Oxide film characteristics of Al–7Si–Mg alloy in dynamic conditions in casting

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'New' oxide film which forms in a very short time in the casting process was studied. Samples for the study were prepared based on a technique in which an oxide–metal 'sandwich' could be made. Alloy A356 (Al–7Si–0·4Mg) was selected for the study. Features such as thickness of the oxide film, its morphology, rigidity and presence of eutectic phase have been examined and shown by SEM study. Possible consequences of the morphology of the oxide film are discussed. IJCMR/513

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1 **Keywords**:

Introduction

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 that is being rapidly created. The entrainment of the newly created oxide into the bulk of the molten aluminium necessarily occurs in a dry surface to dry surface mode (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 folded film represent an unbonded interface in the liquid and therefore effectively constitute a crack.[1] Turbulent transfers of molten aluminium are common in casting operations, thus, if care is not taken, aluminium castings can be filled with cracks. Figure 2 shows such a case.[3]

In addition to constituting crack like 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 other films are known to have a wide range of sizes and shapes, cracks in the liquid can clearly be extremely serious, often constituting by far the most frequent defects in the casting. They can easily be envisaged as reaching from wall to wall of a casting, causing a leakage defect in a casting required to be leak-tight, or causing a major structural weakness in a casting requiring strength or fatigue resistance.[1,6]

Although the presence of oxide films has been known and studied for decades,[7–16] the relation between oxide films and casting defects does not seem to have been appreciated. The all-important link between oxide films and the quality of cast materials has only been made in recent years.[1]

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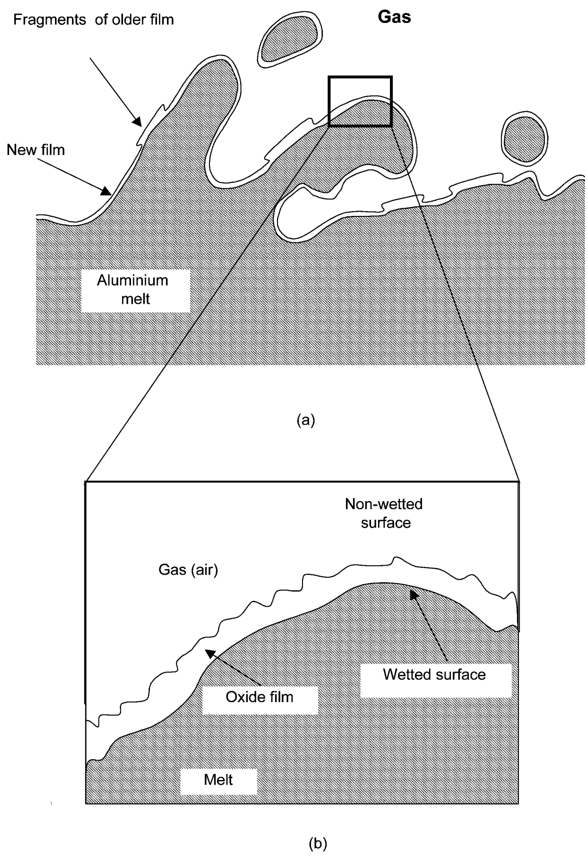
It seems that a general acceptance among researchers[17–20] is gradually growing that oxide films and inclusions play a major part in reducing the quality and reliability of aluminium casting alloys. It has even been suggested that entrainment defects could account for as much as 80% of the total effective problems in castings.[1,17] There is therefore a considerable interest in characterising the surface films of various casting alloys.[21,22]

Oxidation of 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.[7,23] After a further



1 *a* Schematic view of oxide film on surface of aluminium alloy. Note possible tearing (and immediate re-growth) in film as a result of stress. *b* Detailed view of surface oxide film contrasting interface with melt with that of air or other gas

