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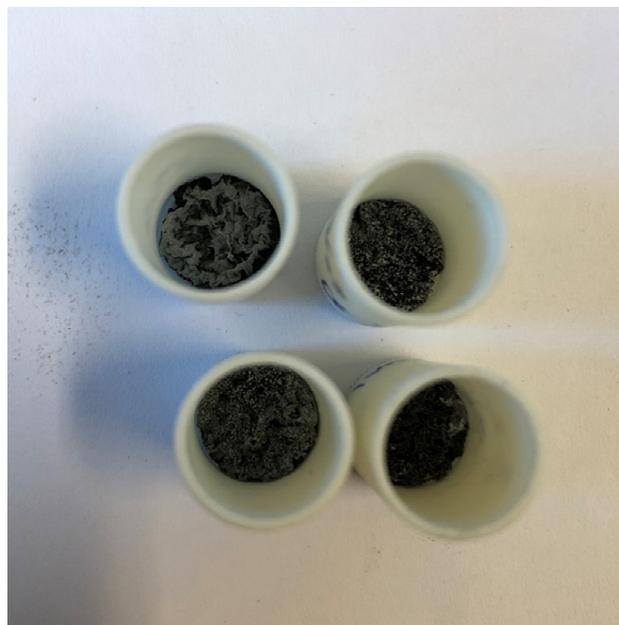
Report

Effect of micro-alloying elements on the oxidation of a 5 % Mg aluminium alloy

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Report

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ABSTRACT

The addition of beryllium to an AlMg alloys to inhibit oxidation is a long known industrial practice. The addition of Be brings with it potential health risks as Be and Be-containing compounds are known health hazards. Therefore, an alternative micro-alloying element to beryllium is desired. To highlight any potential replacement, screening tests of selected elements were carried out to determine the effect on oxidation and breakaway time. Ca, Ce, Ga, Gd, La, and Sc were investigated as potential replacements. Only Ca and Sr showed potential to act as an oxidation inhibitor in AlMg alloys

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1 Introduction

The oxidation of molten aluminum during melting, refining, and casting represents a significant loss and cost for the aluminum industry. In addition to a loss of material the oxides can result in cracks and defects in the final product such that the material cannot be sold and must be remelted. Problematic oxidation is known to increase with increasing magnesium concentration. Historically, alloys that are prone to problematic oxidation have been treated with beryllium additions. Additions of as little as 2 ppm of beryllium have been known to reduce the oxidation to an acceptable level(1, 2). However, the continued usage of beryllium has begun to be questioned due to beryllium's negative health effects. It has been well documented that beryllium and beryllium containing compounds can cause lung disease and cancer, especially in plant workers who are routinely exposed to beryllium dust. As a result, an alternative alloying element to beryllium is desirable. This report outlines the results of testing on several different alloying additions to see the potential effects on the oxidation.

2 Selected alloys

The list of potential replacement elements for beryllium is relatively small as any replacement element must have a higher reactivity with oxygen than magnesium in the melt and be able to form a protective layer to inhibit oxidation(2). Further, one of the largest advantages of beryllium is that additions of only a few ppm are required to inhibit the oxidation.

To test the potential of any alloying element at reducing the oxidation it was decided to produce model alloys with 5 % Mg and 1000 ppm (0.1 %) of a given alloying element. Based on discussions with industry partners (Alcoa, Hydro, Novelis and KBM alloys) it was decided to test: Ca, Ce, Ga, Gd, La, Sr and Sc. Alloying elements were provided as aluminum master alloys by KBM alloys with exception of the Sr which was added as a pure metal. Based on initial results alloys with 3 % Mg and 1000 ppm of La or Sc were also produced for testing.

