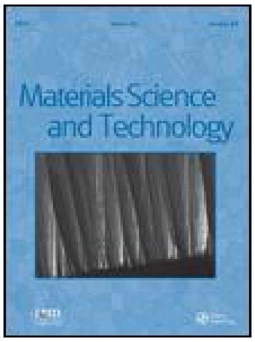

Materials Science and Technology

ISSN: 0267-0836 (Print) 1743-2847 (Online) Journal homepage: https://www.tandfonline.com/loi/ymst20

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To cite this article: R Gopalan & Narayan K Prabhu (2011) Oxide bifilms in aluminium alloy castings – a review, Materials Science and Technology, 27:12, 1757-1769, DOI: 10.1179/1743284711Y.0000000033

To link to this article: https://doi.org/10.1179/1743284711Y.0000000033

REVIEW

Oxide bifilms in aluminium alloy castings – a review

R. Gopalan and Narayan K. Prabhu*

Aluminium alloy castings are most widely used in automobile industry because of their light weight, better castability and improved properties. The liquid aluminium surface easily oxidises during melting, transferring and pouring operation which may entrain oxide films into the casting. Research work has shown that the entrainment of this surface film and formation of bifilms in castings appear to be the source of most of the casting defects leading to a significant reduction in the mechanical properties of aluminium alloy castings. In this paper, the phenomenon of formation of oxide bifilms in aluminium alloy castings, effect of these bifilms on casting properties and their assessment techniques are discussed. For enhancing the quality of casting, research should focus towards development of process techniques for healing of bifilms in liquid metal during solidification.

Keywords: Oxide bifilms, Aluminium alloys, Castings, Casting reliability, Review

Introduction

Casting process is the most common route for the production of components in manufacturing industry because of its near net shape capability and versatility. Foundry engineers aim and strive for the production of zero-defect castings. Numerous techniques have been developed over the years to optimise casting parameters in order to produce defect free castings. Even with the present knowledge of science and engineering of metal casting processes, casting defects are observed and pose significant challenge to the metal casting industry. An understanding of the evolution of various casting defects, causes and effects of these defects on performance of components are very much necessary for developing prevention techniques to minimise the occurrence of defects and achieve production of quality castings.

The various defects generally observed in castings are inclusions, hot tears, blow holes and pin holes, shrinkage, misrun, cold shut and rat tail, etc. Defects in castings impair the properties of components and it is very difficult to eliminate them by post-treatments, resulting in rejection of the component, loss of production and increase in operational cost. Aluminium alloys are characterised by high specific strength, excellent corrosion resistance, good castability and better thermal and electrical conductivity. They replace the traditional materials in the area of transportation, packaging, construction, electrical conductors and machinery to achieve greater weight reduction.[1] When aluminium alloys are cast, there are many potential sources of defects which can harm the quality of the cast part. All aluminium alloys are subject to[2]

(i) shrinkage defects: Al alloys shrink by 3·5–6·0% during solidification (depending on the alloy type)
(ii) gas porosity: molten aluminium readily picks up hydrogen which is expelled during solidification giving rise to porosity
(iii) oxide inclusions: molten Al exposed to air immediately oxidises forming a skin of oxide which may be entrained into the casting.

The pioneering work by John Campbell on the entrainment of surface film in the casting has shown that most of the casting alloys, especially aluminium and its alloys appear to be the suspension of bifilms. During the casting process, the hot liquid metal reacts with its environment/surroundings and forms surface film which can fold over itself and become entrained into the bulk melt, forming doubled over film defect, hence called bifilm whose internal surfaces are not bonded and have a layer of trapped gas.[3,4] Bifilms in the aluminium alloy can exert major control on the cast microstructure, including grain size, dendrite arm spacing (DAS) and morphology of eutectic silicon, serve as a nucleation site for gas and shrinkage porosity, act as cracks to initiate failures resulting in significant impairment of the tensile strength and fatigue life of the aluminium alloy cast component. None of the familiar casting defects seem to occur without the presence of an initiating bifilm.[3] Therefore it is important to understand the entrainment of bifilms into aluminium alloy castings, its effect on casting properties and control of these defects in order to ensure more efficient use of castings.

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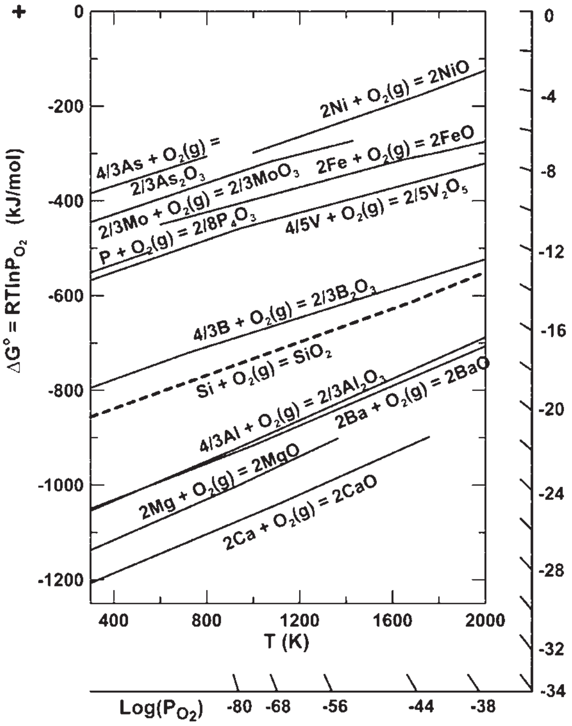
Published by Maney on behalf of the Institute
Received 16 March 2011; accepted 4 April 2011
DOI 10.1179/1743284711Y.0000000033



1 Ellingham diagram illustrating free energy of formation of oxides as a function of temperature[9]

Discussion

Double oxide film/bifilm formation

The formation of bifilms in aluminium and its alloy castings are mainly due to the combination of two actions:

(i) formation of surface oxide films
(ii) folding of these surface oxide films.

Formation of surface oxide films

Casting of aluminium alloy involves melting, pouring and solidification. During pouring of the casting, the liquid aluminium alloy is normally exposed to the atmosphere and moisture on the mould lining which results in the oxidation of liquid melt surface leading to the formation of oxide films. The driving force for these processes is the striving of the melt to come into equilibrium with its surroundings.[5] The Ellingham diagram (free energy versus temperature) can be used to predict the possibility of melt to form oxides with respect to temperature (Fig. 1). The rate of oxidation increases with molten temperature of the casting. The pure liquid aluminium melts at normal casting temperature and forms thin amorphous or crystalline γ-Al_2O_3 or η-Al_2O_3. Further transformation of γ-Al_2O_3 or η-Al_2O_3 to α-Al_2O_3 may occur with time and temperature. The presence of magnesium (approximately above 2%) in the aluminium alloy results in the formation of pure magnesia (MgO) surface film. When the magnesium content of the aluminium alloy is between 0·005 and 2%, it can cause the mixed oxide to form as $MgO.Al_2O_3$ known as spinel.[5,6] Alloying elements such as Cu, Fe, Si, Mn have a minimal effect on the oxidation of molten aluminium, whereas Mg, Na, Se and Ca enhance the rate of oxidation.[7] The protective action of the film may be determined by the ratio of the molecular volume of the oxide to the atomic volume of the metal contained in the compound. If this ratio is greater than unity, a dense continuous film is formed; if this ratio is less than unity, a discontinuous film is formed; that is[8]

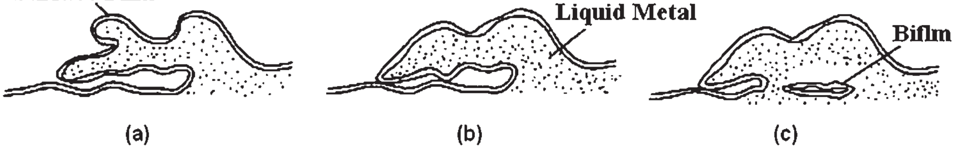
$$\frac{W_O d_M}{W_M d_O} \rangle 1 \rightarrow \text{continuous film} \quad (1)$$

$$\frac{W_O d_M}{W_M d_O} \langle 1 \rightarrow \text{discontinuous film} \quad (2)$$

where $W_{O/M}$ and $d_{O/M}$ are the molecular weight and density of the oxide/metal respectively.

