

## Oxidation of Manganese-Containing Aluminum Alloys

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Keywords: aluminum manganese, thermogravimetric, oxidation

### Abstract

During remelting of aluminum alloys, industrial experience has shown a tendency toward increased oxidation losses with manganese-containing alloys. A goal of this work is to increase current knowledge of oxidation of Mn-containing aluminum alloys and relate this knowledge to reducing oxidation losses.

An oxidation study was performed on 99.99% Al, Al-1%Mn and Al-5%Mn materials in a thermogravimetric furnace with different atmospheres, and in a muffle furnace with air. The mass gain behaviour for these materials was studied and compared for different temperatures and surface preparations.

The results show that there was no Mn in the oxide on either the extruded or heated Al-1%Mn samples. The mass gain at 800 and 1000°C for O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> atmospheres (with and without H<sub>2</sub>O) and for different surface treatments was less than 0.35%, and does not appear to explain increased oxidation losses experienced in industry when remelting Mn-containing alloys.

### Introduction

While oxidation of pure Aluminum and Mg-containing alloys is well-studied and reported, very little information is available in the literature about oxidation behavior of Mn-containing Al alloys.

Thiele [5] showed in 1962 the influence of varying alloying elements on aluminum oxidation at 800°C; from highest oxidation to lowest: Mg, Na, Se, Ca, Zn, Mn, Si, Fe and Cu.

Cochran[1] studied oxidation of Mg-containing Al in atmospheres containing Ar, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> (with and without H<sub>2</sub>O) and concluded that both CO<sub>2</sub> and “flue gas” (CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O<sub>(g)</sub>) delayed oxidation.

Lee [2] showed that moist air increased oxidation in Al-1.8%Mg. More recently, Stevens [4] showed that water vapour in Ar can oxidize aluminum through dissociation, and reported mass gains of up to 10% for an Al-4.5% Mg alloy at 800°C in dry air.

Rossel [3] showed a correlation between scrap

thickness and metal loss when remelting, but found that there was very little difference between Al99/5 and AA3103 (0.9-1.5% Mn)

As seen from Table 1, the thermodynamic oxidation potential of Mn is approximately 70% of that of Al, and the calculated activity coefficients for 1% Mn in Al in Table 2 indicate a strong negative deviation from ideality. Therefore, it is expected that for an ideal solution, the Al would oxidize before the Mn, and little oxidation of Mn should occur.

**Table 1:** Gibbs free energy change and equilibrium constants for Al and Mn oxidation reactions, calculated using FactSage [7].

	Al oxidation	Mn oxidation
$\Delta G_{800^\circ\text{C}}^\circ, \frac{\text{kJ}}{\text{mol}}$	-952	-667
$K_{800^\circ\text{C}}$	1.43E+62	3.32E+43
$\Delta G_{1000^\circ\text{C}}^\circ, \frac{\text{kJ}}{\text{mol}}$	-908	-633
$K_{1000^\circ\text{C}}$	2.52E+47	1.19E+33

**Table 2:** Activities and activity coefficients of Al and Mn in Al-1%Mn alloy at 800°C and 1000°C, calculated using FactSage [7].

	Al	Mn
mass%	99	1
mole frac	9.95E-01	4.94E-03
$\alpha_{800^\circ\text{C}}$	9.95E-01	8.48E-06
$\gamma_{800^\circ\text{C}}$	1.00E+00	1.72E-03
$\alpha_{1000^\circ\text{C}}$	9.95E-01	2.81E-05
$\gamma_{1000^\circ\text{C}}$	1.00E+00	5.68E-03

However, industrial experience has indicated increased dross formation when remelting Mn-containing alloys. The present thermogravimetric study investigates the oxidation behaviour of Al-1wt%Mn to understand if and why the addition of Mn significantly increases oxidation in the context of dross formation in Al remelting furnaces.

