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QUALITY COMPARISON BETWEEN MOLTEN METAL FROM REMELTED SHEETS; MILL FINISH AND COATED

Anne Kvithyld[1], Arne Nordmark[1], Derya Dispinar[2], Sara Ghaderi[3], Kyle Lapointe[1]
[1]SINTEF Materials and Chemistry, Trondheim, N-7465, Norway
[2]University of Istanbul, Metallurgical and Materials Engineering, Istanbul, 34320, Turkey
[3]University of Bergen, 5020 Bergen, Norway

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Abstract

Deterioration of metal quality caused by contamination (e.g. coatings) is an issue in remelting of aluminium scrap. Therefore molten metal quality from remelting sheet material with and without coating is compared. In the experiments the crucibles are placed inside a resistance furnace to ensure that the charges are melted under the same conditions at the same time, measuring temperature and hydrogen. The melts was subjected to (i) settling overnight (ii) blowing air through a porous plug for 2.5 min to generate oxides (iii) settle overnight and adding turnings and (iv) adding carbon. The bifilm index is used as a measure of metal quality. The results show a statistically significant difference in the quality of the samples comparing coated and non-coated for all the melt treatments (i) – (iv), even if the charge material only contained approximately 0.4 % coat.

Introduction

Gathering, sorting and processing of aluminum scrap are economically beneficial provided there is a high melting yield and high metal quality. Recycling saves energy and resources that otherwise would have been used to process new aluminum. Thus, recycling represents a precious component in the sustainability of aluminum.

As recycled materials often are contaminated with coatings, plastic and foreign elements, deterioration of melt quality is an issue. Contaminations also lower the metal yield.

Metal yield numbers are difficult to compare as they are affected by the melting technologies. However, in laboratory experiments [1] stacking of the aluminum plates in the crucible before heating gave reclaiming mass ratios 96%, for mill finished, 90% for flash anodized aluminum and 70% for coated materials. Laboratory experiments [2], where the aluminum plates were submerged into a molten metal pool, gave higher melt recovery. However, the coated materials show a much higher metal loss (6 %) compared to flash anodized and mill finished samples (both around 1%). In the same paper we also concluded that the quality of the mill finish material may be slightly better than the flash anodized and coated. More sampling is needed to support this conclusion. The focus in this work is the quality assessment of remelting clean versus contaminated scrap.

Theory- Statistical analysis

Previously, results are presented as the mean and standard deviation [1, 2]. In previous works, average ± standard deviation of measurements was calculated and if there were no overlap between the intervals, it was concluded that measurement means were different. This is not a reliable method since the error rate associated with this comparison is high [11]. Therefore a t-test was employed to investigate the quality difference of our measurements. A t-test is any statistical hypothesis test in which the test statistic follows a student's t distribution if the null hypothesis is supported. In this paper an unpaired t-test for two independent samples was used; equal variances were assumed. By applying the t-test we have introduced standard error in our results. The standard error is defined as:

$$\text{Standard error} = \text{Standard deviation} / \text{sqrt}(n)$$

Where n is the number of measurements. With help of this measurement we can produce confidence intervals which are defined as average (mean) ± standard error. This approach is beneficial since it provides information regarding the measure of central tendency (mean) and variability (standard error) in our experiments [12].

The null hypothesis in our t-test is that the molten metal quality is the same, choosing a 95% confidence interval, that is:

> If $P<0.05$, we reject the hypothesis that the two samples have equal quality, thus there is a statistical difference.
>
> If $P>0.05$, we accept the hypothesis that the two samples have equal quality, thus there is no statistical difference.

Where P is the probability of sampling the data we sampled (or more extreme) given that the null hypothesis is true.

The statistical package PASW Statistics 18 (SPSS Inc. 2010, Chicago, IL) and Excel were used to perform the t-test.

