head of the pore. Thus, the left hand of Eq. (10) can be given as

$$
\frac{d(r\rho^h_r)}{dt} = \frac{2.58 \times 10^{-7}}{\delta} \left\{ (P^0 + \rho_L gh) \frac{dr_p}{dt} + r_p \rho_L gh \right\}
$$

In Fig. 3, the melt level increased while the pore was growing, leading to an increase in static pressure inside the pore. From the measured data of melt level to the center of the pore, the change of $h$ vs. $t$ can be approximately described by

$$
h = 2.27 \times 10^{-4}t + 1.67 \times 10^{-3} \text{ (m)}
$$

and hence

$$
\frac{d(r_p \rho^h_r)}{dt} = (5.33 \times 10^{-4} + 1.36 \times 10^{-6}t) \frac{dr_p}{dt} + 1.36 \times 10^{-6} r_p
$$

Here, $P^0 = 0.02 \text{ atm} = 2026.4 \text{ Pa}$, $\rho_L = 2.370 \text{ kg/m}^3$ and $g = 9.8 \text{ m/s}^2$ are used.

On the right hand of Eq. (10), as temperature merely changed during the initial growth stage of the pore, $D_{H_2}$ is constant. The value of $\rho^h_r$ changes with $P^0$, but since $\rho^*_{H_2} \ll \rho^0_{H_2}$, the change of $\rho^h_r$ does not affect the final result much. It is assumed that the flow inside the bulk melt during solidification is negligible, and, in this pure diffusion system, the change of boundary layer thickness with time is determined by

$$
\delta = 4\sqrt{D_{H_2} t}
$$

On the other hand, the change of $\rho^h_r$ with time can be given from the combination of Eqs. (1) and (7) as

$$
\rho^h_r = \frac{H_i}{1 - \rho_i} = \frac{2.37 \times 10^3 H_i}{0.766 - 7.83 \times 10^{-4} t}
$$

since $H_i \ll H_f$ according to the analysis in Sec. 4.1 about the pore nucleation. Therefore, considering that $\rho^h_r \ll \rho^0_{H_2}$, the right hand of Eq. (10) reads

$$
\frac{D_{H_2}}{4} \left( \frac{2.37 \times 10^3 H_i}{0.766 - 7.83 \times 10^{-4} t} \right) \frac{1}{\sqrt{D_{H_2} t}} = \frac{8.76 \times 10^{-7}}{(0.766 - 7.83 \times 10^{-4} t)^{3/2}}
$$

by assuming $H_i = 0.27 \text{ ppm = } 2.7 \times 10^{-7}$ (see Sec. 4.1) and taking $D = 3 \times 10^{-7} \text{ m}^2/\text{s}$. Thus, Eq. (10) can be rewritten as

$$
\frac{dr_p}{dt} + \frac{1.36}{(533 + 1.36)t} r_p = \frac{8.76 \times 10^{-2}}{(533 + 1.36)(0.766 - 7.83 \times 10^{-4} t)^{3/2}}
$$

The Eq. (11) which is in the form of

$$
\frac{dr_p}{dt} + P(t) r_p = Q(t)
$$

is a linear first order equation with

$$
P(t) = \frac{1.36}{(533 + 1.36)t} \quad \text{and} \quad Q(t) = \frac{8.76 \times 10^{-2}}{(533 + 1.36)(0.766 - 7.83 \times 10^{-4} t)^{3/2}}$$
Fig. 10. Comparison of calculated correlation between $r_p$ and $t$ after Eq. (12) with observed correlation.

The solution of the linear first order equation is:

$$r_pe^{|P(t)|dt}=\int Q(t)e^{|P(t)|dt}dt+C$$

Here, $C$ is a constant. From the integration of the above equation, it can be learned that $C=0$ since $r_{p|t=0}=0$.

Therefore, the relationship between $r_p$ and $t$ is deduced as:

$$r_p=\frac{3.58}{(533+1.36)}\ln\frac{0.766+0.0245\sqrt[3]{t}}{0.766-0.0245\sqrt[3]{t}}$$  \hspace{1cm} (12)

Taking the time change during the initial growth stage of the observed pore in Fig. 3 from 0 to 50 sec, as shown in Fig. 4, the change of $r_p$ vs. $t$ after Eq. (12) is plotted in Fig. 10, and the regression of the curve gives:

$$r_p=4.46\times10^{-4}t^{0.47}$$  \hspace{1cm} (13)

In the above analysis, the contribution of volume shrinkage during solidification is not included. It can be seen that both the time power index and the numerical factor in Eq. (13) are very close to those in Eq. (2), suggesting that hydrogen diffusion in the initial growth stage of the observed pore is the prime, or dominant growth mechanism. In Fig. 10, the calculated pore growth curve is slightly below the observed curve. Obviously, the theoretical analysis results may not be sufficiently precise since there are some approximations and simplifications made in the above analysis. For the observed pore, the solid/pore interface area increased gradually, but in calculation, this S/P interface is ignored, which will cause an over-estimation of the calculated results. However, in the first 50 sec, either the S/P interface area or the growth rate of the area is much smaller than the L/P interface area, and hence this effect can be expected small.

