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To cite this article: W D Griffiths et al 2016 IOP Conf. Ser.: Mater. Sci. Eng. 117 012070

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Oxide film defects in Al alloys and the formation of hydrogen-related porosity

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Abstract. Double oxide film defects have also been held responsible for the origins of hydrogen porosity, where hydrogen dissolved in the Al melt passes into the interior atmosphere of the double oxide film defect causing it to inflate. However, this is in opposition to long-established evidence that H cannot readily diffuse through aluminium oxide. To investigate this further, samples of commercial purity Al were first degassed to remove their initial H content, and then heated to above their melting point and held in atmospheres of air and nitrogen respectively, to determine any differences in H pick-up. The experiment showed that samples held in an oxidising atmosphere, and having an oxide skin, picked up significantly less H than when the samples were held in a nitrogen atmosphere, which resulted in the formation of AlN in cracks in the oxide skin of the sample. It is suggested that double oxide film defects can give rise to hydrogen-related porosity, but this occurs more quickly when the oxygen in the original oxide film defect has been consumed by reaction with the surrounding melt and nitrogen reacts to form AlN, which is more permeable to H than alumina, more easily allowing the oxide film defect to give rise to a hydrogen pore. This is used to interpret results from an earlier synchrotron experiment, in which a small pore was seen to grow into a larger pore, while an adjacent large pore remained at a constant size.

1. Introduction

Double oxide film defects occur in Al alloy castings when, during mould filling or other metal transfer operations, the oxidised surface of the liquid metal folds over onto itself and is entrained in the liquid metal. Since the oxidised surfaces are at a temperature thought to be too low for sintering, the defect consists of unbonded oxide surfaces between which is trapped a thin layer of the local atmosphere, trapped when the liquid metal surfaces folded over onto themselves. The thickness of the defects is probably just a few µm’s, but their area can be several mm². These gas-filled crevices with an area of several mm², present in the solidified casting as defects, can bring about a considerable reduction in mechanical properties. The randomness of the fluid flow effects occurring during their formation, and their subsequent dispersion and orientation, means that oxide film defects have a considerable effect on the reproducibility of cast Al alloy properties [1-3]. Figure 1 shows a sketch of the formation of a double oxide film defect, and figure 2 shows an example of such a defect on the fracture surface of a tensile test bar.

Double oxide film defects in Al alloys have also been associated with the formation of other defects, such as shrinkage porosity, hydrogen gas porosity, hot tears and the nucleation of low melting point phases such as Fe-rich intermetallics [2]. It has been claimed that the nucleation of porosity during solidification, both shrinkage porosity and gas porosity, is best explained by the presence of...
double oxide film defects, as their internal atmosphere acts as a precursor pore, avoiding the problem of accounting for the initial nucleation of a pore [1-3].

Experimental evidence by Griffiths and co-workers supports the possibility of hydrogen diffusing through the oxide layer of a double oxide film defect into the interior atmosphere [4-5]. However, obstacles to this interpretation are to be found in the reports by other researchers of the difficulty for hydrogen to diffuse through an oxide layer. For example, alumina, in layers as little as 20 nm thick, has been proposed as a barrier to the permeation of hydrogen through steel [6,7]. Furthermore, in early experiments to measure hydrogen dissolved in solid Al, considerable problems were experienced due to the presence of an alumina layer on the sample surface [8]. Most interesting were experiments reported by Campbell [1], in which water was placed on the surface of an Al alloy melt while the hydrogen content was being continuously measured. No change in hydrogen content was observed.

The results presented here derive from an experiment in which samples of commercial purity (CP) Al alloy were heated in either an oxygen or a nitrogen atmosphere, to change their surface characteristics, and then held in a hydrogen atmosphere, followed by measurement of hydrogen pick-up. The results were used to interpret the behaviour of pores observed by synchrotron X-ray tomography in small samples of Al held in the liquid state [9].

![Figure 1. Sketch showing the formation of a double oxide film defect in liquid metal [3].](image1)

![Figure 2. SEM image of one side of a double oxide film defect on the fracture surface of a tensile test bar, (arrowed). The diameter of the test bar is 6 mm.](image2)

2. Experimental procedure

Samples of commercial purity (CP) Al alloy of dimensions 8 mm in diameter and 50 mm in length were used in the experiment, as they had suitable dimensions for measurement of hydrogen in a LECO instrument. (The LECO instrument heats up the sample and extracts out dissolved hydrogen into a nitrogen carrier gas; the thermal conductivity of the N\textsubscript{2}/H\textsubscript{2} gas mixture is measured in order to determine the hydrogen content of the Al alloy sample).

