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SURFACE FORMATION ON VDC CASTING

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Abstract

Surface Defect Characterisation

A range of surface defects commonly formed on vertical direct chill (VDC) cast products have been examined by various metallographic techniques. Whilst the presently accepted model for the formation of cold folds on the cast surface can be reconciled to the details observed in these examined samples, the suggested explanations for the formation of other common surface defects could not. This paper describes current research efforts aimed at measuring the strength of the molten aluminium alloy oxide skin under various conditions. This data is used as the basis for understanding the behaviour of the melt surface in the meniscus region of a VDC mould during casting. The results obtained from the surface skin strength tests and the metallographic examination of the cast samples are discussed and a framework of possible factors responsible for the formation of various surface defects is proposed.

Introduction

The surface finish and surface structure of VDC cast products is of critical importance to the downstream processing of such products. Despite technical advances, a large percentage of VDC cast products are scalped prior to further processing. Surface defects also result in variable, and at times, high percentages of cast product scrap. Advanced technologies such as air-pressurised casting of extrusion billets and reduced mould lengths for rolling block (LHCTM process) have been developed to improve surface properties of the cast product[1,2]. Despite such developments there is still no accepted explanation for the formation of each of the defects observed, except that for cold folds; and consequently, no accepted corrective procedures. The work described in this paper forms part of a project designed to formulate a coherent framework for understanding the mechanisms of surface formation in DC casting that includes the different defects observed. The paper describes the characteristic features of typical surface defects and the determination of some of the critical properties of the molten metal meniscus (surface tension and film strength). It is suggested that the formation of the surface defects occurs in this region of the mould (fig. 1).



Fig. 1. Schematic of hot top billet mould, showing position of meniscus.

Examples of a range of cast surfaces formed on VDC billets were obtained from a number of production plants. The samples included billets cast using a number of different technologies including the two main variants of gas pressurized casting (AirSlipTM and AirSol VeilTM), and also a range of billet diameters, alloys and casting conditions. Over 30 samples were examined. Typical cast surfaces that commonly form on VDC cast products are shown in fig. 2.



Fig. 2. Typical surfaces observed on the range of VDC cast billet samples examined. a) smooth to slight lapping: b) cold folding + lapping: c) "sand paper": d)" blebbing".

The surfaces were examined in detail using common macroscopic techniques. Metallographic samples were also taken from the surface region of the castings and examined by optical microscopy. The results obtained from these samples can be summarized as follows:

Regardless of casting technology used, diameter, or alloy, all samples had a surface layer that was significantly higher in solute than the bulk material. This layer is commonly referred to as a segregate layer [2,3]. (fig. 3).

The "segregate" layer varied in thickness from $\sim 50\mu m$ to $>500\mu m$. Generally the thickness of the segregate layer decreased with increase in surface smoothness. The thickness of the layer was relatively constant and continuous on the surface of each sample. The layer was also contiguous with the bulk structure, i.e., not marked by a boundary. When the surface finish changed from smooth to defective along the length of a billet, the thickness of the segregate band changed accordingly.

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In dilute alloys, e.g. 1050, 6063, the surface "segregate" layer was enriched in solute, with a predominance of iron/silicon, and, if present in the alloy, magnesium compounds (fig. 4). A 390 alloy had a surface layer that was eutectic at the surface versus hypereutectic for the bulk material. (fig. 5).



Fig. 3. Cast surface of 6063 alloy billet showing "segregate" layer.



Fig. 4. Cast surface of 6061 alloy billet showing compounds high in silicon, iron and magnesium at the surface.



Fig. 5. Cast surface of A390 alloy billet showing fully eutectic type microstructure at the cast surface.

The "sand-paper" finish (fig.2) is similar in macroscopic and microscopic appearance to the vertical drag type defect observed on cast product. The surface protrusions of both types of defect were high in solute, and at the completion of a cast, were often found on the curved surface that was the original meniscus during casting of the billet. (figs. 6 & 7).

No visual microstructural evidence of a solute depleted layer between the segregate layer and the bulk material was observed. Whilst cross section analyses have been reported in the literature [2,3], such scans have not been on the micro-scale required to detect differences in solute concentration over a 50 - 100 μ m boundary that would be typical of the samples examined. More commonly, spectrographic methods are used that clearly are incapable of resolving concentration differences on this scale.

"Blebby" surfaces often contained multiple layers of segregate, and usually showed a distinct band between the outermost layer and the next (fig. 8).

