

# Light Metals 2011

**CAST SHOP for  
ALUMINUM PRODUCTION**

**Dross Formation, Control and  
Handling**

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## OXIDATION OF AlMg IN DRY AND HUMID ATMOSPHERES

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### Abstract

Thermal oxidation of Al5%Mg was carried out in dry and humid atmospheres with a thermogravimetric analyzer (TGA), and the composition of off-gases was measured with a mass spectrometer. It was found that when water vapor participates in oxidation, hydrogen gas is produced. A humid atmosphere (7 mol% H<sub>2</sub>O) does not affect total oxidation mass, but seems to catalyze oxidation in both air and air containing 5 mol% CO<sub>2</sub>. In an air atmosphere containing 5 mol% CO<sub>2</sub>, total oxidation is approximately 50-75 % less than in air alone. Some samples in humid air (7 mol% H<sub>2</sub>O) containing 5 % CO<sub>2</sub> did not oxidize significantly, which may be due to a strong oxide layer which forms around the liquid aluminum sample. A carbon powder coating was shown to protect the aluminum from oxidation for an extended period of time compared to an unprotected sample and humidity extended this protection. This work has potential applications in industrial thermal decoating units.

### Introduction

In aluminum (re)melting, the formation of oxide i.e., dross, reduces the yield. The formation of dross is higher in a hotter melt, due to increased oxidation. The effect of humidity and carbon residue on oxidation is examined.

Aluminum is lost not only by oxidation, but also from the large metal content of the dross [1,2]. The high oxide strength [3] allows for pure liquid aluminum to be trapped within the dross during skimming. If the formation of dross can be minimized, recycling yields increase.

Some recyclers use a thermal decoating process, which consists of two stages; (i) evaporation of the volatile organic compound leaving carbon residue behind and (ii) reaction of this carbon with oxygen in the atmosphere [4]. Carbon powder is used to simulate carbon residue during oxidation.

Aluminum-magnesium alloys are known to oxidise more readily than pure aluminum [5,6] and are investigated in a TGA with humidity control and a mass spectrometer.

Attention has been given to the work of Impey, whose thesis contains an impressive literature review, including work by Thiele on the nature of aluminum oxide formation and growth [7,8]. Thiele's review gives an overview of the fundamental research which has been conducted, as well as more complex systems of oxidation. Thiele points to the inherent difficulty of studying aluminum oxidation.

Surface finish has an effect on the oxidation of aluminum, as reported by Aziz and Godard [9]. Oxidation increases on a

machined surface as compared to a surface polished with 600 grit emery paper because of a larger effective surface area.

### Material and Sample Preparation

The composition of the alloy oxidized (Table I) was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Table I. Composition of Sample Material.

Element	Quantity [wt%]
Mg	4.62
Si	0.07
Fe	0.25
Mn	0.33
Ti	0.02

The samples were machined into discs from a large ingot of the alloy. Table II contains the average dimensions of the samples after final preparation. It is assumed in this work that the effective surface area is the same as the geometric surface area because 1 micron polish gives a flat surface. This assumption is validated by experimental data gathered by Cochran and Sleppey [10].

Table II. Important Sample Dimensions.

Dimension	Average Value	Standard Deviation
Diameter	7.98 mm	0.02
Thickness	1.93 mm	0.03
Surface Area	148.5 mm <sup>2</sup>	1.0
Mass	257.4 mg	1.60

Electric discharge machining was used to form the sample discs. This technique was necessary as the material was too soft for mechanical machining at the small size required.

To clean the samples and homogenize the surface, manual grinding and polishing down to 1 micron was carried out. Between each grinding and polishing stage, the samples were cleaned with soapy water and rinsed with water, ethanol, and acetone, then dried. In order to keep the samples cylindrical, only the top and bottom surfaces were polished; the sides were left as-machined.

The samples were wrapped in lens paper to protect the polished surface, rather than isolate the samples from humidity. The time between sample preparation and experimentation varied between several hours and several days.

Samples were photographed, measured, and weighed before each experiment, to determine the change which occurred during

oxidation. Figure 1 shows a sample as machined, after polishing, and after oxidation.

