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Hydrogen, porosity and oxide film defects in liquid Al

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Abstract This article reports results from an experiment where a bubble of air was held at a constant temperature in a liquid Al melt, with the volume of the bubble monitored continuously using real-time X-ray equipment. When the H content of the surrounding melt was low, the volume of the trapped air bubble reduced with time, as the O and N in the bubble atmosphere reacted with the Al to form Al_2O_3 and AlN. When the H content of the melt was increased to about 0.3 ml 100 g^{-1} Al, the H in solution passed into the air bubble causing its expansion. In an Al casting the same effect would cause an entrained double oxide film defect to act as a site for the growth of H-driven gas porosity. The way in which the oxide film defects might behave in forming H porosity has been discussed.

Introduction

The mechanical properties of Al alloy castings are significantly reduced by the presence of porosity, formed by either solidification shrinkage, the precipitation of H during solidification, or both acting concurrently [1–4]. The literature on H porosity in nonferrous metals was reviewed by Talbot in 1975 [5]. It was there pointed out that, in the case of solid Al, its surface oxide film significantly retarded the diffusion of H into and out of the metal [6, 7], and that diffusion rates were considerably increased by surface treatments that reduced or removed the oxide, such as physical abrasion.

A similar reduction in the rate of passage of H through the surface oxide film of liquid Al was first noted by Ransley and Neufeld [8] in their original measurements of H solubility in liquid and solid Al. A more detailed investigation was carried out by Weigel and Fromm [9] who made careful measurements of the H content of a pure Al melt using a probe inserted into the liquid metal through which a carrier gas was passed which came into equilibrium with the dissolved H. When the surface oxide film was disturbed or removed, (which was done by a ceramic rotor), the rates of absorption of H from the surrounding atmosphere to the melt were measured to be around 10^4–10^5 ml m^{-2} h^{-1}. However, with an undisturbed oxide film on the surface of the melt the rate of absorption of H was reduced by several orders of magnitude, to around 1 ml m^{-2} h^{-1}. Significantly, even when a droplet of water was placed on the oxidized surface of the liquid Al, this did not result in an increase in the H content of the melt. In addition, for melts containing significant quantities of H in solution, desorption to the atmosphere was measured to occur at rates of 1–3 ml m^{-2} h^{-1}. The evidence from experiments with both solid and liquid Al has therefore shown that the presence of an unbroken surface oxide film significantly reduces the flow of H into and out of the metal.

Another type of defect to be found in Al alloys are double oxide films. The surface of liquid Al in contact with air is covered by a thin oxide film and, as the liquid metal flows, this oxide skin is continuously broken and reformed by reaction with oxygen in the atmosphere. Splashing of

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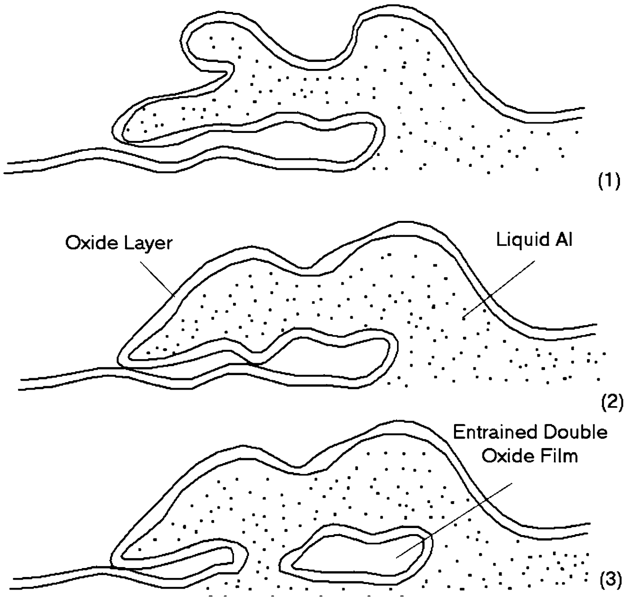