The curvature from the cast surface to the top surface formed on completion of the cast (fig 6 (b)), varied around the circumference of the billet, even though there was no evidence of cooling differences (as evidenced from the "cooling rings" left in the solidified top surface). This curvature difference of the original meniscus resulted in a height difference around the circumference of up to 5mm on a 178mm diameter billet ("X" fig. 6(b)). (a) (b)



Fig. 6. (a) Cast surface/top surface junction (meniscus region) of a 6063 alloy billet showing the ends of vertical drag and sand paper defects that extend down the cast surface of the billet.
(b) Schematic of cast surface/top surface junction showing curvature variation, X ~ 5mm (minimum to maximum distance).



Fig. 7. Section through a vertical drag nodule showing high concentration of solute elements. Similar microstructures were observed in surface nodules that made up a "sand-paper" surface.



Fig. 8. Surface structure of A356 alloy billet with surface blebbing showing multi-layer structure present, including segregation bands.

The generally accepted mechanism for the formation of cold folds on the cast surface, involves the progressive movement of the solid/liquid interface into the meniscus with inward contraction of the meniscus due to shrinkage contraction, to a point where the molten metal then overflows the thin solid skin, to form the fold. This mechanism is well illustrated by Bergmann [4] and again by Grandfield [3]. It is suggested that the cold fold formation is just an extreme example of meniscus movement and it is probable that the "lapping" and similar defects commonly observed are formed in a similar manner, by meniscus movement, although without overflow of the liquid metal. The general acceptance of the "cold fold" mechanism permits a reasoned approach to the correction, or prevention of this defect. A readjustment of the temperature balance through metal temperature, or cast speed, increase is all that is generally required, although rectification of lapping defects is often more difficult (less responsive to these changes).

When the metallographic structures present for the "sandpaper", "vertical drag" and "blebbing" type defects are considered objectively, it is difficult to explain these structures using the model whereby high solute, interdendritic material is exuded through the surface under the metallostatic pressure [5]. The thin shell formed during the initial solidification of the surface is ruptured and high solute, interdendritic material is exuded onto the surface. It is not disputed that this mechanism reasonably accounts for "bleed-outs" and some of the "blebby" surfaces observed on long length, open moulds, however, the defects shown in fig. 1 were all formed in short length, hot top moulds. Indeed, even some defects observed in longer length, open moulds possess features that also do not match the structure that may be expected from the defect being the result of exudation of interdendritic segregate. These features include segregation bands parallel to the cast surface (fig. 8) and definitive boundaries, e.g., fig 4 of Benum et al [5].

It is not disputed that the surface segregation originates from the solidification mechanism; what is questioned is the location of this segregation with respect to the solidifying interface and how it reports at the solid cast surface. A framework that reasonably links the above observations and others, described below, with the various factors acting in the meniscus region of the casting, is the subject of on-going work, including that described below.

Measurement of Surface Tension and Skin Strength

In order to improve the understanding of the factors influencing the formation of the surface defects, equipment was commissioned to measure the strength of the liquid meniscus by determining the surface tension and the strength of the oxide film on a molten drop of metal. The measurement of the surface tension of molten aluminium is known to be difficult due to the formation of an oxide film on the surface of the metal, even at high vacuum. This film is known to reduce the surface tension by ~ 10% [6,7]. Whilst a range of surface tension values are available for pure aluminium, very little work has been published on the effect of alloying elements on the surface tension [8]. The recently published work of Anson on AI-Si alloys modified with strontium, adequately details the difficulties involved in reproducibly and accurately obtaining such data [7].

Experimental Details

The present work on surface tension and skin strength measurement uses the sessile drop method in a similar manner to that described by Anson [7]. A series of alloys prepared from commercially available metals, were melted in an induction furnace and cast into bars that were then machined into cylindrical samples with rounded ends. Samples weighing 4 - 6 g. were etched in 5% HF, transported under acetone to a tube furnace operating at a vacuum of 1.3×10^{-5} Pa and transferred to an evacuated condition as quickly as possible. The sample, resting on a fused alumina plate coated with boron nitride, was melted and the temperature raised to T_{Liquidus} + 50°C (alloy liquidus temperature, measured with a thermocouple located adjacent to the surface of the drop), equilibrated for 5 minutes, then the meniscus shape was digitally recorded. Calculation of surface tension from the drop geometry used Bashforth and Adams tables, as described in the literature [6,7].