Materials and Methods

Material Characteristics

The remelted material was obtained from a 0.9 mm thick wrought 1050 coil; the composition of which is given in Table I. A protective coating was applied to the wrought aluminum. Samples of clean aluminum (uncoated surface) and coated aluminum were collected for this work. The coating thickness is approximately 0.004 mm on both sides. Its density is 1.21 g/cm^3, and is approximately 0.36 % mass of the aluminum sheets.

Table I: The chemical composition of wrought 1050 coils (wt%)

Si	Fe	Cu	Mn	Mg	V	Zn	Ti	Al
0.06	0.34	0.001	0.002	0.0007	0.01	0.005	0.01	99.5 (min)

Turnings from machining were collected from alloy AA6060-35. The turnings were covered with Omega 658 lubricant. Two thirds of the turnings were held at 300°C for 16 hours to dry.

The aluminum sheets and machine turnings were analyzed using thermogravemetric furnace. Circular samples from an Al sheet ~0.12 g, and turnings ~0.26 g, were heated in sintered alumina crucibles to a final temperature of 800°C. The samples were held for 7 and 4 hours for the Al sheet and turnings, respectively, at this temperature.

The thermogravimetric data from coated and uncoated aluminum sheets is displayed in Figure 1. Two parallel trials were completed for each sample type. The coated material has a mass loss mean value 0.09%, equivalent to the amount of coating evaporated. The coated sheets oxidized much less (+ 0.30 %) compared to the uncoated sheets (+ 0.80%). In addition, it should be noted that the variance in mass gain between the coated samples is, ±0.15% compared to only ±0.001% for the uncoated samples.

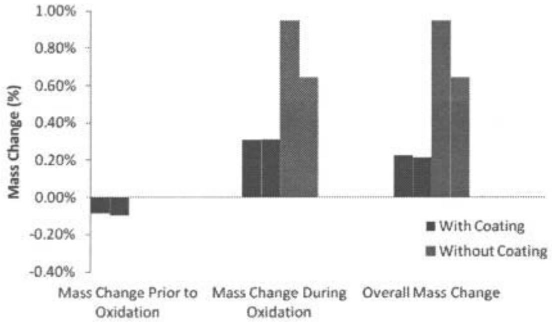

Figure 1: The mass change of the remelted aluminium with and without coating.

The mass changes with respect to temperature on dried and not dried machine turnings are given below in Figure 2. The dried turnings did not loose mass. From the thermogravimetric data, it seems that the lubricant composed approximately 0.32% mass of the turnings.

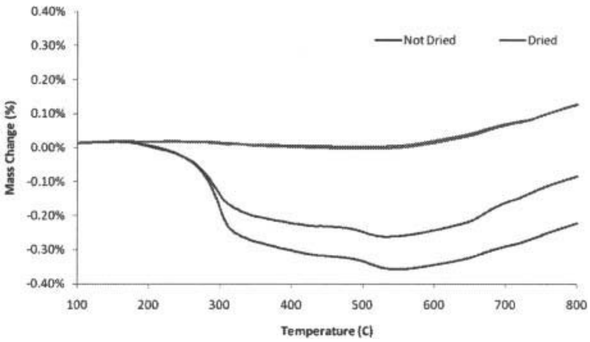

Figure 2: Mass change results of dried (two parallels) and not dried (two parallels) turnings.

Experimental Procedure

Before melting, the material was cut in 100 x 100 mm square sheets. The melting was performed in three crucibles shown in Figure 3. The crucibles were placed inside a resistance furnace that was preheated to 750 °C and held for the remainder of the experiment. 4 kg of plates were charged in each crucible. Uncoated sheets were charged in crucible 1, and coated sheets were charged into the remaining two crucibles (Crucibles 2 and 3) in order to check the reproducibility of the experiments.

When the starting material was molten, an additional 7 kg of sheets were charged into each crucible by dipping 5 sheets at the same time. The temperature in the molten metal was recorded continuously. During the experiments the temperature was 720 – 740 °C. After each treatment of the melts, hydrogen was measured with AlSPEK.

