Proceedings of the 9th International Conference on Aluminium Alloys (2004)
Edited by J.F. Nie, A.J. Morton and B.C. Muddle

The Role of Surface Tension and Oxide Film Strength on the Surface Formation of Vertical Direct Chill Cast Products

I.F. Bainbridge, J.A. Taylor, A.K. Dahle

Cooperative Research Centre for Cast Metals Manufacturing (CAST)
Division of Materials, The University of Queensland, Brisbane, Queensland, 4072, Australia.

Keywords: surface tension, VDC casting, aluminium, surface formation, oxide films

Abstract

The surface tension of several aluminium alloys and the strength of the oxide film formed on them have been measured by the sessile drop technique and a modified-Wilhelmy plate method respectively. This paper describes the methods and equipment employed and the results obtained, with particular emphasis on the effect of alloy composition on these two characteristics. The results are applied to the development of an hypothesis for the formation of as-cast surfaces on vertical direct chill (VDC) cast product.

1. Introduction

The as-cast surface of a vertical direct chill (VDC) cast aluminium product (billet or rolling ingot) plays an important part in the subsequent processing of that product. Any defects in the surface section of the casting, which includes the microstructure adjacent to the surface, may impact on the surface finish and properties of the semi-fabricated product, and add to the overall process costs. The behaviour of the molten metal surface in the meniscus region within the VDC casting mould is thought to play an important part in the formation of some types of cast surface defects [1]. The meniscus region is the molten metal surface within the mould adjoining the solidifying section of the casting and projecting back to the point of metal entry into the mould (fig 1.).

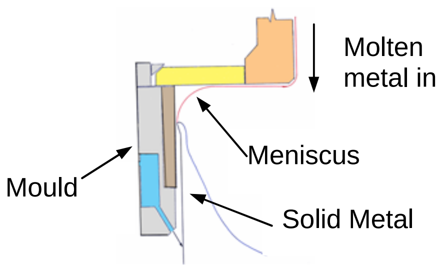

Figure 1: Meniscus region of the VDC casting system.

It is known that the formation of folds or laps on the cast surface is due to an unstable meniscus surface as a result of a specific set of solidification conditions [2, 3]. The mechanism responsible for this type of defect is generally understood and hence practical control procedures are relatively easy to implement. However, other forms of meniscus instability, or breakdown, may contribute to the formation of other types of surface defects, hence an understanding of the factors affecting the properties and behaviour of the molten metal meniscus is considered to be important. Properties that may influence the behaviour of the meniscus, "apparent surface tension" [1], and "skin strength", have therefore been subjected to closer investigation, particularly the effect of alloying elements on these properties.

2. Surface Tension/Skin Strength

The surface tension of a molten metal is defined as the surface free energy per unit area [4]. There are a number of methods of measuring the surface tension of liquid materials. One of the most common methods used for molten metals is the sessile drop method [5, 6]. The surface tension of pure aluminium has been measured by a number of investigators and these results were reviewed by Keene [7]. The surface tension of molten aluminium is significantly influenced by any oxide film formed on the surface of the metal [8] and this factor has to be taken into account in any measurement of the surface tension. Generally accepted values for the surface tension of pure aluminium are 1050 and 870 mNm for the un-oxidised and oxidised surfaces, respectively [7, 8].

Whilst the surface tension is generally taken to be a measure of the strength of the surface of the molten metal, it is a measure that does not easily relate to a molten metal surface in a mould (e.g. metal meniscus, Figure1), and the effect of contaminants, such as oxides, that may be on that surface. Kahl and Fromme therefore attempted to derive a measure of surface strength of such contaminated surfaces [9]. Although they developed two different measuring systems and reported results on both pure aluminium and commercial alloys, no attempt was made to relate the results to surface tension and cast surface properties.

The surface tension of pure aluminium has been well reported, however there has been little work carried out on the effect of alloying elements on surface tension, apart from the work of Anson et al. [10] who reported the results for alloy A356. Some work related to the preparation of molten metal composites at high temperatures (>1000°C) has also been reported [11], but this work is difficult to translate to the temperatures and conditions found in VDC casting.