The standard sessile drop apparatus was further modified to permit an aluminium titanate probe (4mm dia.) to be inserted into the molten drop, with the probe being part of a lever system, including a sensitive load cell, to attempt to record the force required to penetrate and also to extract the probe from the drop. A schematic of the apparatus is shown in fig. 9. In addition to measurements under vacuum, which was used, not to try to exclude the effects of any oxide that may be formed, but to establish a constant experimental base, measurements were made in atmospheres of dry air, argon and nitrogen, and with the alumina plate coated with graphite.



Fig. 9 Schematic of Sessile Drop and Oxide Strength Apparatus (not to scale).

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The experimental procedure employed included; melting the sample in vacuum with minimum disturbance of the molten surface and recording the profile obtained. The probe was inserted into the sample and the drop distortion observed, plus surface adhesion to the probe as the probe was withdrawn. The signal from the load cell was recorded. The profile of the drop was again recorded, dry air admitted to the system and the drop profile recorded. Finally the probe was re-introduced into the drop and again profile changes and surface adhesion recorded. The reported results are the average of five samples for each alloy.

<u>Results</u>

The experimental work is on-going with the results from the sessile drop work providing the basis for further experimentation. The most significant observations made to date are summarized below:

The ability to obtain a uniform, or symmetrical drop shape on melting in vacuum and the "mobility" of that drop varied according to the alloy (table 1). Pure aluminium (99.999%) easily melted to a symmetrical drop and was mobile on the plate on which the drop rested, i.e., the drop would readily roll around should the apparatus be vibrated in any way. The drop often rolled off the plate, terminating the test. Some alloys required prodding with a probe and extensive agitation to achieve an approximately symmetrical drop (fig. 10) and the drop was immobile, even with considerable vibration of the apparatus. Drop mobility following admission of air also differed with different alloys. The type of coating on the alumina plate had no apparent influence on these properties.

Table 1. Observations made on sessile drops during the initial melting phase of the experimental sequence.

| molting phase of the experimental coduction | | |
|---|-------------------------|---------------|
| Alloy | Drop Symmetry | Drop Mobility |
| 99.999% AI | As melted | Mobile |
| 99.8% AI | Some agitation required | Just mobile |
| AI-Si, AI-Fe, | Agitation required | Not mobile |
| AI-Cu, AI-Zn | | |
| AI-Mn (0.5%) | Agitation + prodding | Not mobile |
| AI-Mn (>0.5%) | As melted | Not mobile |
| AI-Mg (<0.5%) | As melted | Not mobile |
| AI-Mg (>0.5%) | As melted | Mobile |
| AI-Cr, AI-Zr | As melted | Just mobile |



Fig. 10. Typical drop shape obtained in the "as melted" state showing a symmetrical drop on the left and a non-symmetrical drop on the right.

The term "surface tension" is applied to the description of the observed combined effects of the actual surface tension of the molten metal, plus the additive effect of any surface oxide film. It is acknowledged that all of the measurements made, were the sum effect of both components. The average value obtained for

99.999% AI under vacuum, of 1050 mNm, compares well to published values of 1050 - 1100 mNm [6,7,8].

The surface tension obtained after inserting the probe into the molten drop, was always lower than the as melted value, and for pure aluminium at 970mNm, was similar to published values for "oxidized" pure aluminium. This was attributed to the establishment of a stable, albeit thin, oxide film as the restricting and determining factor for the surface tension value obtained. On all of the solidified drops, oxide of a different colour outlining a "surface fracture" pattern was evident, suggesting that the probe fractured the initial oxide surface permitting a new skin to exert the major influence (see also for example fig. 13).

The surface tension obtained after admitting dry air to the system did not show a significant decrease. For most of the alloys, the change obtained was within the experimental accuracy. This was attributed to the fact that the probe had already broken the surface of the drop. Presumably any re-oxidation had already taken place, with additional exposure to oxygen having little effect. Admitting air did have the effect of changing the behaviour of the drop from mobile to non-mobile in most, but not all, alloys.

The effect of the re-introduction of the probe into the drop after admitting dry air into the system was variable. In some alloys the change was minor, whilst for others it was significant, e.g., 20% additional reduction in surface tension.

