Proceedings of the 2013 International Symposium on Liquid Metal Processing & Casting
Edited by: Matthew J. M. Krane, Alain Jardy, Rodney L. Williamson, and Joseph J. Beaman
TMS (The Minerals, Metals & Materials Society), 2013

THE BEHAVIOUR OF ENTRAINMENT DEFECTS IN ALUMINIUM ALLOY CASTINGS

[1]W. D. Griffiths, [1]A. J. Caden and [2]M. A. El-Sayed
[1]School of Metallurgy and Materials Science, College of Engineering and Physical Sciences, University of Birmingham, Edgbaston, Birmingham, United Kingdom. B15 2TT.
[2]Department of Industrial and Management Engineering, Arab Academy for Science, Technology and Maritime Transport Abu Qir, P.O. Box: 1029, Alexandria, Egypt

Keywords: Aluminium alloys, oxide films, entrainment, mechanical properties.

Abstract

The results of experiments are reported in which air bubbles were held for varying lengths of time in melts of three different Al alloys, (commercially pure Al, Al-7Si-0.3Mg, (2L99), and Al-5Mg alloy), with the air bubbles acting as analogs for the behavior of the interior atmosphere of double oxide film defects. After solidification a Pore Gas Analyser was used to measure the contents of the bubble, to determine how their oxygen, nitrogen and hydrogen content varied over time in the different alloys. The results showed that, firstly, oxygen should be consumed by reaction with the surrounding melt to form an oxide, followed by nitrogen, forming a nitride, probably AlN. Simultaneously, hydrogen dissolved in the melt passed in to the air bubble. At the end of the 40 minute holding period the air bubbles, and by analogy the interior atmosphere of a double oxide film defect, largely consisted of a nitrogen/hydrogen atmosphere. The reaction rates obtained from these experiments were used to estimate the time taken for the interior atmosphere of a typical double oxide film defect to be consumed, which was found to vary with alloy type, and to be about 25 minutes in the case of a defect in the Al-7Si-0.3 Mg alloy.

Introduction

The transfer of liquid Al alloys, and the action of pouring into a mould, is often accompanied by entrainment of the oxidized surface skin of the alloy. The very high reactivity of liquid Al with oxygen in the air means that the surface of the liquid metal can be considered to be permanently coated with an oxide film. Therefore, as the oxide film is ruptured by movement of the liquid metal underneath, the rupture must be almost instantaneously sealed by reaction between the Al and oxygen in the air. Pouring or transfer of the liquid metal results in considerable splashing of the liquid metal, (which has a viscosity similar to that of water), and as the splashes coalesce and merge with the bulk liquid, a doubled-over oxide film can be carried into the liquid metal. The sides of the double oxide film defect are unbonded, and the defect would capture a portion of the local atmosphere to be carried into the melt, from where it may be swept into the mould cavity, (see Figure 1) [1].

Double oxide film defects therefore consist of a crevice in the solid metal, formed by the unbonded oxide films, and containing a layer of gas. They form a defect in the final solidified casting of variable size, and with variable orientation with respect to any applied load experienced by the casting in service. It is therefore thought that double oxide films play a major role in influencing the variability of mechanical properties in Al alloys, [2], Mg alloys, [3], and possibly other alloys as well [4].

Since the defects consist of unbonded oxide surfaces containing a layer of gas, this gives rise to the speculation that the interior atmosphere of the defect can continue to react with the surrounding bulk liquid metal once it has been entrained. If the interior atmosphere becomes consumed, it may be possible for the oxide surfaces of the defect to be brought together where they may bond in some way, reducing the deleterious effect of the oxide film defect.

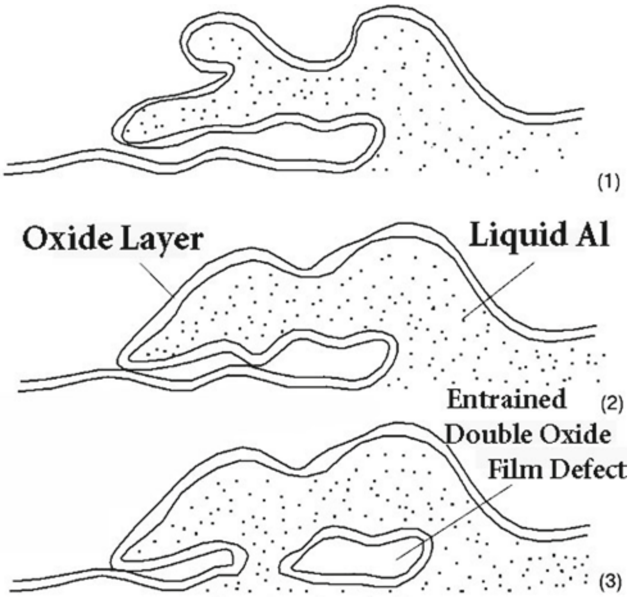

Figure 1. Sketch of the formation of an entrained double oxide film defect.

