

OXIDE SKIN STRENGTH MEASUREMENTS ON MOLTEN ALUMINUM – MANGANESE ALLOYS WITH AND WITHOUT SALT ON SURFACE

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Abstract

The strength of the oxide skin on molten aluminum is important in many metal processing steps. Among others, it affects the surface finish of DC-cast ingots through the dynamics of the meniscus, feeding in low pressure die casting, and the yield of metal recovery when dross is processed.

This paper presents recent measurements of oxide skin strength on molten aluminum. The measurements were done on Al + 1%Mn and Al + 5%Mn, and are compared to earlier measurements on pure aluminum. Also the effect of a commercial salt mixture on the oxide skin strength on AlMn alloys is presented.

Introduction

Dross is a non-uniform mixture of aluminium metal and oxides where the metal content can be up to 90%. The dross is skimmed off the furnace and into dross pans. With rapid treatment of the dross, it is possible to recover some of the metal before the dross is shipped to other plants for processing. It is important to understand the dross formation and why it can encapsulate much metal. To help understand the process of dross formation, various characteristic of the dross must be measured. One such characteristic is the oxide skin strength on the molten aluminium. The author has earlier published work regarding measurements of oxide skin strength on various aluminum alloys [1].

It has been mentioned by some industrial remelters that manganese containing alloys seem to give increased dross formation. Therefore it was decided to measure the oxide skin strength on molten aluminium – manganese alloys.

Salt has for a long time been used in industrial melting furnaces for various melt treatment purposes. Dissolved elements such as sodium and calcium can be removed to a salt phase with the use of a proper salt mixture. One other important purpose (and relevant to this paper) is to use salt for reducing the amount of aluminium in the dross.

Considerable work has been published on the coalescence properties of aluminium and the influence of salt. Roy and Sahai studied the effect of an equimolar NaCl-KCl salt mixture without or with a long list of other chloride or fluoride containing salts [2] and found an improved effect of the various salt mixtures. Also Beson and co-workers [3] studied the effect of cryolite as addition to a NaCl-KCl salt and found that even 1% addition was enough to significantly increase the coalescence of aluminium droplets.

In this work the effect of addition of small amounts of salt to the melt surface during oxide skin strength measurements was studied.

Previous oxide skin strength measurements

The oxide skin strength has been measured earlier on some alloys where both alloy composition and temperature have had an effect [1]. Generally the oxide skin strength on molten aluminium was constant up to temperatures from about 710°C for pure aluminium (as shown in Figure 1) and to about 770°C for an alloy containing 11% silicon (see Figure 2), and then starts to increase linearly with temperature.

Figure 1 shows a measurement of the oxide skin strength on pure molten aluminium in contact with air as function of temperature. This measurement series is used as reference later in the paper.

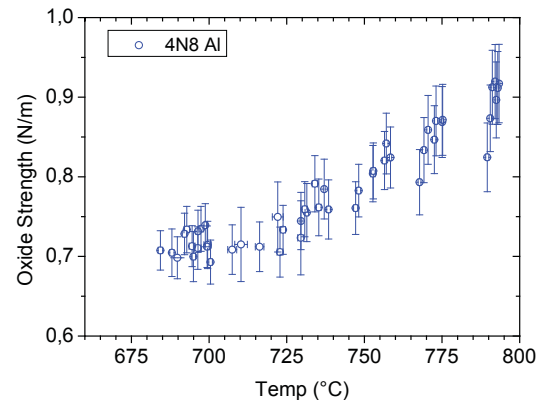


Figure 1: Measured oxide skin strength on pure aluminium (99.998 %) [1].

Not only the temperature affects the oxide skin strength. Figure 2 shows measurements on Al + 11% Si with and without 0.3% Mg. At lower temperatures, the oxide skin strength is significantly reduced due to the magnesium addition. This is probably due to formation of spinel in the oxide layer and hence reducing the mechanical strength.

