Journal of Engineering Technology

Volume 8, Issue 2, July 2019, PP. 117-126

RESEARCH ARTICLE -ENGINEERNG TECHNOLOGY

Oxide Film Age and Mechanical Properties of Aluminium Alloys

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Abstract: Double oxide films (bifilms) are serious defects in the castings of light metals. These flaws have been reported to increase the variability of the fracture strengths of Al and Mg alloy castings. This means that shape castings in light alloys can have inconsistent properties, which makes designing structures employing shape castings more difficult. It has been suggested that the air entrapped inside a bifilm can react with the surrounding melt leading to its consumption, which might improve the mechanical properties of the castings. In this work the effect of holding an Al casting in the liquid state for 20 minutes before solidification was studied using a two-level full factorial design of experiments. Two responses were considered; the UTS and %elongation of the resulting castings. The results showed that the holding treatment had no significant influence on the UTS while it had a trivial decreasing effect on the % elongation of the castings produced. SEM investigation of the fracture surfaces of the test specimens detected many alumina layers at different locations, most of which were found inside pores, reflecting the role of entrained defects in the formation of porosity. The results hence could be a suggestion of two opposite phenomena that may take place during the holding treatment. The consumption of air inside the entrained defects due to reaction with the surrounding molten metal may lead to improvements in mechanical properties, but this may be accompanied by hydrogen passing into the defects, which has a deleterious effect on properties.

Keywords: oxide film; aluminium casting; hydrogen; Design of experiments

Introduction

The mechanical properties of Al castings were greatly affected by their inclusion contents [1-8], especially what is called double-oxide film defect or bifilm [9-13]. This defect is created due to surface turbulence of the liquid Al, which is a common foundry practice during metal handling, transfer and/or pouring. If liquid aluminium entered a mould cavity with a velocity greater than a critical value, the surface oxide film of the liquid metal would fold over onto itself (but not fuse) and be submerged into the bulk liquid with a volume of air entrapped, creating crevice-like pores, with an oxidised interior surface [10-18].

Entrained double oxide film defects represent the easiest possible initiating features for cracks and pores, since they are not in atomic contact with the liquid and their dry inner surfaces can be separated with minimal effort [19-23]. Also the strength of these features is much lower than the rest of the matrix and the fracture path is expected to preferentially go through them. In addition, double oxide films are considered to be favourable sites for the initiation of pores [24] and for the nucleation and growth of a wide variety of intermetallics [25-27]. These defects not only reduce the elongation, tensile strength and fatigue limit of the aluminium casting, but also increase their variability [28]. Oxide films also were suggested to increase the variability in the fluidity of Al melts during the casting process [29].

Nyahumwa et al. [30] suggested that, due to the transformation of the oxide layer from γ-Al_2O_3 to α-Al_2O_3, (a process thought to take about 5 hours), cracks are introduced into the oxide skin which allows the liquid aluminium to come into contact with, and react with, the atmosphere inside the defect (mainly oxygen and nitrogen). This mechanism could result in the consumption of the atmosphere inside the bifilm and possibly lead to its deactivation.

This explanation was further supported by Griffiths and Raiszadeh who trapped an air bubble (as a proxy for a bifilm) inside liquid Al and monitored its change in volume with time using real-time x-ray radiography. Their results showed that the oxygen in the trapped air should be consumed first, to form Al_2O_3, then the nitrogen would react to form AlN. These reactions started immediately, (with no need for an initiating phase transformation). They also reported an increase in the volume of the bubble when the initial hydrogen content of the melt was higher than the equilibrium associated with the ambient atmosphere, which was suggested to be due to hydrogen diffusion into the bubble [31].

A more detailed experiment, using a Pore Gas Analyser to investigate the change in the composition of an air bubble trapped in different Al alloys [32, 33], has demonstrated that hydrogen can diffuse through an oxide layer showing how a double oxide film defect can grow into a hydrogen-filled pore.