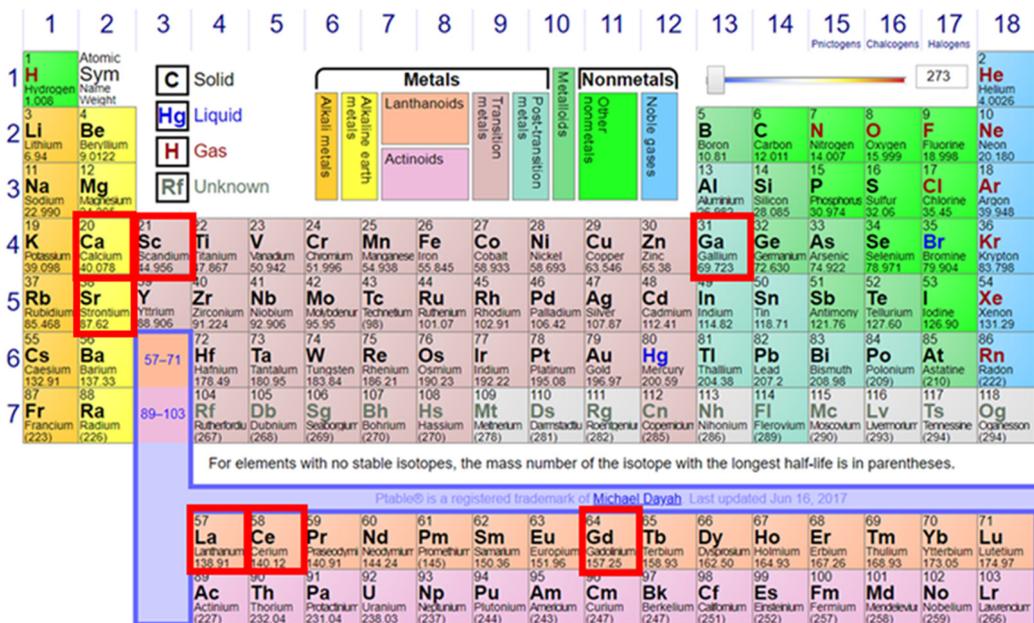


Figure 1 Periodic table showing selected micro-alloying elements(3).

Hypothesis:

By testing at 1000 ppm any effects on the oxidation should readably be seen. If no positive effect is observed at 1000 ppm it is assumed to be unlikely that the effect will be positive lower levels. However, if a positive effect is seen at 1000 ppm the element may have a positive effect at lower concentrations. In this case a positive effect is defined by a significant longer time until the start of breakaway oxidation or lower total mass gain after breakaway.

3 Alloy production

Two different methods were investigated to produce an aluminum alloy with 5 % Mg and 1000 ppm of the desired alloying element. The first method involved making small samples in a bench top arc melter. The arc melter did not yield usable alloy samples as the high temperature resulted in significant Mg evaporation and loss, as such it will not be discussed further. In the second method the alloys were melted in an induction heated crucible and the samples were cast into a sand mold. This method is given in more detail below.

3.1 Casting

The individual alloys were cast as a 4 mm thick plate in a sand mold in the casting lab at SINTEF. The sand mold used is shown in Figure 2, this mold gave a sheet measuring 10 cm x 7 cm x 0.4 cm as shown in Figure 3. Sand with a binding agent was mixed and filled into the form and compacted. The sand was left to cure for about 10 minutes. The sand mold was then removed from the form, and the process was repeated as a new sand mold was used for each alloy.

To cast the alloys a small-scale induction coil setup was used. This set-up could melt up to 300 grams of Al at a single time. Using the small-scale induction coil allowed for small batches of the alloys to be made quickly without having to melt a large amount of metal like is generally required for the larger furnaces. To produce the alloy the crucible was first coated (Velvacoat ST 802) to prevent the metal from sticking. The aluminum metal was placed in the crucible and melted. It took approximately 15 minutes for the aluminum to melt. Once the aluminum was liquid the oxide layer was scraped off and the alloying elements were added. The crucible was then heated until the crucible was glowing red which took approximately 5-10 minutes. The power to the induction coil was then shut off and the sample was cast into the sand mold. In addition to the casting the samples for oxidation experiments in the TGA, a small sample was cast in a standard sampling apparatus for chemical analysis via spark OES. After the castings had cooled, they were removed from the sand molds.