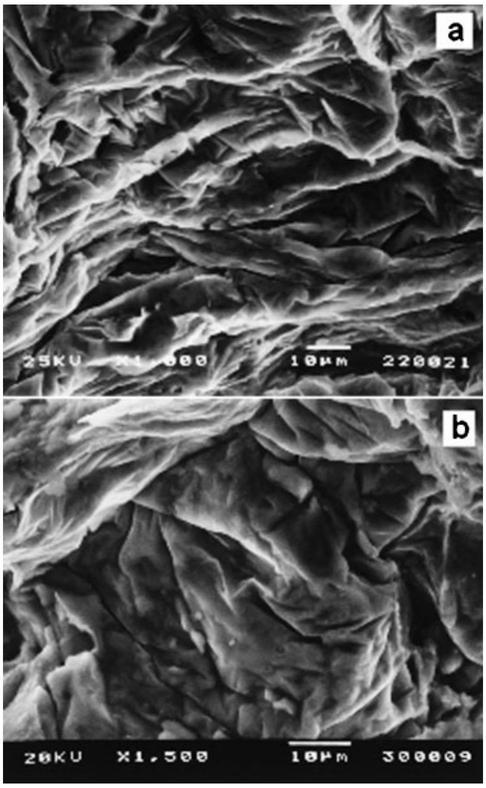
Folding of surface oxide film

Surface oxide film of aluminium melt is not harmful as long as it remains on top of the surface. The problem with an oxide film only occurs when it becomes a submerged film.[1] When the molten aluminium containing the surface oxide film is poured into the mould, the surface oxide film may be folded over or broken by the action of a breaking wave or by droplets forming and falling back into the melt which results in entrainment of the surface film in the bulk liquid. These folded films will trap gas (a mixture of N_2, O_2, Ar, etc.) between the dry interfaces and the outer side and are strongly bonded (surface oxide have grown atom-by-atom from the melt) with the matrix when metals solidify. These folded oxide films in the casting are known as double oxide films or bifilms (Fig. 2). The folding of the surface film also occurs simply by the contraction of a free liquid surface where the area of film itself is not able to contract. Thus the excess area is forced to fold.[5,4,7] Once the bifilm is formed into the casting, the internal atmosphere between the halves of the bifilm is consumed by the gradual continued oxidation and nitridation and thus the normal thickening of the film occurs which is controlled by diffusion of ions through the film. Impey *et al.*[10] has described that thin surface oxide of γ-alumina forms rapidly on melts of commercially pure aluminium at 750°C providing a highly effective barrier confining the molten aluminium. Localised failure of this protective oxide film results in exudations forming on the melt surface, the size and number of which increase with exposure time. Based on this study Raiszadeh and Griffiths[4] suggested a possible process that the original amorphous surface oxide film which is folded as bifilm



a breaking wave is formed by surface turbulence; *b* two unwetted sides of oxide films contact each other; *c* double oxide film is submerged into bulk liquid as crack-like defect[4]

2 Entrainment of double oxide film defect



3 Secondary electron micrograph showing *a* young oxide film and *b* old oxide film in Al–7Si–Mg alloy casting[14]

would transform to crystalline γ-Al_2O_3 and then α-Al_2O_3. This transformation results in a 24% reduction in oxide volume leading to stresses in the film and formation of crack within it. The aluminium melt can then exude through these crack to come into contact with the internal atmosphere where it reacts with oxygen to thicken the existing Al_2O_3 film.[4,11] They also studied the consumption of internal atmosphere of the bifilm in aluminium alloy. They held a known volume of air in the liquid aluminium and found that first oxygen and then nitrogen in an air bubble trapped in a melt was consumed by aluminium to form aluminium oxide and aluminium nitride respectively.[4] Furthermore, a semi-empirical model was proposed by them to estimate the duration of the atmosphere within a bifilm. This model suggested that the oxygen and nitrogen in the atmosphere of a bifilm defect in an aluminium melt may be consumed in less than about 3 min depending on its dimensions specifically volume and surface area.[12]

Young and old oxide film

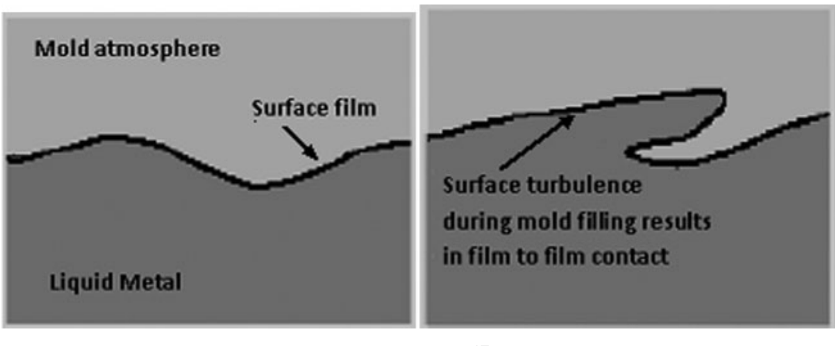
The double oxide film in the casting exhibits different morphologies such as tangled or network, layer oxide or globular oxide and cloud or strip clustering particles.[13] Based on the thickness and time of oxidation, Campbell classified the oxide film into two types namely young oxide film and old oxide film (Fig. 3). Table 1 shows different forms of oxide in liquid aluminium alloys.[1] The oxide films formed in very short oxidation time are known as young oxide films and characterised by very thin thickness some hundreds of nanometres thick. They are formed during pouring and mould filling and appear as fine wrinkles. The oxide films formed during extended time period are known as old oxide films which developed from the thickening of the oxide that originally exists on the surface of ingots during the melting process and also during the transport of the liquid from a furnace to a crucible. They are generally thick oxide films having thickness up to several millimetres and appear as coarse wrinkles.[5,7,15,16]

Entrainment of surface oxide film into casting

The entrainment of surface oxide films into the bulk of the melt and formation of bifilm occurs for a number of reasons. Quality of the melt charge and generation of surface turbulence during the casting process appear to be the most important parameters to submerge the surface oxide film into the melt.

Surface turbulence

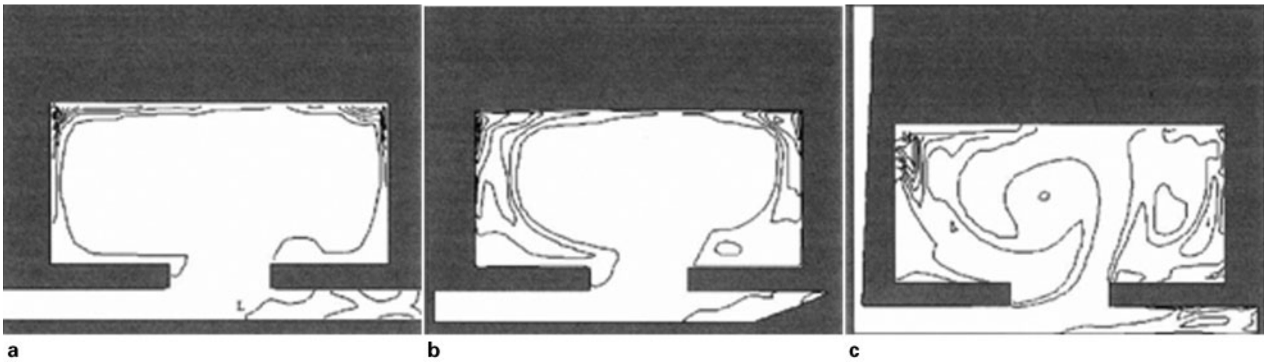
Surface turbulence during the casting increases the potential for the excess area to be entrained into the casting (Fig. 4). Since oxide films have deformability and flexibility, they will be compressed or bent by the surface turbulence.[7] During such actions as pouring,



4 Entrainment of surface film into melt due to surface turbulence[17]

Table 1 Forms of oxide in liquid aluminium alloys[1]

Growth time	Thickness/µm	Type	Description	Possible source
0·01–1 s	1	New	Confetti-like fragments	Pour and mould fill
10 s–1 min	10	Old 1	Flexible, extensive films	Transfer ladles
10 min–1 h	100	Old 2	Thicker films, less flexible	Melting furnace
10 h–10 days	1000	Old 3	Rigid lumps and plates	Holding furnaces