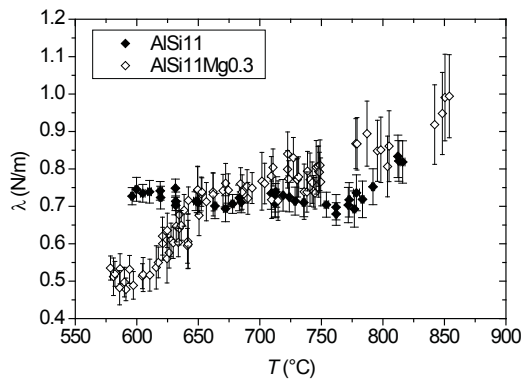


Figure 2: Oxide skin strength on an Al + 11% Si alloy with and without 0.3% Mg [1]. Remember that the liquidus temperature of these alloys is about 580°C.

Sodium is another element which has been shown to have large effect on the oxide skin strength.

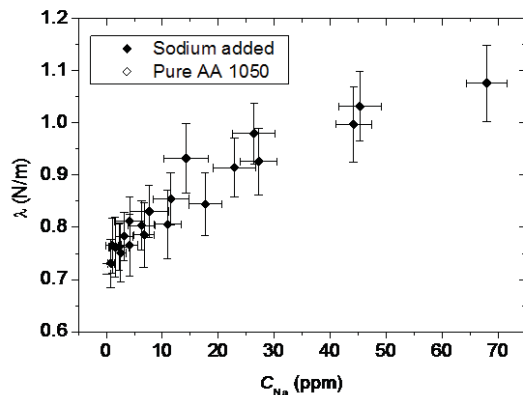


Figure 3: Oxide skin strength on industrially pure aluminium as function of sodium content. The temperature for all measurements was about 690°C – 700°C.

Experimental method

Principle of measurement

The apparatus was developed by Kahl and Fromm [4]. A sketch and a photograph of the apparatus are shown in Figure 4. In short, a cylindrical probe is rotated so the oxide skin is stretched between the probe and an fixed outer ring. When the force (torque) from the probe becomes too large, the skin around the probe breaks up. The torque is measured and the oxide skin strength is calculated by the use of the probe size and a calibration curve.

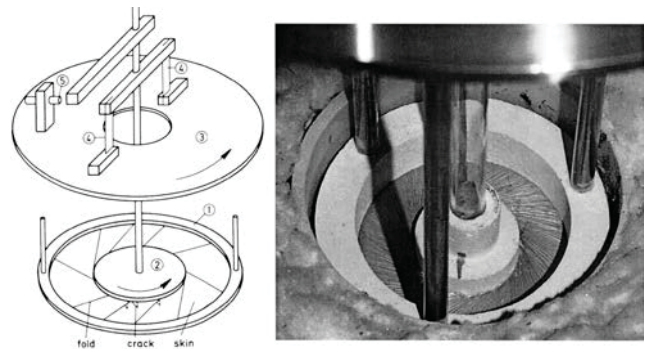


Figure 4: Schematic and close-up picture of apparatus for measurement of the strength of the oxide skin. The rotation was counter clockwise when the picture was taken, as can be seen by the stretch marks on the oxide skin.

Because the oxide skin strength is dependent on the temperature, a thermocouple is lowered approximately 10 mm into the melt through the stationary ring. The millivolt signals from the torque measurement system and melt temperature are logged by a Data-taker DT80 [5]. The logger is connected to a PC where the time series are displayed in real time. The sampling frequency is 1 Hz.

Measurement definitions

A typical measurement series is shown in Figure 5. The measuring probe is lowered onto the surface at time = 0.4 min. The probe is then started to rotate so the signal rises. The signal is constant until the rotation is reversed at time = 4 min. The rotation direction is reversed two more times before the probe is lifted from the surface at time = 13 min. There is some noise in the measurements from electric motor, gear-box, and cooling water.

When analyzing the measurement signal the oxide skin strength is calculated from half the distance between two plateaus as indicated in Figure 5. The uncertainty in a plateau value is taken to be the standard deviation of the measurements of that plateau.