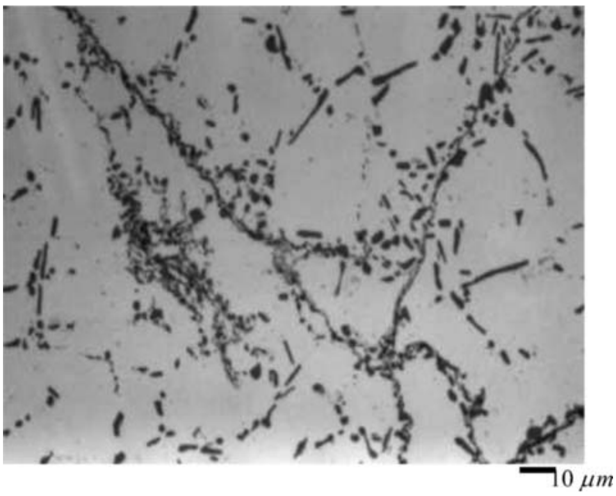
incubation period, the oxide structure converts to α-alumina, accompanied by a decrease in the volume of the oxide. Cracks can then form in the oxide layer, and combined with a higher mobility of aluminium ions in the α-alumina, lead to a faster rate of oxidation.[13]

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 effects 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, magnesia aluminate spinel ($MgO.Al_2O_3$) forms, probably via the metastable prespinel $MgAl_2O_4$.[10,11]

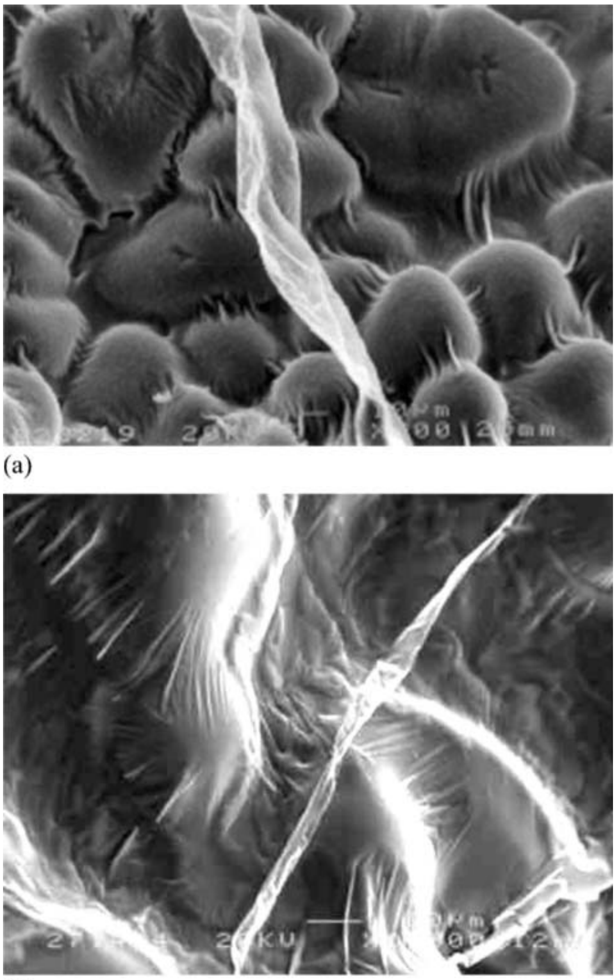
Most of the research on the oxidation of liquid aluminium has been carried out on stagnant melts.[7–16] However, in the aluminium casting processes, the molten metal is in motion, travelling at local velocities often measured in metres per second. Thus, the oxide film layer is continuously subjected 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]

Preliminary work

A series of experiments was carried out to study the effect of passage of air bubbles in solidifying aluminium castings to determine the consequential damage to the cast structure.[2] On the inner surface of an air bubble which has been trapped in a cast aluminium alloy sample, the oxide films were clearly visible draped over the dendrite tips. Figure 3*a* and *b* shows this case in Al–5Mg and Al–7Si–Mg alloy, respectively. The morphology and the scale of wrinkles in the oxide films are quite different in different alloys.[24]



2 Optical image showing tangled oxide film in A356 alloy[5]



(a)

(b)

3 SEM micrograph taken from inside trapped bubble in *a* Al–5Mg and *b* A356 alloy revealing oxide films draped and folded over surface of dendrites. Note differences in morphology and thickness of films

Experimental procedure

Samples studied in this work were taken from A356 alloy (Al–7Si–0·4Mg). Details of the experimental technique are explained elsewhere.[24] In brief, bubbles are artificially introduced via a silica tube into the base of a casting, and observed by video X-radiography. Bubbles are formed and grow as they rise over about 0·2 s. If a bubble is seen to collide with another bubble, 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 trapped in between. The authors call it an 'oxide–metal sandwich'. The sample studied in this work is shown in Fig. 4.