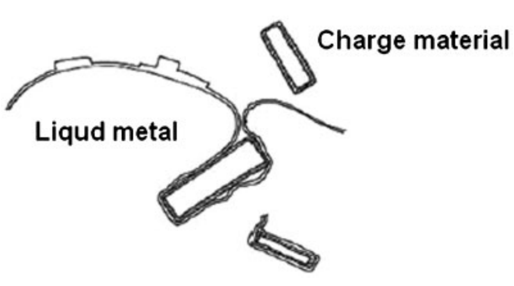


5 **Scalar variable distribution plots of three runner systems for *a* vortex-flow runner (VR) system (t=2·61 s); *b* rectangular runner (RR) system (t=2·58 s); *c* triangular runner (TR) system (t=2·20 s)[13]**

splashing, and stirring, the surface oxide films may also be broken and the new oxide film will form on the freshly exposed surface of the liquid metal. All such actions fold the surface film, over-run it with the liquid metal and submerge it.[5,7] The improper design of the filling system results in an undesired higher metal flow velocity and surface turbulence.[18] According to Campbell if the velocity of flow is sufficiently high at some locality for the melt to rise enough above the general level of the liquid surface to subsequently fall back under gravity then it would entrap a portion of its own surface.[19] The critical velocity for the liquid aluminium and its alloy is found be 0·5 m s^{-1}.[6] Above this critical limit, there will be surface turbulence which may cause the surface to fold over and entrain itself in the bulk of the melt. Studies on different types of runner systems during Al–7Si–Mg castings by Dai *et al.*[13] found that liquid metal flow in rectangular runner and triangular runner in which ingate velocity is well above 0·5 m s^{-1}, exhibits an undesirable behaviour with the possibility of generating surface turbulence whereas liquid metal flow in the vortex-flow runner system was smooth and no splash and folding over of the melt (Fig. 5). Dispinar and Campbell observed the non-quiescent filling conditions (fast and turbulent) of LM 24 resulting in high value of bifilm index (total pore length) which reduce the quality of casting.[20]

Melt preparation

Introduction of defects into aluminium alloy castings begins at the primary alloy production where hydrogen gas and bifilms become incorporated.[21] In the case of aluminium and its alloys, scraps, machining chips and foundry return components are recycled. The stability of the bifilm remains in suspension for a long period because of its nearly neutral buoyancy.[16] Therefore, the recycling of aluminium alloy components which already contain bifilms further increases the population of bifilms in casting. Liu and Samuel[22] observed that the main type of inclusion in the recycled A356·2 alloy was the large number of oxide films. Also, when the solid charge materials were added directly into a melting furnace or into a liquid pool, heavy oxide layer on the charge material becomes necessarily submerged. It is expected that the act of passing through the melt surface to be incorporated in the bulk melt will wrap the thin new film on the liquid surface around the old piece of film as it is submerged resulting in an asymmetrical bifilm consisting of one half of old thick film and one half of new thin film (Fig. 6).[16] Fluxing and degassing were commonly employed in aluminium foundry in order to improve melt cleanness. Fluxing and degassing studies with LM 27 by Dispinar and Campbell observed that introduction of bifilm because of the high gas flowrate creates violent turbulence and inert gas used to carry out the degassing operation can never be truly inert, so that its content of oxygen and water vapour would be expected to further contribute to the generation of oxides.[21] Mechanical stirring and agitation of liquid during melting breaks the surface oxide film and incorporate them into bulk of the melt.[22]



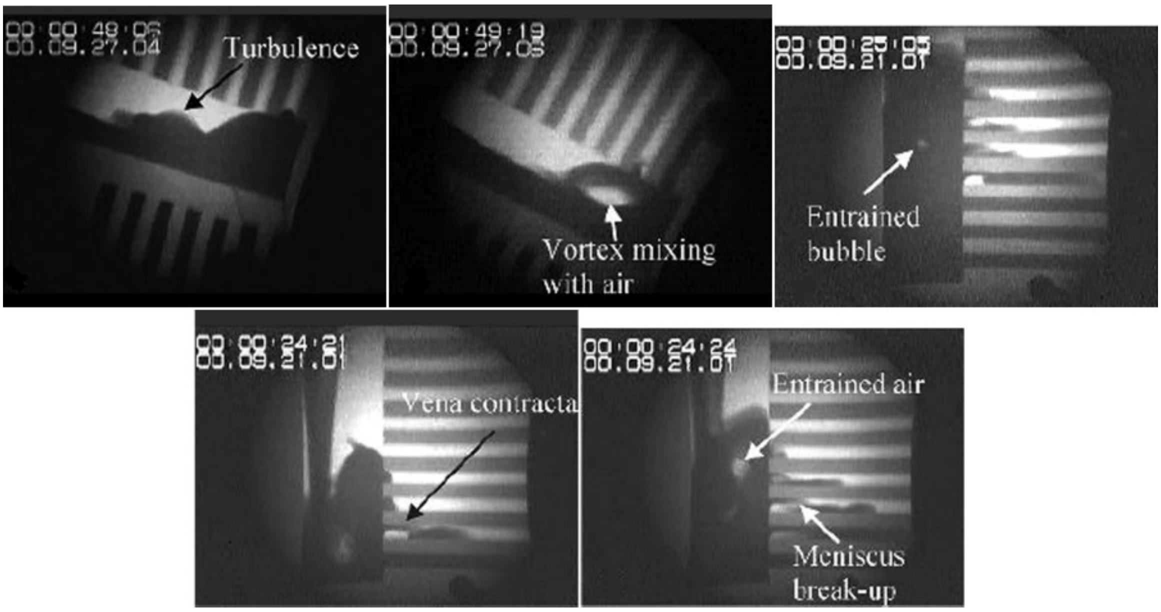
6 **Addition of charge material containing oxide film into melt entraining a wrapping of young film around their old oxide and young oxide to form asymmetrical bifilm[16]**

Other sources

When the pouring height of the melt stream increases, the stream of melt has more time to react with air and be contaminated with oxides. Also, the stream which is falling down from longer distance has higher kinetic energy and will cause larger turbulent movement as compared to the stream that is falling from smaller distance. Influence of the pouring distance between the basin and ladle at different heights (1, 5, 10 and 15 cm) on the melt quality of AlSi7MgCu alloy during top casting was studied by Pavlak.[23] He observed that the increase in pouring height results in the higher density index, i.e. the sample has more pores and oxide inclusions. The density index D_i of the casting is defined as

$$D_i = \frac{D_a - D_v}{D_a} \tag{3}$$

where D_a and D_v are the densities of samples solidified in air and under partial vacuum respectively. Another action that forms a double oxide film in the casting is surface flooding, i.e. when an advancing liquid front is stopped for any reason, allowing the liquid metal to flood over the film and the dry sides of the films come



7 X-ray video radiograph of Al–4·5%Cu during mould filling[25]

into contact.[1] The effect of passage of air bubble in solidifying aluminium alloy casting was studied by Divandari and Campbell.[24] They artificially introduced bubbles via silica tube into a base of the casting and monitored their movement by video X-ray radiography. The passage of numerous bubbles results in a tangle of bubble trails with fragments of bubbles trapped in the mass of oxide films.

Assessment of bifilms in casting

In general, oxide bifilms formed in the aluminium alloy casting were in the order of only nanometres or at the most micrometres even though they may be extensive in area, typically of diameter 0·1 to 10 mm. Because of their extreme thinness, normal casting inspections including nondestructive inspection technique fails to detect bifilms in the casting.[24] Some of the special techniques which were used to identify the bifilms are described below.

X-ray video radiography

Continuous monitoring of the liquid melt flow in the mould during casting by X-ray video radiography allows identification of the critical casting defects such as creation of surface turbulence, entrainment of air, vena contracta, etc. (Fig. 7). However, it is not possible for this technique to determine the complete flow field and to provide quantitative data about the free surface generated during the filling.[25]

Modelling and simulation

Computational fluid dynamics (CFD) is one of the most important tools used to investigate the liquid metal filling and distribution of oxide films in the casting.[13] The results of this simulation generally agree closely with the actual flow patterns as revealed by real-time X-ray radiography of mould filling.[25] Many researchers have used the code of FLOW-3D with the volume of fluid method to track the moving free surface of liquid aluminium. The excess free surface film obtained this way can be thought of as the free surface film that has the potential to be entrained into the bulk of the liquid metal during the filling. Dai *et al.*[13] employed the scalar variable distribution method of the FLOW-3D to predict the potential distribution of entrapped oxide films. Yang *et al.*[18] developed a numerical algorithm, oxide film entrainment tracking (OFET, 2D) in which tracking points were introduced on the free surface area for predicting the oxide film defects distribution in the liquid aluminium throughout the filling. The results attained using the proposed numerical algorithm was in good agreement with those using the CFD code – Flow-3D and qualitatively consistent with the experiments.[18] Reilly *et al.* developed an algorithm along with FLOW-3D to place marker particles that allows identification of the final location of entrained defect.[26] However, the mentioned place of tracking points to define the bifilm was allowed to move with the velocity of the fluid, but the mechanical resistance of the bifilm to deformation was not considered. In order to model bifilm deformation in the bulk of the melt, Pita and Feliceli proposed immersed element-free Galerkin method. In this method, the fluid domain was modelled using the finite element technique and the solid domain was modelled using the element-free Galerkin method. This method shows a good potential for application to the problem of oxide bifilm unfurling during solidification processes.[27]