Fig. 1 Sketch showing the formation of a double oxide film defect

the liquid metal during mould filling is highly likely in gravity casting operations, in which case metal streams separating from the bulk liquid would almost instantaneously, and continuously, come to have their own surface oxide films. When the liquid metal streams recombine, as shown in the sketch in Fig. 1, their individual oxidized surfaces meet but do not fuse together, and trap a region of the local atmosphere between them. These folded-over surface oxide films become entrained in the bulk liquid metal, and upon solidification can be found as crevice-like pores, with an oxidized interior surface, containing an atmosphere that was trapped during the entrainment event [10]. It has been pointed out that the encapsulated pockets of gas so formed could serve as ideal sites into which H dissolved in the melt could diffuse [10] and attention has turned to the role of these double oxide film defects as initiators for H gas porosity. Raiszadeh and Griffiths [11] observed that a bubble of air deliberately inserted into a liquid Al melt with a high H content underwent expansion, as the dissolved H diffused into the bubble atmosphere. In addition, Campbell [12] has interpreted the results of a study of porosity size distribution and solidification rate by Tynelius et al. [13], to show that a relationship between double oxide film content and H content could be responsible.

In the modelling of porosity in Al alloy castings that has been carried out, (for example, references [14, 15]), the origins of the H pores were not included, with the models being aimed at simulating pore growth. In this article the nature of the diffusion of hydrogen into double oxide film defects has been considered, in order to suggest ways in which pore formation involving double oxide film defects could be modelled.

Experimental procedure

In order to mimic the behaviour of a double oxide film defect in a liquid Al alloy melt, an air bubble was deliberately trapped in liquid Al, and its change in volume with time monitored and recorded using a real-time X-ray imaging system. The experimental arrangement has been shown schematically in Fig. 2, and was carried out as follows. A calcium silicate fibre tube was placed inside a resistance-heated tube furnace, placed inside a real-time X-ray imaging system. The fibre tube was sealed at one end with a metal plug, and had internal dimensions of depth = 225 mm and diameter = 45 mm. A 700 g melt of commercial purity liquid Al, (>99.7 wt% Al), was held in the liquid state in the tube, (at a temperature of about 700 °C), for periods of several hours. A silicon nitride or silica rod, with an external diameter of 21 mm, having a hole at the lower end, was plunged into the liquid Al in the fibre tube and clamped in place, thus trapping a bubble of air in the hole in the rod which could be seen in the real-time X-ray. The change in volume of the air bubble over time was video recorded in the real-time X-ray system for subsequent examination. Examples of images from the recordings have been shown in Fig. 3. Further details of the experimental procedure are given in reference [16].

Experiments were carried out to determine the rate of change of the bubble volume with two different H contents in the Al melt, and two different bubble sizes. The two values of initial H content used were 0.1 ml 100 g^{-1} Al and 0.3 ml 100 g^{-1} Al, (measured by a Severn Science HyScan^{TM} device). The holes at the end of the inserted rods were 14 mm diameter, but holes of two depths were used, 40 mm and 10 mm, giving bubbles with initial volumes of about 5000 mm^3 and 2000 mm^3, respectively.

Results

Figure 4 shows a graph of the change in volume of a large air bubble with time, (height 40 mm, diameter 14 mm), when contained in the commercial purity Al melt with an initial hydrogen content of 0.11 ml 100 g^{-1} Al. The error in the determination of the volume of the bubble was estimated to be about ±1%. This graph showed that, initially, O was consumed by reaction with the surrounding liquid Al to form Al_2O_3, and then N was consumed, forming AlN. This was confirmed by examination of the reaction products after the experiment was completed [11, 16]. The transition between the two reactions

