Investigation on thickness of short time oxide films in Al–1Mg and Al–2Mg alloys

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The melts of aluminium alloys are very sensitive to oxidation during casting, and the surface oxide film formed during casting can be folded and entrained into the melt due to melt surface turbulence. In this research, sandwiches of oxide–metal–oxide (OMO) formed in a very short time within the cast during solidification were investigated in order to see the effect of magnesium content (i.e. 1 and 2 wt-%) on the oxide film thickness. To form OMO sandwiches within the cast, a certain amount of air was blown into the melt every 0·5 s during casting time by means of a compressor at 0·5 atm pressure. Where bubbles of air collided, they formed a sandwich which later was used for investigating purpose. Both the thickness and the surface of oxide films were studied via SEM. The results showed that the thickness of the short time oxide film varies in the range of 150–250 and 200–300 nm for Al–1Mg and Al–2Mg alloys respectively.

Keywords: Surface oxide films, Al–Mg alloys, Short time oxidation, Oxide–metal–oxide sandwich

Introduction

The safe use of aluminium alloy castings, especially Al–Mg alloys, in automotive and aerospace industries is a critical issue and must be dealt with care. It is necessary to produce safe and reliable casting and to to understand the possible casting defects which might affect the mechanical properties of these alloys severely. The sensitivity of Al–Mg alloys to oxidation is known as one of the main source of casting problems.

Although the long time oxidation of aluminium alloys has been investigated by a number of researchers,[1–5] there is only a little data available about short time oxidation of these alloys during casting.[6–9] Therefore, it seems that more investigations in this issue can be very useful.

According to the reports[1–5] published about the long time oxidation of aluminium alloys, the fresh surface of melt oxidises rapidly and a thin oxide layer forms on it. At the beginning of solidification, the surface oxide film is amorphous; but later it transforms to crystalline oxide film.

Alloying elements in the melt can influence the rate of oxidation. Silicon, copper, zinc and iron have minimal effect on the oxidation behaviour of molten aluminium, whereas magnesium, sodium, selenium and calcium increase its rate of oxidation (Fig. 1).[4] Freti *et al.*[5] reported that adding 3 wt-% of magnesium to aluminium melt can increase its oxidation rate by 30 times at 700°C before breakdown oxidation. They also claimed that the oxidation rate of some aluminium alloys can be increased by 2–3 times when they are exposed to temperature range 700–800°C.

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Al liquid metal oxidises in a very short time, i.e. 0·1 s when bubble trails are generated and even at much shorter time of 0·01 s for severe surface turbulence condition in die cast process.[10] In this situation the surface oxide film, which is strongly bonded to the melt, folds upon itself due to surface turbulence of melt; hence a double oxide film can be created in the melt.[7–9,11,12]

The oxide–metal–oxide (OMO) sandwich technique has a great potential in investigation of surface morphology of oxide film and measuring the double oxide film thickness (Fig. 2).[7–9,13] Therefore, in this research, the OMO sandwiches formed via air bubble blowing were used to measure the thicknesses of both folded oxide films and the double oxide films.

Experimental

Commercially pure aluminium and magnesium bars were used for producing the cast alloys in this research. Melting was performed in an induction furnace at 800°C. Sodium silicate binder cured with carbon dioxide was used as the moulding material. Air bubbles were blown into the melt via a silica tube having a bore of 1 mm. Air bubbles blown into the mould cavity every 0·5 s during casting time by means of a compressor having a pressure of 0·5 atm. Using this technique caused some air bubbles to move upward in a row, when the first bubble stopped on colliding with the partially solidified melt, other bubbles in the row collided with one another and made at least one OMO sandwich (Fig. 3). After cutting the casting and finding a suitable OMO sandwich sample, the thickness of oxide films within the sample were measured using scanning electron microscopy (SEM).

Results and discussion

A typical section of an OMO sandwich in Al–1Mg alloy is shown in Fig. 4. The dark area in Fig. 4*a* shows a

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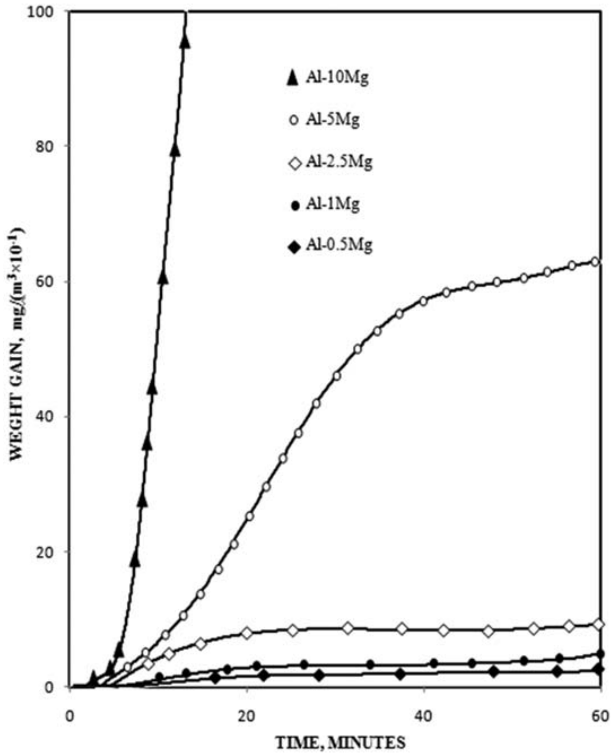