Microscopy

Because of the extremely fine thickness of the bifilm, the optical microscope is usually not capable of resolving bifilms and higher magnification is needed. The sample preparation and requirement of small sample in the transmission electron microscopy results in lower probability of detection of bifilms in the sample. Scanning electron microscope is widely used to study the bifilms. Careful examination is needed to detect these oxide bifilms. Even on fracture surfaces they are often apparently invisible and are so thin that the metallic structure is visible through the film. These films usually reveal itself by minute rucks and folds that are visible only at highest magnification.[28,29] Some thick films show charging effects in secondary electron imaging mode.[30]

Reduced pressure test

Fox and Campbell proposed a novel test and a radically new mechanism for the development of macroscopic defects from pre-existing or process related metal damage within aluminium alloy. The bifilm which contains entrapped gases between the inner sides would expand when the pressure above the melt was reduced. Thus the expanded bifilm could be clearly identified in a radiographic study.[30.] Dispinar proposed a parameter to quantify the quality of casting termed bifilm index. It is the total length of bifilms on the sectioned surface of the RPT sample solidified at 100 mbar[8]

$$\text{Bifilm index} = \sum(\text{pore length}) \tag{4}$$

Weibull analysis

The Weibull distribution is a useful means of describing data that are skewed about their mean value. The two parameter Weibull distribution is normally used to characterise the scatter in mechanical properties of the casting which is given as[25]

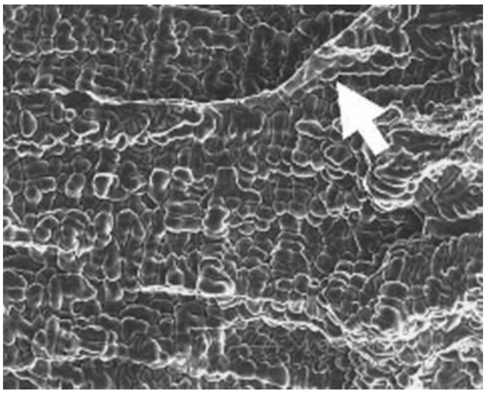
$$P = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^{\mathrm{m}}\right] \tag{5}$$

where, P is the fraction of specimens that fail at or below a given value of σ, σ is the variable being measured (e.g. tensile strength, fatigue life), σ_0 is scalar parameter (a characteristic value of σ at which 63·2% of specimens have failed), and m is a width parameter.

Taking the natural logarithm twice, the above equation becomes

$$\ln\left[\ln\left(\frac{1}{1-P}\right)\right] = \lambda \ln\sigma - \lambda \ln\sigma_0 \tag{6}$$

By plotting $\ln\left[\ln\left(\frac{1}{1-P}\right)\right]$ against $\ln\sigma$, the resultant straight line obtained gives the slope m which is termed as Weibull modulus. This Weibull modulus is a criterion that can assess quantitatively the reliability of a casting caused by the entrainment of surface films during filling. A high Weibull modulus is an indication of increased homogeneity and less spread in the flaw population. The described two parameter Weibull analysis assumes that threshold value σ_T (below which no specimen is expected to fail) is zero and it is easier to estimate the parameters. The three parameter Weibull distribution of the mechanical data sets for the casting showed non-linear Weibull plots. For such data there is often a minimum threshold value (either positive or negative). Futhermore, Tirayakioglu showed that high value of m does not necessarily mean higher repeatability or reliability of casting in two parameter Weibull analyses.[31] Tirayakioglu and Campbell explored the importance of the threshold value in the Weibull analysis and inefficiency of the interpretation of data when assuming $\sigma_T=0$.[32] They showed that, in three Weibull distribution plot, the trend of the curve at low values of ln σ is influenced by the value of the threshold σ_T. A positive threshold results in higher slope at low values of ln σ and when the threshold is negative, the slope decreases with decreasing ln σ. The cumulative probability function of the three parameter Weibull distribution is expressed as follows



8 Fractured surface of aluminium alloy reveals dendrites responsible for straightening of bifilm by their mechanical pushing action[3]

$$P = 1 - \exp\left[-\left(\frac{\sigma-\sigma_T}{\sigma_0}\right)^{\mathrm{m}}\right] \tag{7}$$

They recommended that both versions be considered, and even small details should receive attention, especially when the threshold is not too far away from zero. Furthermore, they also described about Weibull mixture also known as bi-Weibull for multiple casting defect distributions. This analysis is more useful when formation of new defects especially the formation of young oxide films during filling of castings.[32]

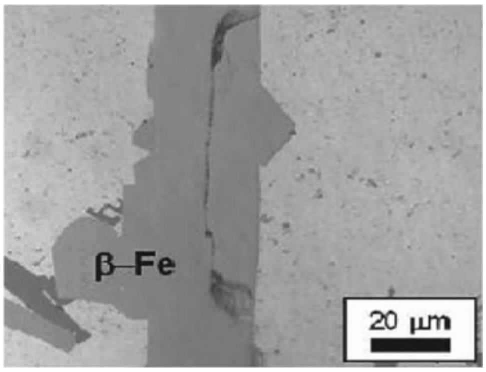
Effect of bifilm on properties of aluminium alloy casting

Bifilm as a crack

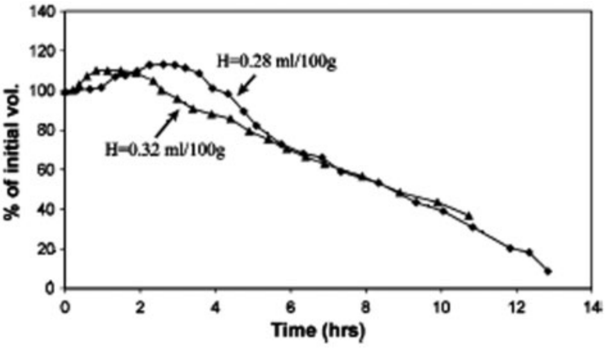
The inner sides of the bifilm do not bond together and there exists a gap between them. These dry sides of a double oxide film in cast aluminium alloys constitute a crack.[25,33] Campbell described that during solidification of casting, the entrained bifilm may straighten or unfurled and mechanically flattened by the growth of dendrites (Fig. 8).[3] The dendrite pushing process creates large planar areas which are separated by the planar unbonded interface between the two films, thus forming extensive transgranular and sometimes intergranular cracks. The transgranular cracks exhibit the accurately planar crystallography defined by the dendrites, whereas the bifilms pushed into intergranular planes exhibit the typical curved surfaces of grain boundaries.[3] The unfurling of bifilms can also occur by hydrogen precipitation in the air layer between the films, shrinkage reducing the pressure acting on the films and iron precipitation in the form of β phases.[8]

Precipitation of secondary phase/intermetallics

The outer surface of bifilm is in perfect atomic contact with the matrix and the only solid surface available at an early stage of cooling of the liquid. Therefore, they are probably favoured substrates for the precipitation of second phases as intermetallic compounds. Because the intermetallic compound usually grows on either side of the double film, the central unbonded interface of the bifilm often appears as a crack along the centre of the growing particle.[35] The experimental work on the aluminium alloy evidenced these by the presence of crack-like defects within the intermetallics (Fig. 9).[36] Cao and Campbell have shown that primary α-Fe