Design of experiments (DoE) is a systematic method to determine the relationship between factors affecting a process and the output of that process [34-38]. In other words, it is used to find cause-and-effect relationships. This information is needed to manage process inputs in order to optimize the output. A common experimental design is one with all input factors set at two levels each. These levels are called `high' and `low', 'Good' and 'Bad' or `+1' and `-1', respectively. A design with all possible +1/-1 combinations of all the input factors is called a full factorial design in two levels. If there are k factors, each at 2 levels, a full factorial design has 2^k runs [39].

The purpose of current study is to explore how the holding time of the casting in the liquid state before solidification (oxide film age) can affect the amount and morphology of bifilm defects, and by implication the tensile properties of the resulting castings. In the present study, general factorial design was used for the modelling of the casting process. The results of this investigation could lead to the development of techniques by which oxide film defects might be reduced or eliminated in aluminum castings.

Experimental

This study was aimed at investigating the effect of the age of entrained bifilm defects within an Al casting on the mechanical properties of such casting. Castings from 1100 Al alloy were produced via gravity casting. To perform the design of experiment, Design-Expert Software Version 7.0.0 (Stat-Ease Inc., Minneapolis, USA) was used and the two-level factorial design was adopted to analyze the effect of the selected parameter.

The two-level factorial design was selected because the parameters could be easily varied at two discrete levels and statistically analyzed using only two total experiments, making the DoE easy to regulate and execute due to low complexity. In this work the studied parameter (oxide film age) was varied at a "-1" and "1" value and its effect on the UTS and % elongation was evaluated.

The experimental work involved carrying out two experiments to produce castings from 1100 Al alloy that containing bifilms of different lifetimes; 0 and 20 minutes. Chemical composition of alloy is given in Table 1. In each experiment about 10 kg of the aluminium were melted in an induction furnace.

Table 1. Chemical composition of 1100 Al alloy

Element	Si	Fe	Cu	Cr	Al
%	0.3	0.6	0.15	0.1	Bal.

The liquid metal was then prepared in such a way as to promote surface turbulence and splashing, by being poured from a height into preheated ceramic shell moulds, and being stirred in an induction furnace, (using a power setting of 7.5 kW and frequency of 2350 Hz, for one minute). This was intended to cause the creation and entrainment of new bifilm defects, and their introduction into the melt.

In one experiment the casting was allowed to solidify immediately to preserve any bifilm defects created during the melt stirring or mould filling. In the other experiment it was maintained in the liquid state by placing the filled ceramic shell mould in a resistance-heated furnace for 20 minutes, before removing it to allow solidification. Thus any bifilms generated in these cases were known to be about 20 minutes old. During holding of the melt, the hydrogen content was evaluated.

After solidification, each of the castings was machined into 20 tensile test bars, for determination of their Ultimate Tensile Strength and %Elongation at failure. The tensile tests were conducted using a WDW-100E universal testing machine using a using a crosshead velocity of 1 mm min^{-1}. To evaluate the H content of the castings, a Leco sample was cut out from the running bars of the solidified castings from each experiment. The samples were machined to the dimensions of standard Leco samples (8 mm diameter and 49 mm length), and analysed to determine the hydrogen content of the castings from different experiments. Finally, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) studies were carried out on the fracture surfaces of the tensile test specimens using a Philips XL-30 SEM with Oxford Inca EDS, for the evidence of bifilm.

Results

The H content of the solidified castings from these experiments was determined to be 0.22 and 0.51 cm^3/100g respectively for the castings that contained zero and 20-min. age oxide films. The values of ultimate tensile strength (UTS) and % elongation for commercially pure Al alloy have been presented in Table 2. For each alloy, 40 test bars were tested (20 test bars for each holding time).