Results

Figure 5*a* and *b* shows the SEM images taken from the contact area between the bubbles (the oxide–metal sandwich region). The dark areas are the dendrites of solidified aluminium alloy trapped between the two layers of oxide film (the light areas).

From the observed cracks in the films, the oxide appears to be brittle (Figs. 5 and 7).

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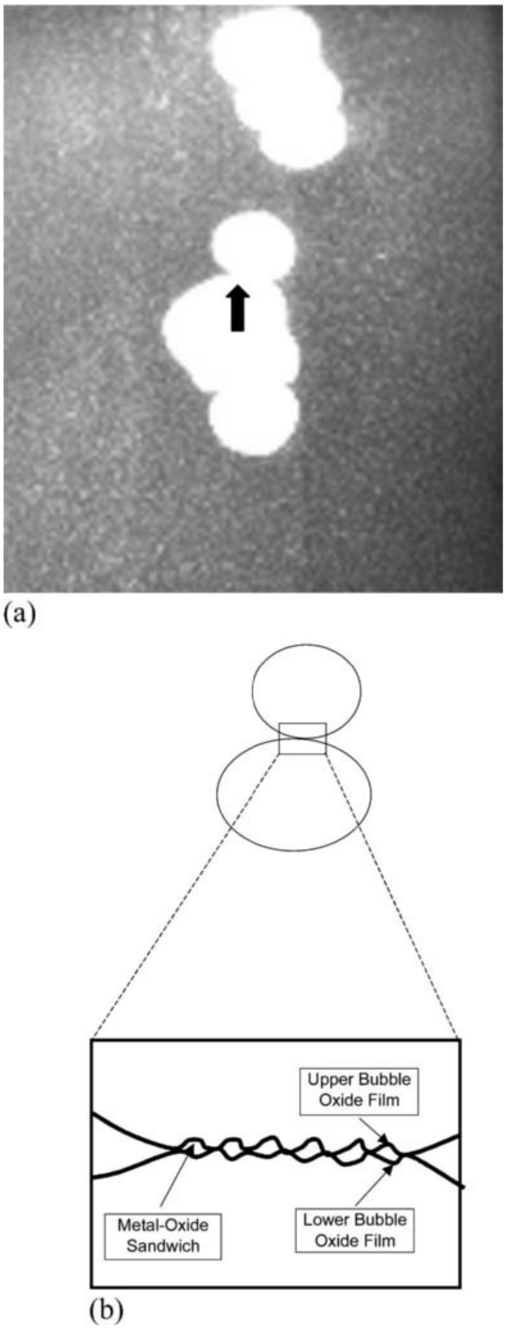
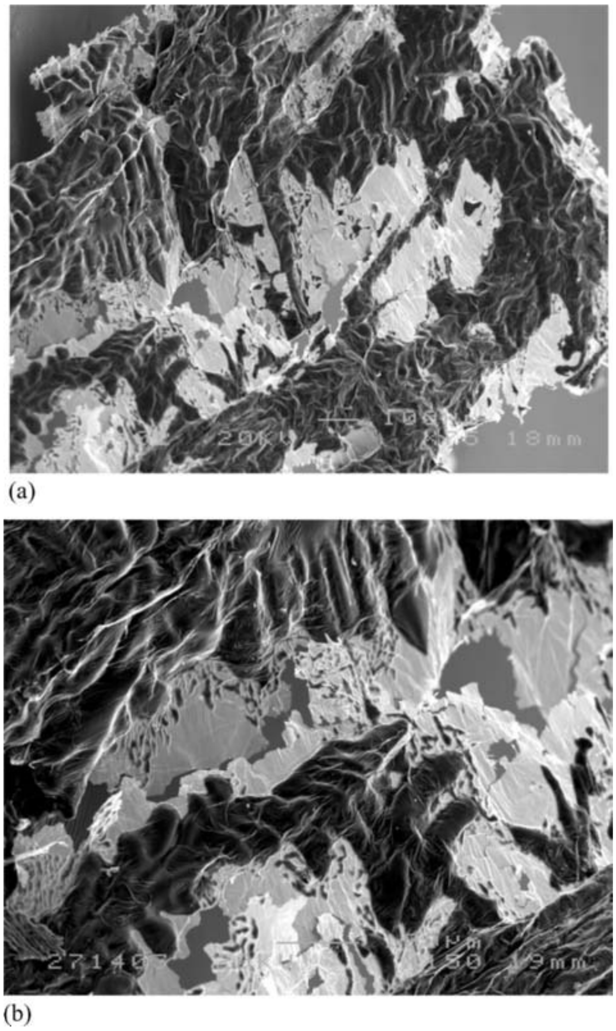