9 Microphotograph of Al–11·6Si–0·37Mg showing presence of crack-like defects within intermetallics[36]

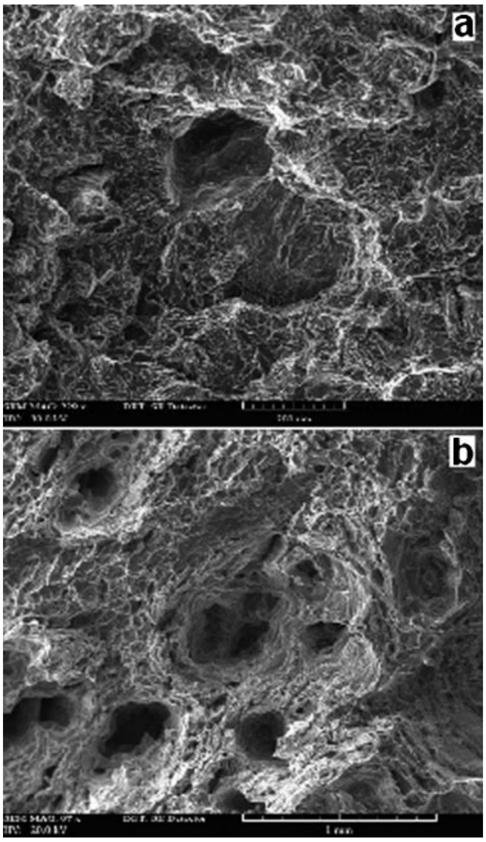


10 Change in volume of air bubble with time in liquid commercial purity Al, with high initial hydrogen contents of about 0·3 mL 100 g^{-1} Al[41]

nucleates on the wetted external sides of the entrained oxide films. The possibility of α-Fe phase nucleation on the oxide film was assessed by planar disregistry. They found that good matching between α-Fe phase and several of the main oxides in Al–Si–Mg alloy and have shown that γ- or η-Al_2O_3, α-Al_2O_3, MgO. Al_2O_3 and MgO are good substrates for the nucleation and growth of the α-Fe phase.[6,33] The crack-like defects were generally observed to be associated with the Fe-rich intermetallics and there is no direct evidence that the primary Fe-rich intermetallics actually nucleate on the wetted surfaces of the double oxide films. Hence, Miller *et al.* conducted experiments on Al–11·6Si–0·37Mg under the conditions of low and high melt agitation to alter the nature and content of oxide films in the melt. Furthermore, direct additions of oxide particles (α-Al_2O_3 and $MgAl_2O_4$) were made to investigate the nucleation dynamics of Fe-rich intermetallics on oxide particles. The microstructural observation of experimental alloy shows both blocky α-Fe and β-Fe plates, with the β-Fe phase being more predominant. They found that a large proportion of β plates from the agitated samples contain crack-like defects, whereas the β plates in the carefully prepared sample appeared defect free. The crack-like defects were observed only within the β plates in samples that were heavily agitated and therefore expected to contain many entrained oxide films. When samples were solidified in the presence of certain oxide substrates, preferential growth of Fe-rich intermetallics appeared to occur from the oxide substrate surface. These experiments suggested that bifilms in castings were favourable substrates for nucleation of intermetallics.[36] Liu *et al.*[37] observed aluminium and strontium oxides act as favourable sites for the precipitation of β-Al_5FeSi iron intermatallic phase in Sr-treated Al–Si alloy system. Miresmaeili *et al.*[38] investigated A356 alloy melts modified by the addition of 0·004 wt-%Sr. The scanning electron microscopy and its associated line scan microanalysis pattern of the casting at upper and lower part revealed old oxide (spinel) and new oxide (alumina) film associated with Sr-rich compounds. The Sr-rich compounds were situated at depths of 10 to 400 nm beneath the surface oxide film which was similar to the estimated thickness of the oxide film and this confirms that the Sr-rich compounds were located on the wetted side of the oxide film and nucleated there. The planar disregistry of matching planes of the oxide films and the Sr-rich compounds show that the Sr-rich compounds were most probably the Al_2Si_2Sr intermetallic. Oxide films of γ-Al_2O_3 and Al_2O_3.MgO appeared to be good substrates for the nucleation and growth of Sr-rich compounds.[38]

Initiation of porosity

The classical theory explains that gas porosity in aluminium alloy castings is caused by the rejection of dissolved hydrogen from the solidifying phase into the liquid phase, which becomes increasingly enriched in the gas. This dissolved hydrogen exerts a pressure and a pore is formed when this pressure is equal to the sum of the atmospheric, metallostatic and surface tension pressures.[36] Campbell showed that the initiation pressure that is required for the nucleation of pore in aluminium casting is 30 000 atm. Therefore the homogeneous nucleation of pore is practically very difficult to occur and heterogeneous nucleation of pore is expected to occur. In heterogeneous nucleation, the presence of non-wetting particles (required internal pressure of the bubble becomes an inverse function of the wetting angle) such as inclusions, refractory and mould wall act as excellent nucleation sites.[1] Campbell argued that even the most non-wetting condition (contact angle of 160°) yields a reduced pressure for nucleation by a factor of 20. Although this is a large reduction, it is not large enough to facilitate nucleation on any common non-wetted substrates in any known liquid metal.[28] Hence, the pressure required for both homogeneous and heterogeneous nucleation of pore is extremely high and Campbell proposed a new mechanism of pore initiation on bifilms.[28,29] The unbonded inner side of the bifilm together with the trapped gas act as pre-existing cavities in the melt and these oxide films could be inflated (under practically zero stress) to become the porosity in the casting. Naturally, gas in solution in the liquid will diffuse through the alumina film into the central bifilm gap until the gas in this location reaches the pressure in equilibrium with the liquid. In this way the bifilm is expanded and gas driven microporosity is generated. By analogous process of tensile stress operating on the outside of the bifilm, the expansion of the bifilm will lead to the creation of shrinkage driven microporosity.[28] Fox and Campbell observed the inflation of the double oxide film nuclei and become complete expanded spheres in the reduced pressure test of Al–7Si–0·4Mg alloy with increasing hydrogen content.[40] Griffiths and Raiszadeh conducted experiments to study diffusion of H into the double oxide film.[4,41] They deliberately trapped an air bubble into the liquid aluminium and monitored the

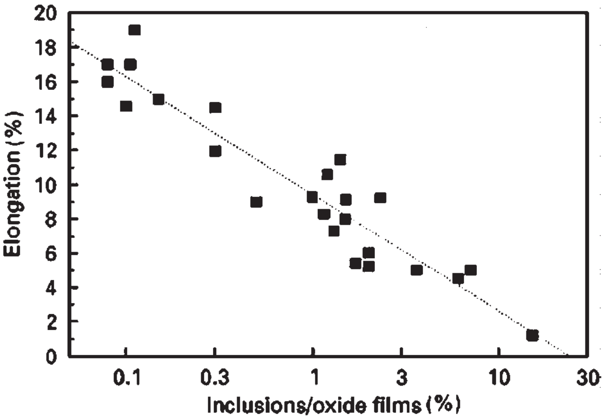


11 Scanning electron micrograph of fracture surface of *a* A356, *b* commercially pure liquid aluminium solidified immediately after pouring shows pores associated with oxide film network[42]

change in volume of air with time using real time X-ray imaging system. They observed that when the H content of the melt was increased to about 0·3 mL 100 g^{-1} Al, the H in solution passed into the air bubble causing its expansion (Fig. 10). In an Al casting the same effect would cause an entrained double oxide film defect to act as a site for the growth of H-driven gas porosity. Initially, the diffusion of H into an oxide film defect would be slow as the oxide film provides a barrier to the diffusion of H. Later more rapid diffusion of H could occur into an oxide film defect through surface ruptures which is caused by convection or other sources of fluid flow or the change in volume of the interior atmosphere due to H ingress or reaction of the interior gases with the surrounding melt. They also conducted experiments on melts of commercially pure liquid aluminium and Al–7Si–0·3Mg alloy were cast into moulds designed to produce entrainment of oxide film defects. The fracture surfaces showed pores that were associated with oxide film networks (Fig. 11).[42] The fatigue study on Al–7Si–Mg alloy by Nyahumwa observed that in unfiltered castings, fatigue cracks initiated at gas pores which were associated with young oxide films.[43]

Other microstructural change

The presence of bifilm affects the grain refinement in the aluminium alloy casting. The straightened bifilm by the growth of dendrites constituted as large planar barriers through the casting section. These would have prevented convection, so that thermal or mechanical perturbations were suppressed and large grains could grow undamaged. During solidification, the oxide films will be rejected by an advancing solid interface because the matrix solid will not nucleate on its own oxide. Thus isolated region of undercooling of several hundreds of degree Celsius is routinely achieved which solidify rapidly. This would result in finer DAS adjacent to regions of coarse DAS.[3,28,29]