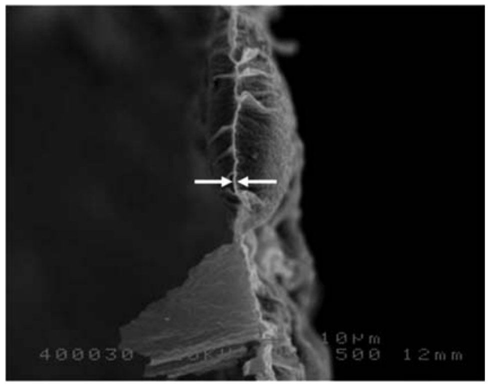
1 Effect of Mg on oxidation of Al–Mg alloys[8]

metal layer with a thickness in the range of 10–15 μm entrapped between two transparent oxide layers. The bright area seen in this figure shows the parts of sandwich with less and/or without any entrapped metal. In other words, the bright colour of these areas is caused by the oxide film.

The schematic presented in Fig. 5 demonstrates how the dark and bright areas were formed in OMO sandwich samples during solidification process. When a nucleus forms in the entrapped melt in between the oxide layers of an OMO sandwich (region A in Fig. 5*c*), the extent of its growth is dependent on the amount of the melt available there. Moving the surrounded melt toward the nuclei causes melt depletion in some regions located between two adjacent growing nuclei, so that oxide layers can move closer together in those regions and form a double oxide layer (regions B and C in Fig. 5*d*).

Returning now to Fig. 4, folds observed in the right hand side of Fig. 4*a* and *b* are formed possibly perpendicular to the direction of the upward flow of bubble. These folds seem to have some flexibility at the initial stage of their formation on the melt. In other words, oxide films have lower resistance to deformation at primary stage of its formation, relative to their final form.[14] Therefore, when the melt beneath the oxide film experiences some sort of stresses, this situation can end up to either of the following: oxide film may become separated from the melt, or surface oxide films can remain cohesive to the melt. What has been commonly seen is that an oxide film usually folds over and over under the stress without losing its cohesiveness to the underneath melt.

It has been reported[15] that the surface energy for the wetting of alumina and aluminium is 0·64 N m^{-1} at 750°C, while the surface tension of non-oxidised aluminium melt at 700°C is ~1·13 N m^{-1}.[16] Therefore, it



2 Potential of OMO sandwich for investigating short time oxide film thickness[8]

seems separation of the surface oxide film from the melt is very unlikely.

The folding of the oxide film can be explained by the contraction in size of the bubble. Contraction will occur for various reasons:

(i) the bubble will slightly change its shape during its flotation stage, so that contractions in its area will necessarily occur during any wobbly perturbations to its (smooth) shape
(ii) there may be some slight cooling of the entrapped air in the bubble during freezing; this could result in a reduction in volume by several per cents, and thus a corresponding reduction in area of the bubble
(iii) there will be loss of oxygen from the bubble by oxidation of the melt, the growth of the oxide skin of the bubble.

All of these reductions in volume will lead to a reduction of the area of the bubble; however, of course, no reduction in the area of the oxide skin, which will therefore necessarily crumple and fold.

The folds observed in the left hand side of Fig. 4*b* occurred in a radial form around a nucleus. In this case, stresses generated due to different contraction behaviour of the surface oxide films and the melt during solidification tend to fold the surface oxide films over and over again.

Folds could also be seen with less clarity in bright areas of OMO sandwich images. By focusing on Fig. 4*a* it is obvious that at least one of the edge sides of the most folded films in bright areas ends up to high stress regions of dark areas. This is an indication of mechanical stresses existed in dark areas where nucleation has started and caused contraction around the nucleation site.

Figure 6 shows a part of OMO sandwich in Al–2Mg alloy. The extension of the entrapped metal in this part of OMO sandwich can be understood by considering dark in the SEM image.

In previous studies,[7–9,13] the thickness of double oxide film has been estimated on the base of measurement made from the single folded oxide film thickness. However, various folds thicknesses can be affected by the type of materials trapped inside the folds, local stress severity in each folds, strength and flexibility of oxide film, sensitivity of the alloy to oxidation and the amount of available oxygen in any particular region of the melt. Some researchers[7–9,13] tried to measure the thickness of oxide films in the thinner sections of the folds which