Table 2. UTS and % elongation of specimens of commercially-pure Al alloy held for different periods in the liquid state prior to solidification

Sample No.	Holding time (minutes)			
	Zero		20	
	UTS (MPa)	Elongation %	UTS (MPa)	Elongation %
1	46	34	52	31
2	50	39	51	23
3	52	31	58	30
4	47	40	52	31
5	48	30	55	27
6	51	27	57	25

7	53	34	56	28
8	49	21	49	29
9	54	31	62	29
10	56	26	53	25
11	56	34	48	33
12	45	30	50	24
13	42	28	56	19
14	57	25	54	23
15	55	47	51	32
16	55	33	43	22
17	53	27	54	31
18	50	35	46	28
19	54	32	47	32
20	56	28	45	29
Average	51	32	52	28

The normal probability plots of the residuals for both the UTS and % elongation are shown in Figures 1 (a) and (b), respectively. The observed points on both plots are distributed relatively near to the straight line. This could suggest that the residuals follow a normal distribution for the two responses evaluated in this study.

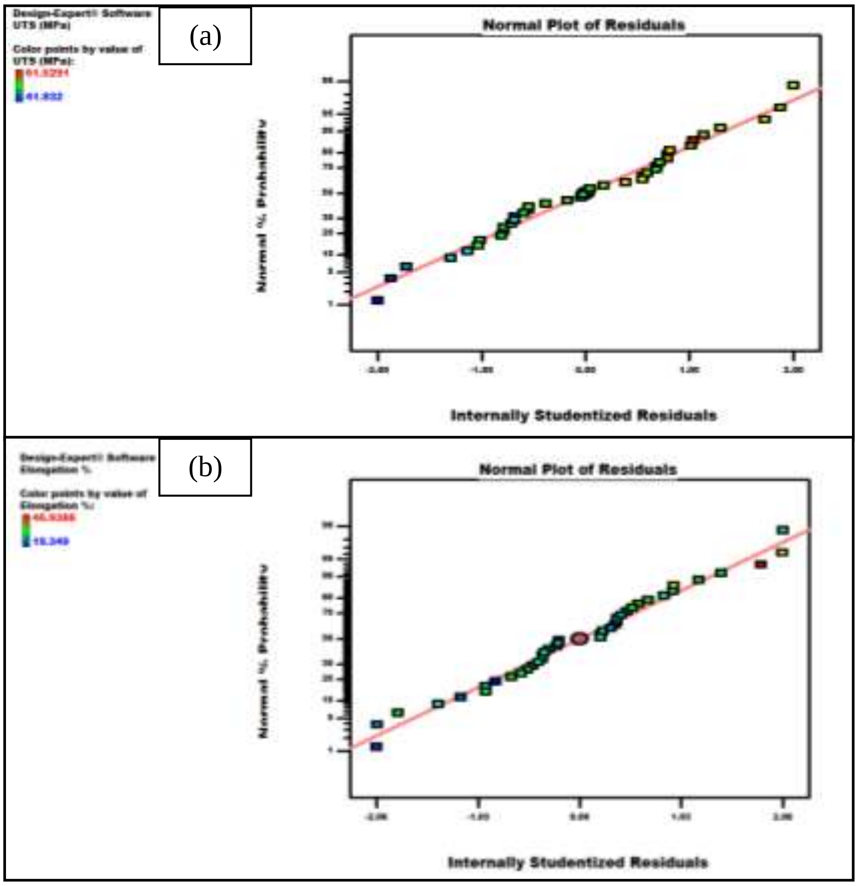

Figure 1. Normal probability plots of the residuals of (a) UTS, and (b) % elongation

1- Analysis of UTS

Table 3 shows the **Analysis of Aariance** results for the UTS values shown in Table 2. The "Model F-value" of 0.10 implies that the model is not significant relative to the noise. In other words, there is a 75.07 % chance that a "Model F-value" this large could occur due to noise. Therefore, the results of the model suessted that the age of the oxide films has no significant effect on the UTS of the castings procdued.