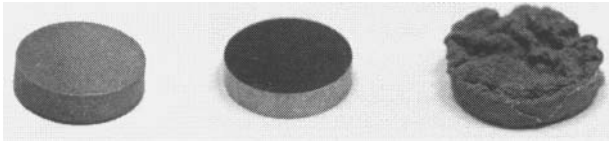


Figure 1. Sample progression; as machined, as polished, and after oxidation.

The preparation of the samples is a source of error in this work. The samples were ground using SiC abrasive paper, so SiC particles were most likely embedded in the soft aluminum. It is unknown whether the SiC particles affected oxidation of the aluminum, but SiC oxidation was assumed to be insignificant at the temperatures of this work. The ethanol and acetone used to clean the sample may have affected oxidation behavior.

For experiments conducted with a carbon coating, Thermax® Powder Ultra-pure N991 was used. The powder was applied manually by rubbing the surface with small amounts of the powder using tweezers. The powder did not adhere well to the polished surfaces, so unpolished samples cut with a band saw were used. It was important to use only carbon powder without an adhesive agent, such as ethanol, to avoid contamination of the off-gases.

### Apparatus

To study the effect of atmosphere on the oxidation of aluminum, a Setaram Setsys 2400 TGA, coupled with a Setaram Wetsys humidity generator and Pfeiffer Quadrupole mass spectrometer was used. The TGA measured the mass change of a sample with respect to temperature and time. More in-depth descriptions of the fundamentals of TGA can be found in Brown [11] and Speyer [12].

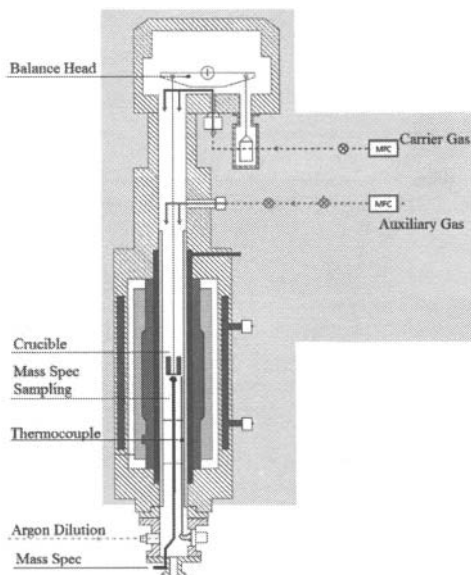


Figure 2. Schematic of TGA Apparatus.

A schematic of the TGA apparatus is shown in Figure 2. The carrier and auxiliary gases come from a common source and have identical compositions. The dry carrier gas flows through the balance head (10 ml/min) to protect the balance from exposure to humidity and mixes with the auxiliary gas before passing through the furnace tube and around the sample. The auxiliary gas passes through the WetSys apparatus (50 ml/min) and flows into the TGA above the furnace tube, giving identical flow patterns for dry and humid atmospheres. The mass spectrometer samples gases from just below the sample crucible in the furnace tube. 100 ml/min argon is introduced at the furnace outlet, diluting the humid gas to prevent condensation.

The interior of the furnace and gas flow patterns is shown in Figure 3. Note that sizes are approximate.



Figure 3. Diagram of the sample within furnace tube.

The top surface of the sample was assumed to be the most active surface, but the sides of the sample are clearly exposed and oxidation was also present on the underside of the sample.

### Experimental Procedure

The prepared samples were measured and weighed before oxidation. Three measurements of the diameter and thickness are taken with a Vernier caliper and averaged. These measurements were used to calculate the surface area. The initial and final masses of the sample were obtained by weighing the sample crucible with the sample and subtracting the mass of the empty sample crucible. It was assumed that the crucible mass would not change during an experiment.

For carbon coated samples, the amount of carbon used was determined by weighing the sample before and after coating, as well as the carbon powder itself. The two values were averaged, giving an approximate mass of carbon on the sample.

Alumina crucibles, 10 mm tall with a 12 mm inner diameter and a 0.75 mm wall thickness were used, connected to the balance with platinum suspension wires. With each run, some oxidized material remained in the crucible that could not be cleaned out. This material accumulated in the crucible and fused to the sample which prevented it from being removed, approximately every four runs. New crucibles were used when the sample could not be removed from the old crucible.

The sample and furnace chamber was evacuated and backfilled with argon before beginning each experiment.

Samples were heated in the atmospheres shown in Table III. The air used was synthetic air, not ambient air.

