

Morphology of oxide films of Al–5Mg alloy in dynamic conditions in casting

M. Divandari and J. Campbell

The Iran University of Science and Technology, Narmak, Tehran, Iran(16844) E-mail Divandari@iust.ac.ir , Department of Metallurgy and Materials, The University of Birmingham, Birmingham, UK B15 2TT

Al–Mg alloys are reported to be sensitive to turbulence during casting, creating plentiful drosslike defects. New oxide films that form very quickly during casting seem to be one of the main reasons. The characteristics of these new films were studied. Samples for the study were prepared based on a technique in which an oxide–metal sandwich was made by the bubble impingement technique. Features of the oxide film such as thickness, morphology, rigidity and presence of nuclei in the matrix alloy have been examined by SEM. Possible consequences of the morphology of the oxide film are discussed.

IJC/558

© 2005 W. S. Maney & Son Ltd. Manuscript received 18 July 2004; accepted 21 February 2005.

Keywords: Oxide films; Al–Mg alloys; Folded double films; Oxidation; Metal–oxide sandwich

Introduction

Al–Mg alloys are reported to be very sensitive to turbulence during pouring, leading to characteristic defects in the castings. When liquid aluminium is exposed to air, the surface oxidises extremely quickly. Thus when the liquid is poured, surface oxide forms on the new surface very quickly. The entrainment of the newly created oxide into the bulk of the molten aluminium necessarily occurs in a dry surface to dry surface mode creating a double film (Fig. 1).^{1,2} The interfaces wetted by (i.e. in atomic contact with) the melt are on the outside of the folded double film. The inner, unwetted surfaces of the doubled film are folded face to face, representing an unbonded interface in the liquid and therefore effectively constitute a crack.¹ Such a description of events in the melting and handling processes involved in casting is becoming generally accepted. However, such effects seem to be especially critical in the casting of Al–Mg alloys.

Turbulent transfers of molten aluminium are common in casting operations, thus, if care is not taken, such transfers can fill the castings with cracks (Fig. 2).³ In addition to constituting cracklike defects in their own right, the gas coated films can act as excellent initiation sites for the subsequent growth of gas bubbles or shrinkage cavities.^{1,3–5} Since the folded oxides (and possibly other films) are known to exhibit a wide range of sizes and shapes, the cracks in the liquid can clearly be extremely serious, often constituting by far the largest defects in the casting. They can easily be envisaged as reaching from wall to wall of a casting, causing a leakage defect in the casting

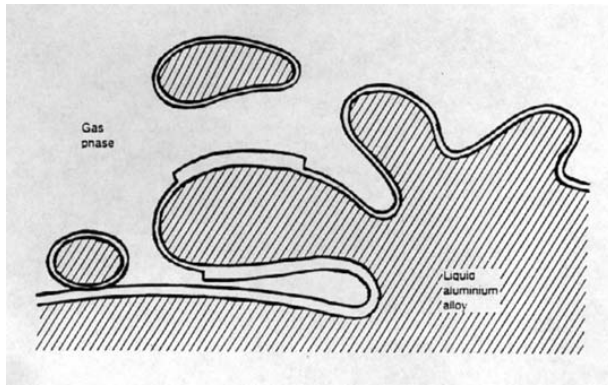
required to be leak-tight, or causing a major structural weakness where strength or fatigue resistance is required.^{1,6}

Although the presence of oxide films has been known about and studied for decades,^{7–16} the intimate and necessary relations between oxide films, casting defects and properties do not seem to have been appreciated. This all-important link between oxide films and the quality of cast materials has only been made in recent years.¹ However, it seems that a general acceptance among researchers^{5,17–19} is gradually growing that oxide films and inclusions play the major part in reducing the quality and reliability of aluminium castings. It has even been suggested that entrainment defects could account for as much as 80% of the total effective problems in castings.^{1,17} There is therefore a considerable interest in characterising the surface films of various casting alloys.^{20,21}

Oxidation of a pure aluminium melt is thought to start by the rapid formation of an amorphous alumina layer. After an initial incubation time, the amorphous alumina changes to crystalline γ -alumina, slowing the rate of oxidation.^{7,22} After a further incubation period, the oxide structure converts to α -alumina, accompanied by a decrease in the volume of the oxide. Cracks can then form in the oxide layer, and combined with a higher mobility of the aluminium ions in the α -alumina, lead to a faster rate of oxidation.¹³

Alloying elements in the metal can influence the rate of oxidation by incorporation of the oxides of these elements into the oxide layer. This can result in an increase in the density of the alumina film, the covering of the alumina by another protecting oxide layer or an increase in mobility of the ions in the oxide. Silicon, copper, zinc and iron have minimal effect on the oxidation behaviour of molten aluminium whereas magnesium, sodium, selenium and calcium increase the rate of oxidation.^{8,9} At high alloying concentrations, magnesium oxidises preferentially forming magnesia (MgO) whereas at magnesium levels typical of many Al casting alloys, magnesium aluminate spinel (MgO·Al₂O₃) forms, probably via the metastable pre-spinel.^{10,11} The effect of magnesium content on oxidation rates is shown in Fig. 3.