On the other hand, because of the limitation of the specimen thickness, the observed pore may not be a round sphere but an elliptical sphere with the short axis parallel to the direction of visualization. Thus, the observed radius of the pore is larger than the calculated sphere radius used in this analysis. At the same time, the volume shrinkage contributes also to the deviation of both curves.

4.3. Growth Mechanism of Pore in the Second Growth Stage

In the second growth stage, Fig. 4, the pore growth rate has slowed down. In this stage, a large part of the surface of the pore is solid Al. Since the hydrogen diffusivity in solid Al is one order of magnitude lower than that in the Al melt, the contribution of hydrogen diffusion to the pore growth will be decreased greatly in kinetic view, although the hydrogen diffusion from the melt into the pore continues until the end of solidification. Therefore, it can be expected that the volume shrinkage will mainly control the pore growth in this stage and the hydrogen diffusion becomes subordinate. Theoretically, since the present solidification process is linear with time, i.e., $df/dt=$ constant, the total volume change, $\Delta V$, during solidification is also linear in time. Hence, if all of the $\Delta V$ is considered to contribute to the increase of the pore volume, a relationship between $r_p$ and $t$ can be described as

$$r_p \propto \frac{3}{3}\Delta V \propto t^{0.33}$$  \hspace{1cm} (14)

It should be noted, however, that the $\Delta V$ does not happen exclusively in the pore volume but in the entire remaining melt portion of the specimen, i.e., the actual contribution of the total volume change to the pore growth, $\Delta V_p$, will be less than $\Delta V$. Taking this factor into account, i.e., $r_p \propto \sqrt{\Delta V_p}$, it becomes understandable that the power index of $t$ in Eq. (3) (=0.25) is less than that in Eq. (14) (=0.33). In fact, for the pure shrinkage void described by Eq. (5), the power index (=0.29) is close to 0.33, where, as expected, the contribution of the total volume change to the void growth, $\Delta V_p$, is greater. Although a quantitative analysis on volume shrinkage can be hardly carried out, the similarity of the power indices of time among Eqs. (3), (5) and (14), and the similarity of the numerical factors in Eqs. (3) and (5) show that the second growth stage of the pore is mainly controlled by volume shrinkage.

The measured time of 50 sec of the transition from dominantly diffusion growth to dominantly shrinkage-induced pore-growth is related strictly to the specimen size and shape. Although the observed pore in the present experiment is much larger than the actual size of most pores in commercial castings of Al alloys, the fundamentals of porosity formation are considered the same for the pores in micro-scale (<200 µm) in castings. In the initial stage, pore growth is primarily and predominantly determined by hydrogen diffusion; and in the following stage, volume-shrinkage contributes predominantly to the pore growth. The results of the present study strongly support the conclusions from Lee and Hunt\(^6\) with statistical analysis, showing that the hydrogen diffusion growing mechanism plays the dominant role in pore formation of Al alloy castings. Therefore, in Al alloy casting practice, the control of the initial hydrogen content by gas bubbling or vacuum degassing will be the primary requirement to reduce the porosity.

5. Conclusions

(1) The real-time radioscopic observation of a pore growth process during pure aluminium solidification indi-
icates that the growth of a pore is divided into two stages. In the first stage, the radius of the pore increases very fast, expressed by time to the power of 0.53. In the second stage, the growth of pore slows down and its radius changes with time to the power of 0.25.

(2) Kinetic analysis of the pore growth based on the present observation shows that, in the initial growth stage, growth is primarily controlled by a hydrogen diffusion mechanism; and in the second stage, the volume shrinkage of the Al-melt contributes predominantly to further pore growth.

Acknowledgements

The authors thank M. G. Chu of the ALCOA Technical Center for providing financial support and aluminium for this study.

Nomenclature

- $D$: binary diffusivity
- $d$: thickness of a substance
- $f$: fraction of a phase
- $h$: static pressure head
- $H$: hydrogen concentration
- $I$: X-ray intensity
- $M$: molecular weight
- $P$: pressure or partial pressure
- $r$: radius
- $R^2$: regression coefficient
- $R$: ideal gas constant
- $S$: super-saturation
- $t$: time
- $T$: temperature
- $\Delta V$: volume change
- $\delta$: thickness of boundary layer
- $\rho$: density
- $\sigma$: cross section

Subscripts

- 0: original or input
- $i$: initial
- $H$: hydrogen
- $L$: Al melt
- $M$: substance
- $P$: pore
- $S$: Al solid
- $V$: void

Superscripts

- °: ambient
- *: equilibrium
- L: in Al melt
- P: in pore

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