## Experimental

### Materials

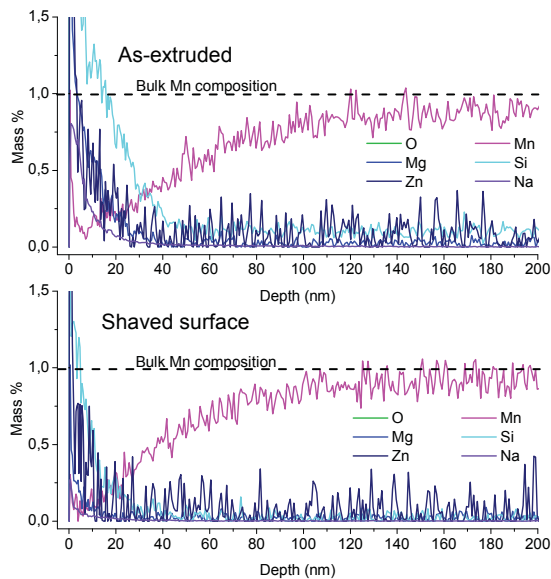
99.99% pure Al was used as a reference material. Al1Mn represents the upper range of Mn content in commercial Al alloys, and Al5Mn was chosen as an “extreme” content to investigate if (or how) Mn affects Al oxidation or cross formation.

The Al1Mn alloy was prepared from 99.8% Al and a commercial master alloy containing Al and 20 weight% Mn, while the Al5Mn alloy was prepared from 99.99% Al and the same 20 wt% Mn master alloy. In both cases the alloys were cast into ingots that were allowed to cool in air.

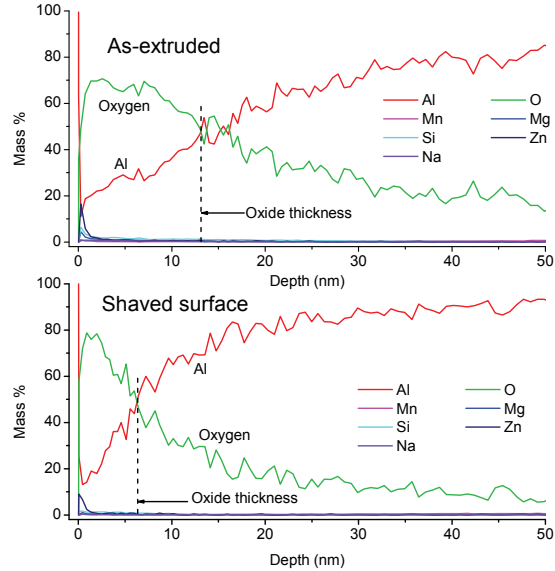
A portion of the Al1Mn ingot was machined into a 95 x 200 mm cylinder that was subsequently extruded into a 1.6 x 78 mm strip. This extrusion was used for the thermogravimetric (TGA) oxidation work.

Material from the remaining Al1Mn and Al5Mn ingots, as well as from some 99.99% pure Al were used for the muffle furnace oxidation experiments.

Glow Discharge Optical Emission Spectroscopy (GDOES) was used to measure the concentration profile of the surface of the as-extruded Al1Mn strip; Figures 1 and 2 show the measurement results.



**Figure 1:** GDOES measurements of Mn profile for as-extruded (top) and shaved (bottom) Al1Mn extrusion. Mn is depleted to a depth of 80-100 nm in both samples [7].



**Figure 2:** GDOES measurements of oxide thickness for as-extruded (top) and shaved (bottom) Al1Mn extrusion before heating. The oxide thickness is between 5 and 15 nm thick [7].

It was found that Mn was depleted in the surface of the as-extruded material to a depth of some 75 nm, and the oxide layer (defined here as the region with > 47 mass% oxygen) was between 10 and 15 nm thick. A carpenter’s hand plane was used to shave approximately 100  $\mu\text{m}$  from both surfaces of the extruded strip, to remove the oxide layer and Mn deficient region from the surface of the extrusion. The shaved surface was then measured again with GDOES; the oxide layer was thinner, as expected, but the Mn profile was nearly identical to that of the as-extruded material.