4 ***a*** **Radiograph taken from casting showing entrapped bubbles.** ***b*** **Schematic view of sandwich taken for study**

Figure 6*a* and *b* shows a closer view of the sandwich in which the folded oxide film on the surface of dendrite is visible. The films are sufficiently thin that the dendrite structure can be clearly seen through the upper film. In Fig. 6*b*, the thickness of the wrinkles in the Al–7Si–Mg alloy can be observed to be rather less than 1 μm indicating the individual films to be less than 0·5 μm thick. In fact, if the specimen is rotated to view the sandwich on its edge (Fig. 8), the thickness of the oxide film can be measured directly. In places where the metal has been excluded, the remaining double oxide layer can be clearly seen. The thickness of the individual oxide films appears to be approximately 50 nm. Thus the method of estimating film thickness by halving the measured thickness of folds is seen to give estimates too large by an order of magnitude in this case. The reason is partly the additional material trapped inside the folds, such as metal, and partly the residual rigidity of the film that helps it resist its conformance to a sharp bend.



5 ***a*** **Oxide–metal sandwich of Al–7Si–Mg alloy. White areas are double layer of oxide film. Dark areas are dendrites covered with oxide films from two sides, front and back.** ***b*** **Shows same area at higher magnification. Films are stretched over light areas resulting in fewer folds. Note patches of eutectic phase in light areas, possibly the result of being squeezed out from between solidifying dendrites but remaining captured between double layer of films**

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, one can see, in the sandwich, the different phases formed during the solidification of the alloy. For instance, the Al–Si eutectic that forms in Al–7Si–Mg alloys is visible in Fig. 7.

Discussion

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

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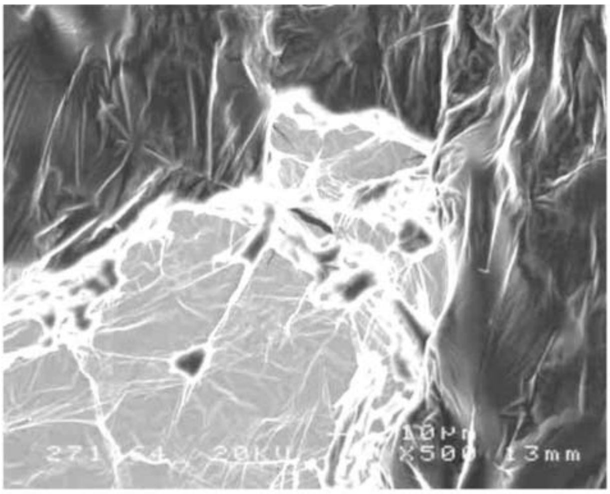
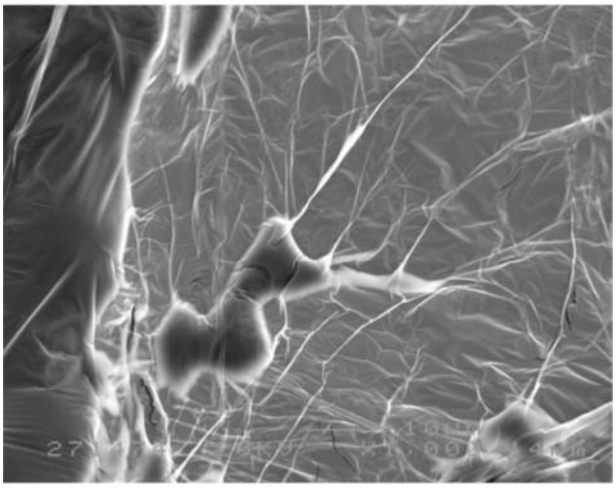
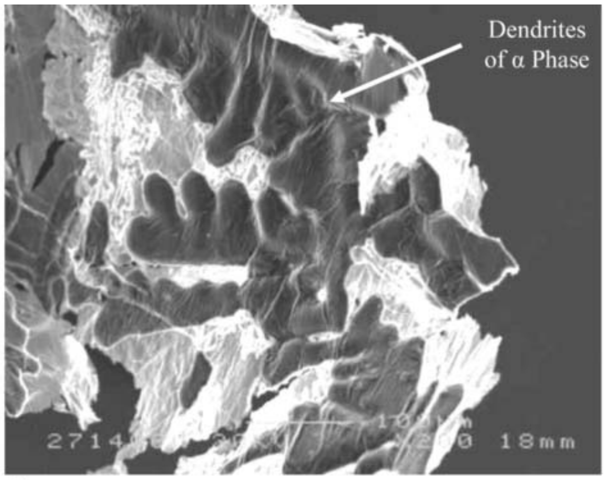