Nyahumwa et al. [5] speculated that if the interior gas in the defect was air, then, initially, the oxygen would react with the surrounding liquid metal to form alumina, and once all of the oxygen was consumed, the remaining nitrogen would react with Al to form AlN. Once all the internal atmosphere was consumed, Ar would remain, (air consists of 1 vol.% Ar), which would be inert and insoluble. The entrapment of an atmosphere consisting of air would be reasonable if a die casting is considered. In the case of a sand casting, the breakdown of the binder would produce a local atmosphere containing gases such as water vapour, hydrogen and hydrocarbons, of varying amounts, depending on whether a greensand or chemically-bonded sand was used.

Raiszadeh and Griffiths performed an experiment in which a bubble of air, acting as an analogue for a double oxide film defect, was held in a melt of commercial purity Al for several hours [6].

The volume of the air bubble was monitored using a real-time X-ray instrument, which showed a reduction in the bubble volume corresponding to the reaction of the air bubble with the surrounding melt. It was inferred that the air bubble contracted initially due to the reaction of Al with oxygen to form Al_2O_3, followed by the reaction of Al with nitrogen to form AlN. Examination of the surfaces of the solidified sample of the air bubble surface confirmed the occurrence of Al_2O_3 and AlN. It was suggested that these reactions occurred as the skin of the air bubble was ruptured and resealed, rather than by diffusion of the interior gases through the oxide skin of the bubble.

In melts containing relatively low hydrogen contents the bubble volume initially contracted, and then steadily shrank. In melts containing relatively high hydrogen contents, the bubble volume initially expanded, and then contracted, and from this it was inferred that hydrogen was passing through the oxide film into the air bubble, showing how double oxide film defects could be initiators of hydrogen-related porosity. Reaction rates obtained from observation of the rate of reduction of the bubble volume were used to infer likely lifetimes of the interior atmosphere of double oxide film defects of a couple of minutes, about the typical solidification time of an Al casting.

El-Sayed et al. suggested the occurrence of two competing mechanisms during the holding of Al castings in the liquid state before solidification that could affect any entrained bifilms. The first mechanism was the consumption of the air inside bifilms, which reduced their size and in turn improved mechanical properties. The other mechanism was the diffusion of H into the defects, increasing their size and making the properties worse [7,8].

The work presented here is a more detailed study of the behaviour of air bubbles held in Al melts, as a method of understanding the behavior of double oxide film defects. Previous work mostly employed commercial purity Al alloy, which would form Al_2O_3 on its surface. Commercially used alloys would form different oxides, and in this work other alloys were also used, namely, an Al-7Si-0.3Mg alloy, (2L99), where the surface oxide film would be spinel, (Mg_2AlO_4), and Al-5Mg, where the surface oxide film would be expected to be MgO. Such different oxide films would have different characteristics, and this may affect double oxide film defect behavior. In the previous work, reaction rates were inferred by changes in bubble volume, whereas in this work the air bubbles held in the melt were preserved by solidification of the surrounding liquid metal, and the contents of the air bubbles subsequently analysed using mass spectroscopy.

The results obtained allow a more detailed understanding of double oxide film defects in commercial alloys, and may point towards methods of eliminating the defects once they are formed.

Experimental Procedure

Air bubbles, to represent double oxide film defects, were trapped inside Al alloy melts by immersing a steel strip of length 50 mm, containing two blind holes of height 5 mm and diameter 6 mm. The steel strip was immersed in a melt to a depth of 20 mm, and then rotated at 540 rpm, giving an angular velocity at the position of the trapped bubbles of 1.4 ms^{-1}, (see Figure 2). This procedure was intended to represent the shearing action that might occur as a double oxide film defect was carried through the melt during mould filling.