Initial tests on the first series of castings showed a large variation in the oxidation results this is believed to be due to beryllium contamination from AlMg master alloy that was used and surface segregation. To overcome these issues new alloys were cast using pure Mg as an alloying element to eliminate the contamination. Further, 1 mm from each side of the casting was removed by grinding to achieve a uniform surface and remove any surface segregation layer that resulted from the casting and cooling.



Figure 2 Sand mold used for casting samples.



Figure 3 Samples in as cast form.

4 Results from OES

The composition of the cast alloys was analyzed by a spark-OES calibrated and used for analysis of aluminum samples. The results are given in Table 1. The OES must be calibrated for the elements being tested, as the micro-alloying elements tested here are not commonly seen at the 1000 ppm level the OES results from them are not available or have a large uncertainty. The results do show that the targeted Mg content was achieved and that the micro-alloying elements were successfully added for the Ca and Ga alloys. For the other microalloying elements it was not possible to determine the concentration via spark-OES. Based on the results for Mg, Ca and Ga it is assumed that the concentration of the micro-alloying elements in the samples are in the desired range of 100s to 1000s of ppm, which should be sufficient to prove or reject the hypothesis. This assumption is supported by the fact that, with exception to Sr, all the alloys were added as aluminium master alloys with composition close to the eutectic point. This should give a similar melting point and dissolution behaviour for the different alloys. For Sr containing alloys pure Sr metal was used. As a clear effect on the oxidation rate was seen on the samples containing Sr it is assumed that these samples contained sufficient Sr to confirm the hypothesis.

Table 1 Spark OES results of as cast alloys in weight %.

	Si	Fe	Cu	Mn	Mg	Na	Ca	Be	Ga	Li	Al%
AlMg5 Gd 1-2	0.0948	0.0952	0.0036	0.0021	5.1319	0.0007	0.0006	0.00007	0.0100	0.0000	94.6273
AlMg5 Ce 1-2	0.0899	0.0879	0.0035	0.0022	5.0594	0.0003	0.0007	0.00007	0.0093	0.0000	94.7125
AlMg5 La 1-2	0.0918	0.0889	0.0037	0.0023	5.1191	0.0000	0.0004	0.00007	0.0094	0.0000	94.6481
AlMg5 Sc 1-2	0.0929	0.0977	0.0036	0.0021	4.9957	0.0002	0.0006	0.00007	0.0099	0.0000	94.7568
AlMg5 Ca1-2	0.0944	0.0944	0.0036	0.0024	5.0729	0.0006	0.0626	0.00007	0.0097	0.0000	94.6243
AlMg5 Ga1-2	0.0909	0.0908	0.0036	0.0022	4.9257	0.0008	0.0007	0.00007	0.1523	0.0000	94.6980
AlMg5-2	0.1031	0.0934	0.0035	0.0021	5.1501	0.0011	0.0004	0.00007	0.0099	0.0000	94.6008

5 Thermogravimetry (Oxidation)

5.1 TGA setup

To evaluate the effect of the alloying elements on the oxidation a thermogravimetric balance (TGA) was used to measure the weight change over time. A Setaram Setsys evolution TGA was used, this TGA has a resolution of 0.1 mg. To produce the oxidation, samples measuring 8.5 mm in diameter were punched out by hand from the ground castings. The sample was rinsed in ethanol to remove any surface oils of contamination. A standard oxidation program for all runs was used to ensure all samples were oxidized under the same conditions. The furnace chamber was evacuated and Ar purged 2 times to remove any atmospheric oxygen. After which it was heated at 10 °C/minute to 750 °C under a high purity argon atmosphere (6.0). Once 750 °C was reached the atmosphere was replaced with synthetic air. The sample is held at 750 °C under air flowing at 20 mL/min for 16 hours. Followed by cooling to room temperature under argon. The same synthetic air and argon bottles were used for all runs thus reducing atmospheric variations.