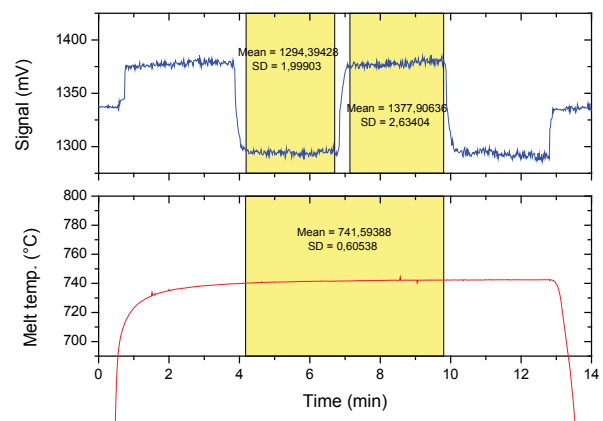


Figure 5: Typical measurement series on an aluminum alloy. The upper graph shows the voltage signal from the displacement probe and the lower graph the measured melt temperature. The mean and standard deviations are calculated within their own yellow areas.

Force balance

From a global point of view, the forces act tangentially on the rim of the probe; new surface should therefore ideally not be produced. However, as indicated in Figure 4, it was observed that small cracks in the oxide layer along the rim of the probe were produced continuously during the measurements. (See also Kahl [4] pp. 34 – 37.) This means that locally, the forces are acting perpendicular to the opening of the cracks.

The force, F , acting on the rim of the probe gives a torque, T , equal to

$$T = F \cdot R \quad (1)$$

where R is the radius of the probe. The relation between the measured oxide skin strength, λ , and the acting force is

$$\lambda = \frac{F}{2\pi R} \quad (2)$$

or in terms of the torque:

$$\lambda = \frac{T}{2\pi R^2} \quad (3)$$

By using the torque transducer T20WN from HBM [6] connected to the system, the voltage signal from the displacement probe is calibrated. The calibration data is shown in Figure 6.

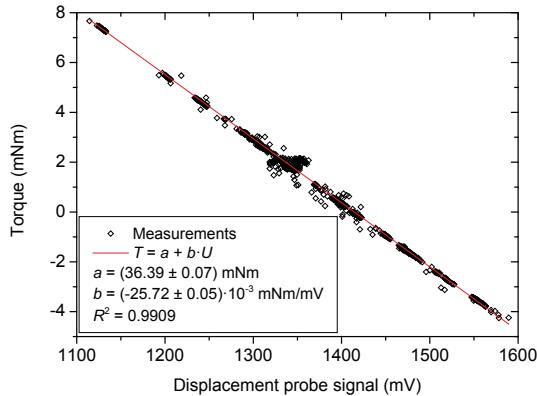


Figure 6: Calibration data for the displacement probe.

Using the slope in the calibration curve and a probe radius of 15 mm gives the relation between the measured signal and the oxide skin strength of:

$$\lambda = 9.097 \cdot 10^{-3} |U_1 - U_2| \quad (4)$$

where λ has unit of N/m, and U_1 and U_2 units of mV. As an example, considering the measurement series in Figure 5, $U_1 = 1294.4$ and $U_2 = 1377.9$ giving an oxide skin strength of $\lambda = 0.76$ N/m.

Measurement uncertainty

As shown in Figure 5, during measurements there are variations both in the logged voltage signal from the displacement probe and the measured temperature. These signal variations are used to give uncertainties in the oxide skin strength and temperature measurements respectively.

By considering propagation of errors [7], the uncertainty in the oxide skin strength is

$$\Delta\lambda = 9.097 \cdot 10^{-3} \sqrt{\Delta U_1^2 + \Delta U_2^2} \quad (5)$$

which in the example in Figure 5 gives $\Delta\lambda = 0.03$ N/m.

Experimental materials

Aluminium alloy containing 1% and 5% Mn was mixed in the laboratory using industrially pure aluminium and Al + 20% Mn master alloy. The aluminium and master alloy were melted and mixed in a small (about 20 kg aluminium) induction furnace which ensured good mixing before it was skimmed and cast into cast iron moulds. Samples for spectrographic analysis were taken from the melt prior to casting. The samples were analyzed at SAPA Heat transfer in Finspång, Sweden. The major components of the alloys are shown in Table 1. The content of Mn in the Al + 5% Mn alloy was too high for the spectrograph used for the analysis. However, the Al + 1% Mn alloy was produced and analyzed before the Al + 5% Mn alloy and the result was as aimed for. Therefore, it is assumed that the content of manganese in the Al + 5% Mn alloy is not far from the target.

Table 1: Spectrographic analysis of the alloys mixed in the laboratory.