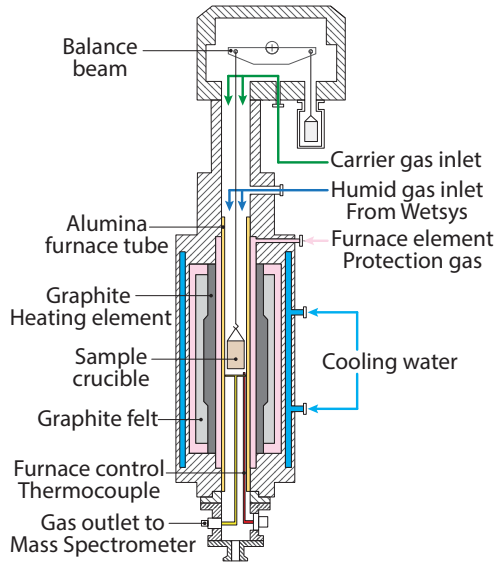
### Thermogravimetric Oxidation

Setaram SetSys 2400 Thermogravimetric Analyzer Thermogravimetric (TGA) measurements were carried out using a Setaram SetSys 2400 TG-DTA; an equipment schematic is shown in Figure 3.

The gases used in the TGA were 99.9999% Ar and N<sub>2</sub>, and 99.999% O<sub>2</sub> and CO<sub>2</sub>. A Setaram Wetsys gas humidifier was connected to the inlet gas, and 7 mol% deionized water vapour was added to the gases in some of the experiments to simulate conditions in the combustion-heated remelting furnace.

The outlet gases directly below the sample crucible can be analyzed using the attached quadrupole mass spectrometer (MS) to give more information about any reactions that take place. When water vapour

is present, hydrogen peaks provide evidence of accelerated (breakaway) oxidation. In experiments with H<sub>2</sub>O vapour, the MS data also shows when the desired humidity level is reached in the furnace.



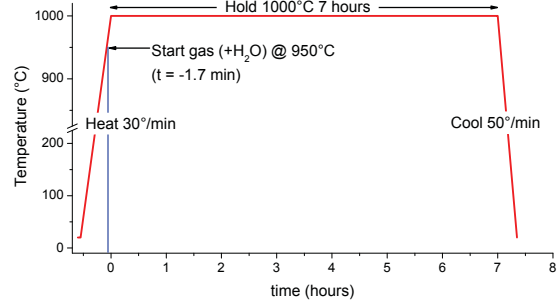
**Figure 3:** Schematic of Setaram Setsys 2400 TGA

TGA procedure 8.5 mm diameter discs were punched from the 1.6 x 78 mm Al1Mn extruded strip using a hand punch with a flat face, giving a 225 mg sample. The sample lay flat in the bottom of the 10 mm alumina crucible so that the sample shape was maintained when it melted. The upper side of the sample was openly exposed to the furnace atmosphere, while the lower surface was not.

The samples were heated according to the profile shown in Figure 4, with a 7 or 14 hour isothermal period at 1000°C. The Setsys program started with a vacuum - Ar backfill cycle so that the sample did not react during the furnace heating phase. At  $t = 0$  in Figure 4, the furnace atmosphere was changed to the experimental gas, and this atmosphere was maintained for the remainder of the measurement.

The following operating procedure was used for the thermogravimetric experiments:

1. Weigh sample and crucible on external balance
2. Load sample and crucible in Setsys
3. Start Setsys and MS programs simultaneously
4. When experiment is finished, weigh sample and crucible on external balance



**Figure 4:** TGA sample heating profile, with 7 hour isotherm [7].

### Muffle furnace

For a rapid comparison of oxidation characteristics between pure Al and the Al1Mn and Al5Mn alloys, and to better simulate the conditions of a remelting furnace bath with larger size samples, three groups of oxidation trials were conducted in a muffle furnace under a normal air atmosphere, in the sequence shown in Table 3.

The surface of the Series 1 samples was prepared using an abrasive belt sander, while the Series 2 and 3 samples were prepared by machining. In each series of trials, 7 samples of each alloy were prepared. The samples were loaded into alumina crucibles, then all of the crucibles for the series were loaded into the preheated furnace. One crucible of each alloy was removed from the furnace at the times indicated in Figure 9 and allowed to cool in still air.