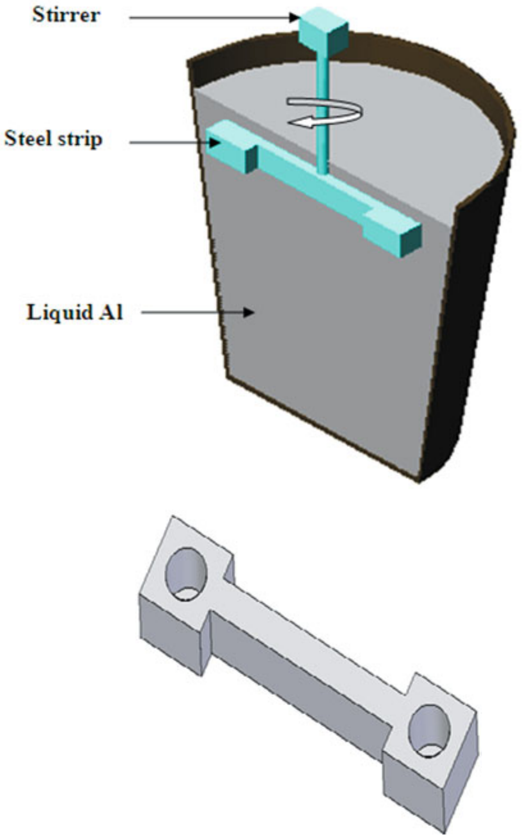

Figure 2. (a). Schematic of the experimental technique. (b). Illustration of the steel strip immersed in the melt.

The steel strip was rotated in the melt for periods of time ranging from 2 to 40 minutes, during which time the contents of the air bubble reacted with the surrounding Al alloy melt. Following the desired holding period the rotation was halted, and the alloy melt quickly solidified by the insertion of cold alloy blocks. The trapped air bubble was then sectioned out of the solidified melt and placed in a Pore Gas Analyser, (built by Hiden Analytical Ltd., Warrington, UK).

The Pore Gas Analyser was evacuated to a pressure of less than about 10^{-8} bar, and then the air bubble was pierced, and its contents passed through a mass spectrometer for analysis. In order to test the accuracy and reproducibility of the Pore Gas Analyser, air was trapped inside a piece of Cu tube of similar dimensions, which was soldered shut at both ends, and then its contents analysed in the same way. Table 1 shows the measurement of the composition of the air trapped inside three Cu tubes, with the different samples agreeing largely with the expected analysis of air, although the oxygen content, about 18%, was slightly lower than expected. However, the reproducibility and relative accuracy of the measurements gave confidence in the method used. The determination of the composition of the bubbles held in the melt for varying time periods was obtained from the Pore Gas Analyser by comparison with the results obtained from the analysis of air.

Experiments were carried out using bubbles of air trapped in three alloys having variable Mg contents, namely, commercial purity Al alloy, 2L99 alloy, (Al-7Si-0.3Mg), and Al-5Mg alloy. The varying Mg contents meant that each alloy should form a different surface oxide film. These reactants, formed on the surface of the alloy melt exposed to the air bubble, were analysed using scanning electron microscopy and EDX spectroscopic analysis.

Table 1. Measured compositions of samples containing air, as measured using the Pore Gas Analyser.

	Vol.% of gases inside bubble			% Variation
Gas	**Sample 1**	**Sample 2**	**Sample 3**	
Ar	0.98	0.96	0.96	2.0
H	0.71	0.73	0.73	2.0
N	79.47	78.68	78.68	1.0
O	18.24	18.42	18.42	1.0
H_2O	0.59	0.59	0.59	1.0

The change in composition of the air bubbles was used to estimate the rates of reaction of the bubble contents with the surrounding melt, (i.e., the change in oxygen and nitrogen content), and the rate of diffusion of hydrogen into the bubble. From these estimated rates of reaction, estimates were made of the time taken for consumption of the interior atmosphere of a double oxide film defect.

Results

Figure 3 shows a typical output from the Pore Gas Analyser, showing the variation in pressure obtained from the mass spectrometer as it analysed a sample of an air bubble in an Al-7Si-0.3Mg alloy melt, after 2 minutes holding. The largest peak was associated with nitrogen, as was to be expected, followed by oxygen, and hydrogen and argon, with a trace amount of water vapour.