Table III. Oxidation Gas Compositions, mol %.

Atmosphere	Ar	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
Argon	100	-	-	-	-
Humid Argon	93	-	-	-	7
Air	-	21	79	-	-
Humid Air	-	19.5	73.5	-	7
Air + CO <sub>2</sub>	-	13	82	5	-
Humid Air + CO <sub>2</sub>	-	12.1	76.3	4.7	7

The sample was heated at 30°C/minute up to 800°C and held for 4 hours. The holding time of 4 hours was chosen based on preliminary results from oxidation of a similar aluminum alloy. After 4 hours, the sample was cooled to room temperature at the maximum rate allowed by the furnace, approximately 50°C/minute.

Figure 4 shows the temperature and humidity profiles used in the experiments.

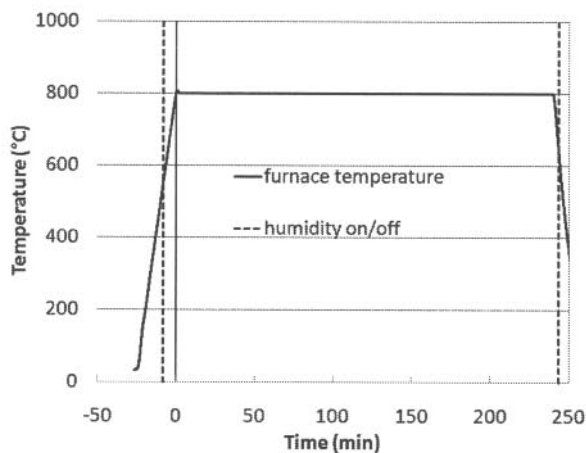


Figure 4. Temperature profile. Time zero is the beginning of the 800°C isotherm.

The solid line shows the temperature profile, while the dashed lines indicate when the humidity is switched on and off. Humidity reached the desired value shortly after being switched on, effectively instantaneous for the time scale of the experiments. Time zero was chosen at the beginning of the 800°C isotherm.

At -8 minutes, when the sample was at approximately 550°C, the humidity was switched on. This was done before the start of the 800°C isotherm because it was found that oxidation occurred before the holding temperature was reached. Humidity was not introduced at the beginning of the experiment as the water would condense, damaging the delicate balance head. The humidity was switched off during cool-down of the furnace before the dew point of the gas was reached.

Baselines were run for each atmosphere with empty crucibles, and were subtracted from sample runs to isolate sample oxidation data.

### Results and Discussion

The off-gas was monitored for hydrogen during oxidation in humid argon. The correlation between mass gain and hydrogen production is evident (Figure 5).

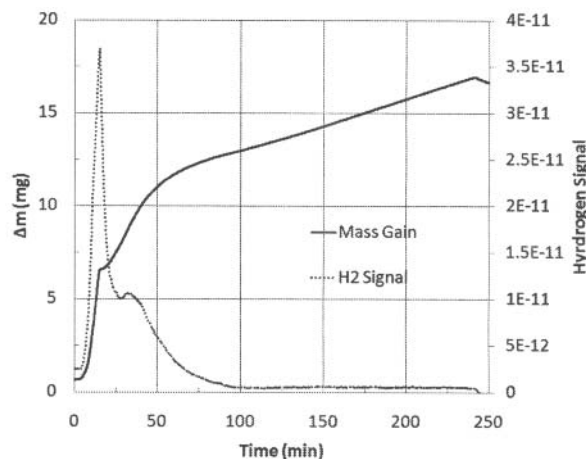
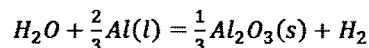


Figure 5. Mass gain, approximately 7%, and hydrogen signal curves from oxidation in humid argon, (see Table 3).

The hydrogen peak occurs during the rapid initial oxidation. The hydrogen signal intensity decreases to a constant value, corresponding to the linear mass gain. It is postulated that the following reaction takes place [13].



Oxidation in dry argon resulted in negligible weight gain, since there is no oxidizing agent present.

Figures 6 and 7 show the results of two dry and two humid oxidation experiments, respectively.