3. Experimental Procedures

Initial experimental work used the sessile drop method to measure the surface tension, basically as outlined by Anson et al [10]. This work was sufficient to confirm both the published figures for 99.999% aluminium, and the influence of the oxide film on the surface tension values obtained. Although the work was performed in a vacuum of ~ 1.3×10^{-5} Pa, the variability of results and the diverse behaviour of samples under slightly different experimental conditions suggests that the static sessile drop method yields results that are difficult to extrapolate to practical casting conditions.

The experimental procedure was therefore modified to provide for a cylindrical aluminium-titanate probe to be inserted into the sessile drop, fracturing the surface in the process. This more dynamic form of surface tension measurement, similar to that of the Wilhemy plate method [4], may be more representative of surfaces formed in practice, where repeated rupture of the surface film is known to occur. The test apparatus and general

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[1] It is suggested that the property measured in the work described is not a true surface tension, as this cannot be determined under the experimental conditions used. The measured surface tension is a measure of the strength of the surface of the molten metal with that surface being modified by an oxide film, whether a simple or complex form.

procedure have been described elsewhere [1]. Samples were initially melted under vacuum (1.3 x 10^{-5} Pa), and the sessile drop profile recorded digitally for subsequent analysis. The probe, attached to a load cell via a lever system, was then slowly (~5mm/min) forced into the drop and the mV trace from the load cell recorded. The changed profile and general behaviour of the drop, including mobility [2] were also recorded. The above procedure was repeated subsequent to admitting dry air into the vacuum furnace. The load system was calibrated using known weights. At least five measurements were carried out for each alloy. The surface tension was calculated from the drop profile using the Bashford and Adams [12] system of geometric measurements and associated tables. The contact angle of the drop with the substrate (fused alumina, coated with boron nitride) was measured using imaging software. Finally, the colour of the solidified drop was recorded.

4. Results

The results obtained from each test represent four separate conditions: as-melted in vacuum; fracture and reformation of the surface under vacuum; molten drop exposed to dry air; and fracture and reformation of the surface in dry air. Figure 2 shows the surface tension results obtained for 99.999% aluminium and 99.85% aluminium, whilst Figure 3 shows the effect of iron and silicon additions to 99.85% aluminium on the surface tension.

The addition of magnesium to 99.85% aluminium also significantly lowered the surface tension, whilst the effects of Cu, Mn, Ti and Cr were less pronounced and dependent on concentration. The results obtained for some of the alloys tested are shown in Table 1.

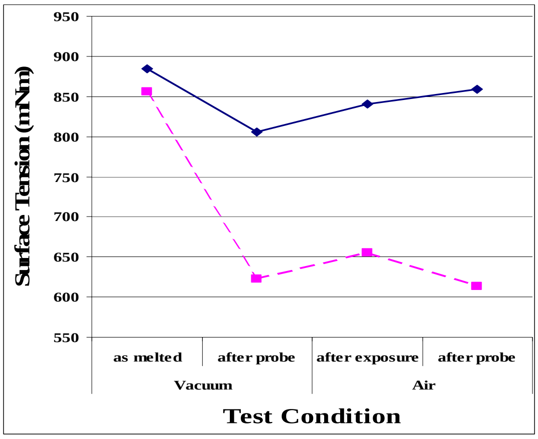

Figure 2: Average surface tension for 99.999% (solid line) & 99.85% Al.(dashed line).

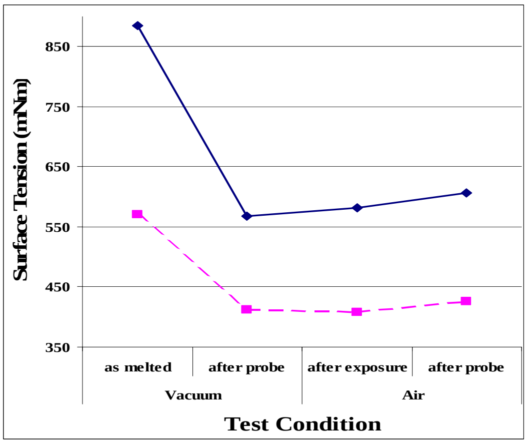

Figure 3: Average surface tension for 0.5% Si. (solid line) & 0.7% Fe (dashed line).