Naturally, most of the research on the oxidation of liquid aluminium has been carried out on stagnant melts.^{7–16} However, in the aluminium casting processes, the molten metal is in motion, travelling at



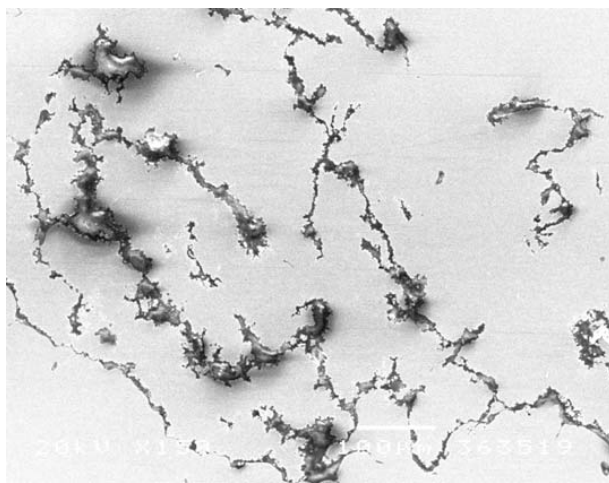
1 Schematic view of oxide film on surface of aluminium alloy; note possible tearing (and immediate re-growth) in film as a result of stress

local velocities often measured in metres per second. Thus, the oxide film layer is continuously subjected to deformation forces. Since the aluminium oxide film is expected to have little or no plasticity (being a ceramic), it will fracture (i.e. tear) when subjected to tension. On exposure to the atmosphere the freshly revealed aluminium will quickly oxidise.¹⁶

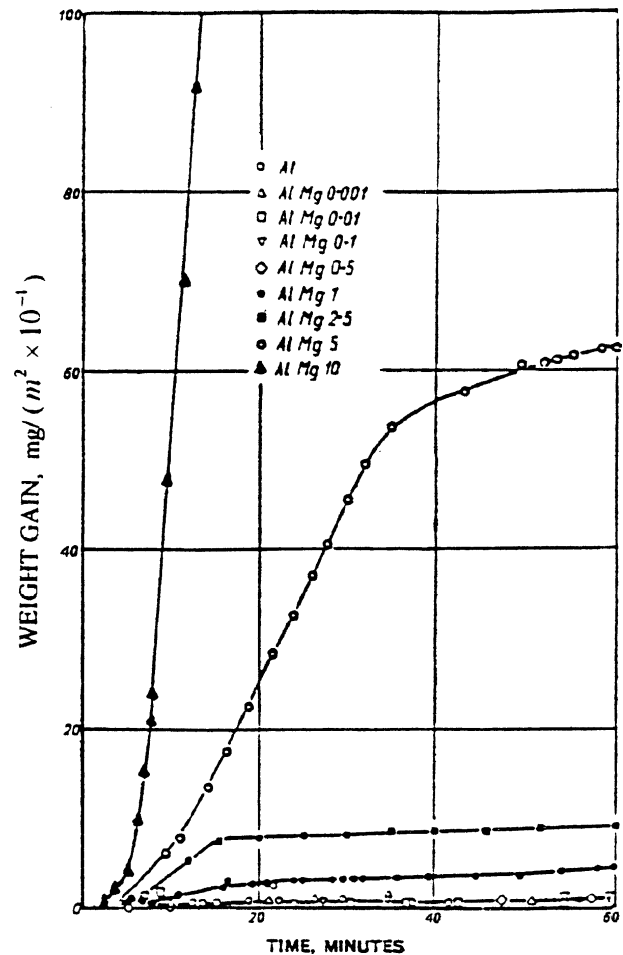
Earlier work revealed the inner surface of an air bubble, trapped in an Al–Mg alloy casting, covered in oxide; the film was clearly visible draped over the dendrite tips (Fig. 4a and b). This observation indicated the clear presence and potential importance of the new oxide film and provided the impetus for this work. A series of experiments was therefore carried out to study the effect of the passage of the air bubbles in solidifying Al–Mg alloy castings to determine the consequential damage to the cast structure.^{2,23}