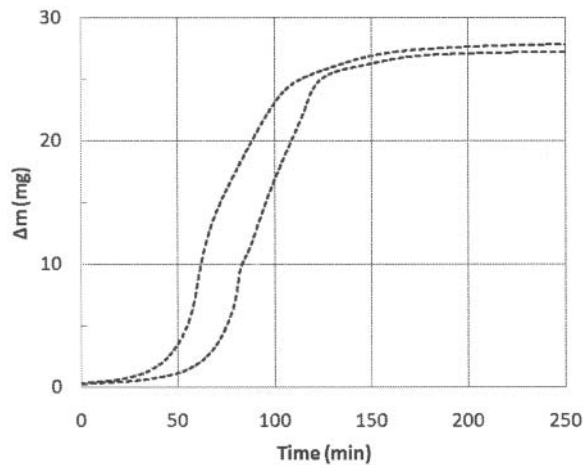


Figure 6. Mass gain curves of oxidation in dry air, (see Table 3), 10 % mass increase.

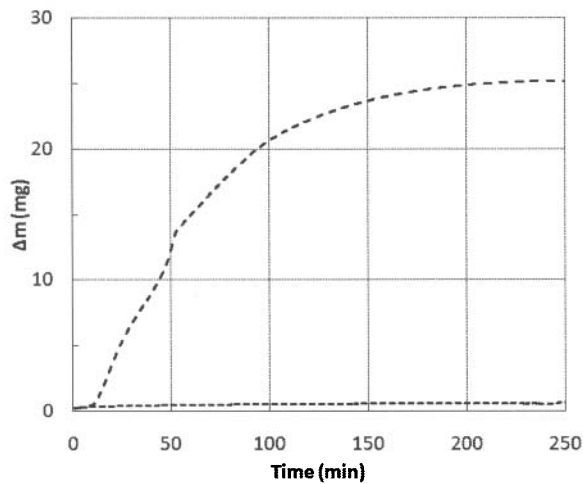


Figure 7. Mass gain curves of oxidation in humid air (see Table 3), 10 % mass increase.

Significant hydrogen signals were not obtained for oxidation in humid air, therefore water did not react. The aluminum reacted preferentially with oxygen, forming an oxide layer which the water vapor could not react with. Out of two experiments in humid air, only one oxidized significantly.

Samples were oxidized in air containing 5 % carbon dioxide. Dry and humid conditions were used, Figure 8 and 9, respectively. Figure 8 contains data from 4 experiments and Figure 9 contains 7 experimental sets of data.

Samples oxidized in air containing 5 % carbon dioxide gained less mass than in air, for both dry and humid conditions. Hydrogen production was not observed for oxidation in humid air and air containing carbon dioxide. While the water did not react, it appears to have catalyzed the reaction as the mass gain for humid conditions occurs sooner than in dry conditions.

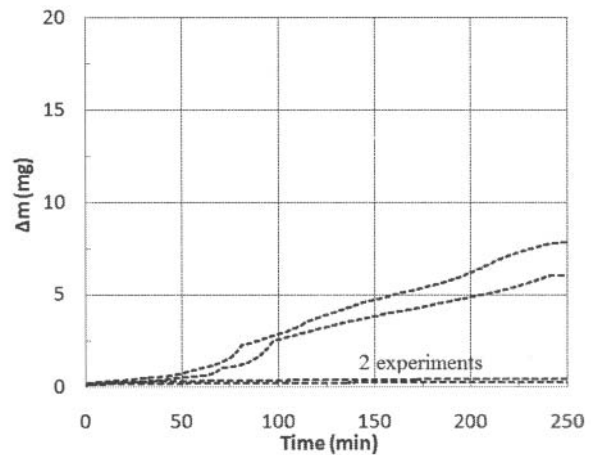


Figure 8. Mass gain curves of 4 experiments, oxidation in dry air +5 % carbon dioxide (see Table 3), 3 % mass increase.

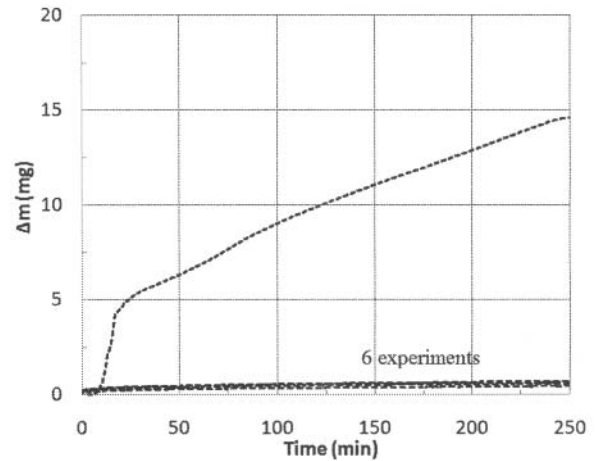


Figure 9. Mass gain curves of 7 experiments, oxidation in humid air + 5 % carbon dioxide (see Table 3). Lone mass increase 6 %.