The strength of the surface film, as measured by the load required to force the probe into the drop, varied considerably with the type of alloying addition, and whether tested in vacuum, or air. Figure 4 shows load curves obtained for 99.999% aluminium, and an Al-0.5%Si alloy. The former shows one major load peak with one or two smaller spikes, whilst the latter shows a number of spikes. Many of the mV traces recorded for the other alloys tested were similar to the Al-Si alloy. The maximum pressure exerted by the probe (calculated from the load cell mV traces) to penetrate the skin of the drop is shown in Table 1. Table 1 also summarizes other observations such as molten drop mobility and solidified drop surface colour, for some of the alloys tested.

[2] Mobility of the drop is the propensity of the drop to roll across the surface of the plate on which it is resting, when the apparatus is subjected to minor vibration.

Table 1: Measured and Calculated Test Data for Selected Alloys

Alloy	Surface Tension {air + probe} (mNm)	Probe Pressure {vacuum} (mN/mm^2)	Drop Mobility {in vacuum}	Contact Angle {vac.+ probe}	Drop Colour
99.999%Al	859	1304	highly mobile	48°	dk. grey
99.8% Al	614	363	mobile	41°	dk. bronze
Al-0.5% Si	607	941	mobile	46°	dk. bronze
Al-0.7% Fe	426	784	mobile	42°	mid bronze
Al-0.5%Mg	341	1500	not mobile	48°	silver
Al-0.4%Cu	553	990	not mobile	44°	dk. grey
Al-0.5%Mn	422	1000	not mobile	51°	dk. bronze
Al-0.08%Ti	646	824	mobile	38°	silver grey
Al-0.06%Sr	348	1079	just mobile	52°	silver

All tests were carried out with the sessile drop resting on a fused alumina plate coated with boron nitride. The contact angle was found to be relatively constant for all of the alloys tested for the vacuum and initial dry air conditions, but the contact angle increased with the condition of dry air plus probe (Figure 5).

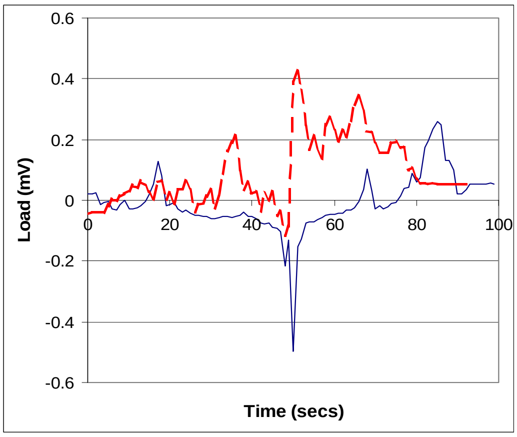

Figure 4: Plot of load vs time for 99.999% Al (solid line) & Al-Si alloy (dashed line) in vacuum.

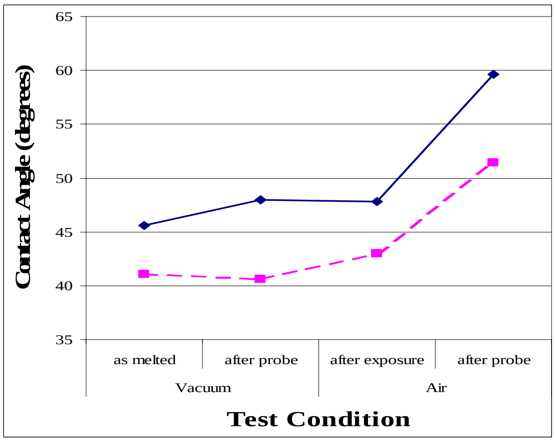

Figure 5: Average contact angles of sessile drops on BN coated Al_2O_3 substrate for various test conditions. 99.999% Al (solid trace) & 99.85% Al (dashed line).