Experimental

Samples studied in this work were made from Al–5Mg. Details of the experimental technique are explained elsewhere.²⁴ However, in brief, a steady succession of bubbles is artificially introduced via a



2 SEM image showing tangled double oxide film in Al–Mg alloy; note size of oxide films; they act like cracks in casting



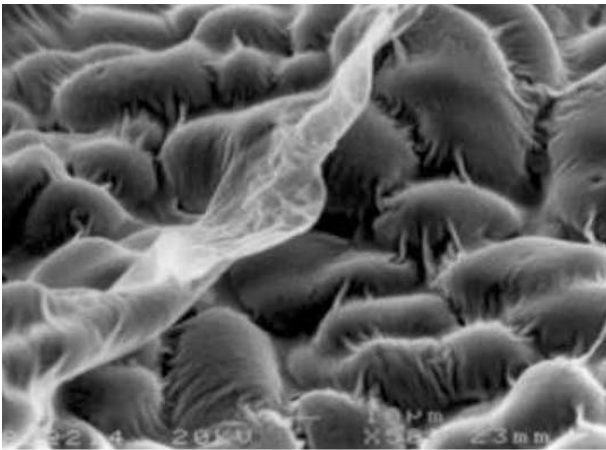
3 Effect of Mg on oxidation of Al–Mg alloys

silica tube into the base of a casting, and their trajectories observed by video X-radiography. Bubbles are formed and grow as they rise, taking about 0.2 s to rise through the casting of 100 mm height. If a bubble is caught by solidifying material, so that the next bubble collides with it, bubble formation is arrested and the sample is allowed to freeze. The contacting region between the bubbles consists of a triple layer composed of the oxide films from each of the bubbles, and residual metal that happens to be trapped in between. The authors call it an 'oxide–metal sandwich'. The sample studied in this work is shown in Fig. 5.

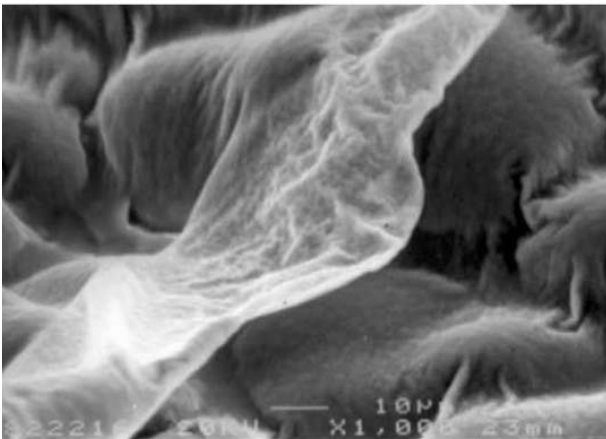
Results

Figure 6a and b shows the SEM images taken from the contact area between the bubbles (the oxide–metal sandwich region). The films are sufficiently thin that the dendrite structure can be clearly seen through the upper film. The dark areas are the dendrites of solidified aluminium alloy trapped between the two layers of oxide film (light areas). From the observed cracks in the films, the oxide appears to be brittle (Figs. 6 and 7).

Figure 7a and b shows a closer view of the sandwich of the alloy in which folds in the film on the surface of dendrites are clearly visible. The morphology and scale of wrinkles in the films are quite different in different alloys.²⁴ The size of



(a)



(b)

4 SEM micrograph taken from inside trapped bubble in a Al-5Mg and b at higher magnification; oxide film is present over whole surface, and is draped and folded over surrounding dendrites

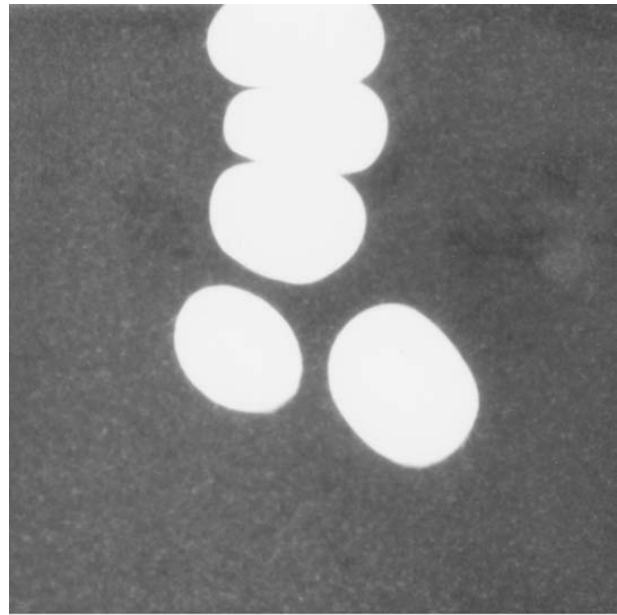
the wrinkles in the Al-5Mg alloy seen in Fig. 7b is in the range of micrometres.