There was some difficulty in oxidizing the aluminum in air containing carbon dioxide. It can be seen in the figures above that several curves show minimal oxidation. Indeed, out of 11 experiments, only 3 oxidized significantly. It is tempting to conclude that the limited oxidation is due to the presence of the 5 mol% carbon dioxide.

An oxide layer forms on the surface of the melted aluminum, trapping liquid aluminum inside a solid oxide layer. This is similar to what occurs during dross skimming [1]. The layer must crack or break, exposing fresh aluminum, in order to obtain significant oxidation. The curves in Figures 8 and 9 which show only a slight mass gain correspond to the formation and thickening of this oxide layer.

Figure 10 shows two oxidized samples. The sample on the left did not oxidize significantly, while the sample on the right gained significant mass.

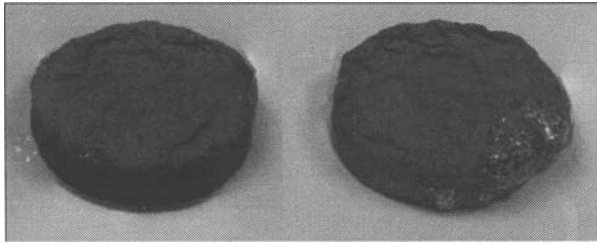


Figure 10. Surface appearance comparison of two samples oxidized in dry air + 5 mol% CO<sub>2</sub> (see Table 3).

The sample on the right of Figure 10 contains localized cracks, indicating that the oxide layer has broken, providing access to the liquid aluminum for oxidation. This finding is supported by Akagwu [14], who conducted oxidation of aluminum with a TGA.

Samples coated in carbon powder were oxidized in air, under humid and dry conditions (Figures 11-14). The loss of mass in Figures 11 and 13 corresponds to the amount of carbon that was on the sample.

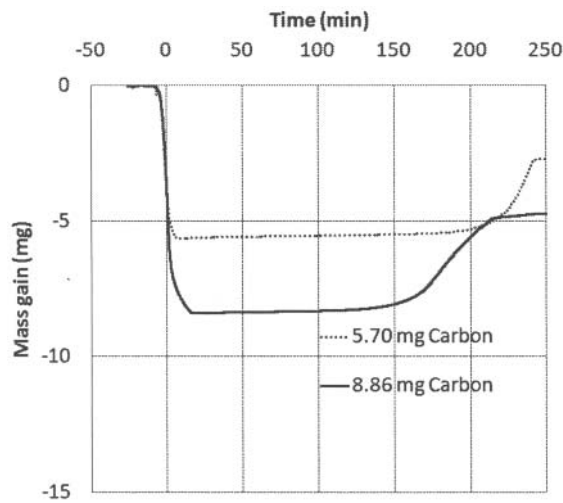


Figure 11. Mass gain curves of oxidation in dry air with a carbon coating (see Table 3).

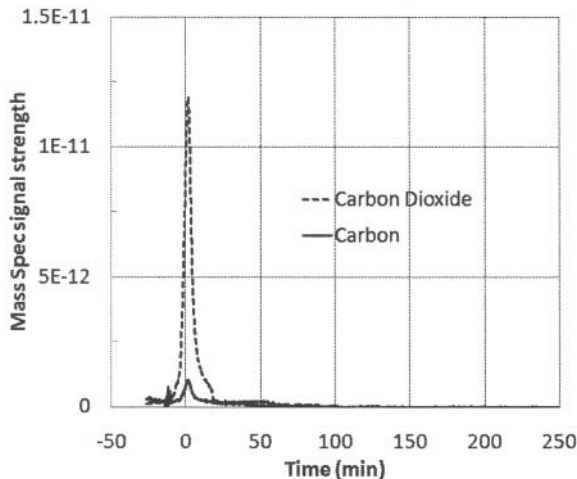


Figure 12. Typical carbon and carbon dioxide signals corresponding to Figure 11.