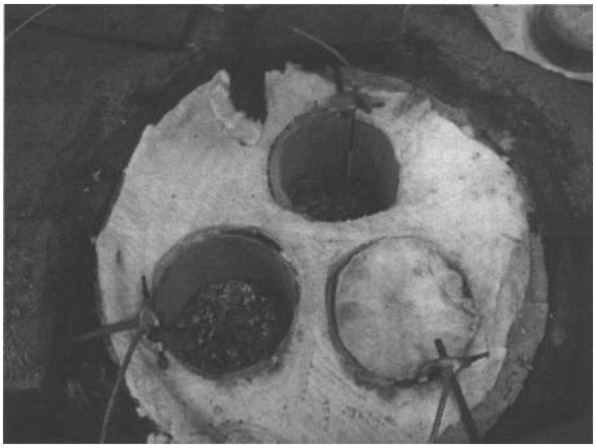

Figure 3: Three crucibles with molten aluminium from uncoated and coated sheets placed inside a resistance furnace to ensure otherwise equal conditions.

Below, the treatments in the three crucibles are listed:

(o) Once the melt initially reached a homogeneous temperature of 720 °C, 10 samples were collected via the reduced pressure test (RPT) for the purpose of a bifilm index measurement. For simplicity, these samples will be referred to as "Melting".

(i) The melt was then held 18 hours at 670°C. Another 10 samples were collected referred to as "Holding". Each crucible was recharged with 2 kg sheets by dipping 10 sheets into the melt at a time.

(ii) The melt was left for 18 hours and then purged with air for 5 minutes at a rate of 1.6 l/min. 10 samples were collected 5 minutes after purging and named "Gassing". The melt was again left for 18 hours and held at 670°C.

(iii) Aluminium turnings were added 50 g at a time, wrapped up in aluminium foil. A total of 250 g of dried turnings were added into crucibles 1 and 2. In crucible 3, 250 g of not dried tunings were added. After the melting completed, 10 samples were collected and named "Turnings".

(iv) Carbon powder was added 10 g at the time, wrapped in aluminium foil. The packages oxidized and had to be manually mixed into the melt with a ladle. After adding 20 g to each crucible, 10 samples were collected and named "Carbon".

Bifilm Index

To be able to measure the melt quality, samples were collected in pairs. Approximately 80g of molten aluminium was cast from a ladle into a sand mould with two compartments. The sand moulds were placed inside a vacuum chamber and left for 2 ½ minutes at 100 mbar absolute pressure. Vacuum conditions enhance pore formation in the metal. The samples are then machined with fine face milling to the centre. Image analysis is carried out on the surface analyzing the length and size of pores. The bifilm index [3] is given as the sum of the maximum length of the pores, giving a total length for a given surface area as seen in Figure 4. Bifilm index can be used as a measure of melt quality. Many studies have been carried out examining the bifilm index's relation to melt quality and have shown it to be a sensitive method [4-9].

As rule of thumb, a length of 10 mm is of good quality, 10 - 50 mm is satisfactory, and over 50 mm is poor quality. The rule of thumb for bifilm index is based on extensive research all summarized in [7].

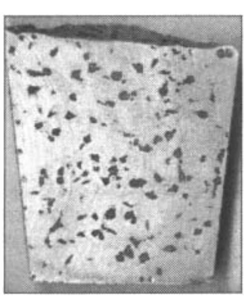

Figure 4. The sum of maximum length of the pores is measured to give bifilm index (40x55x15mm)

Results

The chemical composition of the melt did not change; that is the melt from the coated plates were not significantly different from the uncoated plates.

Tables' II to IV below, give the measured hydrogen content and temperature together with the mean, standard deviation and standard error of the bilfilm measurements for the remelted coated and uncoated sheets.