When the melt trapped between two layers of film starts to solidify, the whole process of solidification occurs between these two nearly transparent films. As a result, the various phases that form during freezing can be observed with unusual ease. The α phase, which is the first phase that starts to precipitate in Al-5Mg alloy, is visible in Fig. 8 in dendritic form. Also in the middle of Fig. 8b, a nucleus of the α -Al phase is clearly visible. It seems quite possible in principle to analyse and identify the nucleus, although this was outside the scope of the present study.

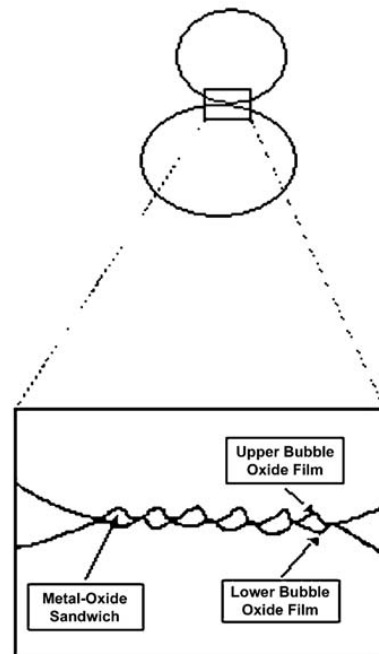
By rotating the specimen to view the sandwich on its edge (Fig. 9), the thickness of the oxide film could be measured directly. In places where the metal had been excluded, the remaining double oxide layer could be clearly seen.

Discussion

In Al-Mg alloys, the rate of oxidation is reported to be especially fast.^{8,9} However, practically all studies of oxide film characteristics have been carried out on a sample of molten metal held at rest in a crucible. This technique is valuable for information on the



(a)

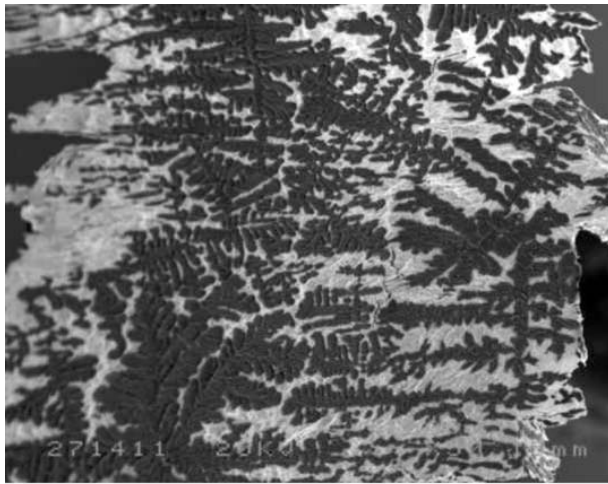


(b)

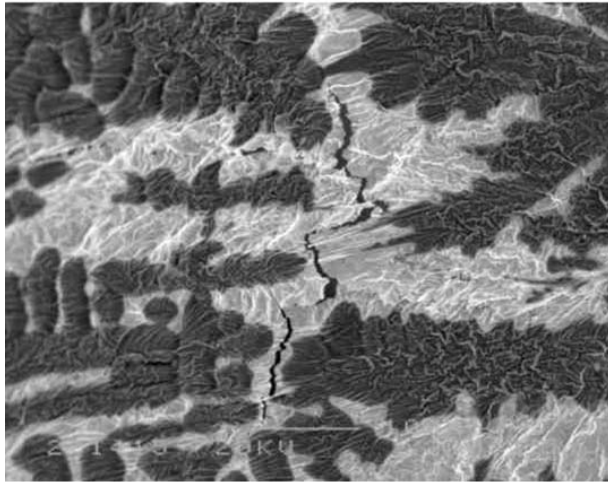
5 a radiograph taken from casting showing examples of entrapped bubbles; b sandwich taken from between two contacting bubbles

build up of thick films over periods of minutes, hours or days. In contrast, those films entrained during the pouring of molten metals are typically formed and submerged within milliseconds. Films formed during the creation of bubble trails represent an intermediate case. The present study attempts to capture films for study that are typical of these intermediate times.