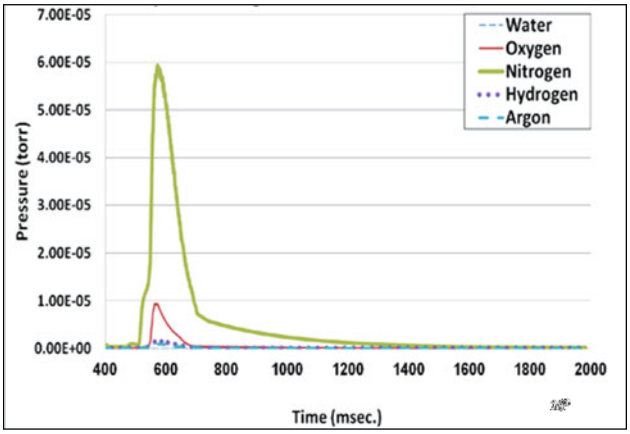

Figure 3. An example of the output from the Pore Gas Analyser. (The largest peak is due to nitrogen, the smaller peak is due to oxygen. There was little hydrogen in this sample).

Figures 4(a) to (c) show the change in volume for air bubbles trapped in the three different alloys. In the case of the commercially purity Al alloy, and the Al-5Mg alloy, the bubble volume decreased to about 40% of its original volume, with 40 minutes holding time, (see Figures 4(a) and 4(c)). In contrast, in the Al-7Si-0.3Mg alloy (Figure 4(b)), the reduction in bubble volume was much less, reaching about 70% of its initial volume.

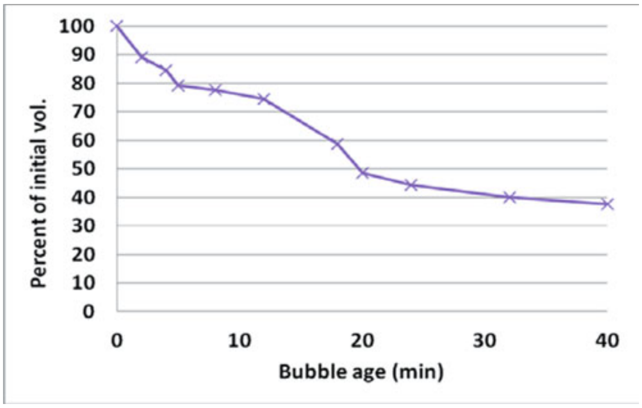

Figure 4 (a). The reduction in air bubble volume with time for the commercial purity Al alloy melt.

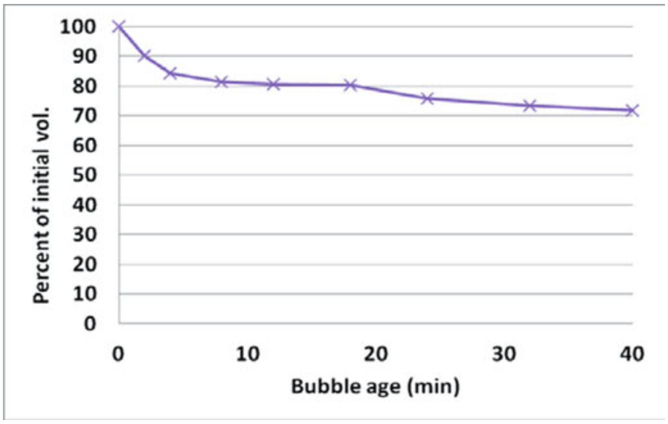

Figure 4(b). The reduction in air bubble volume with time for the Al-7Si-0.3Mg alloy melt.

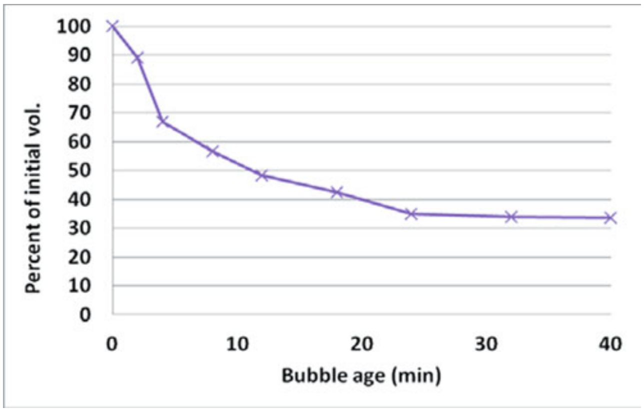

Figure 4(c). The reduction in air bubble volume with time for the Al-5Mg alloy melt.