The most significant change in surface tension was obtained by the alloy additions, with iron and magnesium having the greatest effect. Magnesium reduced the surface tension to <40% of the value for pure aluminium "as melted". The surface tension results for alloying element additions of up to $\sim 0.5\%$, is shown in fig 11. The trends observed for different levels of addition of a particular alloying element varied, with some elements showing a continued reduction of the surface tension with increasing additions, whilst others suggested that minor amounts of the element (<0.5%) had the greatest effect, e.g., iron. Whilst only a limited number of ternary alloys have been tested, it is probable that one element will tend to exert an over-riding effect compared to the other element. This is evident in the Mg-Si combination where the effect of silicon appeared to predominate, resulting in a higher surface tension than the binary AI-Mg alloy. Fig 11 shows the results for the "as melted" and "after admitting air and inserting the probe" condition, being the two extremes of the results obtained for each alloy. The results for the "as melted" condition showed a greater variation than for the other three conditions, this being attributed to the effect of the probe on drop symmetry and uniformity of the skin. It is suggested that the "air + probe" results approximate practical casting conditions where skin rupture may be expected, with, of course, no vacuum protection.

Also included in Fig 11 are the preliminary results for several commercial alloys. These were "as melted + agitation" but without deliberate rupture of the surface. Of note is the difference in measured surface tension between 6063 and 6061 alloys with the latter containing a higher magnesium content, but more importantly chromium. The same observation applies to 7150 alloy that contains zirconium. The binary Al-Zr alloy in the as melted state has a relatively high surface tension and a strong oxide film. This effect may compensate the weakening effect of magnesium on the oxide film in these alloys.



Fig 11. Surface tension results obtained for some of the alloy systems and commercial alloys tested.

The colour of the oxide formed on the drop varied according to the alloying elements added. This aspect of the work is to be examined further using an SEM.

The results obtained from the measurement of the force needed to penetrate the drop by the probe, and again on withdrawal of the probe are yet to be analysed in detail. However when the force, as measured in mV is plotted against time (recording the time over which the probe is inserted and then withdrawn from the drop), markedly different behaviour for the different alloys was observed (fig. 12). It would appear that in some alloys multiple fracturing of the skin occurs as the probe is inserted, whereas for others, only one or two skin ruptures are recorded. In addition, it was possible to observe the distortion of the drop during insertion of the probe (fig. 13). The higher the recorded force required to insert the probe, the greater the drop distortion. This also correlated with the behaviour during melting as reported in table 1, where those alloys that required prodding and agitation to achieve a symmetrical drop exhibited larger drop distortion and a high probe insertion force.



Fig. 12. Load curves for three different alloys in the "as melted" condition.



Fig. 13. Drop distortion due to probe penetration (AI-Mn alloy). Cracking of the original skin is apparent.

Considerable variation was noted between alloys in the amount of skin adhesion to the probe as it was withdrawn from the drop.

Of particular note was the effect of magnesium on the formation and behaviour of the drop and the measured surface tension. At low magnesium contents (< 0.5%) a uniform drop shape was readily obtained on melting in vacuum but the drop was not mobile. At higher magnesium contents (>0.5%) the drop was not only mobile, but appeared to be unstable in terms of the surface tension. The drop left undisturbed would suddenly change from a low profile (low surface tension value) to a high profile. In addition, during the melting phase of the test, the sample melted in a completely different manner to all other alloys. The magnesium containing alloys melted by small blebs appearing on the surface (fig. 14) with these then expanding to join together, with the sample then collapsing into a molten drop. All other alloys slumped within an enveloping skin as melting occurred.



Fig. 14. An AI-0.5% Mg sample during initial stages of melting showing protrusions through the surface.

Discussion

Movement of the meniscus during casting, particularly in open mould VDC casting where observation of the molten metal surface is relatively easy, and in hot top VDC casting, has been reported previously [9]. Baker and Grandfield [14] linked the surface tension with the movement of the meniscus in a hot top mould and accounted for the gas escape in an air-pressurized mould causing the familiar bubbling or pulsing.

The results obtained from the surface tension work suggest that any segregation in the liquid metal in the meniscus zone may significantly affect the strength of the meniscus and hence the ability of the meniscus to withstand variations in the position of the solid/liquid interface at the surface of the casting. Should, for example, the point of solidification move downwards (due to a number of reasons e.g., cast speed increase, change in primary cooling, etc.) then the meniscus will be stretched and may rupture, particularly if the skin strength is reduced due to the effects of a concentration of alloying elements. The rupture may be minor, a bleb or "sandpaper" pimple, or it may be larger, resulting in a "bleb", for example.