Table 3. ANOVA results. *Values of "p-value" less than 0.05 indicate model terms are significant. Values greater than 0.1 indicate the model terms are not significant.*

Source	Sum of Squares	Degrees of Freedeom (df)	Mean Square	F-Value	p-value
Block	321.04	19	16.90		
Model	2.45	1	2.45	0.10	0.7507
A-Oxide Film age (min.)	2.45	1	2.45	0.10	0.7507
Residual	447.71	19	23.56		
Corresponding Total	771.20	39			

Figure 2 shows the effect oxide film age on the UTS of the test bars cut from different castings (with different holding times before solidification). It is clear that there is no significant influence of the age of oxide films on the UTS of the produced Al casting. As shown in the graph increasing the oxide film age from zero to 20 minutes increased the average UTS of the castings from 51.4 to 51.9 MPa (<1%).

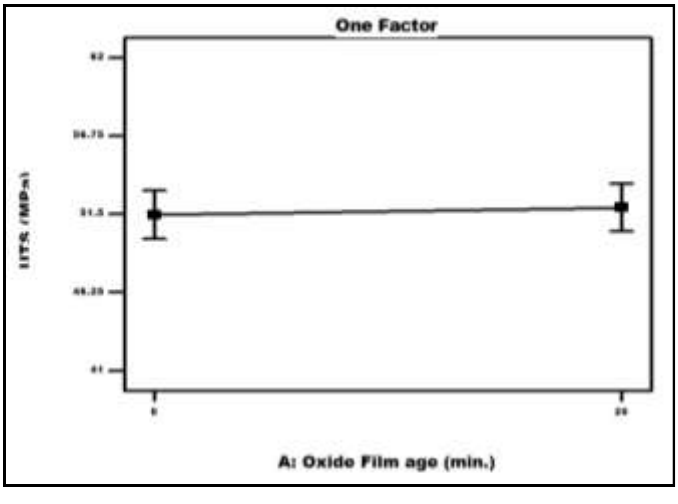

Figure 2. Effect of oxide film age on the UTS of the Al alloy.

2- Analysis of %elongation

Table 4 shows the **Analysis of Aariance** results for the % elongation values shown in Table 2. The Model F-value of 9.67 implies the model is significant. In other words, there isonly a 0.58% chance that a "Model F-Value" this large could occur due to noise. Therefore, the results of the model suessted that the age of the oxide films has, to some extend,an inlfuence on the % elongation of the castings procdued (note that the p-value of that test is betweeb 0.05 and 0.1).

Table 4. ANOVA results. *Values of "p-value" less than 0.05 indicate model terms are extreamly significant. Values greater than 0.1 indicate the model terms are not significant.*

Source	Sum of Squares	Degrees of Freedeom (df)	Mean Square	F-Value	p-value
Block	614.47	19	32.34		
Model	165.92	1	165.92	9.67	0.0058
A-Oxide Film age (min.)	165.92	1	165.92	9.67	0.0058
Residual	325.83	19	17.15		
Corresponding Total	1106.22	39			

Figure 3 shows the effect oxide film age on the % elongation of the test bars cut from different castings (with different holding times before solidification). It could be stated that the age of oxide films showed an effect on the % elongation of the produced Al casting. As shown in the graph increasing the oxide film age from zero to 20 minutes decreased the average % elongation of the castings from 31.7 to 27.6.

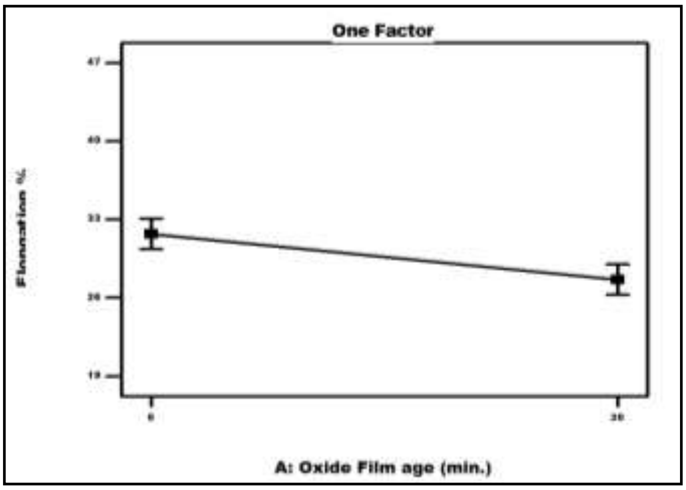

Figure 3. Effect of oxide film age on the % elongation of the Al alloy.