Table II: Summary of the bifilm results for crucible 1 (uncoated)

	Melted	*Holding*	*Gassing*	*Turnings*	*Carbon*
H_2 (ml/100g)	0.2	0.17	0.22	0.16	No Data
Temp (°C)	715	745	735	740	740
Mean	22.20	16.24	30.96	24.95	128.05
Std. Dev.	9.97	7.19	18.64	21.11	28.32
Std Error	3.15	2.27	5.89	6.68	8.95

Table III: Summary of the bifilm results for crucible 2 (coated)

	Melted	*Holding*	*Gassing*	*Turnings*	*Carbon*
H_2(ml/100g)	0.19	0.2	0.22	0.18	No Data
Temp (°C)	715	740	735	735	735
Mean	43.40	112.86	159.16	67.21	61.05
Std. Dev.	29.56	79.99	110.51	34.82	47.18
Std Error	9.35	25.30	34.95	11.01	14.92

Table IV: Summary of the bifilm results for crucible 3 (coated)

	Melted	*Holding*	*Gassing*	*Turnings*	*Carbon*
H_2 (ml/100g)	0.2	0.22	0.22	0.21	No Data
Temp (°C)	720	750	735	740	740
Mean	70.47	47.82	153.86	77.57	79.48
Std. Dev.	43.00	13.73	92.73	63.21	33.18
Std Error	13.60	4.34	29.32	19.99	10.49

As seen in the above tables, there is generally a large variance in the bifilm measurement results. The results are graphed with standard error and shown in Figure 5.

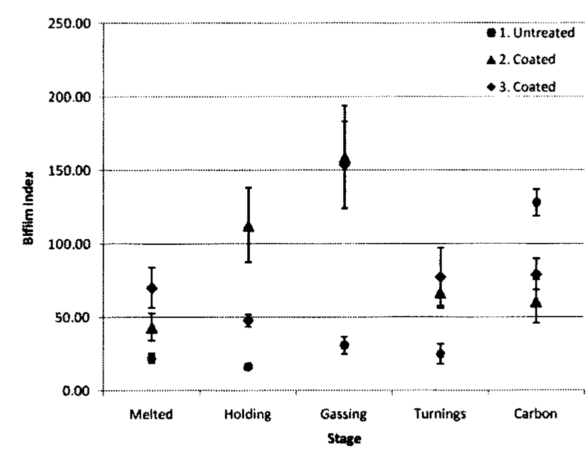

Figure 5. The bifilm index results for uncoated and coated aluminum together with the mean and standard error.

As seen in Figure 5, the confidence ranges do not overlap for the uncoated and coated samples. Both the coated samples (crucibles 2 and 3) show overlapping error bars for the gassing, turnings and carbon stages.

To statistically compare the relationship of melt quality and stages – student t-tests were performed. The results from a t-test comparing the three crucibles are shown below in Table V. Both, Excel and SPSS produced the same P values.

Table V: The P value from the t-test comparing the three crucibles bifilm index at the various treatments.

	1 vs. 2	1 vs. 3	2 vs. 3
Melted	0.046	0.003	0.118
Holding	0.001	0.000	0.021
Gassing	0.002	0.001	0.909
Turnings	0.004	0.022	0.655
Carbon	0.001	0.002	0.326

There is a significant difference in the quality between uncoated and coated aluminum coils. However, crucibles' 1. (uncoated) vs. 2. (coated) produced P values are near the 0.05 limit.
There was no significant difference in the quality between the two crucibles containing the coated aluminium, except for the "Holding". Crucibles' 2 vs. 3 "Holding" gave a P value of 0.021(<0.05), indicating that the melts are not of equal quality. However, the data suggests that all other treatments for the two coated sample indicate the melts are identical. We will therefore in the following sections combine the coated samples as one sample pool.

A summary of a t-test comparing treatments and melt quality is given in Table VI. Note that each stage has been compared to the previous stage, i.e. "Gassing" compared to "Holding" and "Holding" compared to "Melted". However, "Turnings" were compared to "Holding" as the melt was left over night after purging with air. The dried and not dried turnings showed no significant affect on quality and are combined into one sample pool.