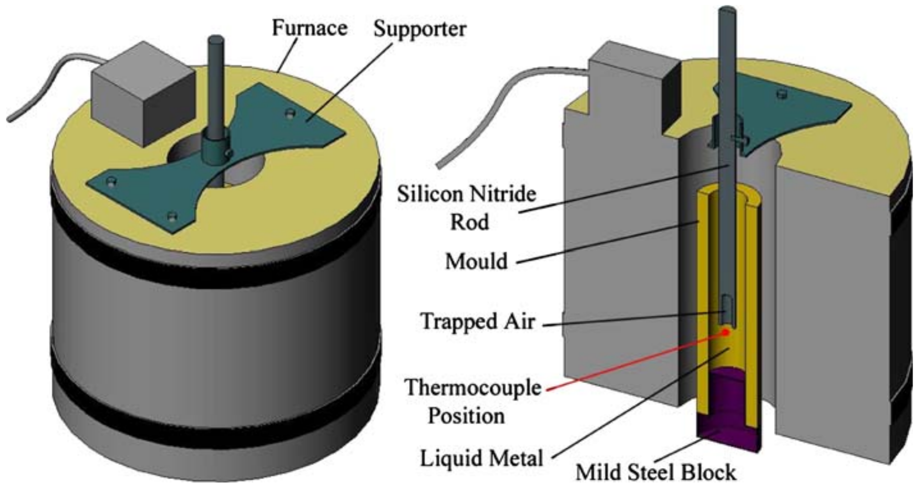

Fig. 2 Sketch of the experimental arrangement placed in the real-time X-ray system, for determination of the change in volume of a bubble of air trapped in liquid Al

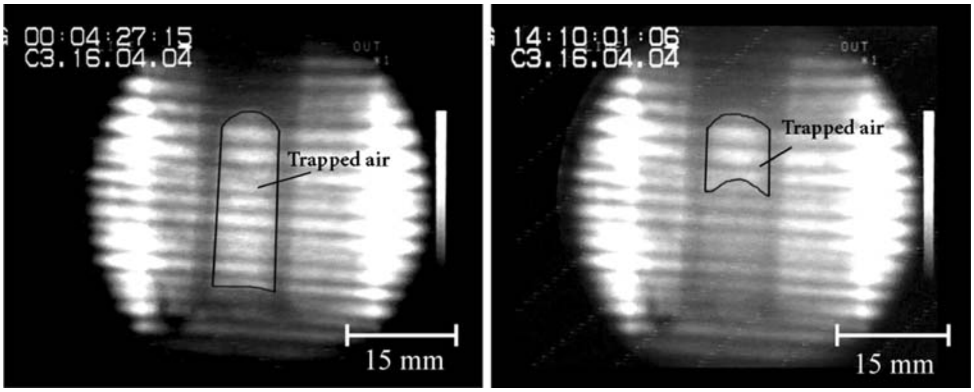

Fig. 3 Typical images from a recorded real-time X-ray video showing the change in bubble volume with time

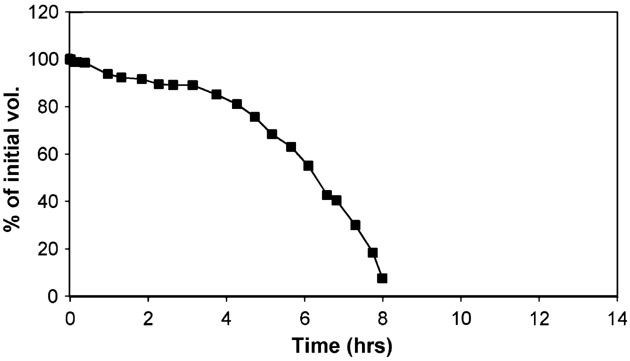

Fig. 4 The change in volume with time of an air bubble maintained in liquid commercial purity Al, with an initial hydrogen content of 0.11 ml 100 g^{-1} Al (The initial bubble volume was about 5000 mm^3)

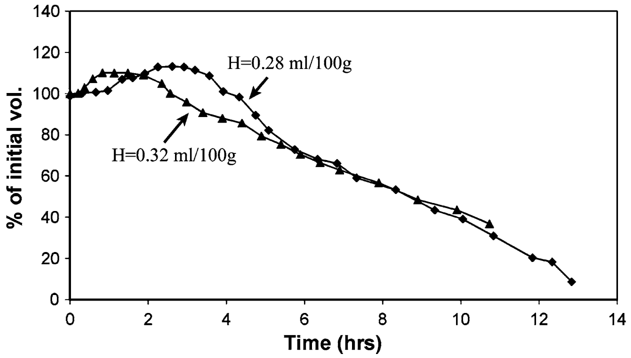

Fig. 5 The change in volume of an air bubble with time in liquid commercial purity Al, with high initial hydrogen contents of about 0.3 ml 100 g^{-1} Al (The initial bubble volume was about 5000 mm^3)

presumably occurred at the point at which there was a change in gradient of the curve in Fig. 4 to a more rapid rate of reduction in volume, occurring at around 3 h. Note that it appears that it was not necessary for the entire O content in the bubble to be consumed, before the reaction with N began.