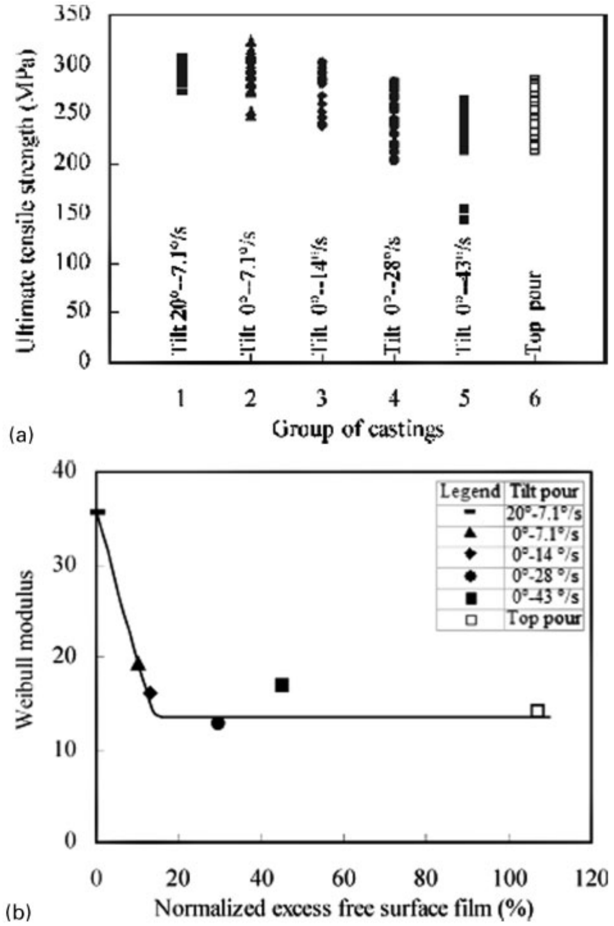
12 Percentage elongation–log area percentage inclusions/oxide film relationship[22]

Mechanical properties

The crack-like nature of bifilms suspended in aluminium alloy castings leads to premature failures and thus reduces the mechanical properties (tensile strength, ductility and fatigue life) of castings. The decrease in tensile ductility and strength of Al–Si–Mg cast aluminium alloys correlates with the area fraction of defects (porosity and oxide films) in the fracture surface of the samples.[44] Campbell found that the overall elongation to failure was only 0·3% for the bar that was taken from a aluminium alloy casting, in which a folding-over surface wave was observed during X-ray video observation of mould filling. In the same casting, at its far end just 250 mm away, another test bar was observed to fill without surface turbulence. Thus, no large bifilms were expected to be present and the elongation to fracture was measured to be 3·0%.[3] Liu and Samuel poured A356·2 castings under different conditions such as fresh alloy, recycled alloy, melts with different stirring time, different holding time of melt and melts with and without degassing. They observed that oxide films have a much more deleterious effect on the mechanical properties compared to that expected from other inclusions and established a linear relationship between percentage elongation and log area percentage inclusions/oxide films as shown in Fig. 12.[22] The best fit equation is given by

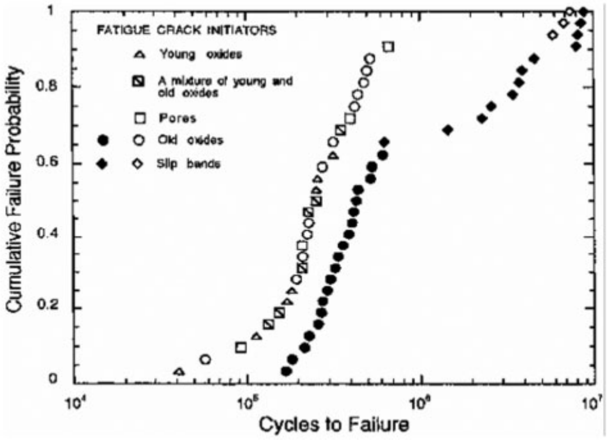
$$\begin{aligned}&\text{percentage elongation} = 9.5 - 2.98 \log\\&(\text{area percentage inclusions/oxide films})\end{aligned} \tag{8}$$

Mi *et al.*[25] measured the ultimate tensile strength of Al–4·5Cu casting produced with various filling sequences. The spread of the ultimate tensile strength increases from the casting with tranquil flow to the casting with turbulent flow. The Weibull moduli for the tensile strength dropped abruptly from 36 to 13 when about 15±2% of excess free surface film was available for entrainment and remained virtually unchanged thereafter (Fig. 13). Jiang *et al.*[15] observed that fatigue cracks



13 ***a*** **scatter in UTS of Al–4·5Cu casting produced at different filling sequences and** ***b*** **their normalised excess free surface film on Weibull moduli of tensile strength[25]**

initiated from oxide films (exhibited as folded or tangled form) which were located at or near the surface specimen of Al–7Si–Mg. Nyahumwa conducted fatigue experiments on Al–7Si–Mg alloy. Test bars were cast using bottom-gated filling systems with and without filtration. Polished cast test bars produced by the bottom gated filling filtered system were relatively sound. However, extensively tangled networks of oxide films were observed to be randomly distributed in almost all polished sections of unfiltered castings. The measured fatigue lives of the unfiltered castings ranged from 0·04 to 7 Mcycles, whereas those of the filtered castings ranged from 0·2 to 9 Mcycles at 150 MPa (Fig. 14). The fractured surface showed that fatigue cracks were



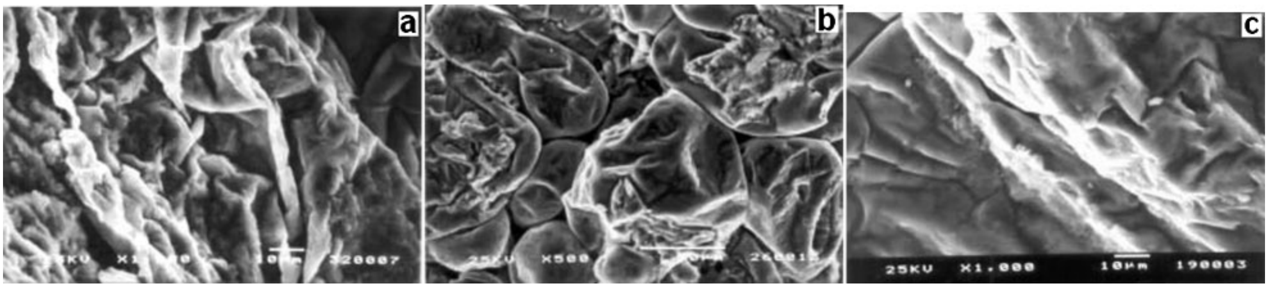
14 Correlation between fatigue crack initiators and fatigue life distributions for 150 MPa unfiltered (open symbols) and filtered (solid symbols) Al–7Si–Mg alloy castings[45]

initiated by oxide film defects. Old oxides acted as fatigue crack initiators in both unfiltered and filtered castings but the young oxide film defects and pores attached to oxide films were only found to act as fatigue crack initiators in the unfiltered castings (Fig. 15). The slip mechanisms were found to operate more in the filtered castings. Further they applied the two parameter Weibull distribution to describe the fatigue life data of the castings associated with oxide film defects. This analysis indicates that the young oxide films were more damaging than the old oxide film.[43,45] Haberl *et al.*[46] observed that the fatigue life cycle with a survival probability of 90% of the LM25 castings increased from 120 000 to 220 000 with the decreasing amount of bifilms as oxides in the melt.[46]

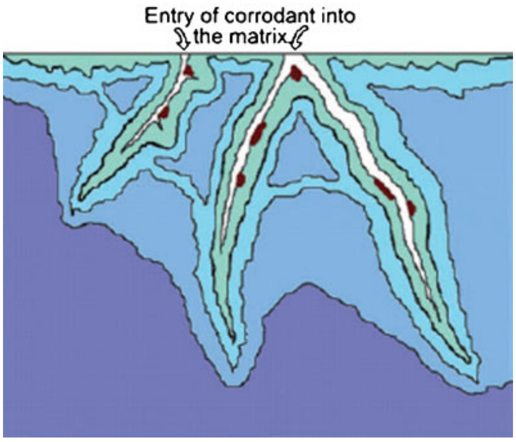
Deterioration of electrochemical/corrosion properties

The crack-like nature of bifilm provides a channel to permit the corrodant to penetrate deep into the interior of the metal and creates a localised galvanic cell with the intermetallic (specially Fe-rich and Cu-rich intermetallics) which is precipitated on bifilm affecting the corrosion behaviour of aluminium alloy.[28] In order to study the effects of bifilm on the electrochemical behaviour, Emamy *et al.* conducted experiments on Al–5Zn–0·002In sacrificial anode. The following three artificial methods were employed to introduce oxide bifilms in castings:

(i) addition of Al–Zn–In chips with an average diameter of 0·5–3 mm up to 60 wt-%
(ii) increasing the pouring height from 30 to 480 mm



15 Secondary electron micrograph showing ***a*** **young oxide film,** ***b*** **pore attached to oxide film initiated fatigue crack in unfiltered casting and** ***c*** **old oxide film defect initiated fatigue crack in filtered casting[43]**



16 Schematic illustration of penetration of electrolyte into biflms and arrival of electrolyte at sites of intermetallic precipitates at random locations on biflms[16]

(iii) melt agitation carried out using mechanical stirring action by means of a graphite impeller rotating at 4 Hz (250 rev $\min^{-1}$) for different times between 20 and 300 s.