The morphology of the oxide films in Al-5Mg is such that Fig. 10 seems to be more realistic for Al-5Mg in comparison to the representation in Fig. 1. In Fig. 10, the outer surface of the oxide film in contact with the air has been shown to be rough. There seems to be a relationship between the thickness of the oxide film and its morphology. In the alloy Al-5Mg, the thickness of



(a)



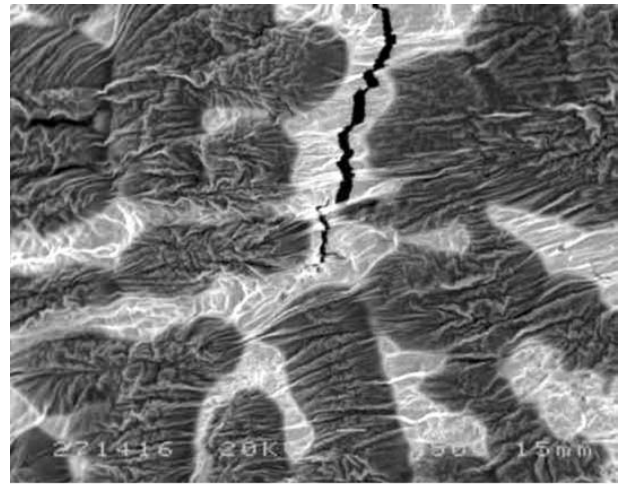
(b)

6 a oxide-metal sandwich of Al-5Mg alloy; white areas are double layer of oxide film that have collapsed together; dark areas are dendrites covered with oxide films from both sides, front and back; b same image at higher magnification; note cracks visible in white areas, that are the result of brittle nature of double layers of oxide film in these areas

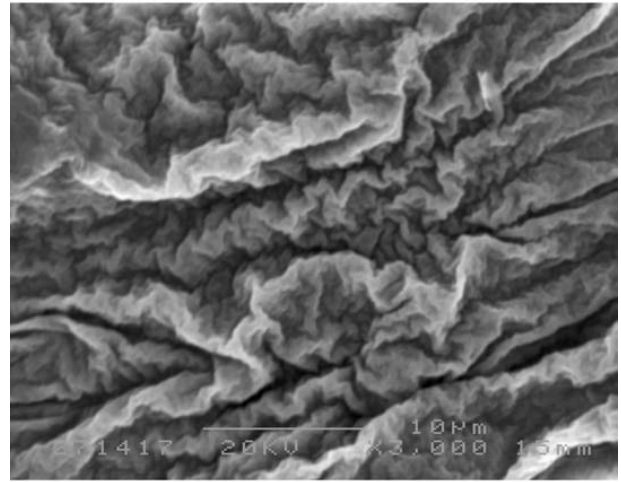
the surface oxide film is about 10 times greater than that of Al-7Si-Mg alloy.²⁵

The rough and wrinkled morphology of oxide films in Al-Mg alloys and Mg-base alloys has been reported previously.²² The microscopic folds, as well as the macroscopic folds, would be expected to retain air, contributing to gas porosity in the melt by forming excellent initiation sites for the precipitation of hydrogen. In addition, of course, the nature of the oxide film with its entrained layer of air between folds would act as a crack in the solidified casting. One can envisage the future use of physical and/or mathematical modelling techniques to estimate the amount of the air and/or gas that might be entrapped between wrinkles.

The thickness of the oxide film seems to be an important factor in the possibility of the formation of defects. It is well known that some alloys, particularly those based on Al-Mg, are very difficult to cast without defects.²⁶ It seems that many of the defects which are related to the fluid flow are somehow under control of



(a)



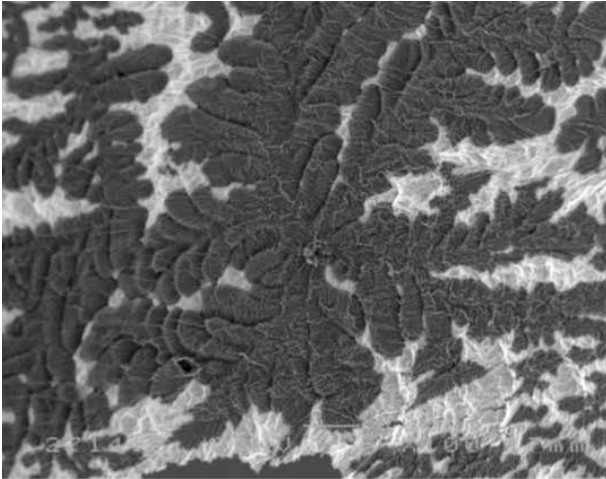
(b)