Figure 5 shows the change in volume with time for two experiments with large air bubbles trapped in the melt, but with high initial H contents of 0.28 and 0.32 ml 100 g^{-1} Al, respectively. The volume of the trapped air bubbles expanded to about 110% of their initial volume, and then began to shrink after about 2–3 h of expansion. These

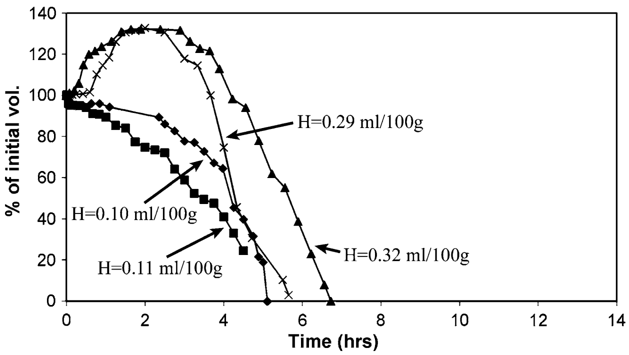

Fig. 6 The change in volume of an air bubble with time in liquid commercial purity Al, with an initial bubble volume of about 2000 mm^3, and low and high initial hydrogen contents

results showed that the H dissolved in the liquid Al had passed into the air bubble, with the two experiments in Fig. 5 showing good reproducibility.

Figure 6 shows the change in volume for two further experiments carried out with smaller bubbles of height 10 mm and diameter 14 mm, with low and high initial H contents of around 0.11 and 0.30 ml 100 g^{-1} Al, respectively. The initial and maximum volumes of the air bubbles have been summarised in Table 1, which shows that the absolute increase in bubble volume for the two bubble sizes was similar, about 600 mm^3. The smaller air bubbles therefore expanded to about 130% of their initial volume when in the melt with the higher H content.

The increase in volume of the trapped air bubbles showed that, initially, their volume increase due to the rate of transfer of H from the melt to the bubble atmosphere was greater than the volume reduction due to the reaction of O with the surrounding Al. (At this stage, according to Fig. 4, reaction of N with Al would not be expected.) Once the H content of the bubble was such that the rate of further diffusion of H into the bubble was balanced by the loss of O by reaction with the melt, the peak expansion of the bubble was reached, and continued reaction of the O then caused an overall decrease in bubble volume.

The reaction of O (and N, when it occurred later) would itself cause diffusion of H from out of the bubble atmosphere back into the melt. Once the H content of the bubble reached equilibrium, further consumption of O and N would increase the partial pressure of H in the bubble atmosphere, driving it out of the bubble back into solution in the Al melt. Furthermore, while H was passing into the interior of the air bubble its content may be lowered in the melt by diffusion to the surrounding local atmosphere in the furnace, through its exterior surface oxide film, and this would also cause diffusion of H from out of the bubble back into the melt.

The previous experiments referred to in the Introduction had suggested that an oxide film was an effective barrier to the passage of H. Therefore, the mechanism of exchange of H between the Al melt and the atmosphere of the trapped bubble, and the mechanism of reaction between the interior atmosphere of the bubble and the melt, would depend upon the extent to which the oxide film at the interface of the bubble atmosphere and the melt experienced rupture. At points of rupture the liquid metal would be in direct contact with the atmosphere, and exchange of H would be unhindered, at least for the short time until the rupture was sealed by reaction of the bubble atmosphere with the melt. An example of such a ruptured film is shown in Fig. 7, derived from these experiments. This shows a film that was originally Al_2O_3, but had later been torn open at a time after the bubble had lost its initial O content, resulting in the reaction of Al and N to form AlN.