Figure 5 shows the change in composition of the air bubbles trapped in the different alloy melts. Figure 5(a) shows that for commercial purity Al alloy, there was an initial reduction in oxygen content, from about 20% to nearly 0%. As the oxygen content declined there was a corresponding increase in nitrogen content. Once most, (but note, not all), of the oxygen had been consumed, the nitrogen content began to decrease, presumably due to the formation of AlN.

As first the oxygen content was decreased and then the nitrogen content decreased, the hydrogen content steadily increased. At the end of the 40 minute holding period, the bubble consisted of approximately 50% nitrogen and 50% hydrogen.

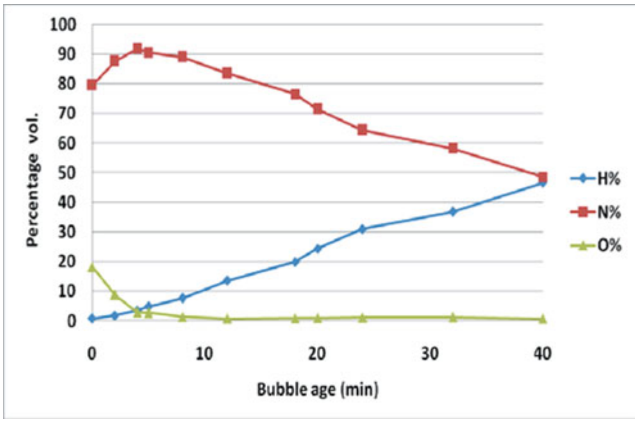

Figure 5(a). The change in composition for an air bubble held in a commercial purity Al alloy melt for up to 40 minutes.

Figure 5(b) shows the change in composition with the air bubble being held in a melt of Al-7Si-0.3Mg alloy. As Figure 4(b) showed, the rates of reaction were much less, but with the same trends. There was an initial reduction in oxygen, and a corresponding increase in nitrogen content until most of the oxygen was consumed, followed by a reduction in nitrogen content. During this time there was also an increase in hydrogen content. At the end of the 40 minute holding period the air bubble had a composition that was about 80% nitrogen, and 20% hydrogen.

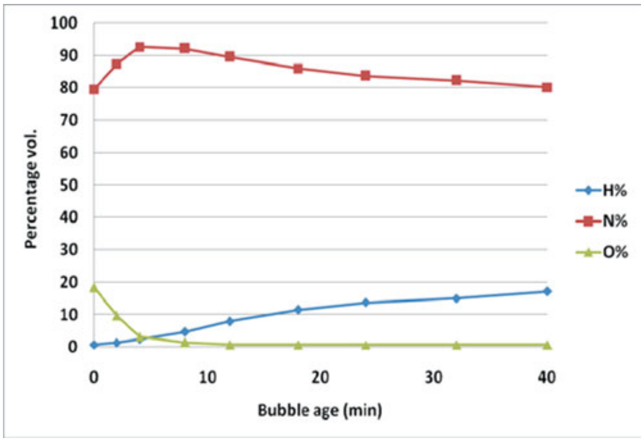

Figure 5(b). The change in composition for an air bubble held in an Al-7Si-0.3Mg alloy melt for up to 40 minutes.

Figure 5(c) shows the change in composition of an air bubble held in an Al-5Mg alloy melt. This also showed a reduction in oxygen content to almost 0% over the first five minutes, and a corresponding increase in nitrogen content, followed by a decrease. The hydrogen content also increased during this period, but slowed after about 25 minutes. The final composition of the bubble after 40 minutes holding time was about 70% hydrogen and about 25 to 30% nitrogen.

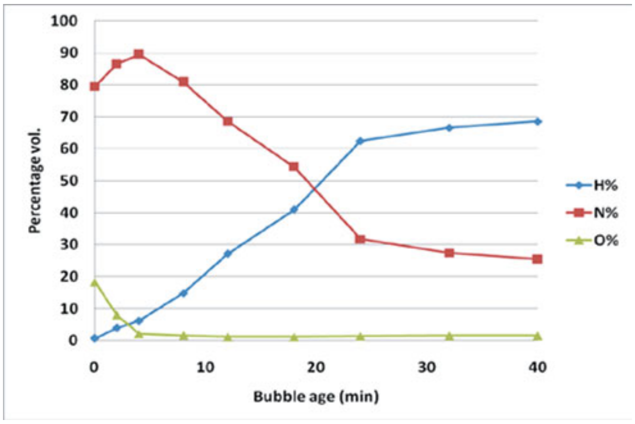

Figure 5(c). The change in composition for an air bubble held in an Al-5Mg alloy melt for up to 40 minutes.