5. Discussion

The surface tension results suggest that whilst the formation of the oxide film reduces the surface tension, once formed, any further exposure to oxygen does not appear to have any significant effect. The reduction in surface tension due to the formation of the oxide layer (~ 10%) is less than the reduction due to specific alloying elements (~ 60%). Iron, silicon and magnesium were all found to significantly reduce the surface tension. The presence of magnesium also affects the type of oxide formed on the surface [13], which may account for the low value obtained. Limited work on ternary alloys suggests that there is no additive effect on the reduction of surface tension by iron, silicon and magnesium. Al-Fe-Si alloys have surface tension values closer to the binary Al-Si alloy than to the binary Al-Fe alloy.

The Laplace-Young equation [4] (eq.1) describes the pressure differential across a surface (P) in terms of the surface tension (γ) and the radius of curvature in both the horizontal (R_1) and vertical planes (R_2).

$$P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (1)$$

For practical VDC casting, R_1 is much larger than R_2 and hence $1/R_1 \sim 0$. Ackerman et al.[3] related the height of the meniscus in the mould (b) to the surface tension (eq.2),

$$b = \sqrt{\frac{2\gamma}{\rho g}} \qquad (2)$$

where ρ is the density of the molten metal and *g* the gravitational acceleration. Based on these relationships, any variation in the surface tension of the molten metal will directly affect the maximum radius of curvature of the meniscus that can be maintained under the particular casting conditions. Any change in casting conditions that requires a larger radius may cause rupture of the meniscus and the formation of a surface defect. This effect may be localized (and differences in the radius of curvature around the circumference of a billet have been observed [1]), or it may affect the total circumference of the billet. A change in casting speed, sub-mould cooling conditions, or molten metal temperature, will move the point of solidification, i.e., the junction of the meniscus with the solid product (Figure1). Similarly, any change in the height of the molten metal (metallostatic pressure) feeding the mould will also change the maximum tolerable radius of curvature of the meniscus before rupture occurs. In addition, it is known that a solute segregate layer, high in Si, Fe, and if present Mg, exists on the surface of most VDC cast product [1]. Contrary to the currently accepted inverse segregation mechanism of formation, should this segregation rather originate at the interface between the meniscus and the solidified metal, it would be expected to have an adverse effect on the strength of the molten metal meniscus and hence the formation of surface defects.

The strength of the surface film, as measured by the force required to push the probe into the sessile drop, is also affected by the presence of alloying elements. The results, however, do not reflect the same trend as recorded by the surface tension measured in the conventional manner (compare columns 2 and 3 in Table 1). The significance of these differences is yet to be resolved. Whilst this procedure in the test sequence did provide an alternate measure of surface tension or skin strength, the main benefit was considered to be the creation of a test more representative of the dynamic conditions that exist during practical VDC casting. In addition, fracture of the initial film formed on the sessile drop reduced the standard deviation, with the value for the “as melted” condition being greater than that for any of the other test conditions. Further analysis of the probe load results is in progress.

The mobility of the sessile drop was affected most by the surface oxidation. Apart from 99.999% aluminium, for all other alloys tested, the sessile drop was immobile after the admission of dry air to the system. Ekenes et al. [14] reported that the formation of a smooth cast surface on “hot-top” VDC cast product, was dependent upon the surface film on the molten metal in the meniscus region being “mobile”. The exact connection between the mobility of the sessile drop and the surface film mobility in the meniscus area, and the effect of this on the formation of surface defects, is yet to be established.

Surface colour of the solidified drops varied with alloy composition (see Table 1). Colour may be related to oxide composition and thickness. Significant variations in the nature of the surface film may affect the heat transfer coefficient of the air/oxide interface in the meniscus region, which will then impact on the mould heat balance and the maximum radius of curvature of the meniscus that is stable.

6. Conclusions

The surface tension testing regime used in this work has reproduced published surface tension results for 99.999% aluminium and provided a test environment that was more representative of conditions in a VDC mould, where repeated molten metal surface rupture may occur. The significant reduction of the surface tension of molten aluminium by iron, silicon and magnesium provides for a possible mechanism for the formation of particular surface defects on VDC cast aluminium products. Work is in progress to verify these mechanisms and to derive approaches to minimize these effects.

Acknowledgement

The CRC for Cast Metals Manufacturing (CAST), was established by and is funded in part through the Australian Government's Cooperative Research Centre Scheme.

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