The results from the high H melts have been compared in Table 1, which shows, for both bubble sizes, the increase in bubble volume, the time taken for the bubbles to reach maximum size and the rate of volume increase, derived from the curves in Figs. 5 and 6. The rate of expansion of the bubble volumes was about 2 to 4 × 10^3 ml m^{-2} h^{-1} (where the area term refers to the area of reaction of the bubble, assumed to be the cross-sectional area of the hole in the bubble holder).

The absolute increase in volume was similar for both the large and the small bubbles, between 525 and 670 mm^3. This may be explained by the fact that the flux of H into the smaller bubble would cause this bubble to come more rapidly to equilibrium with the melt than in the case of the larger bubble. (This assumes that gaseous exchange was controlled by the same mechanism in each case, the rupturing illustrated in Fig. 7). The smaller bubble, for the same H content in the liquid Al, should show a smaller

Table 1 The rate of increase of the volume of the bubbles shown in Figs. 5 and 6

Bubble size	Initial volume (mm^3)	Maximum volume (mm^3)	Maximum increase in volume (mm^3)	Percentage increase in volume	Time taken to reach maximum volume (h)	Rate of change of bubble volume (ml m^{-2} h^{-1})
Large	5381	6051	670	12	1.96	2.2 × 10^3
Large	5158	5683	525	10	0.83	4.1 × 10^3
Small	1967	2600	633	32	1.89	2.2 × 10^3
Small	1806	2397	591	33	2.00	1.9 × 10^3

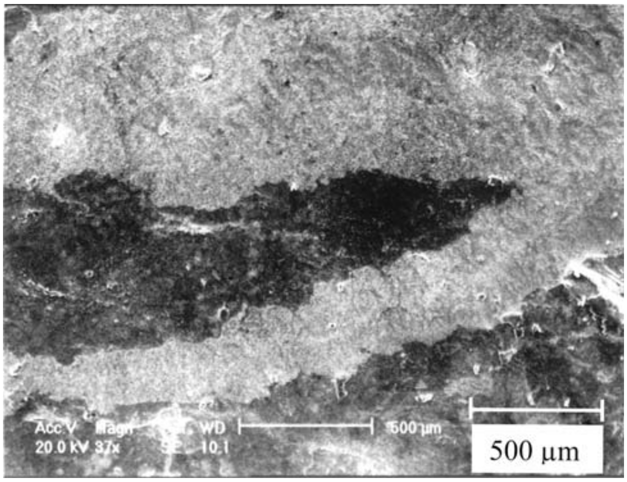

Fig. 7 A SEM micrograph showing an example of rupture of the surface film of an air bubble. The dark phase was identified by EDX as Al_2O_3; the light phase was identified as AlN

expansion. However, at the same time, the smaller bubble had a lower rate of O consumption due to reaction with the melt, due to the more rapid dilution of its O content by the H diffusing in (estimated to be about 1.5×10^{-6} mol h^{-1} [17]). In the case of the larger bubble, the ingress of H into the bubble would produce a larger expansion, but this was accompanied by a larger rate of consumption of O (estimated to be about 3×10^{-6} mol h^{-1} [17]). These two effects on bubble volume may have led to approximately equal increases in absolute volume, despite their different initial sizes. Of course, when expressed as a percentage of their initial volume, the smaller bubbles expanded more (about 33%, compared to about 12%, for the larger bubbles). Note that it is not suggested that N is consumed within this period, but that the effects described are due to H and O alone.

The results of the trapped bubble experiments therefore showed that double oxide films in Al alloy melts can act as initiators of H porosity. Furthermore, since it has been shown that an oxide film on the surface of a melt considerably reduces the rate of passage of H [9] the mechanism by which the dissolved H passes into (and out of) the bubble atmosphere, and by inference the mechanism by which dissolved H can pass into (and out of) a double oxide film defect, should involve physical damage to the oxide film.