Table VI: Results from the t-test comparing the treatments for the uncoated and coated aluminum

	Melted vs. *Holding*	*Holding* vs. *Gassing*	*Holdings* vs. *Turnings*	*Turnings* vs. *Carbon*
Not coated	Equal	Not Equal	Equal	Not Equal
Coated	Equal	Not Equal	Equal	Equal

The results show that between melting and holding stages, the molten metal quality does not change significantly. Purging with air lowers the quality of the melt. Adding turnings to the melt causes no significant changes after "Holding". From Table II it is seen that adding carbon to uncoated aluminum causes a lower molten metal quality, whereas adding carbon into the coated crucibles has no significant impact.

No significant difference was found in the order of pouring of the paired samples in the sand mould in all instances.

Discussion

Taking representative samples from a 10 kg non-homogeneous melt are challenging; our sample sizes are limited to approximately 80g. The large spreads of bifilm indexes between our paired samples highlight this effect.

However, since we managed to find a significant difference in the data, our t-test the sample size is fine. There exists no rule of about how many measurements are needed. In the case of more than 60 measurements one can assume normal distribution. (not the our case).

Bifilm index results of the uncoated coil material are given in Figure 5. The experimental setup appears to be successful. The fact that we obtain similar results for two crucibles containing coated aluminum indicates that our experimental setup is robust.

The procedure by submerging seems successful in entraining the oxide and coating film on the surface. There was no need to skim metal from the crucibles.

There was a large variation in bifilm index between the coated and uncoated aluminum. The coated aluminum consistently produces larger bifilm index compared to the uncoated aluminum. This large difference is surprising as the charge material only contained approximately 0.4% mass of coating. Overall, the untreated aluminum displays good bifilm quality, with small standard error.

An increase in bifilm index is especially present after purging in air; the coated sample index increases to 157 mm, which is poor quality. To compare, the uncoated sample has a bifilm index of 31mm after the same treatment. In both cases, the purge rate of air was 1.6 L/min. This rate is quite low and may not cause any disturbance on the surface. No splashing or violent stirring was observed during the gassing procedure. The mean bifilm index value before purging was 64 mm for the coated molten metal pool compared to 16 mm. This may be the reason for the large difference.

Based on coating thickness and density the amount of coating is approximately 0.36% of the sample mass, yet, in our experiments, the measured mass loss due to coating gasification only amounted to 0.09%. This discrepancy is most likely residual carbon left from the coating. In other studies, carbon on the surface significantly reduced mass gain due to oxidation [10]. This may also explain the low mass gain during oxidation of the coated samples shown in Figure 1.

After 18 hours of holding, the bifilm index drops for the uncoated melt from 22 to 16 mm; this change is not statistically significant (p =). The same treatment resulted in an increase of bifilm index from 57 to 80mm for the coated aluminum, which is also not statistically significant. There are two possible events that can take place during holding: (i) oxides may sediment to the bottom of the furnace, or (ii) float to the surface. These effects are highly dependent on density differences, as well as convection in the melt.

Interestingly, there was no effect of addition of dried or not dried turnings to the molten melt quality compared to holding (Table VI). Comparing the hydrogen content reported in Table's III and IV, there is a slight increase in the melt with not dried turnings: 0.18 compared to 0.21 ml/100g of H_2. The lubricant on the turnings seem to increase the hydrogen content of the melt.

Carbon addition had the greatest effect on the bifilm index of the melt, increasing it from 31 to 128 mm in the uncoated molten metal pool. Carbon addition did not seem to affect the bifilm index, which remained around 70 mm for the coated aluminum. The procedure in adding carbon involved manual stirring, which is difficult to reproduce consistency. These effects need further investigation.

Conclusions

The bi-film index can be used to investigate parameters that effect molten metal quality, such as coatings and melt treatments. Use of the bifilm index in the present experiments indicates that:

1. There is a statistically significant difference in the molten metal quality between remelting uncoated and coated aluminium. The coated aluminum consistently produces larger bifilm index compared to the uncoated aluminum.

2. Purging with air lowers the quality of the melt.

3. Holding the melt and adding turnings did not cause a significant change of quality in the melt.

4. Adding carbon to uncoated aluminum lowers the molten metal quality. Adding carbon into the coated melt has no significant impact.

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