7 a another region of specimen shown in Fig. 6; b at higher magnification showing roughness of oxide film

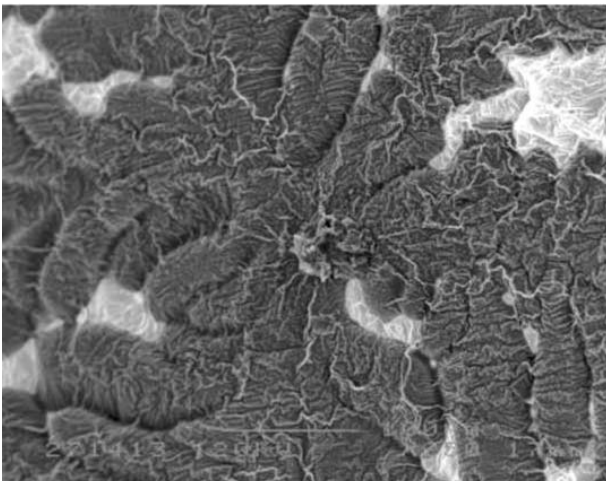
the oxide film thickness and its strength.^{27,28} The thickness of oxide film is a function of alloying elements. Mg clearly thickens and thus probably strengthens the oxide film. Defects related to the presence of films are likely therefore to be enhanced.

The thickness of the individual oxide films is not easily characterised because of the different length scales of folds of the film. The total thickness of the film appears to be approximately 500–700 nm because of macroscopic folding and roughness, whereas the side view seen in Fig. 9 shows that the real thickness is nearer 20–30 nm. Thus the method of estimating film thickness by halving the measured thickness of folds is seen to oversimplify and usually overestimate the thickness of the film. The overestimation is compounded by the additional material trapped inside the folds, such as metal, and partly from the residual rigidity of the films that helps it to resist conformance to a sharp bend.

With entrained films of such characteristics of thickness and morphology, it is understandable that the attainment of good castings from Al-Mg alloys is difficult when they are commonly poured via turbulent running systems. Returning now to Fig. 2, this shows that if such oxide films bridge



(a)

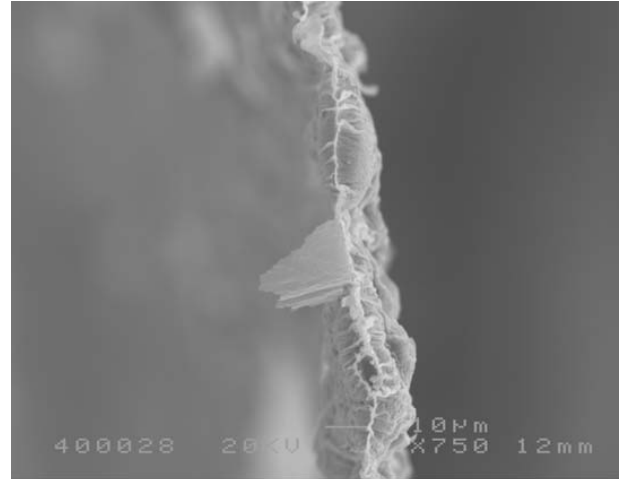


(b)

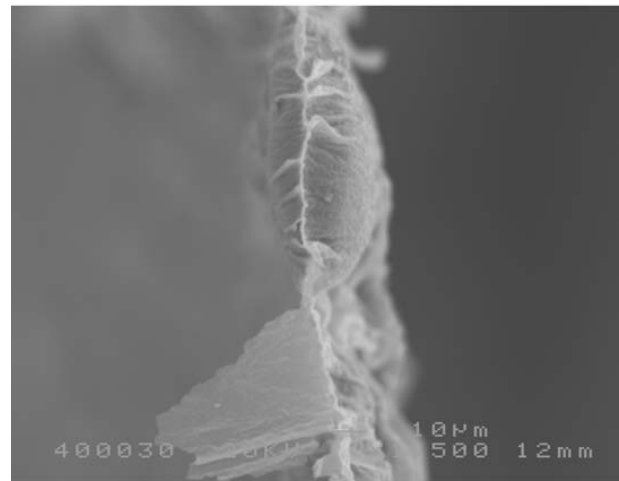
8 *a* oxide-metal sandwich of an Al-5Mg alloy in more detail; Al matrix dendrites covered with a thin folded oxide film are clearly visible; *b* possible nucleation site of α -Al phase

from wall to wall of a thin wall casting, the result would be a crack in the wall, and/or a through-wall leakage defect. Other effects of such a rough morphology would be the higher levels of porosity resulting from the ease of precipitation of hydrogen, added to the air, as gas porosity. The presence of air as a contributor to the total gas porosity in Al alloys has been shown to be likely from other recent work.²⁹