Figure 6 shows the changes in composition for each element in the case of the different alloys. Figure 6(a) shows the change in oxygen content over time, which shows that for each alloy the reduction in oxygen occurred over about 5 minutes, with the Al-5Mg alloy, expected to have a porous MgO interface, having the quickest rate of loss.

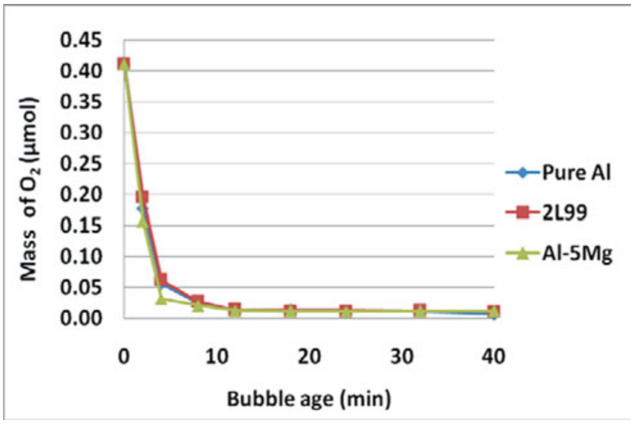

Figure 6(a). Change in oxygen content in the three alloys.

Figure 6(b) shows the change in nitrogen content over time for the three alloys, with the rate of reduction being greatest in the Al-5Mg alloy, and the least rapid being in the Al-7Si-0.3 Mg alloy.

Figure 6(c) shows the change in hydrogen content of the three alloys, with hydrogen passing into the air bubble most quickly in the case of the Al-5Mg alloy, almost reaching equilibrium, and least quickly in the case of the Al-7Si-0.3Mg alloy.

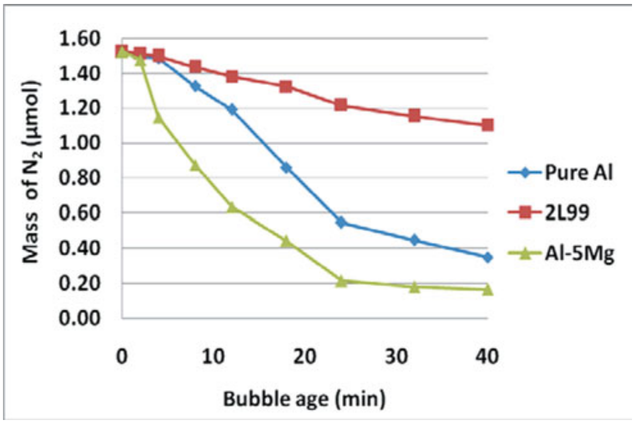

Figure 6(b). Change in nitrogen content in the three alloys.

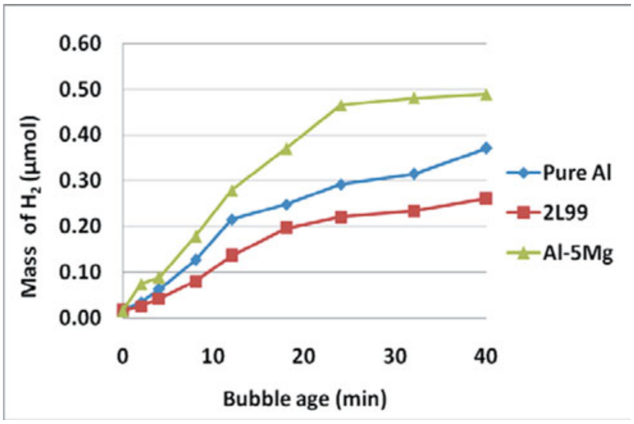

Figure 6(c). Change in hydrogen content in the three alloys.

Following analysis of the air bubble contents the interface of the alloy with the air bubble was examined using scanning electron microscopy and EDX to infer the compounds formed by reaction between the bubble and the melt. The oxides formed in the case of the three alloys appeared to be as expected, namely, alumina in the case of the commercial purity Al alloy, spinel ($MgAl_2O_4$) in the case of the Al-7Si-0.3Mg alloy, and MgO in the case of the Al-5Mg alloy. A nitride, probably AlN of Mg_3N_2, was also detected in all of the three cases.