Due to changes in the temperature, gas flow and oxidation from impurity oxygen in the argon changes in the mass were seen during heating. The mass gain curves were corrected for these changes and so that the mass gain was set to 0 at the point where the air flow had stabilized after the temperature reached 750 °C.

5.2 TGA results of selected elements

The results from the TGA tests on the 5 % Mg alloys containing 1000 ppm of Ca, Ce, Ga, Gd, La and Sc are given in Figure 4. The dashed line at 3.3 and 13.2 % show the theoretical mass gain if 100 % of the Mg is oxidized to MgO and MgAl₂O₄, respectively. For Mg containing alloys the complete conversion of Mg to MgAl₂O₄ is considered the upper limit for oxidation as any further oxidation would be that of Al directly to Al₂O₃. This occurs at such a low rate that the oxidation can be assumed to stop after the consumption of Mg. It can be seen that the addition of Ca had a strong inhibiting effect on the oxidation, whereas the other micro-alloying elements did not show a clear inhibiting effect. The inhibiting mechanism behind Ca was not investigated in this work, therefore it is not possible to say why calcium inhibited the oxidation. Additionally, La and Sc potentially gave a small delay in the onset of breakaway oxidation, and thus were tested with a lower Mg content as described in section 5.4.

Most alloys were tested 2 times and only a small variation was seen between the 2 runs. For clarity, only the first run is shown in Figure 4. This indicates that the sample preparation method used gives good results. The only exception to this is the sample with Ce where the oxidation stopped at 7.5 % instead of 11 % as seen on the other tests. This is likely due to the sample having a lower Mg content but has not been confirmed.