Another use of the sandwich technique, employing its unique ability to provide thin sections of solidified material, is the possibility of studying the nucleation sites and the phases that occur during freezing of the matrix alloy. The whole sandwich including its encapsulated metal is nearly transparent in the SEM. One can speculate that it would be an interesting sample for study in the transmission electron microscope (TEM), although, once again, this was outside the scope of the present investigation. The detail morphology of phases in 3D form can be seen. Figure 8*a* indicates that dendrites appear to have started to grow from a nucleus in the centre of the image. One might speculate that studies to size nuclei, and check the distribution and effectiveness of different nuclei may be possible.



(a)



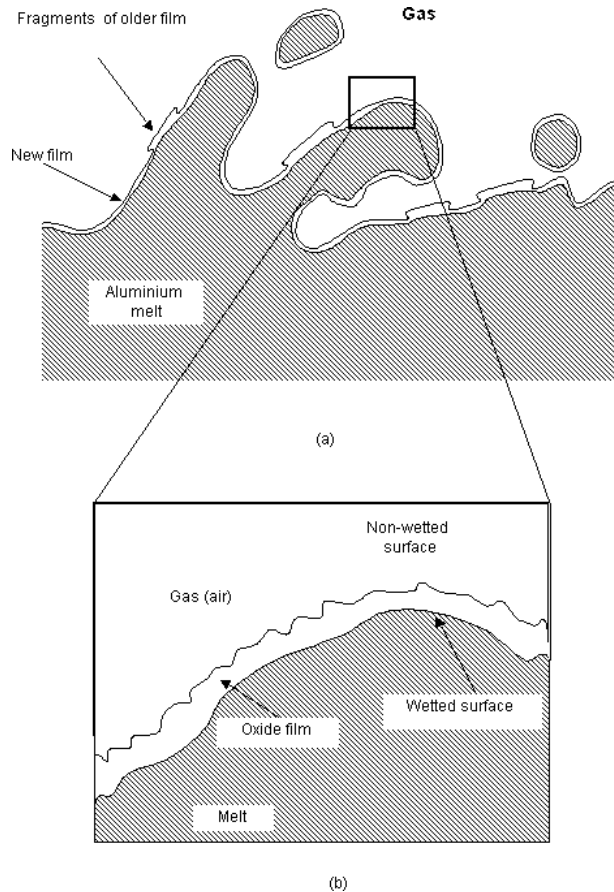
(b)

9 *a* oxide-metal sandwich viewed from its edge; thickness of specimen is seen to be 10–20 μm ; *b* double oxide film which, from cracks present, seems to be brittle; folds in film have thickness of the order of micrometres

Allowing a modest further speculation, the technique used in the present study is expected to be useful for other gas/metal systems. For instance, the entrained surface of the liquid alloy in vacuum-casting of nickel-based superalloys is expected to consist of oxide, and/or possibly nitride, films. This is because the vacuum contains sufficient air and water vapour to react with the major alloying element (that happens to be aluminium) in these alloys; the aluminium effectively 'getters' any available oxygen (and nitrogen at these high temperatures) present in the vacuum. The defects entrained turbulently in this way would be expected to control the reliability and life of turbine blades. In cast irons, mould gases that are rich in hydrocarbons decompose on the surface of the melt, depositing films of carbon as graphite or diamond.¹ It is hoped to investigate and report on these systems in due course.

Conclusion

From the present study of surface films in molten aluminium alloys, the following conclusions can be made:



10 a proposed schematic view of oxide film on surface of liquid metal that may be more realistic for Al–Mg alloys; b speculative detailed morphology of surface film

1. The contacting interface between impinged bubbles represents an elegant and powerful means for studying surface films on liquid metals.

2. This technique could be used to make comparisons between the thickness and morphologies of the films in different film-forming alloys like aluminium alloys, magnesium alloys, ductile iron and super-alloys.

3. The morphology of oxide films could be indicative of the amount of air that could be retained by the film, entrained in the roughness of its surface at the time of pouring.

4. The volume of this entrapped air might be a criterion for the seriousness of folded oxide film defects to act as cracks and provide the free space for better initiation of gas porosity.

5. In the case of Al–Mg alloys that are sensitive to critical gate velocity, it seems that there would be a relation between the morphology and thickness of oxide films and the casting defects as a result of turbulence in the casting process.