	Al + 1% Mn	Al + 5% Mn
Mn (%)	0.989	> 3
Si (%)	0.09	0.057
Fe (%)	0.075	0.069

Before the measurements started, about 1.5 kg of alloy was melted in an electrically heated furnace. The furnace temperature was controlled by a thermocouple placed between the crucible and heating wires. The temperature used and presented in this paper was measured with a thermocouple placed about 10 mm below the outer ring as shown in Figure 4.

Figure 5 shows a typical measurement series. For a relatively pure aluminium alloy, it is possible to run the measurements for four plateaus before the probe has to be lifted from the surface and the surface is skimmed. Finally too much oxide granules will build up around the probe, giving increased noise in the measurements.

Salt additions

A commercially available salt for fluxing in furnaces was used to test the influence on the oxide skin strength. The salt was a mixture of 79% NaCl, 19% KCl, and 2% Cryolite (all given in mass %) and added manually to the surface. According to thermodynamic calculations with FactSage [8], the liquidus temperature of this salt mixture is about 740°C.

Results and discussion

Oxide skin strength on Al – Mn alloys

The oxide skin strength on the two alloys with 1% and 5% manganese was tested at temperature from 700°C and up to 750°C for the 1% Mn and up to 790°C for the 5% Mn. (The furnace used for the 1% Mn alloy was not able to go higher.) Figure 7 – Figure 9 show the measurements for both alloys compared to the oxide skin strength on pure aluminium.

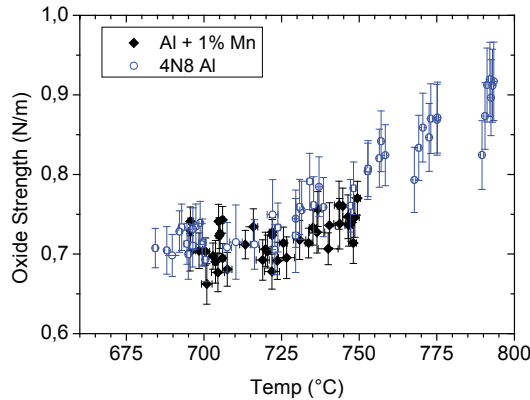


Figure 7: Oxide skin strength on aluminium with 1% manganese and on pure aluminium as function of temperature.

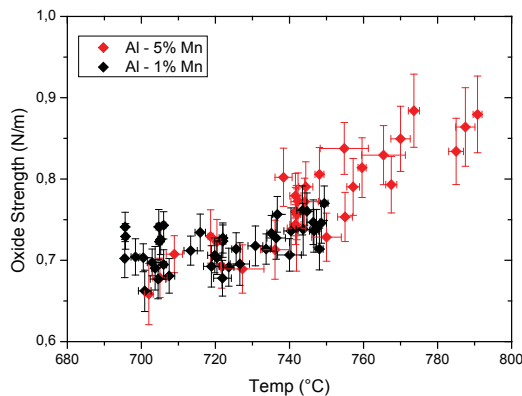


Figure 8: Oxide skin strength on aluminium with 1% and 5% manganese as function of temperature.

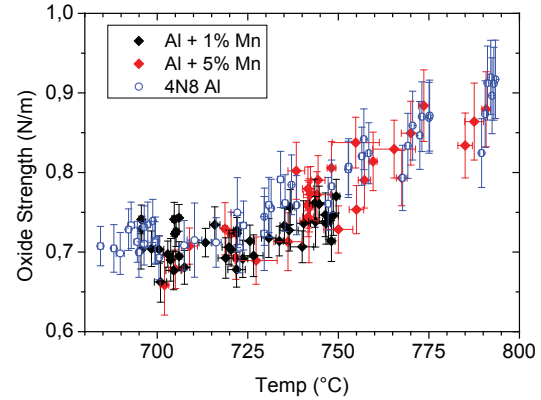


Figure 9: Oxide skin strength on aluminium with 1% and 5% manganese, and on pure aluminium as function of temperature.

There does not seem to be a significant effect of manganese addition on the oxide skin strength. If there is any affect, the manganese might reduce the oxide skin strength slightly.