**Table 3:** Muffle furnace oxidation experimental matrix. Material A = 99.99% Al, B = Al1Mn, C = Al5Mn.

Series	1	2	3
Material	A+B	A+B+C	A
Preparation	Abrasive	Machined	Machined
Temp, C	1000	1200	1000
Mass, g	40.41 ± 0.06	35.55 ± 0.05	38.67 ± 0.04

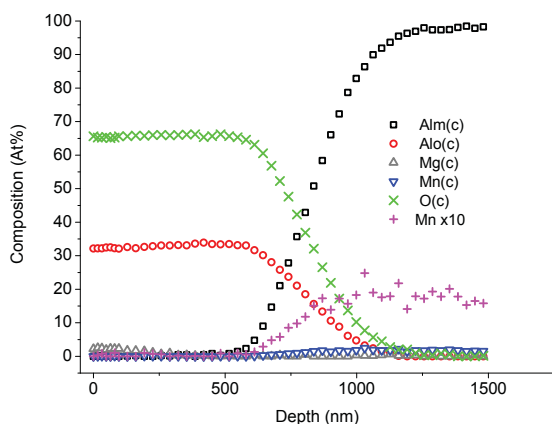
Muffle furnace procedure The following sequence was used for each series of samples:

1. Weigh samples
2. Insert all samples into 1000°C (1200°C) furnace at once ( $t = -8 \text{ min}$ )
3. Allow 8 minutes for samples to heat up and melt;
4. Remove samples at times relative to  $t=0$ , let samples cool in still air
5. Weigh samples

## Results

### Oxidized sample composition profile

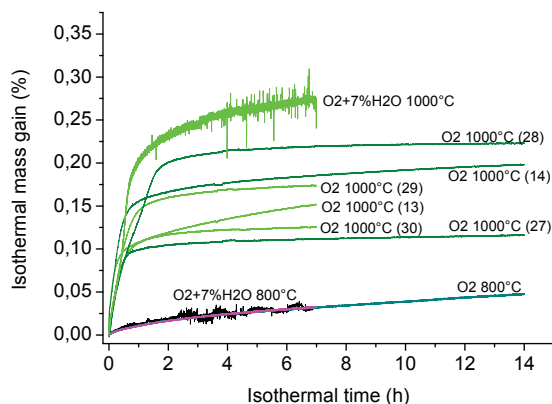
Auger analysis was performed on a few of the oxidized TGA samples. Figure 5 shows the composition of the surface  $1.5\ \mu\text{m}$  of an Al1Mn sample that was heated in  $\text{O}_2$  for 14 h at  $800^\circ\text{C}$ . The oxide layer is approximately  $600\ \text{nm}$  thick and Mn-depleted zone is approximately  $800\ \text{nm}$  thick.



**Figure 5:** Auger analysis of surface of Al1Mn sample heated at  $800^\circ\text{C}$  in  $\text{O}_2$  for 14h. The oxide thickness is approximately  $600\ \text{nm}$ , and Mn is depleted to approximately  $800\ \text{nm}$  [7].

### Thermogravimetric Oxidation

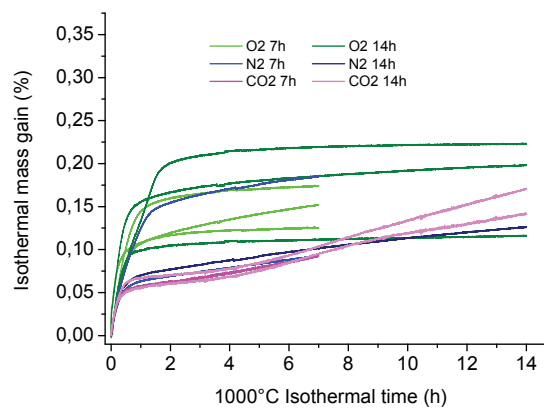
The TGA mass gain curves for oxygen at  $800$  and  $1000^\circ\text{C}$  are shown in Figure 6. At  $800^\circ\text{C}$  the results were very repeatable, and there was no difference when water vapor was added.



**Figure 6:** Al1Mn TGA results for dry and humid  $\text{O}_2$  for  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  isothermal. Experiment sequence number shown in parentheses [6].