(a)

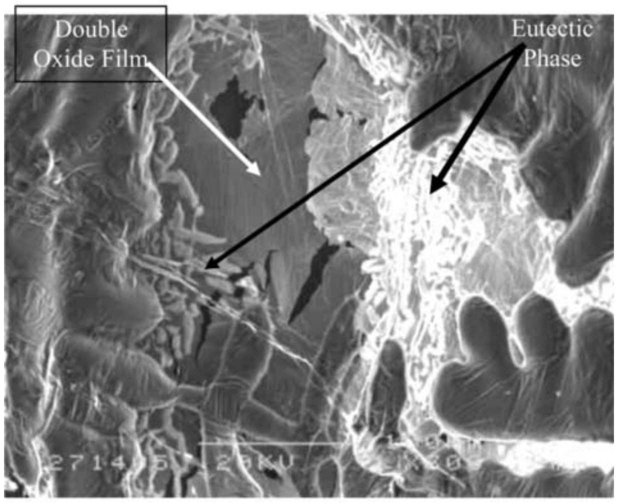


(b)

6 *a* and *b* Closer views of other areas on previous sample seen in Fig. 5. Average thickness of films can be estimated assuming they are approximately half the thickness of observed folds



(a)



(b)

7 *a* Further views of oxide–metal sandwich clearly showing dendrites covered with thin and folded film. *b* Precipitation of eutectic phases in double oxide sandwich. Double films are seen to be torn in places. It is not certain whether this is as a result of solidification contraction or mechanical handling damage

for information on the 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. The present study attempts to capture films for study that are typical of these short times.

The study of aluminium oxide films between impinged bubbles has shown that the nature of the oxide films is quite different in different aluminium alloys,[24] as for instance is illustrated in Fig. 3. The weakness of the film in tension may lead to its easy shredding into smaller fragments, which would be less harmful. In addition, the thinness of oxide film would be expected to confer little rigidity, allowing it to fold and tangle into relatively compact, harmless inclusions. Such tangled films are widely observed in cast Al alloys.[3,4]

The oxide layers can be seen to be capable of retaining air both in the microscopic roughness of the oxide, and in the mesoscale folds and rucks of the film. Such reservoirs of air in the alloy are expected to form excellent initiation sites for the precipitation of hydrogen and, therefore, the growth of micro- and macro-porosity.

Another aspect of the technique is the possibility of studying phases that form during the solidification of the alloy. Nearly all images taken from the sandwich show the Al–Si eutectic phase in the Al–7Si–Mg 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 by transmission electron microscopy (TEM). The detail of characteristic of phases in 3D form can be seen. Furthermore, nucleation sites for the formation of new phases might be studied.