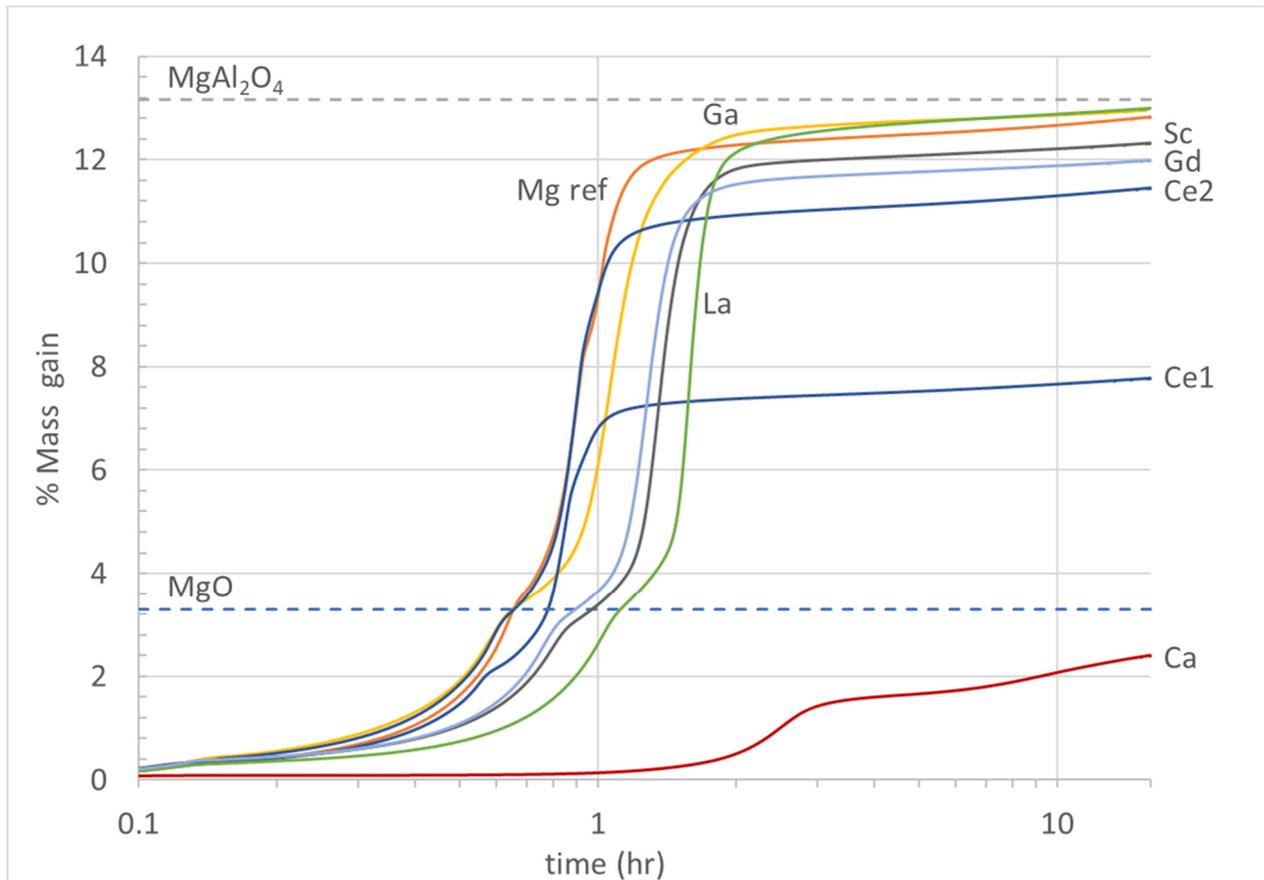


Figure 4 Result of TGA test after oxidation for 16 hours in air at 750 °C. Note logarithmic time scale.

5.3 Ca and Sr investigation

The positive result from calcium was investigated further along with strontium which is another alkaline earth metal element. Ca has previously been shown to have an inhibiting effect on the oxidation, whereas the results for Sr have been mixed with both inhibiting and promoting effects shown in literature(4-7). The alkaline earth elements which include Mg and Be appear to have the largest influence on the oxidation of Al alloys, thus the effects of Ca and Sr are of particular interest. In addition to the 5 % Mg with 1000 ppm Ca alloy tested previously the following alloys were tested:

- 5 % Mg + 30 ppm Ca
- 5 % Mg + 500 ppm Sr
- 5 % Mg + 30 ppm Ca + 500 ppm Sr

The results of the oxidation experiments on these alloys are shown in Figure 5. In addition to the alloys above a reference alloy with only 5 % Mg is given as well as the theoretical lines if 100 % of the Mg was converted to MgO and MgAl₂O₄. The time shown on the x-axis has been corrected so that time 0 is the point after the air flow had stabilized after the furnace had reached 750 °C. The oxidation rate was calculated by change in oxidation mass over a 60 second time frame and is shown in Figure 5. From this figure it can be seen that the oxidation rate for the 5 % Mg and 5 % Mg 30 ppm Ca samples is elevated from time zero, whereas the other alloys have a near zero rate at time zero but increase with longer times.

From these results it is clear that Ca and Sr both can reduce the oxidation rate of Mg containing alloys if sufficient amounts are added. The addition of insufficient amounts of the microalloying element can have a negative effect, though the rate and total amount of oxidation did not go beyond that of the alloy that is free of the microalloying elements (5 % Mg ref). This can be seen by the results for the 30ppm Ca + 500 ppm Sr

sample which showed a higher extent of oxidation than the sample that contained only 500 ppm Sr. This shows that the addition of insufficient amounts of Ca caused the inhibiting effect of Sr to be reduced. However, when 1000 ppm of Ca was added the oxidation rate and extent was similar to the 500 ppm Sr.