Initially samples of CP Al alloy were measured in the LECO instrument three times, in order to reduce the H content to nil, (or less than the measurement accuracy of the instrument, (± 0.005 ppm). The H-free samples were then placed in a sealed glass bottle to minimise H pick-up from the environment, and then placed in a furnace with a controllable atmosphere.

In one experiment the furnace was heated at 40 Kmin\textsuperscript{-1} to 700°C with the samples placed in an atmosphere of air. As the samples of CP Al were heated and expanded, it would be expected that their surface alumina film would crack, and be resealed by the formation of fresh alumina, by reaction between the Al and the oxygen in the air. The samples were held at 700°C for 15 minutes, after which the furnace was evacuated to a pressure of 1 Pa, and then filled with an atmosphere of H\textsubscript{2} at a pressure
of 150 kPa, and held for 1 hour. The furnace was then cooled at a rate of 20 Kmin\(^{-1}\) to 50°C, at which point the hydrogen atmosphere was removed, and the samples taken out for measurement of their hydrogen pick-up by LECO. Two samples were treated in this way.

In a second experiment, two samples of CP Al were similarly completely degassed, by repeated LECO measurement, and then placed into the furnace at room temperature, together with 50 g of Hf turnings, (to act as an oxygen getter). The furnace atmosphere was evacuated to 1 Pa and back-filled with Ar (99.999% purity) to 507 kPa, (5 bar), to minimise the oxygen content in the furnace atmosphere. The furnace was then filled with pure N\(_2\), (99.998% purity), to a pressure of 150 kPa, and then heated to 700°C at the same heating rate, and held for 15 minutes in an atmosphere of N\(_2\). Again it would be expected that heating of the samples would cause them to expand and their oxide film crack, as before, but the cracks in the oxide film should be resealed with AlN, due to reaction between Al and the N\(_2\) atmosphere. The furnace was then evacuated and again back-filled with hydrogen to a pressure of 150 kPa and held at this pressure for 1 hour. The furnace was then cooled and the H content of the samples measured to determine the H pick-up when AlN was present on the sample surface.

In unrelated work, the porosity of samples of 2L99 Al alloy containing porosity was examined using the synchrotron source at the Swiss Light Source. In this work samples of 3 mm in diameter and 6 mm in length, were melted and heated to 727°C in the TOMCAT beamline, and synchrotron X-ray microtomography used to construct 3D images of the porosity and its change in morphology with time. The results of the previous holding experiments were used to interpret the results obtained from the synchrotron imaging. Further experimental details are given in reference [9].

3. Results

3.1 Results of the hydrogen pick-up experiments.

Figure 3 shows the results of the H pick-up experiments. The mean hydrogen pick-up for the two samples heated in air was 0.04 ppm, while for the two samples heated in the nitrogen atmosphere it was 0.08 ppm. Figure 3 also shows the hydrogen pick-up from samples of 5083 alloy, (prepared in the same way), which has a higher Mg content, (4-5wt.%), and therefore should form a surface of porous MgO, as well as having a higher solubility for hydrogen. In this case the hydrogen pick-up was much greater, at 0.28 ppm.

![Figure 3](image-url)

Figure 3. Bar chart showing the relative amounts of hydrogen pick-up in the different experiments.

Figure 4 shows SEM images of the surfaces of the samples heated in the nitrogen atmosphere. At higher magnification, (see figure 4(b)), coupled with EDX analysis, (see figure 4(c)), it was found that the cracks in the surface film contained AlN. The image in figure 4(b) suggested that the structure of AlN would be more permeable than that of alumina. (This type of structure for AlN has been demonstrated in earlier work [4]).
3.2 Results of synchrotron X-ray tomographic microscopy of pores in 2L99 Al alloy.

Figure 5 shows four images obtained in the TOMCAT beamline at the Swiss Light Source, and show the growth of a pore inside a sample of 2L99 Al alloy, held in the liquid state at 727°C for a period of more than 27 minutes. Figure 5(a) shows a pore in the solid state, about 1 mm in diameter, before the experiment began. During heating to the liquid state and holding at 727°C for 16 minutes the pore collapsed to a thinner, irregular form, (see figure 5(b)). Figure 5(c) shows that the pore appeared similar after holding for a further 11 minutes, (a total of 27 minutes). However, the formation of a small spherical pore was noted, (arrowed in figures 5(b-c), adjacent to the large irregular pore. It might be expected that, if this was a hydrogen pore, that the hydrogen would preferentially diffuse into the large irregular pore, whereas growth of the small spherical pore immediately nearby seems to have been preferred. Figure 5(d) shows the same two pores after solidification.