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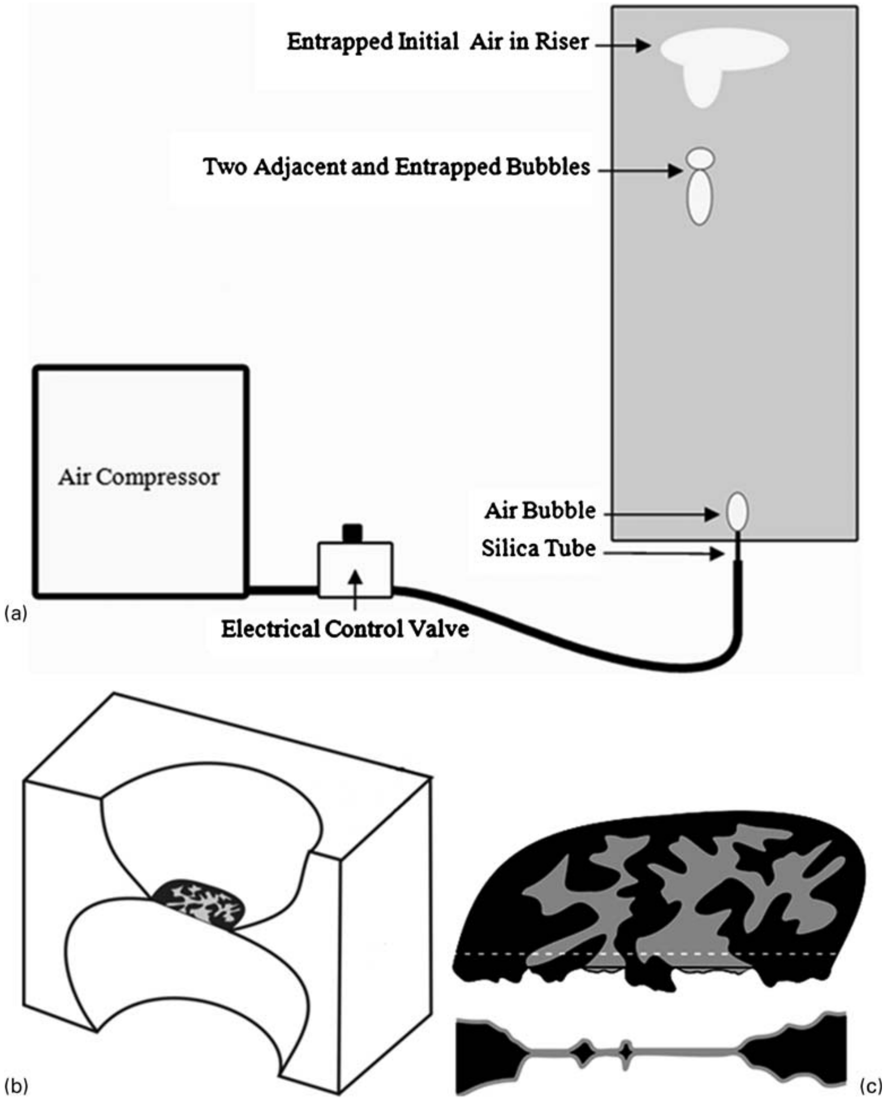
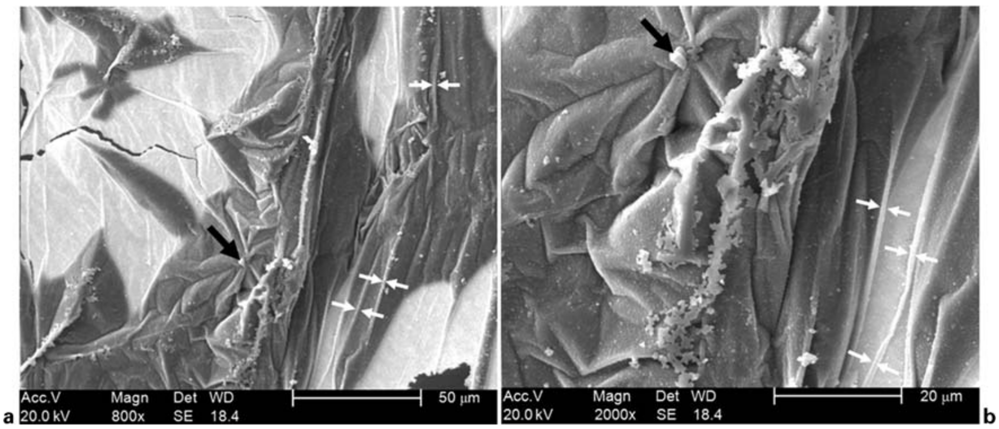


3 Schematic of *a* air blowing system and bubbles colliding, *b* prepared sample and *c* top view of OMO sandwich with cross view of section

were perpendicular to the SEM image in order to reduce the dependences of fold thickness to the above mentioned factors. In this way, the minimum value of folds thickness in each alloy can be a good criterion for the level of its sensitivity to oxidation phenomenon. The more sensitivity of the alloy to oxidation, the thicker will be the oxide film created.

Strength of an oxide film has a direct relation with its thickness.[14] The higher the film strength, the more difficult will be its folding. This causes the amount of



4 *a* part of OMO sandwich in Al–1Mg, *b* same image at higher magnification that shows folded surface of short time oxide film and suitable folds for thickness measurements

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