The thickness of the oxide film seems to be an important factor in the formation of many defects. It has been shown that some alloys such as Al–5Mg are very difficult to cast without defects.[25,26] It seems that this alloy has an oxide film that is expected to be between 5 and 10 times the thickness observed in Al–7Si–0·4Mg alloy.[24,25] Thus its additional rigidity

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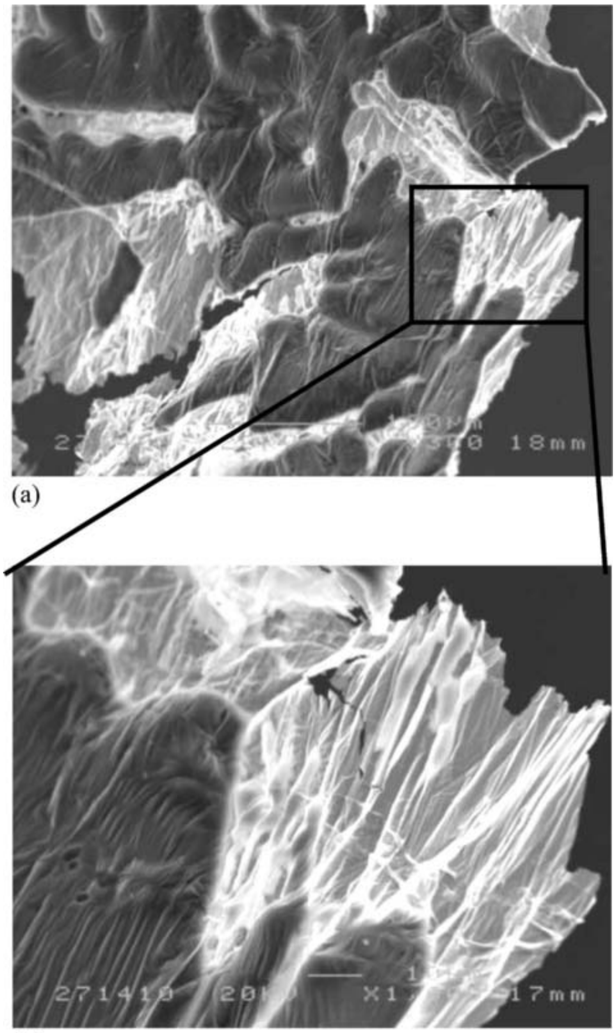

(a)

(b)

8 ***a*** **Oxide–metal sandwich viewed nearly on edge. Total thickness of specimen is approximately 10 μm.** ***b*** **Folds in film have thickness significantly less than 1 μm indicating that thickness of single films is less than 0·5 μm, but direct observation indicates 0·05 μm**

would prevent it crumpling into such insignificant compacted tangles. In addition, the concertina like surface microstructure of this oxide (Fig. 3) will be expected to hold additional quantities of entrained air.

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 the vacuum casting of nickel-based superalloys is expected to consist of oxide films. This is because the vacuum contains sufficient oxygen and water vapour to oxidise the major alloying element that happens to be aluminium in these alloys; the aluminium effectively 'getters' any available oxygen 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.

Conclusions

1. The contacting interface between impinged bubbles represents an elegant and powerful means for studying surface films on liquid metals. The method is relatively easy and effective for measuring the thickness of the surface film especially in dynamic situations. Thus the technique is especially appropriate for the casting industry, but is envisaged to have potential in material science in general.

2. The technique can be used to make comparisons between the thickness and morphologies of the films in different film forming alloys like aluminium alloys. The study of magnesium alloys and superalloys is expected to be similarly possible in principle.

3. The morphology of the surface film gives an indication of the quantity of air that a film can retain in its surface and in its folds. The quantity of entrained air might be a criterion for the significance of folded films acting as cracks. It also provides an unbonded gaseous interface for the initiation of porosity grown by gas or shrinkage.

4. Such study may give a qualitative indication of the tear resistance of the film. A low resistance would be expected, for instance, to be associated with a greater population of smaller entrained fragments.

5. The technique can be used for studying the phases that form during the solidification of an alloy.

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