They observed that in all cases oxide inclusions in the Al anode reduce both the current capacity and anode efficiency. It was postulated that the penetration of the electrolyte into the biflms and the arrival of the electrolyte at sites of intermetallic precipitates at random locations on biflms (Fig. 16) will create a temporary cathodic potential against the aluminium matrix, behaving as a cathode while the localised corrosion cell remains active.[16] Jaradeh and Carlberg[47] observed that presence of oxide film in cut surfaces of direct chill cast billets of extruded AA 6063. They deep etched these cut surfaces by 10 to 20 g of NaOH in 100 mL of water at 60 to 70°C for 5 to 15 min of etch time. They observed that inclusion (Oxide film) develops a large rounded etch pit with increasing etching time which is visible under low magnification/the naked eye. The remainder of the alloy surface remained unattacked by the etchant. This experiment shows the direct evidence of promotion of pitting corrosion by bifilms in the casting.[47]

Techniques for control/deactivation of bifilms

Design of filling system

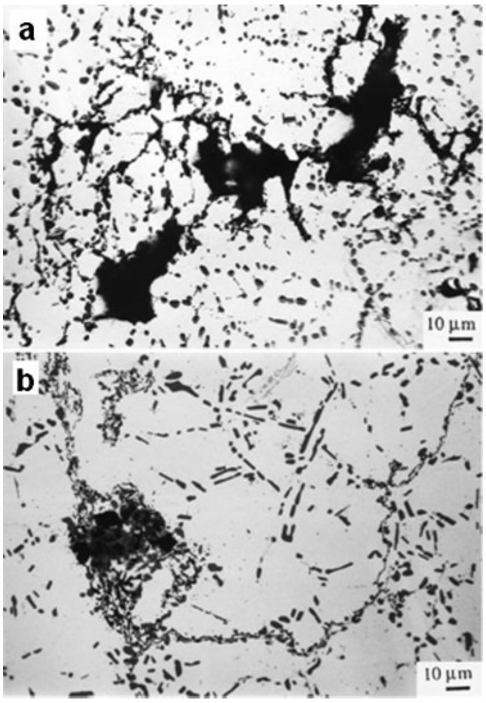
Filling the liquid melt into the mould during casting is a key step which controls the generation of the surface turbulence and hence controls the entrainment of the oxide film into casting. Top gated filling and bottom gated filling are the two typical filling systems normally used in the foundry. In top gated filling the liquid metal falls from above and more or less directly enters the mould cavity at high speeds whereas in bottom gated filling the liquid melt enters the mould at its base and fills the mould cavity in a substantially counter-gravity mode. Li *et al.*[48] have shown that the use of the bottom gated filling design with narrow section channels reduces the potential for surface turbulence whereas top gated filling system causes surface turbulence resulting in the entrained surface film on the liquid. Studies on the tilt pouring and gravity top pouring of Al–4·5%Cu carried out by Mi *et al.*[25] have shown that no surface turbulence generation during tranquil filling resulted from the tilt pouring using an initial mould orientation of 20° and a tilting speed of 7·1° s^{-1}, whereas strong surface turbulence was observed when an initial mould orientation of 0° was used and the tilting speed increased to 14° s^{-1}. The liquid flow became extremely turbulent in top pouring and also when the tilting speed was increased to 43° s^{-1}. Unfortunately, in tilt casting the pouring of melt into initial horizontal position (zero degree) of mould is widely used in casting industry. According to Campbell, if the mould starts from a horizontal position, the metal in the basin is not usually filled to the brim, and therefore does not start to overflow the brim of the basin and enter the runner until a finite tilt angle has been reached. At this stage the vertical fall distance between the start and the far end of the runner is likely to be greater than the critical fall distance. Similarly, if the mould which is tilted downward at the initial condition would result the melt to accelerate under gravity, hitting the far end of the runner at a speed sufficient to cause splashing and entrain the melt surface. The problem can be avoided by stating from a positive angle of up to 20 degrees and proceeding through the critical horizontal stage with care. When the mould is initially tilted slightly uphill during the filling of the basin, there is a chance that by the time the change of angle becomes sufficient to start the overflow of melt from the basin, the angle of the runner is still somewhat above the horizontal. The nature of the liquid metal transfer is now quite different. At the start of the filling of the runner the meniscus is effectively climbing a slight upward slope. Thus its progress is totally stable, its forward motion being controlled by additional tilt. If the mould is not tilted further the melt will not advance. By adopting extremely careful control of the rate of tilt it is possible in principle to cause the melt to arrive at the base of the runner at zero velocity if required.[29,49] The use of filter in the running system can effectively reduce the molten metal flow velocity and surface turbulence. Green and Campbell poured the Al–7Si–Mg alloy into three different systems, namely, top gated filling, bottom gated filling and bottom gated filling with filtered system. A high tensile strength Weibull modulus of 38 was obtained for the casting poured in bottom gated filling with filtered system whereas Weibull modulus of 20 and 11 were obtained for castings poured with bottom gated filling and top gated filling respectively.[50] Nyahumwa used ceramic foam filter with 20 pores per inch in the bottom filling system to give the initial runner velocity of less than 0·5 m s^{-1} with turbulence free conditions and found significant improvement in the fatigue life of the casting.[43,45] Numerical simulation of different runner systems (vortex flow runner and rectangular runner) by Yang *et al.*[18] found that ingate velocities significantly affect the number and distribution of the oxide film defects generated from filling. The reduction of ingate velocity can effectively reduce casting defects. This can be achieved by controlling the chaotic behaviour of liquid metal flow and by the use of a vortex flow regime to dissipate the kinetic energy of the metal in the runner. In order to minimise the turbulence during casting, Dispinar and Campbell made three changes in the casting technique:

(i) lowering of the height of the launder so that the fall of the liquid metal into the ingot mould would be minimised
(ii) altering of the casting device such that the melt was intended to deliver into the ingot mould at the lowest possible point
(iii) changing the tapping procedure of the holding furnace.

These changes in casting technique resulted in the bifilm index lowering from 188 (original design) to 39 mm which clearly showed significant improvement in quality of the casting with minimised turbulence during the casting.[20] Hsu and Lin[51] proposed a new diffusing runner system that could reduce the velocity of flow under the critical velocity of 0·5 m s^{-1}. They created baffle geometry within this diffusing runner. When the flow contacts this obstacle, it could spread laterally and fills the sideways region of the diffuser instead of going straight. Additionally, after impacting the baffle geometry, the flow split into two streams in the centre of the geometry. These streams would be contained fully without having the danger of air and oxides entrapments into the runners.[51] Campbell emphasised the use of counter gravity filling for unconstrained filling of moulds without risk over gravity filling. In counter gravity filling (especially low pressure die casting) the liquid melt in the furnace is pressurised by using air or inert gas which forces the melt to rise up and fill the mould through the riser tube. According to Campbell, 'counter-gravity is such a robust technique that it is often difficult to make a bad casting'. The velocity of the melt filling into the mould can be controlled below critical velocity by good counter-gravity system resulting in no surface turbulence during filling. Also the riser tube positioned at the centre of the melt in furnace can help to prevent the entrainment of surface film formed on the melt. However, the use of clean melt and proper metal handling technique are necessary in order to prevent the entrainment of old oxide film. Cosworth process is a relatively new casting process in which the liquid metal is never poured, never flows downhill, and is finally transferred uphill into the mould.[49]