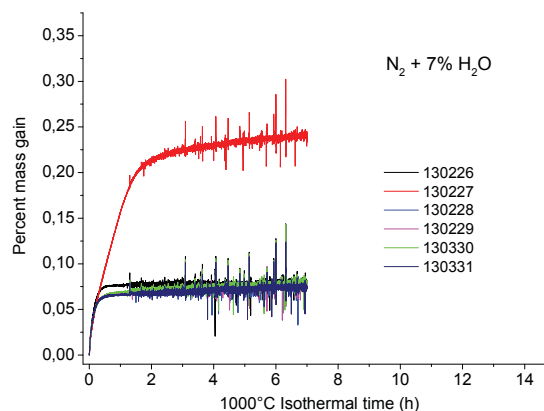
At  $1000^\circ\text{C}$ , there was more mass gain than at  $800^\circ\text{C}$  and there was significant scatter in the results. The addition of water vapor at  $800^\circ\text{C}$  had no effect, while at  $1000^\circ\text{C}$ , water vapor appeared to increase the mass gain.

Figure 7 shows that after seven hours at  $1000^\circ\text{C}$ ,  $\text{N}_2$  and  $\text{CO}_2$  both cause mass gain in the range of  $0.07$ - $0.17\%$ , and are within the same low range as for oxygen.



**Figure 7:** Al1Mn TGA results for 7 and 14h  $1000^\circ\text{C}$  isothermal dry gas experiments [6].

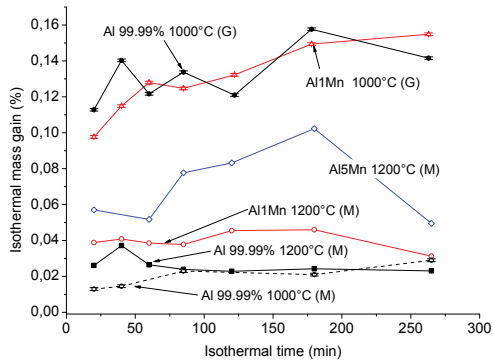
Figure 8 shows the mass gain results for a series of six consecutive, identical Al1Mn samples at  $1000^\circ\text{C}$  in  $\text{N}_2 + 7\%\text{H}_2\text{O}$ , and shows the scatter in the thermogravimetric results. Five of the measurements have nearly identical mass gain, while the sixth (second sample in the series) shows approximately four times as much mass gain.



**Figure 8:** TGA mass gain curves for six identical shaved Al1Mn samples at  $1000^\circ\text{C}$  in  $\text{N}_2 + 7\%\text{H}_2\text{O}$ , showing experimental variation [7].

### Muffle furnace oxidation

The mass gain behaviour of the different muffle furnace trials are shown in Figure 9. The mass gain at  $t = 0$  was not known, since this was during the melting phase.



**Figure 9:** Comparison of muffle furnace oxidation mass gains in air. Samples marked (G) were prepared by grinding with an abrasive belt, samples marked (M) were prepared by machining [7].

The samples that were prepared by grinding - marked (G) in the figure - gained more than the samples that were prepared by machining (M). The ground samples showed no clear difference in mass gain if Mn was present.

The machined samples at 1200°C showed differences in mass gain - Al5Mn showed the most gain while 99.99% Al showed the least, but the mass gain for these samples was one half to one fifth that of the 1000°C ground samples.

To test if the difference was due to temperature or sample preparation, a third series of machined 99.99% Al samples was run at 1000°C; the mass gain results were similar to the machined 1200°C.

The oxidized top surface of the samples was examined using SEM-EDS, and no Mn was found in the oxide layers of any of the samples.

### Discussion

From Figure 2, the oxide on both the as-extruded and shaved materials is around 10 nm thick, however there is no Mn found on the surface. Prior to heating, the bulk concentration of 1% Mn was not reached until 100 nm from the surface (Figure 1). After heating (Figure 5), the oxide thickness has increased some 100x, and the Mn does not reach the bulk concentration until 1000 nm.