Figures 4 (a) and (b) show SEM images, with the corresponding EDX analyses, for inside pores on the fracture surfaces of specimens from castings with different holding times before solidification (zero or 20 minutes holding periods). Many oxide fragments were visible inside the pores. The identity of the alumina film was confirmed by the EDX spectra accompanied with each image, in which oxygen signals were detected at the suspected bifilm layers. This is a suggestion that the origins of the pores were primarily bifilm defects that might have been changed their morphologies during the holding treatment and/or solidification of the casting to form pores. This would be an indication of the role played by bifilms in initiating porosity in light metal alloy castings.

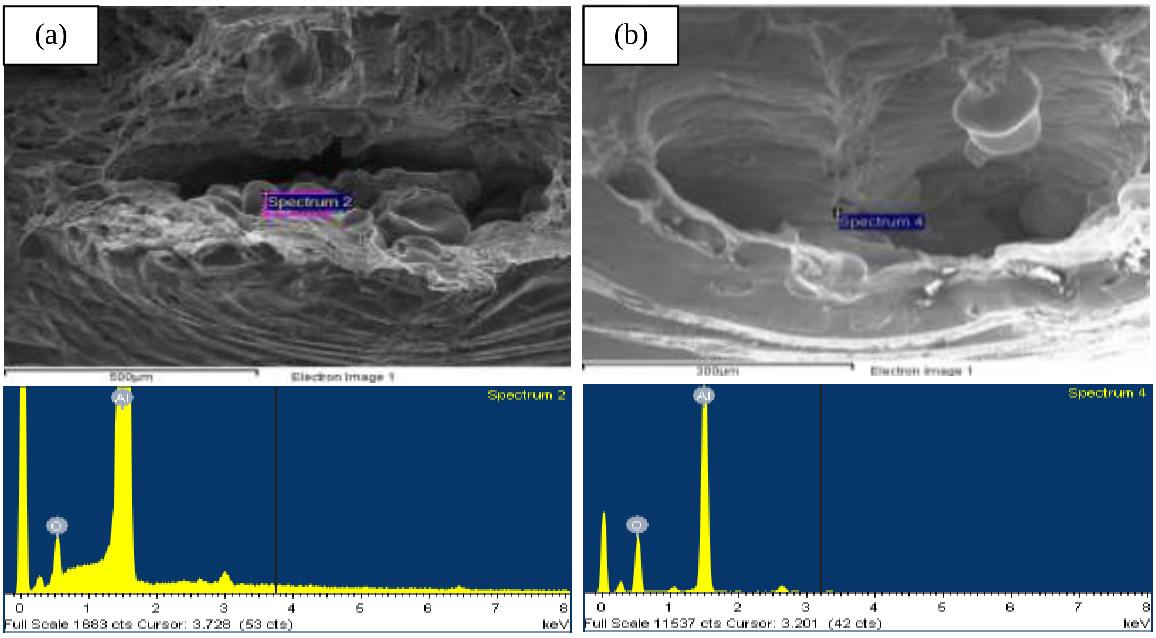

Figure 4. SEM images with corresponding EDX analysis of the fracture surfaces of Al alloy specimens illutrating pores containing oxide films of different ages, (a) zero min. and (b) 20 min.