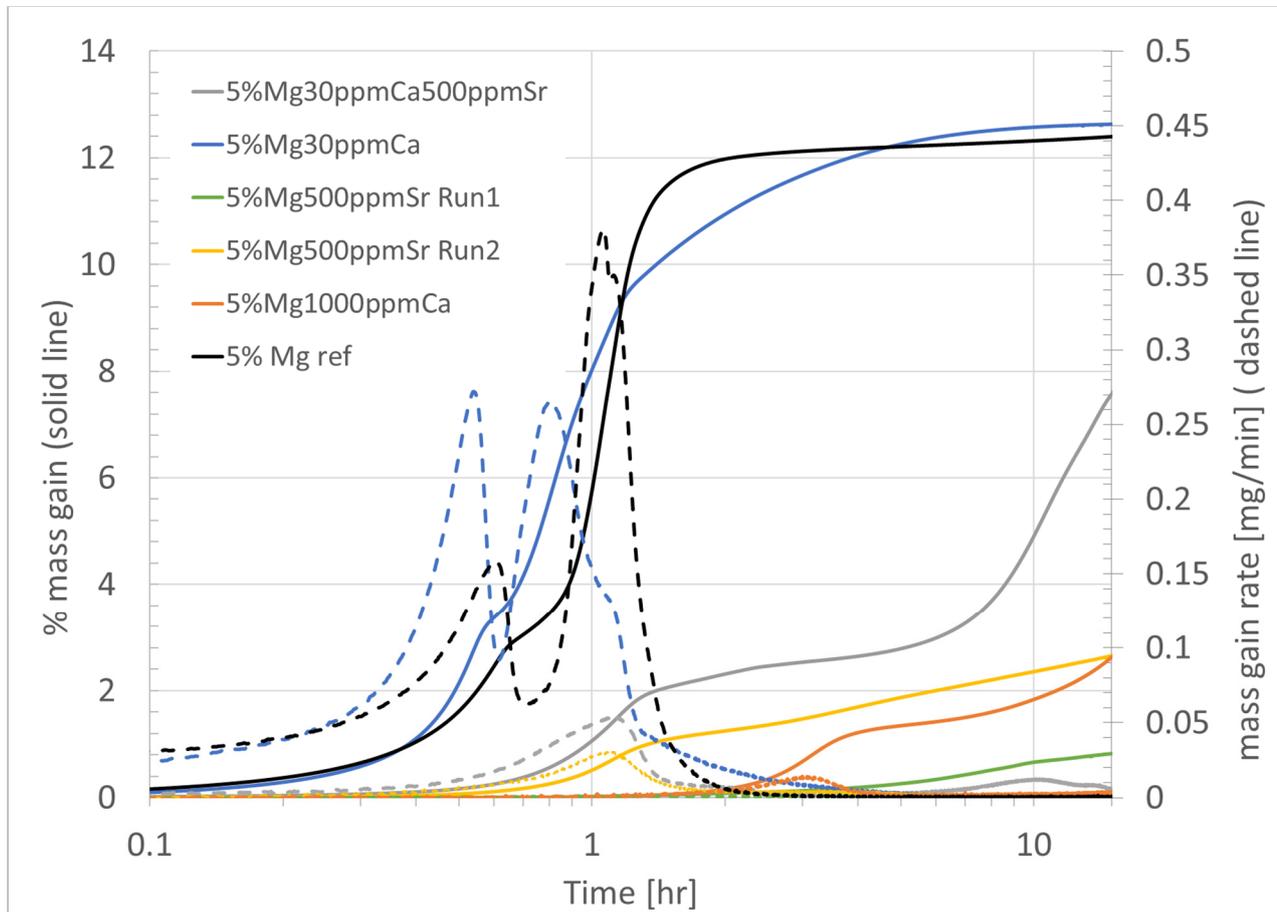


Figure 5 Percent mass gain (solid line) and mass gain rate (dashed line) of the alloys containing Ca and Sr after oxidation at 750 °C for 16 hours. Note logarithmic time scale.

The results show that both Ca and Sr have the ability to inhibit the oxidation of AlMg alloys if sufficient levels are added. The samples for the TGA have a volume to surface area ratio of $1 \text{ mm}^3/\text{mm}^2$, whereas an industrial furnace can have a ratio over $500 \text{ mm}^3/\text{mm}^2$. This means that the TGA samples have a significantly higher surface area compared to the volume of metal compared to an industrial furnace. Thus, they should show a significantly higher oxidation rate, faster breakaway and depletion of alloying elements than would be expected in an industrial furnace. As a result, it is likely that lower concentrations of Ca and Sr would prove effective in larger scale trials. This is further supported by previous work by others that show a reduction in the oxidation in alloys that contain between 20 and 100 ppm of Ca(4). The exact amounts that are required are likely dependent on the oxidation conditions thus the minimum amount of the microalloying element that is required would need to be tested at the industrial scale.