The non-existing effect of manganese on the oxide skin strength is in good agreement with the oxidation rate experiments done by Shawn Wilson et. al. [9]. They melted the same alloys in a TGA (Thermo Gravimetric Analyser) apparatus and kept them at various temperatures and in various atmospheres and measured the weight gain. There was no dependency of the manganese on the weight change relative to pure aluminium. The oxidized samples were also analysed after the experiments and there was very little manganese present in the oxide.

Use of salt on the surface during oxide skin strength measurements

A small amount of salt was sprinkled manually on the surface during the oxide skin strength measurements. The amount was not absolutely fixed, and neither was the salt added perfectly in the same way from test to test. The addition procedure has to be refined in future experiments. The addition was done after a plateau of oxide skin strength measurement was reached. A result is shown in Figure 10. In order to melt the salt, the melt surface temperature had to be higher than 740°C.

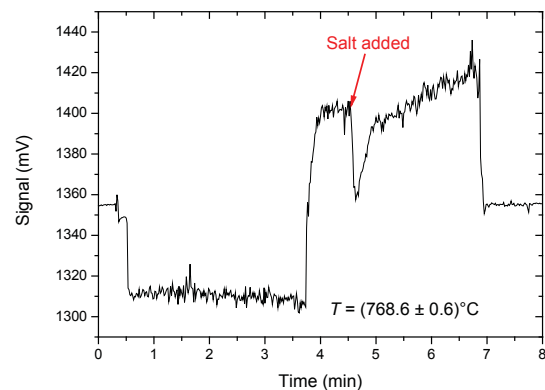


Figure 10: Typical oxide skin strength measurement with addition of salt.

In addition to the temperature, several more parameter are defined and discussed. These parameters are defined in Figure 11 – Figure 13

The minimum voltage signal, ΔU_{min} , is the voltage from a base-line (straight line from signal before and after the series) and to the closest signal right after salt addition as shown in Figure 11.

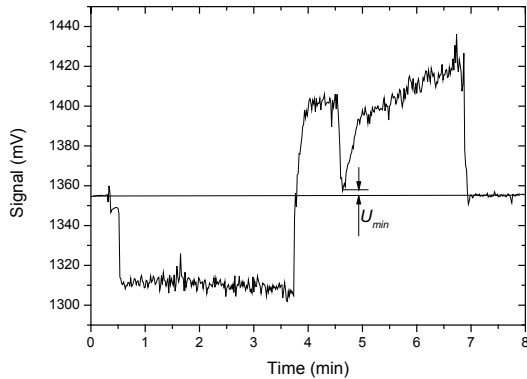


Figure 11: Definition of the minimum signal after salt addition, ΔU_{min} .

After the signal has dropped to the minimum value, it starts to increase with a constant speed. This is illustrated in Figure 12 where the slope S_1 gives the signal increase in units of mV/min. This increase is interpreted as a combination of diminishing of the salt effect on the oxide skin, and the regeneration of the original oxide skin strength.

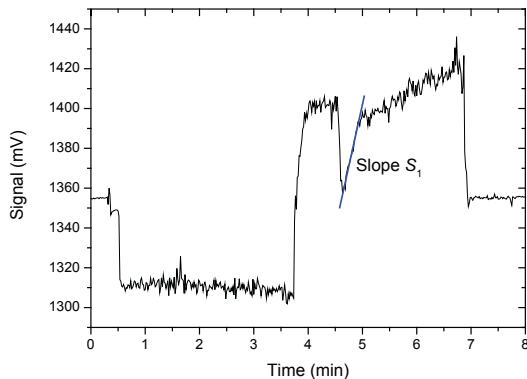


Figure 12: Slope S_1 is defined as the first increase rate of the oxide skin strength increase after salt addition.

During the experiment with the salt addition there always came a sizzling sound from the experiment immediately after the salt was sprinkled on the surface. This sound diminished within 20 – 30 seconds indicating that the effect of salt on the oxide skin decreases with time. This time length was not recorded specifically, but is corresponded quite well with the time length of the first slope.

After the first linear signal increase, the signal increases with a slower rate. This is shown in Figure 13.

It was observed that after every experiment with salt addition, some salt had solidified onto the probe during the experiment. This solidified salt had to be removed before a new measurement could be carried out. It is therefore believed that this second signal increase is a result of growth of salt onto the probe. In this work, the signal increase is calculated to an equivalent increase in probe radius per time with units of mm/min. This is supported by the expectation that as the salt dissolves aluminum oxide, the liquidus temperature of the salt increases.