Discussion

The ANOVA results presented in Tables 3 and 4, and Figures 2 and 3 suggested that holding an Al alloy in the liquid state for 20 minutes before solidification has no effect on the UTS of the casting. On the other hand, the holding treatment showed to have a slight inverse effect on the % elongation of the casting produced. Finally, the hydrogen content of the Al melt was found to increase by about 230% during the 20-minutes holding time.

In earlier studies by Raiszadeh and Griffiths [40] and El-Sayed et al. [32, 33], it was suggested that the interior atmosphere inside a bifilm could be consumed within a few minutes due to reaction with the surrounding liquid Al. This would reduce the size of bifilm defects and hence reduce their deteriorous effects on the mechanical properties of Al castings. In addition, it was also shown that the H soluble in the melt might diffuse into the bifilm gap, increasing its size to form a pore which disproves the properties.

The ANOVA results suggest that two gainsaying situations were taking place simultaneously during the holding of an Al casting in the liquid state prior to solidification and/or the solidification process itself (suggested earlier in a relevant work to take about 4 minutes [22]). The first situation was related to the reaction between oxygen and nitrogen within the bifilm defect with the contiguous melt which decreased their size and in turn enhance the mechanical properties of the casting. On the other hand, another action occurs which may be related to the amount of hydrogen picked up by the liquid metal from the surrounding atmosphere (that increased as the molten metal was spending more time in the liquid state before being completely solidified), and this would lead to a decrease in overall mechanical properties due to increased porosity.

It could be suggested that these two contradicting mechanisms during the holding treatment seemed to cancel one another which made the average values of the UTS of the castings with zero and 20-minutes holding times being almost the same (51 and 52 MPa, respectively).In addition, the second mechanism, related to H diffusion into the bifilm gap, looked to have a more harmful effect on the % elongation as the average values of the elongation of the Al castings decreased from 32% (solidified immediately) to 28% (held for 20 minutes before solidification).

These results is agreeing with the results by El-Sayed et al. [41] that suggested that holding different Al alloys in the liquid state for 20 minutes did not cause a significant improvement in the mechanical properties due to the increasing H content of the melt and hence an increasing H content of the defect and of the porosity size in the final casting.

The SEM investigation of the fracture surfaces of specimens with different holding periods detected many alumina films, as demonstrated by EDX analysis in the SEM, such films, were mostly associated with pores, (as shown in Figure 4, rather than lying on the fracture surfaces.

It was suggested by Griffiths and Raiszadeh [31], that hydrogen dissolved in the Al melt could diffuse into the bifilm causing its expansion into a pore, which might be subsequently torn apart (due to their extremely thinness) leaving only some oxide fragments inside the pores. Therefore, it could be speculated that these oxide-related pores may have been formed due to the diffusion of H from the melt into bifilms. This could be in accordance with the ANOVA results of that suggested a role for the diffused hydrogen into the bifilms in increasing the size of the defects and hence repealing any improving in the mechanical properties of the castings resulted from the consumption of the bifilm atmosphere.

To summarise, the change in mechanical properties suggest that bifilm defects, once formed, quickly undergo changes in their internal atmosphere which influence their effect on mechanical properties by influencing their size and shape. These changes are the consumption of oxygen and nitrogen in the bifilm atmosphere which reduce the size of the defects and then improves the properties, and the diffusion of hydrogen in the bifilms, increasing their size and making the properties worse.

Conclusions

1. SEM examination of the fracture surfaces revealed the presence of oxide films, most of them were associated with pores, which demonstrated a role for such defects in influencing the failure of Al castings.
2. Holding Al castings in the liquid state for 20 minutes before solidification did not cause any significant change in the UTS while cause a slight reduction (of about 12%) in the % elongation of the castings produced.
3. Bifilm defects in liquid Al alloys may have variable effects on casting properties, depending on their morphology (mainly size and shape). This morphology can be influenced by reaction their interior atmospheres with the surrounding melt, and diffusion of hydrogen into the defect. This could cause a planer crack to expand forming a pore.

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