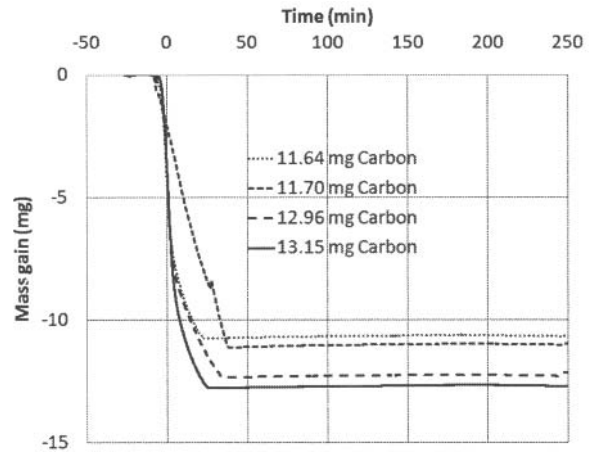


Figure 13. Mass gain curves of oxidation in humid air with carbon coating (see Table 3).

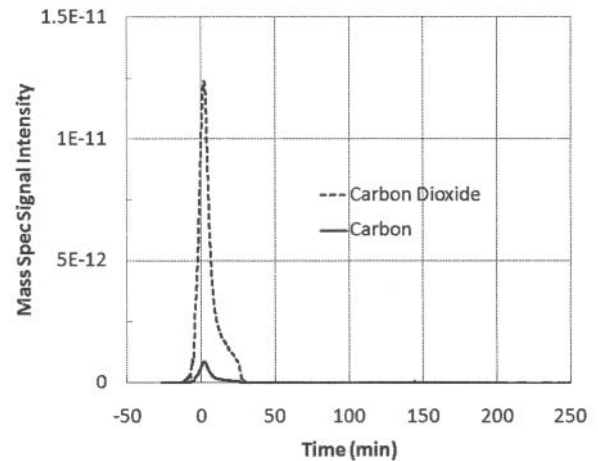


Figure 14. Typical carbon and carbon dioxide signals corresponding to Figure 13.

Carbon powder left the sample initially, leaving a small amount assumed to be a thin layer on the surface. This layer protects the sample from oxidation for some time, approximately 150 minutes in dry air, and over 200 minutes in humid air.

The carbon and carbon dioxide signals in Figures 12 and 14 support the mass loss observations. The presence of carbon dioxide indicates oxidation of the carbon.

A sample with a carbon coating was oxidized in humid argon. The mass gain and corresponding hydrogen signal is shown in Figure 15. The carbon coating did not provide the oxidation protection in argon that it did in the other atmospheres. The carbon was still present on top of the oxidized sample, and no carbon signals were detected. The carbon did not participate in any reactions, highlighting the preferential attraction of water vapor to aluminum with respect to carbon.

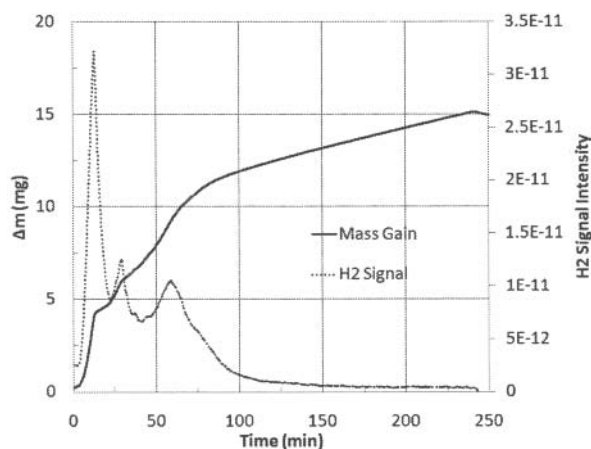


Figure 15. Mass gain, 6%, and hydrogen signal curves of oxidation in humid argon with carbon coating.

### Conclusions

Mass gain by oxidation and composition of off-gases has been measured simultaneously in a TGA. When water vapor is the only source of oxygen available for oxidation, the water reacts with the sample and hydrogen gas is produced.