4. Discussion

The results shown in figure 3 and figure 4 therefore suggest that AlN is more permeable to H than aluminium oxide. Aluminium oxide is evidently not completely impervious to the diffusion of hydrogen, but the more open structure of the AlN would be expected to have the higher diffusion rate, as the results of the H pick-up experiments confirmed. The SEM images of the cracks in the oxide films in which the AlN grew, and the EDX analysis of the region, suggests a complex relationship between alumina and AlN, in which the latter may have grown in cracks in the former, but alternatively, the AlN may have grown on an underlying substrate of alumina. This requires further investigation. The preferential passage of H through AlN compared to alumina may be used to explain the different behaviour of the pores studied in the synchrotron experiment shown in figure 5.
Figure 5(a). X-ray image of a pore in a sample of CP Al at 25°C.

Figure 5(b). X-ray image of the same pore after holding in the liquid state at 727°C for 1000 s.

Figure 5(c). X-ray image of the same pore after holding in the liquid state at 727°C for 1640 s.

Figure 5(d). X-ray image of the same pore after solidification and cooling to 25°C.

The solid sample was obtained from a bar cast in such a way as to contain an entrainment defect, in this case a large, mm-sized pore, shown in figure 5(a). This pore presumably therefore originally contained a mixture of air, (but depleted to some extent of oxygen), arising from the entrainment event, and also some hydrogen, arising from the hydrogen dissolved in the metal, which had passed into the pore during solidification. Upon heating of the sample to the liquid state the pore collapsed, either during melting, or during holding in the liquid state. The extent of the collapse suggests that all of the oxygen contained in the pore would have reacted with the surrounding melt, and the pore atmosphere would now perhaps consist of a mixture of N$_2$ and H$_2$, (strongly suggested by Pore Gas Analysis measurements on air bubbles held in liquid Al alloys [5]. Between 16 and 27 minutes its morphology was constant, (see figures 5(b) and (c)), and the interior atmosphere was perhaps unchanged, and still consisted of nitrogen and hydrogen. However in the same time period, between 16 and 27 minutes, a spherical pore was formed, which then grew slightly to become a spherical pore in the solid state which, if seen in a metallographic section, would probably have been attributed to hydrogen porosity (see figure 5(d)).

It was presumed that the small pore, since it appears to grow independently of the large pore, was not connected. The hydrogen dissolved in the liquid metal appears to have preferentially entered the smaller pore, rather than the larger, tangled pore. The large pore shown in figure 5 had progressed to an age where it should be expected that AlN would have been formed at the pore surface, by reaction between the surrounding Al melt and the nitrogen in the pore. The observation that AlN provides an easy diffusion path for hydrogen into the interior of a double oxide film defect, based on the LECO experiments reported in figure 3, suggests that, since the smaller pore expanded, hydrogen dissolved in the melt passed into the smaller pore because the latter offered the least barrier to diffusion.

The origin of the small pore may or may not have been an entrainment defect. If it originated in an oxide film defect, then the same arguments might apply, the presence of AlN would assist the
diffusion of H into the pore. If the pore origin did not lie with an entrainment defect, no interfacial barrier to diffusion of H would be expected.

These results therefore suggest that the formation of hydrogen porosity during solidification is complex. In these results three different mechanisms have been identified. Firstly, passage of hydrogen through an alumina layer into a double oxide film defect can evidently occur, although this occurs slowly, (figure 3). Secondly, passage of hydrogen through an AlN layer can occur, more quickly than through alumina, (see figure 3). Finally, formation of hydrogen porosity either spontaneously or through the presence of pre-existing pores could be a third mechanism, shown in figure 5. The small pore observed in figures 5(b) and (c) may have been a residual pore from a prior entrainment event, although in this case one might have expected the adjacent irregular pore to behave similarly, so perhaps this may have been a new pore coming into existence.

5. Conclusions
1. Hydrogen can diffuse through AlN at a faster rate than through alumina, suggesting that older oxide films, which have formed AlN at their interface, may be a better candidate for the origins of hydrogen porosity in Al alloys than newer double oxide film defects which still retain oxygen.
2. Synchrotron X-ray tomography has suggested that pore formation in Al alloys can arise for multiple reasons, and a monocausal effect should not be sought.

Acknowledgements
The authors acknowledge the support of the EPSRC LiME grant EP/H026177/1, and the financial support of the School of Metallurgy and Materials at the University of Birmingham.

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