6. The method seems to be an easy and effective method for measuring the thickness of oxide films especially in a non-stagnant situation common in manufacturing, especially where production conditions

are less than ideal. The common technique for estimating the thickness of films assuming the films to be half the thickness of folds is found to overestimate the film thickness.

7. In general, the technique used in this study may be valuable for studying nucleation sites and growth morphologies of metals and alloys. The oxide films act like a transparent medium in the metal–oxide sandwich obtained in this work.

References

1. J. CAMPBELL: 'Casting'; 2003, Oxford, Butterworth-Heinemann.
2. M. DIVANDARI and J. CAMPBELL: *AFS Trans.*, 2001, **109**, 201–212.
3. C. NYAHUMWA, N. R. GREEN and J. CAMPBELL: *AFS Trans.*, 1998, **58**, 215–223.
4. N. R. GREEN and J. CAMPBELL: *AFS TRANS.*, 1994, **102**, 341–347.
5. C. NYAHUMWA: 'Influence of oxide film filling defects on fatigue properties of cast Al–7Si–Mg alloy', PhD thesis, University of Birmingham, Birmingham, 1997.
6. J. CAMPBELL: 'Casting practice'; 2004, Oxford, Butterworth-Heinemann.
7. W. THIELE: *Aluminium*, 1962, **38**, 707–715.(translation
8. M. DROUZY and C. MASCRE: *Metall. Rev.*, 1969, **14**, 25–46.
9. C. N. COCHRAN, D. L. BELITSKUS and D. L. KINOSZ: *Metall. Trans. B*, 1977, **8B**, 323–332.
10. S. IMPEY, D. J. STEPHENSON and J. R. NICHOLLS: *J. Mater. Sci. Technol.*, 1988, **4**, 1126–1132.
11. S. IMPEY, D. J. STEPHENSON and J. R. NICHOLLS: Proc. 1st Int. Conf., University of Cambridge, March 1991, Institute of Metals.
12. W. KAHL and E. FROMM: *Metall. Trans. B*, 1985, **16B**, 47–51.
13. L. RAULT, M. ALLIBERT and A. DUBUS: *Mater. Sci. Forum*, 1996, **2**, 165–170.
14. L. RAULT, M. ALLIBERT and A. DUBUS: *Light Metals*, 1996, **2**, 345–355.
15. D. W. AYLMOORE, S. J. GREGG and W. B. JEPSON: *J. Inst. Metals*, 1960, **88**, 205–208.
16. K. S. AGEMA and D. J. FRAY: 'Preliminary investigations on the deformation behaviour of an oxide scale on molten aluminium'; 1989, Department of Material Science and Metallurgy, University of Cambridge.
17. M. R. BARKHUDAROV and C. W. HIRT: Proc. Materials Solutions Conf. on 'Aluminium casting technology', October 1998, IL, USA.
18. J. RUNYORO, S. M. BOUTORABI and J. CAMPBELL: *AFS Trans.*, 1992, **100**, 225–234.
19. J. L. ROBERGE and M. RICHARD: *Mater. Sci. Forum*, 1996, **3**, 135–140.
20. M. SUZUKI and T. KANEKO: Proc. of 59th Annual Meeting of IMA, May 2002, Montreal, Canada, 84–90.
21. S. P. CASHION, N. J. RICKETTS and P. C. HAYES: *J. Light Metals*, 2002, **2**, 43–47.
22. K. SHIMIZU, A. GOTOH, K. KOBAYASHI, G. E. THOMPSON and G. C. WOOD: Int. Conf. on 'Microscopy of oxidation', University of Cambridge, March 1990, Institute of Metals, 1991.
23. M. DIVANDARI and J. CAMPBELL: 1st Int. Conf. on 'Gating, filling and feeding of aluminum casting', AFS, Nashville, TN, USA, 1999, 49–63.
24. M. DIVANDARI and J. CAMPBELL: *Aluminium Trans.*, 2000, **2**, 233–238.
25. M. DIVANDARI and J. CAMPBELL: *Int. J. Cast Met. Res.*, 2004, **17**, 1–6.
26. D. L. LAVELLE: *AFS Trans.*, 1962, **70**, 642–647.
27. W. BONSACK: *AFS Trans.*, 1962, **70**, 374–382.
28. A. FAKHARI, M. KHOSTAVAN and M. DIVANDARI: 16th Annual Conf. of Iranian Foundrymen's Society, May 2004 (in Persian).
29. D. DISPINSAR and J. CAMPBELL: *submitted to Int. J. Cast Met. Res.*, 2004