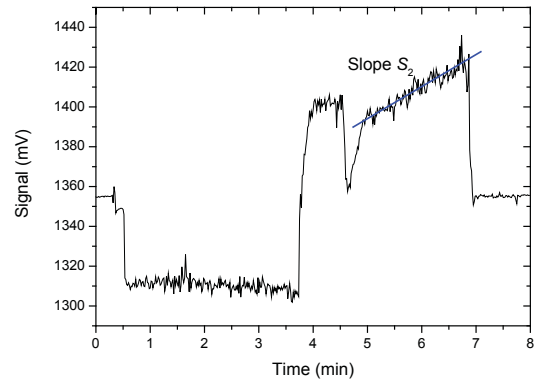


Figure 13: Slope S_2 is defined as the second increase rate of the oxide skin strength increase after salt addition.

It is also interesting to determine the time it takes for the oxide skin strength to regain its value as it was before the salt was added. This time, denoted t_0 , is illustrated in Figure 14.

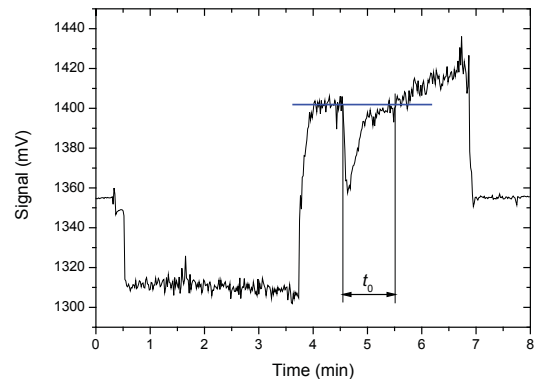


Figure 14: Time t_0 is defined as the time it takes from the salt was added until the oxide skin strength reached the same level as it was before the salt was added.

All the measured and derived parameters as defined in in Figure 11 – Figure 13 are given in Table 2.

Table 2: Measured and derived parameters from the experiments with the salt additions. See text and figures for explanation of the parameters.

Temp °C	ΔU_{min} mV	S_1 mV/min	S_2 mm/min	t_0 s
754	0.6	2.20341	–	24
754	7.1	0.98516	3.06	38
757.1	0.2	3.11209	3.042	70
768.6	2.8	2.24347	2.718	26
771.1	11.8	1.66075	2.052	65
773.7	5.6	3.174	3.33	59
774.6	4.2	2.11054	2.988	50
778.2	5.8	2.14514	3.006	60

The numbers in Table 2 were tested statistically to see if there were any correlations between them. The correlation coefficient matrix was calculated with the Origin 8.6 software [10] and is shown in Table 3.

Table 3: Correlation coefficient matrix calculated for all the measured and derived parameters given in Table 2.

	Temp	ΔU_{min}	S_1	S_2	t_0
Temp	1	0.243	0.232	-0.107	0.153
ΔU_{min}	0.243	1	-0.601	-0.607	0.118
S_1	0.232	-0.601	1	0.419	0.438
S_2	-0.107	-0.607	0.419	1	-0.058
t_0	0.153	0.118	0.438	-0.058	1

From the correlation coefficient matrix, there does not seem to be any clear direct correlation between any of the parameters, at least not within the range of them. The most significant correlations are between ΔU_{min} and S_1 , and between ΔU_{min} and S_2 , with coefficients of -0.6 for both. The correlation between ΔU_{min} and S_2 is easy to explain: Since the salt was sprinkled manually, with a varying salt amount, then more added salt may give lower ΔU_{min} and at the same time faster growth of salt in the probe (increased S_2). The negative correlation between ΔU_{min} and S_1 is somewhat harder to explain if the salt is not starting to grow on the probe already during the S_1 phase.

More experiments are planned to quantify the various effects and also better understand any correlation between them. In these experiments the method for adding the salt to the surface will be improved.

Conclusions

There is no statistical dependence of manganese content on the oxide skin strength. This corresponds with other studies that show there is virtually no trace of manganese in the oxide.

Salt addition to the surface reduces the oxide skin strength significantly. The effect seems to die out within short time.

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