Discussion

The reaction rates of oxygen and nitrogen obtained from the Pore Gas Analysis results were used to estimate the rate of consumption of the interior atmosphere of a typical double oxide film defect. This required an assumption of a typical double oxide film defect size, and specifically dimensions for the surface area of the defect, through which the reactions must occur, and the interior volume of the defect, and hence the amount of gas available for reaction. Previous work, using commercial purity Al, [9] had assumed a defect dimension of 10 x 5 mm with a thickness of 5 µm, based on a suggestion by Campbell [1]. This led to an estimate for the duration of the defect atmosphere of up to around two minutes.

More recently microfocus X-ray studies of porosity in cast Al alloys have been carried out, [10] which suggested dimensions of oxide film defects of around 2.2 x 2.2 x 0.1 mm. The duration of the atmosphere was estimated assuming these dimensions, and found to vary considerably with alloy composition, (see Figure 7). This was presumably due to the different nature of the oxides formed in each case, leading to variations in the reaction rates. Figure 7 shows that the atmosphere in a double oxide film defect in Al-5Mg alloy may have a duration of about 6 minutes, in commercial purity Al about 8 minutes, and in Al-7Si-0.3Mg alloy about 25 minutes. That the shortest predicted duration was associated with the Al-5Mg alloy is suggested to be due to the surface oxide film expected to form on the liquid alloy being (porous) MgO, which would allow a faster reaction rate. Note that the predicted time period for the presence of oxygen in a double oxide film defect was similar, and it was the varying rates of reaction with nitrogen which led to the predicted variation in the time taken for the interior atmosphere to be consumed.

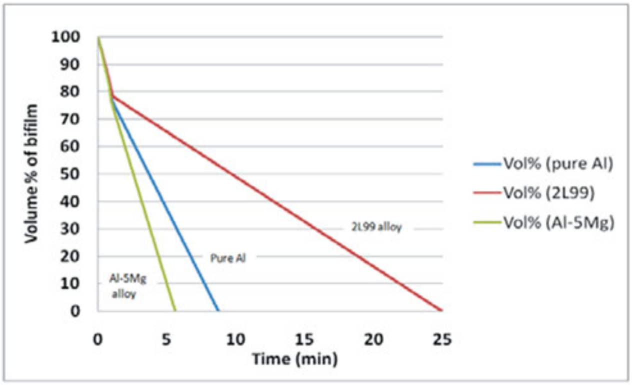

Figure 7. Estimates of the duration of the atmosphere in a double oxide film defect of assumed dimensions, for the three different alloys.

These predicted time periods for the survival of the interior atmosphere of double oxide film defects were longer than the expected solidification times of most thin section Al castings, showing how double oxide film defects formed during pouring would persist into the solidified casting. Furthermore, these estimates of duration of the atmosphere would be greatly extended by the passage of dissolved hydrogen from the melt into the defect, as shown in Figure 5.

Assuming that the melt hydrogen content was approximately equal in the tests, the greatest hydrogen pick-up by the bubble atmosphere occurred in the case of the Al-5Mg alloy, (0.49 µmol, in 40 minutes), while the commercial purity Al alloy was associated with a slightly less hydrogen pick-up of 0.37 µmol, and the Al-7Si-0.3Mg alloy was associated with the smallest hydrogen pick up of 0.26 µmol. Again, the variations in hydrogen pick-up were probably related to the variations in the nature of the oxide film associated with each alloy, with the greatest hydrogen pick-up being associated with the porous MgO film expected to form on the Al-5Mg alloy melt.

Finally, Figure 8 shows an example of an SEM picture taken from a sample of commercially pure Al alloy held for 40 minutes. EDX analyses at points X1, X2 and X3 revealed alumina, probably AlN and pure Al alloy, respectively, one layer over another. At this time, all or most of the oxygen in the air bubble had been consumed, (see Figure 5(a)), and the bare Al alloy surface (labeled X3), would have been in contact with an atmosphere that was largely nitrogen and hydrogen. That the bare Al alloy surface can occur in the presence of nitrogen, suggests that the formation of AlN may require some sort of incubation period, (at least in the case of the commercial purity Al alloy).