Discussion

These experiments suggest how oxide film defects may behave in an Al melt containing H; the passage of H into a double oxide film may be a three-stage process, initially slow, but then rapid. In the first stage, the diffusion of H into an oxide film defect would be slow as the oxide film provides a barrier to the diffusion of H, as shown by Weigel and Fromm [9] and also shown by the results in Fig. 5, in which an initial plateau in the bubble volume before the period of expansion sometimes occurred. The H desorption rate of about 3 ml m^{-2} h^{-1} reported by Weigel and Fromm [9] may be due to the effects of the mechanisms occurring in this stage.

More rapid diffusion of H could occur into an oxide film defect through surface ruptures. In this second stage rupture of the oxide film could be caused by convection or other sources of fluid flow, or the change in volume of the interior atmosphere due to H ingress or reaction of the interior gases with the surrounding melt. H could then rapidly diffuse into the oxide film defect in the brief period before reaction seals the ruptured film. Further expansion and further fracturing of the film could occur in a continuous process, with the rate of passage of H now controlled by the rate at which the film was ruptured and resealed. The time for recoverage of a liquid Al surface by oxide of 1 µm depth has been estimated to be about 0.01 s, in an atmosphere of 1 bar O [9] (and would therefore be presumably longer in the case of a double oxide film with an internal atmosphere with a lower partial pressure of O). The results of the bubble volume experiments may be due to processes occurring in this second stage. The rate of change of the bubble volume, which was due to a combination of expansion due to H ingress, and contraction due to O consumption, was about 2×10^3 to 2×10^4 ml m^{-2} h^{-1}. This was about an order of magnitude below the rates determined by Weigel and Fromm [9], but in their experiments the oxide film on the melt was vigorously and continuously disturbed.

Once all the interior atmosphere (both O and N) of the oxide film has been consumed, any further rupture of the film would not be resealed, and a third stage ensues when only a small residual atmosphere of unreactive Ar (and hydrogen) is left. In the experiments with the air bubbles held in the liquid Al it required several hours for the entire O and N content to be consumed. Extrapolating these results to the estimated dimensions of double oxide film defects in an Al melt, it has been estimated that after about 150 s, only Ar would remain in the interior atmosphere [17]. There would now be no barrier to the passage of H into the defect interior, and the rate of diffusion into the expanding gas pore would be more rapid than in the first and second stages, and perhaps would be governed by the rate of diffusion of H through the liquid metal to the pore-metal interface, and the rapidity with which equilibrium between H in the pore and in solution in the melt was reached. Of course, in this stage, double oxide film defects containing only Ar would possess only a small volume of gas, and any expansion would be small, relative to what would be the case if the oxide film defect atmosphere was larger.

However, during solidification rejection of H from the growing solid causes the H content of the liquid metal to rise to several times its equilibrium concentration [18] and this would greatly increase the driving force for diffusion of H into the atmosphere of the oxide film defect, even if only a small residual volume of Ar remained.

Therefore, for the purposes of modelling double oxide film defects as initiators of H gas porosity in Al alloys, there may be no satisfactory single coefficient to describe diffusion of H through an oxide layer. The rate of diffusion into an oxide film defect would depend upon its local environment (such as local flow conditions, which could lead to rupturing of the oxide skin), the defect structure (such as its volume and surface area, and the nature of its internal atmosphere) and the point it had reached in its evolution.

Finally, it should be borne in mind that Weigel and Fromm [9] used pure Al, and in these experiments, commercial purity Al was also used. In both cases the melt should form an alumina film on its surface, whereas in Al–Si castings containing Mg the oxide film should be $MgAl_2O_4$ spinel [19]. While there may be quantitative differences in behaviour as a result of this, qualitatively the oxide film defects should behave similarly in the presence of H in the melt. However, in alloys containing greater than 2 wt% Mg, the oxide film that forms should be MgO, which is porous [19], and which may therefore offer no barrier to the diffusion of H into such a double oxide film defect.

Conclusions

1. Air bubbles introduced into an Al melt have been shown to expand as the result of diffusion of H into their interior atmosphere.
2. This suggests that double oxide film defects in Al alloy castings would behave similarly, and would act as initiation sites for H gas porosity in castings during solidification.
3. The rate of diffusion of H into an oxide film defect would not be constant, but would be influenced by the local environment of the defect, the structure of the defect, and the stage it had reached in its development.

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