Melt treatment

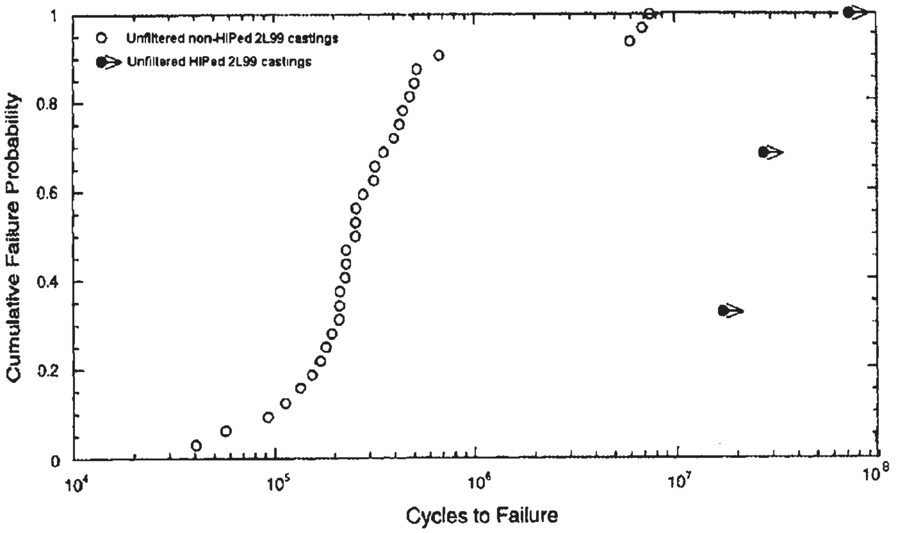
Liu and Samuel[22] observed that holding the liquid A356·2 metal at 735°C for a period as long as 72 h leads to flotation of most of the oxide films to the upper surface of the molten metal which could be removed easily. However, it should be noted that the surrounding humidity may cause absorption of hydrogen. Similarly, in holding experiments of LM 2, Haberl *et al.*[46] observed that the number of pores diminish over time, which suggested that bifilms become inactive over time. Raiszadeh and Griffiths observed that holding an aluminium melt containing double oxide film defects under vacuum for extended periods of time up to 60 min resulted in a gradual decrease in the number of oxide film defects in the melt due to their continuous migration towards the upper surface.[52] According to Campbell an aluminium alloy containing extremely low levels of Mg will exhibit stable alumina film and alloys containing more than about 1·0 wt-%Mg will exhibit a pure magnesia film which is similarly inert. Therefore, the bonding across the internal bifilm interface is very difficult. In alloys of intermediate Mg content an alumina film appears to form first which slowly converts to a spinel, the mixed oxide. During this conversion, the atomic rearrangements might allow a certain amount of diffusion bonding.[28] This was experimentally confirmed by Aryafar *et al.*[53] who investigated the possibility of the bonding of the two layers of a double oxide film defect when held in liquid A356 alloy. They maintained two aluminium oxide layers in contact with each other and the atmosphere trapped between them in the A356 liquid alloy for varying lengths of time of between 30 s and 48 h and observed the bonding of two oxide layers. The bonding would be caused by two different mechanisms. One, which occurs at holding times of a few minutes, is due to the transformation of alumina to spinel and causes the two layers to bond to each other at several points. This bonding is not particularly strong but might reduce the deleterious effect of the defect as a crack. The other happens during the gradual transformation of spinel to MgO in holding times of 13 min or more. This transformation causes a strong bonding between the two oxide layers and may prevent the defect from acting as an initiation site for the formation of other defects, such as gas porosity. However, any bonding can take place essentially only after the oxygen and nitrogen of the atmosphere within the defect is consumed.[53] Campbell proposed the concept of deactivation of Si nucleation and growth on bifilm substrates by modification of Al–Si alloy. In Al–Si alloy, the advancing aluminium matrix will reject and push bifilms ahead of the front and they will become mechanically incorporated in the trench surrounding the Si particle. The silicon particle normally precipitates and grows on the bifilms and thus straightens the bifilm and makes it an effective crack. When modifier such Na and/or Sr added to the Al–Si alloy will cause the alloy to freeze on a planar front, the nucleation of silicon particles ahead of the front is now clearly suppressed. Therefore, that the formation of silicon on bifilms is now no longer favoured. The Si now forced to grows as a eutectic, probably initiated in the regions of significant undercoolings on the mould walls or at the melt surface. Thus bifilms are no longer unfurled by growth of silicon to form planar cracks.[3,29,54]



17 Optical micrograph of network of oxide films and attached pores in bottom gated filled unfiltered *a* non-hipped and *b* hipped Al–7Si–Mg alloy casting[45]

Hot isostatic pressing (hipping) treatment

In foundry, the components are normally subjected to hipping treatment in order to eliminate internal voids



18 Fatigue life distributions for 150 MPa unfiltered non-hipped and unfiltered hipped Al–7Si–Mg alloy castings[56]

and microporosity. The typical hipping temperature and pressure for aluminium and its alloys are about 500°C and 100 MPa respectively.[55] Campbell argued that aluminium alloy casting contains bifilm subjected to a hipping treatment, even though the melting point of oxide film is much higher compared to the hipping temperature. The aluminium alloy at the hipping temperature being active may migrate through the dry side of the bifilm which results in welding of inner sides.[1] This closing of bifilm can still support some shear stress as a result of jogs and folds but cannot of course support direct tensile stress. Nyahumwa *et al.*[45] discussed the concept of oxide film healing mechanism during hipping treatment of aluminium alloy casting by diffusion bonding aided by atomic rearrangements of the oxide lattices. Of course this concept is applicable for the intermediate Mg content of aluminium alloys subjected to hipping treatment. When the applied pressure is at a temperature close to its eutectic temperature a substantial plastic deformation in the casting is introduced causing the oxide films to collapse and their surface to be forced into contact. After an incubation period, which is a function of time and temperature, the entrained Al_2O_3 film transforms to $MgAl_2O_4$. This involves a volume change and atomic rearrangement of the crystal structure, which would be expected to encourage diffusion bonding across the oxide/oxide interface. This bonding appears not to be particularly perfect, but does allow the defects to support some tensile stress. Nyahumwa observed that cracks and pores in the networks of oxide films partially or fully closed/attached when Al–7Si–Mg alloy casting was subjected to a hipping treatment of 100 MPa at 500°C (Fig. 17*a* and *b*). He also observed the presence of some material between two surfaces of oxide films and within a collapsed pore at higher magnification. The measured fatigue lives of non-hipped and hipped castings were 4×10^4–$7{\cdot}4\times10^6$ cycles and $1{\cdot}7\times10^7$–$7{\cdot}6\times10^7$ cycles respectively (Fig. 18). This improvement in the fatigue life of components due to the closure of oxide film defects occurred during hipping treatment.[45,56]

Precipitation and sedimentation of intermetallics

Cao and Campbell proposed a concept to remove oxide film defects from liquid metal by nucleation of primary intermetallic compounds onto the oxide films.[6,33] By controlling the composition of the alloy, the intermetallic particles can be made to solidify before the aluminium solid solution. As these particles have a higher density than the melt, they tend to sink to the bottom of the melt, bringing the oxide films with them. By removing this settled layer, the amount of oxide films in the liquid aluminium can be reduced.[36] Experiments on liquid LM9 precipitated at 600°C for 4 h in convection free condition found to contain the primary α-Fe particles in the central (axial) region of the castings and some oxide films appear to have fully settled to the bottom of the mould.[33] Furthermore, they also showed that the transformation of γ-Al_2O_3 or η-Al_2O_3 to α-Al_2O_3 with the increase in melt superheat of LM9 which had influence on the crystallisation behaviour of primary α-Fe particles. Compared with normal melting at 760°C, an intermediate superheating temperature of 850°C may facilitate the nucleation of primary α-Fe phase and/or hinder its growth, causing clear increases in particle weight and number and a decrease in particle size.[6]

Summary

The high chemical affinity of liquid aluminium and its alloys to oxygen leads to a rapid formation of thin surface oxide film. The surface oxide film can be randomly folded into liquid metal resulting in the formation of bifilms which act as invisible microcracks in the casting. Surface turbulence, charge materials, pouring techniques, surface flooding and bubble trails are the important parameters that lead the surface film to incorporate into the casting. X-ray video radiography, CFD, fractography, reduced pressure test and Weibull analysis are the important tools for the identification and study of bifilms in the castings. Bifilms present in aluminium alloy castings act as cracks, precipitate intermetallics and nucleate porosity. If sufficient care is not taken to remove these bifilms in a casting, it could lead to significant reduction in the reliability of the components. Proper designing of casting systems and maintaining a close control on quality of the melt can prevent the formation of bifilms in castings. Hipping treatment, holding of liquid melts at elevated temperatures for sufficient period of time and precipitation and sedimentation of intermetallics are some of the methods available for healing of biflms in castings. Developing novel process techniques for healing of bifilms are essential for enhancing the reliability of aluminium alloy casting.

Acknowledgements

One of the authors (KNP) thanks Professor John Campbell and Dr Bill Griffiths of the School of Metallurgy and Materials, University of Birmingham, Edgbaston, United Kingdom for introducing him to the wonderful world of oxide film defects.

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