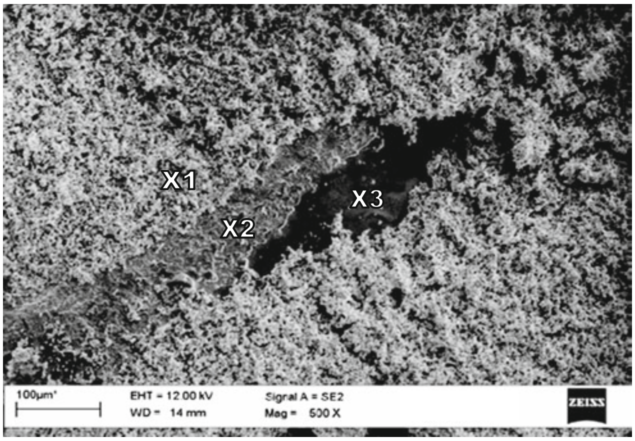

Figure 8. SEM micrograph showing the surface of a sample after holding in commercial purity Al alloy for 40 minutes. EDX analysis revealed the presence of alumina (at position X1), a nitride, probably AlN, (at position X2), and Al, (at position X3).

Conclusions

1. Pore Gas Analysis experiments were carried out on air bubbles held in three different Al alloys for periods of up to 40 minutes, to act as analogues for double oxide film behaviour in liquid Al. The measured changes in bubble composition were used to infer reaction rates to predict the duration of the atmosphere in typical double oxide film defects, leading to estimates of between 6 to 25 minutes, depending upon alloy composition.

2. The Pore Gas Analysis results also showed an increase in hydrogen in the bubble atmosphere, as it diffused in from the melt. The rate of diffusion also varied with alloy composition, and was again most rapid in the case of the Al-5Mg alloy. The estimated durations of the oxide film defect atmospheres would be greatly extended by the presence of hydrogen.

3. Examination of the compounds formed during reaction between the melt and the air bubbles indicated the formation of nitrides. In the case of the commercial purity Al alloy, circumstantial evidence suggests an incubation period may be necessary before the formation of AlN can take place.

Acknowledgements

The authors would like to gratefully acknowledge the technical assistance of Mr. Adrian Caden and Mr. Robert Goodwin of the University of Birmingham, and the financial assistance of Prof. A. Y. Kandeil of the Arab Academy for Science, Technology and Maritime Transport, Alexandria, Egypt, and the technical assistance of Prof. H. Salem of the American University in Cairo, Egypt. In addition, partial support from the EPSRC Centre for Innovative Manufacturing in Liquid Metal Engineering (EP/H026177/1) is acknowledged.

References

1. J. Campbell, *Castings*, Butterworth-Heineman, Oxford, 2003.

2. N. R. Green and J. Campbell, Influence of oxide film filling defects on the strength of Al-7Si-Mg alloy castings, *AFS Trans.,* 102 (1994) 341-347.

3. W. D. Griffiths and N-W Lai, Double oxide film defects in cast magnesium alloy, *Met. and Mat. Trans. A*, 38A, (2007) 190-196.

4. J. Mi, R. A. Harding, M. Wickins and J. Campbell, J., Entrained oxide films in TiAl castings, *Intermetallics*, 11 (2003) 377-385.

5. C. Nyahumwa, N. R. Green, and J. Campbell, J., *AFS Trans*., 58 (1998) 215-223.

6. R. Raeiszadeh and W. D. Griffiths, A method to study the history of a double oxide film defect in liquid aluminium alloys, *Met. Mat. Trans. B*, 37B (2006) 865-871.

7. El-Sayed, M.A., Salem, H.A.G., Kandeil, A.Y., and Griffiths, W.D., Oxide Film Defects in Al Alloy Castings, 22nd International Conference on Computer-Aided Production Engineering, (2011) Edinburgh, Scotland.

8. El-Sayed, M.A., Salem, H.A.G., Kandeil, A.Y., and Griffiths, W.D., Effect of Holding Time Before Solidification on Double-Oxide Film Defects and Mechanical Properties of Aluminum Alloys, *Met. Mat. Trans. B* 42B (2011) 1104-1109.

9. R. Raeiszadeh and W. D. Griffiths, A semi-empirical mathematical model to estimate the duration of the atmosphere within a double oxide film defect in pure Al alloy, 39B, *Met. Mat. Trans. B,* 39B (2008) 298-303.

10. J. M. Park, Behaviour of bifilms in A356 alloy during solidification: developing observation techniques with 3-D micro x-ray tomography, *MRes thesis*, University of Birmingham, 2010.