Analysis of Figure 5 shows that several different mechanisms may be at play. The first peak in the mass gain rate for the 5 % Mg ref and 30 ppm Ca samples correspond well with the 100 % of the Mg being converted to MgO meaning the oxidation rate slowed during the transition from MgO to MgAl_2O_4 before it increased again. Whereas, the peaks for the samples that contained Sr or 1000 ppm of Ca the peak of the curve does not correspond to 100 % conversion of Mg to MgO. This indicates that the microalloying elements are influencing the oxidation rate. Further, the height of the peak is one tenth of the height of the uninhibited tests indicating a significantly lower oxidation rate.

The reduction of the inhibiting effect with the addition of 30 ppm Ca to a 500 ppm Sr alloy needs further investigation as the reason for this is unknown but should be investigated as it indicates that the addition level is critical to maximize the inhibiting effect if two or more microalloying elements are to be added. Further it would indicate that the Ca and Sr influence each other and that preventing unwanted or promoting positive interactions between different trace elements may allow a reduction in the amount of microalloying elements added.

5.4 Reduced Mg content

To see further the effects of Sc and La samples alloys with 3 % Mg and 1000 ppm of either Sc or La were cast per the method described in section 3.1. No notable increase in the oxidation resistance was seen in these 2 alloys as can be seen in Figure 6. Even with a lower Mg content the samples reached the theoretical limit of 100 % of the Mg oxidizing to $MgAl_2O_4$ in a similar time frame as for the 5 % Mg alloys. The reason the samples had a mass gain slightly over the theoretical limit is likely due to a slightly higher Mg content. The plateau in the percent mass gain for the 3 % Mg alloys corresponds to an alloy with 3.3 % Mg. Given the variation in Mg content seen during casting this deviation is within the expected variation. From this figure the effect of Sc and La inhibiting the onset of breakaway oxidation looks to be minimal even with lower Mg contents.