Oxidation in air neither increases nor decreases with the presence of water. Oxidation is delayed in a dry environment compared to a humid environment.

An atmosphere containing carbon dioxide, with and without humidity resulted in approximately 50-75 % less oxidation than in air. Only 2 out of 10 experiments resulted in significant oxidation, which takes place only after the oxide layer has cracked or broken. Humidity may prevent the layer from breaking.

In both air and air containing carbon dioxide, humidity seems to initiate oxidation earlier. The off-gas measurements indicate that water most likely did not participate in oxidation in air or air with CO<sub>2</sub>. Water may act as a catalyst, initiating oxidation but not participating in the reactions.

A carbon coating delays oxidation of the sample. Oxygen preferentially reacts with carbon powder to form carbon dioxide. Humidity seems to extend this carbon protection compared to a dry environment. More experiments are needed to confirm this.

In industry, the formation of dross reduces yield by entrapment of molten aluminum [1,2]. The presented results suggest that metallic aluminum droplets are enclosed in alumina oxide layers, when, upon cracking or bursting, fresh aluminum is oxidized. Furthermore, aluminum is often coated with organic substances. Decoating units are used to remove the coating before thermal melting. The results here indicate that a carbon residue should be left on the surface of the scrap, protecting it from oxidation. A specially designed decoating procedure could achieve this after the organics of the coating have decomposed. This would reduce dross formation and increase recycling yield.

### Future Work

Future work will focus on oxidation of industrial samples with an unmodified surface. Samples with a well understood surface modification, such as anodizing, are of interest.

More experiments of carbon coated samples in various atmospheres will help with understanding mechanisms. A longer holding time will be used to see how long carbon protects the surface.

To improve understanding of surface oxidation, a detailed comparison of pre and post surface oxides will be carried out. Characterization of the surface before and after will help to describe the mechanisms of oxidation.

### Acknowledgement

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### References

1. O. Manfredi, W. Wuth, and I. Bohliger, "Characterizing the Physical and Chemical Properties of Aluminum Dross", *JOM*, 11 (1997), 48-51.
2. Q. Han et al., "Dross formation during remelting of aluminum 5182 remelt secondary ingot (RSI)", *Mat. Sci. and Eng.*, A363 (2003), 9-14.
3. Martin Syvertsen, "Oxide Skin Strength on Molten Aluminum", *Metallurgical and Materials Transactions B*, 38B (2006), 495-504.
4. A. Kvithyld, "Thermal Decoating of Aluminium Scrap" (Doctoral Thesis, Dept. of Mat. Tech., Norwegian University of Science and Technology, July, 2003).
5. A. Kanti et al., "Numerical simulation of early stages of oxide formation in molten aluminium-magnesium alloys in a reverberatory furnace", *Modelling Simul. Mater. Sci. Eng.*, 12 (2004), 389-405.
6. E. Bergsmark, C. J. Simensen, and P. Kofstad, "The Oxidation of Molten Aluminium", *Mat. Sci. and Eng.*, A120 (1989), 91-95.
7. S. A. Impey, "The Mechanism of Dross Formation on Aluminium and Aluminium-Magnesium Alloys", (Doctoral Thesis, School of Industrial Science, Dec. 1989).
8. W. Thiele: *Aluminum*, 38 (12) (1962), 707-715.
9. Philip M. Aziz, and Hugh P. Godard, "The Influence of Surface Pretreatment on the Atmospheric Oxidation of 2S (U.S. Alloy 1100)", *Aluminum, Journal of the Electrochemical Society*, 104, (12) (1958) 738-739.
10. C. N. Cochran, and W. C. Sleppy, Oxidation of High-Purity Aluminum and 5052 Aluminum-Magnesium Alloy at Elevated Temperatures, *Journal of the Electrochemical Society*, 108 (4) (1962) 322.
11. Michael E. Brown, *Introduction to Thermal Analysis*, 2nd edition (Kluwer Academic Publishers, 2001).
12. Robert F. Speyer, *Thermal Analysis of Materials* (CRC Press 1993).
13. T. Abel Engh, *Principles of Metal Refining*, (Oxford University Press, 1992) 332.
14. I. Akagwu, and R. Brooks, "Environmental Reaction of Liquid Aluminium", (Paper presented at Conference for the Engineering Doctorate in Environmental Technology, 2003).