In attempting to address the importance of the meniscus properties on the formation of surface defects the objective is to identify whether the defect formation is above the solid/liquid interface at the surface, or below (as per the "inverse segregation" model). Once this factor is clarified, then methods to correct or prevent the defects occurring may be realistically addressed. Important in this respect is not just the surface tension as classically measured (e.g. sessile drop), but the behaviour of the oxide skin that is formed and the influence this has on the strength and mobility of the metal meniscus. Other attempts have been made to measure the strength of the oxide film on molten aluminium with markedly different results being reported using different experimental techniques [11]. The present work attempted to measure the skin strength using a probe to pierce the skin, with the force required being measured by a load cell. Whilst the load cell used has a load range down to 5 grams, preliminary analysis of the results suggests that this may not be small enough to accurately distinguish and measure the effects visually observed. The load/time traces did suggest different film strengths, however full analysis of these results has yet to be completed. It is probable that more accurate measurement methods may need to be used, or novel methods devised.

The effect of magnesium on the skin strength is significant. Impey [12] reported that with magnesium contents >0.2%, the oxide formed is largely MgO, not Al₂O₃. At a later stage a spinel may be formed. Whilst no data was available it seems probable that MgO may be weaker than Al₂O₃. Further it is not just the overall strength of the film that may be important, but the plasticity of the film and hence the ability to withstand forces that may cause rupture. With magnesium containing alloys, rupture of the film either did not change (< 0.5% Mg) or increased (> 0.5% Mg) the measured surface tension. For all other alloys the effect was to reduce the measured surface tension.

The mobility property of the sessile drop and the possible influence on the meniscus properties is as yet unexplained. Ekenes [9] did refer to a mobile oxide film as being a necessary condition to produce a smooth cast surface. However, whether the two mobilities are the same cannot be confirmed in the static type tests conducted in the present work.

Good agreement with published values for surface tension was obtained for super pure and standard purity aluminium. However, the results obtained for AI-Si alloys and particularly for A356 do not agree with the results of Anson et al, [7] although results for "as melted" 0.5% and 4.3% silicon alloys are of the same order, i.e. ~850mNm. It is suggested that the use of the probe in the experimental sequence introduces a dynamics element to the results, rather than the very passive, undisturbed nature of the normal sessile drop experimentation. Limited published information prevents any other comparisons to be made.

Conclusions

Molten aluminium's surface tension is reduced by many of the common alloying elements. Magnesium has the largest effect,

followed by iron and silicon. Segregation of alloying elements was present at the cast surface of all of the VDC products examined. High solute concentrations were present in "sand paper", "vertical drag" and "blebby" type surface defects. The link to the formation of specific types of surface defects has yet to be established and further work is obviously necessary, including examination of the meniscus surface properties on the amount of primary cooling obtained, and the difference between a liquid surface resting on a substrate and one that is the melted portion of a solidifying casting. The influence of the atmosphere in the region of the meniscus, including volatized lubricant, may also be important.

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References

1. J.Faunce, A Valdo. The Air-slip $^{\rm TM}$ Casting Mould, Light Metals 1985. TMS, 1317-1330

2. F.Wagstaff, et al. *An Improved DC Casting Technology*, Light Metals, 1993 TMS, 709-714

3. J.Grandfield, P.McGlade. *DC Casting of Aluminium: Process Behaviour and Technology*, Materials Forum, 1996, (20) 29-51.

4. W.Bergmann, *Solidification in Continuous Casting of Aluminium*, Met Trans B, 1970, (1), 3361-3364

5. S.Benum et al, *Mechanisms of Surface Formation During DC Casting of Extrusion Ingots*, Light Metals, 1999, TMS, 737-742

6. T.Iida, R.L.Guthrie, *The Physical Properties of Liquid Metals*, (Clarendon Press, UK, 1988), 109-146

7. J.P.Anson et al, *The Surface Tension of Molten Aluminium and Al-Si-Mg alloy under Vacuum and Hydrogen Atmospheres*, Met Trans B, 1999, (30B), 1027-1032

8. B.J.Keene, *Review of Data for the Surface Tension of Pure Metals*, International Materials Reviews, 1993, 38, (4), 157-192

9. M.Ekenes, W.Peterson, Visual Observations Inside an Airslip Mould During Casting, Light Metals, 1990, TMS

10. P.W.Baker, J.F Grandfield, *The Role of Surface Tension Forces in Gas Pressurised VDC Casting*, Seventh Australian Asian Pacific Aluminium Cast House Conference, 2001, TMS, 195-204

11. W.Kahl, E.Fromm. *Experiments on the Strength of Oxide Skins on Aluminium Melts*, Z. Metall, 1984 (75), 957-962

12. S.A. Impey, The Mechanism of Dross Formation on AI. and AI-Mg Alloys, (PhD Thesis, Cranfield Inst. of Technology, 1989)