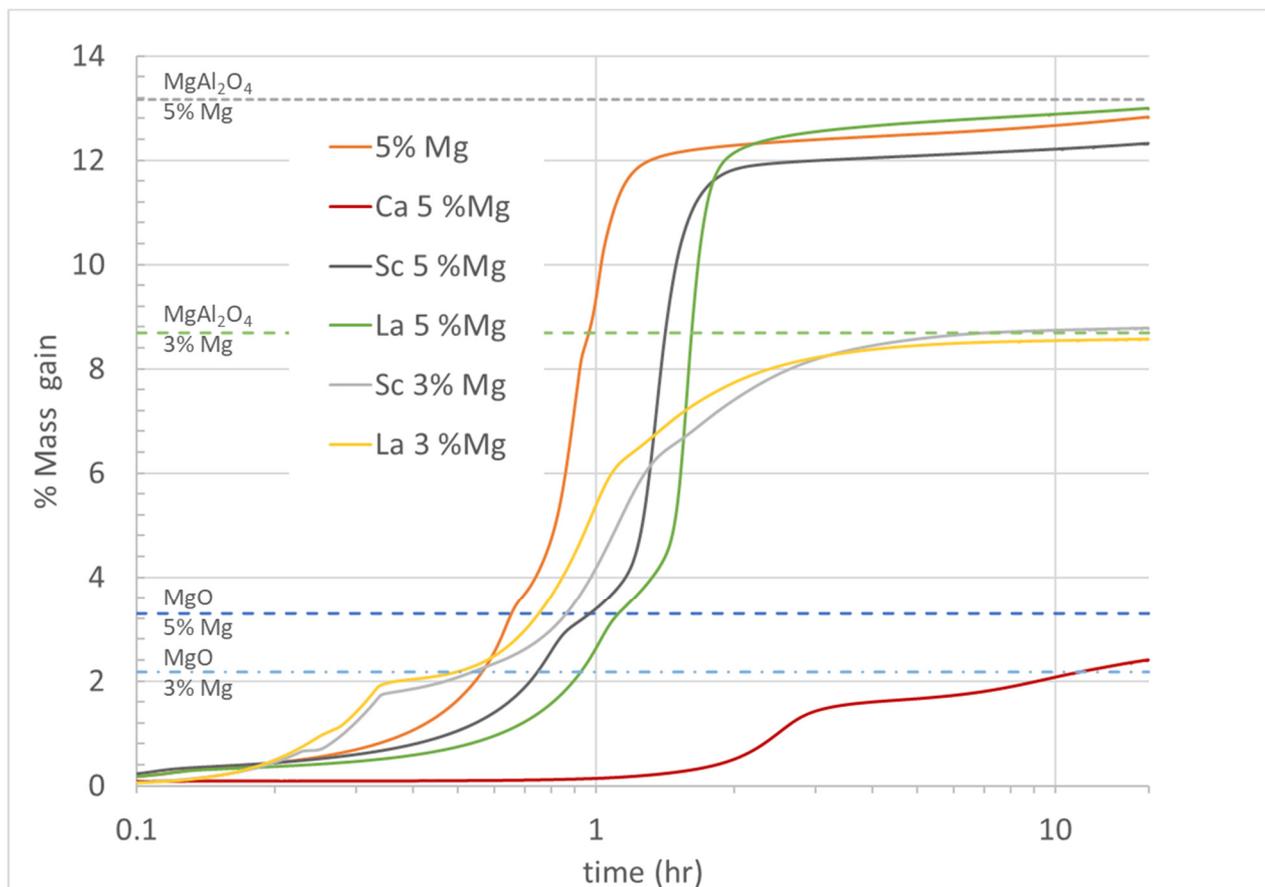


Figure 6 Results of oxidation test on 3 % Mg samples imposed on results from 5 % Mg alloys (Figure 4). Note logarithmic time scale.

5.5 Method evaluation

The sub-gram scale TGA is a well-known and used apparatus for studying oxidation and the effects of time and temperature. For this work the TGA gave clear results as to the effects of the different microalloying elements. The main downside to using a TGA to study the effects of different microalloying elements is that the sample preparation was time and labor intensive. Since each alloy required a separate casting and subsequent grinding step to be carried out the bulk of the time spent on this work was in sample preparation.

Thus, other methods that do not require such detailed sample preparation may be better suited to studying the effects of different microalloying elements. One recommendation would be to test the effects with samples at the kg scale as were the specific alloy does not to be prepared beforehand, but rather can be made at the start of each test.

Analysis of the sample chemistry by spark OES worked well for the major components such as Al and Mg. However, it did not perform well for the microalloying elements as it requires correct calibration for the elements used. An alternative method should be evaluated for determining the concentration of the microalloying elements.

6 Conclusion

Based on the results of the work it was found that:

- Ca and Sr show the strongest potential to act as oxidation inhibitors for AlMg alloys.
- The tests on Ga, Gd, La, Ce and Sc all showed to have none to limited oxidation inhibiting effect.
- Tests with La and Sc with a 3 % Mg alloy also showed no clear inhibiting effect.
- The addition of Ca or Sr in sufficient amounts can cause an inhibiting effect in the oxidation rate.

7 Future work

Future work should be done to optimize the effects of Ca and Sr and understand how these, and other trace elements interact to influence the oxidation of AlMg alloys. Detailed examination of the oxide layer and structure may give clues to the protective mechanism especially if samples from a shorter oxidation time are included to see how the oxide layer develops. Further, larger scale test should be carried out to optimize the required concentrations of Ca and Sr required to protect a melt. Development of a model describing protection time as a function of Mg, Ca and Sr concentrations similar to was previously developed for Be would be beneficial (8).

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