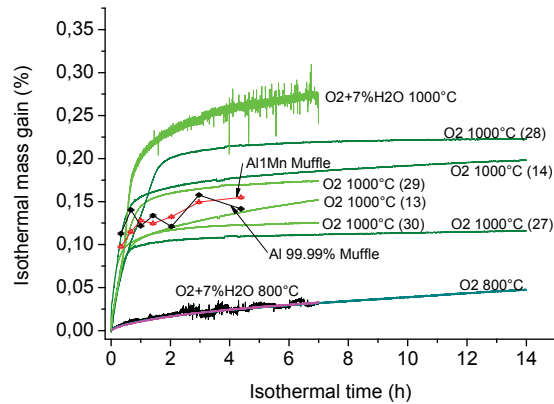
Since Mn is not found on the surface it may not be surprising that the oxidation rate is only 0.1-0.2%,

never exceeding 0.5% mass gain. This also confirms the thermodynamic prediction of minimal oxidation based on reaction potential and activity coefficient.

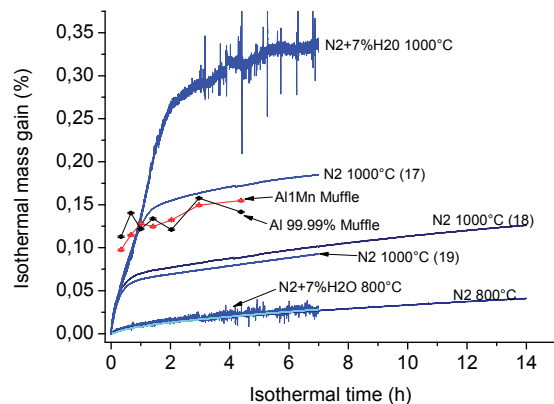
The TGA results indicated that the majority of the sample mass change occurs in the first 60-90 minutes of isothermal heating. However, the thin disc-shaped TGA samples have a high surface area:volume ratio.

From Figures 1, 2 and 5, there is no Mn in the oxide. When comparing the oxide thickness of the oxidized sample (600 nm) to the original extruded material (10-15 nm), the oxide is much thicker.

Figures 10 and 11 show that the oxidation mass gains for the 40 g muffle furnace samples in air are very comparable to those for the 225 mg TGA samples in O<sub>2</sub> and O<sub>2</sub>; the different atmospheres appear to have little effect on the amount of oxidation.



**Figure 10:** Comparison of TGA (O<sub>2</sub>, 225 mg sample) and 1000°C muffle furnace (air, 40 g sample) mass gains [6],[7].



**Figure 11:** Comparison of TGA (N<sub>2</sub>, 225 mg sample) and 1000°C muffle furnace (air, 40 g sample) mass gains [6],[7].

However, the surface of the TGA and muffle furnace samples was not disturbed by the process, so the oxide films that formed would remain relatively intact. It is possible that in the industrial remelt furnace, bath turbulence is a large factor in dross formation; the oxide may be stronger when Mn is added, and this stronger oxide may encapsulate molten metal.

### Conclusions

The major findings of the present thermogravimetric study of a synthetic Al-1wt%Mn alloy are:

1. The oxide on the as-extruded, shaved and re-acted Al-1%Mn samples did not contain Mn.
2. As was predicted by thermodynamics, the oxidation rate of Al-1%Mn is not significantly different from 99.99% Al, and is much less than the oxidation rates of AlMg alloys reported in the literature.
3. The oxidation rate of Al-1%Mn is essentially independent of sample size, atmosphere and method.
4. The oxidation rate of Al-1%Mn found in this study does not seem to explain the increased dross formation experienced in industry when remelting AlMn alloys.

### Future Work

It would be beneficial to investigate if the increased dross formation experienced in industrial remelting of AlMn alloys can be explained by other factors than oxide growth. In the current work, the surface of the sample was still; rupture of oxide films is known to substantially increase oxidation, and the oxide skin strength could be affected by the presence of Mn.

The oxide morphology should also be investigated to determine if the oxides formed with AlMn are structurally different than those for pure Al or AlMg alloys, as well as investigate the stability of different oxide polymorphs with respect to alloy composition.

### Acknowledgements

This research was carried out as part of the Research Council of Norway (RCN) funded RENERGI Project (No. 217617/E20) CastAl (Energy Efficient Aluminium Cast House). It includes the partners: Hydro Aluminium AS, SAPA Heat Transfer AB, SINTEF and SINTEF Energy AS. Funding by the industrial partners and RCN is gratefully acknowledged.

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