

Effects of CO₂ cover gas and yttrium additions on the oxidation of AlMg alloys

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Abstract

AlMg alloys are known to suffer from problematic oxidation that can result in significant gross formation and loss of Mg from the melt. Historically, beryllium has been used to minimize the oxidation as it forms a protective BeO layer at the oxide-metal interface that inhibits further oxidation of the Mg. Alternative protection agents to beryllium are desired due to its strong negative health impacts. The purpose of this paper is to summarize findings in respect to the effectiveness of CO₂ cover gas and yttrium additions as alternatives to beryllium; by examining the rate and product of oxidation using thermogravimetric analysis, electron microscopy and EDS. It was found that additions of as little as 5% CO₂ to air atmosphere can reduce the oxidation of a 5% Mg alloy to nearly the same extent as beryllium additions, while the addition of 100 ppm of yttrium was found to have a limited impact on the oxidation.

Introduction

The addition of select elements to an AlMg alloy in ppm levels is known to have a significant impact on the oxidation characteristics, with beryllium being the most well-known example in literature. The addition of 2 ppm beryllium to a 5000 series alloy was previously found to result in up to a tenfold decrease in the oxidation (1). Further, beryllium additions were found to delay the onset of breakaway oxidation by up to 170 hours (2). The inhibiting effect of beryllium has been attributed to the formation of a BeO layer at the oxide-metal interface. This BeO layer acts as a barrier between the MgO layer and the alloy, limiting the diffusion of magnesium and aluminum metal from the alloy through the oxide layer and thus slowing the oxidation. The use of beryllium brings with it inherent health risks to casthouse operators who breathe or come into contact with beryllium dust (3). The aluminum industry, therefore, desires alternatives to beryllium that provide a similar inhibiting effect, but without the health risks. Two of the options that exist to replace beryllium are reactive cover gases or an alternative alloying element that has a similar effect to beryllium.

The effects of a mixed CO₂/air atmosphere on the oxidation have been previously shown by Cochran et al. (4) and Haginoya et al. (published in Japanese) (5). Cochran proposed that the amount of CO₂ required to protect a specific alloy was a function of the magnesium content. Haginoya showed conclusively that CO₂ additions can effectively delay the onset of breakaway oxidation if added from the start of oxidation. Further, the negative effects of breakaway oxidation can be minimized if CO₂ is added to the atmosphere after an initial period of oxidation in pure air. It was proposed by Haginoya that the adsorption of CO₂ onto

the oxide surface was critical to the inhibiting mechanism. Despite this (single) previous work, a clear understanding of the mechanism behind how CO₂ inhibits the oxidation is not known.

The formation of a protective layer at the oxide-metal interface, as is the case for beryllium, is a viable method to reduce the excessive oxidation. To that end, it has been proposed that additions of yttrium may inhibit the oxidation of AlMg alloys by formation of such a layer. Yttrium is a lanthanoid—a strong oxide former that is known to be surface active. Furthermore, it may react to form the Al₃Y intermetallic phase which has a melting point above what is typically seen in aluminum industrial furnaces. An yttrium concentration of 5.5 at% is required to form the Al₃Y phase at 750 °C. The Al₃Y phase is solid at temperatures below 960 °C (6). If sufficient segregation occurs, the formation of this solid phase at the oxide-metal interface, with an associated melt-protective effect, may be possible. Yttrium has previously been shown to suppress the ignition of a magnesium alloy via the formation of Y₂O₃ at cracks that had formed in the MgO layer, thus preventing the burning of the metal at temperatures up to 730 °C (7).

The aim of the current paper is to summarize our findings of the respective effects of CO₂ in the gas atmosphere and yttrium-alloy additions to the melt in terms of suppressing melt oxidation.

Experimental

Two model alloys were used in this work a 5 % magnesium and a 100 ppm yttrium-5 % magnesium alloy. To produce the model alloys, 99.999 % pure aluminum from Puratronic, 99.98 % pure magnesium from Sigma Aldrich and 99.9 % yttrium from Alfa Aesar were used as raw materials. To generate the 100 ppm yttrium-5 % magnesium alloy, first, a master alloy containing 5 % of yttrium in aluminum was made in a tungsten arc melter under an argon atmosphere. The master alloy plus aluminum and magnesium in proportions to give the desired alloy composition, were charged in to an alumina crucible. The alumina crucible was heated to 850 °C under an argon atmosphere and held for 15 minutes to ensure a homogenous alloy.

To quantify the effects of CO₂ and yttrium on the oxidation, a Linseis PT 2400 a thermogravimetric balance (TGA) with a sensitivity of 10 µg was used to measure the mass change over time at a constant temperature. The model alloys were sectioned to 1.25 mm thick slices using a SiC abrasive saw. The slices were then punched to discs measuring 10 mm in diameter. One side of the sample was ground to a 1 µm finish (CO₂) or 22 µm (Y) finish and washed in ethanol. The sample was weighed and placed in the furnace within 30 minutes of final grinding.

Various CO₂ containing environments were tried, with CO₂ percentages ranging from 5-50 % CO₂ in air with both gasses provided by AGA, the effects were measured over a 7 hour time period at 750 °C. The generated oxide layers were characterized in a DualBeam Focused Ion Beam miller (FIB) and Transmission Electron Microscope (TEM). No special sample preparation was required to examine both the top surface and cross-section in the FIB. TEM samples were selected and prepared in the FIB.

For the tests on the yttrium containing alloy, a standard oxidation program was used across all experimental runs, which consisted of heating from room temperature to 750 °C in 35 minutes under a flowing argon atmosphere, followed by holding of the sample for 16 hours at 750 °C under an atmosphere of flowing air (supplied by AGA). Cooling from 750 °C to room temperature took approximately one hour and was done under an argon atmosphere. The furnace was vacuumed and filled with argon prior to the start of heating and a total gas flow rate of 0.05 liter per minute was maintained at all times. Characterization was carried out in the Scanning Electron Microscope (SEM) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) and the FIB. As a reference a 5% magnesium alloy without yttrium was tested to the same procedure to provide a baseline for comparison.

To investigate the morphology of the oxide layer on the yttrium samples from shorter oxidation times, a horizontal alumina tube furnace was employed. The furnace was vacuumed and filled with dry air two times to ensure a similar atmosphere to the TGA experiments. A sample measuring 24 x 14 x 1.5 mm was prepared with the same method used for the TGA experiments. The prepared sample was placed in an alumina boat that was then slid into the preheated furnace at 750 °C and held for 30 or 90 minutes before removal. This allowed the oxide layer to be examined for shorter time periods than were possible in the TGA, due to the longer heating and cooling time of the TGA.

Results

CO₂ atmosphere

TGA curves

In agreement with previous studies (4) (5), the addition of CO₂ to an air atmosphere was found to inhibit the oxidation of an AlMg alloy to a similar extent as beryllium additions as shown in Figure 1 as both CO₂ and beryllium resulted in a low percent mass gain and delay in the onset of breakaway oxidation. Tests in pure air generally broke away after 210-220 minutes from the start of heating, whereas, the samples oxidized in CO₂ did not breakaway after 7 hours at temperature. Varying the CO₂ percentages between 5-50 % did not have a notable impact on the oxidation. The onset of breakaway oxidation was determined by the criterion below, to determine the point where the mass change over 1 minute departed from linear.

$$mass_t - mass_{t-1min} > 0.02$$

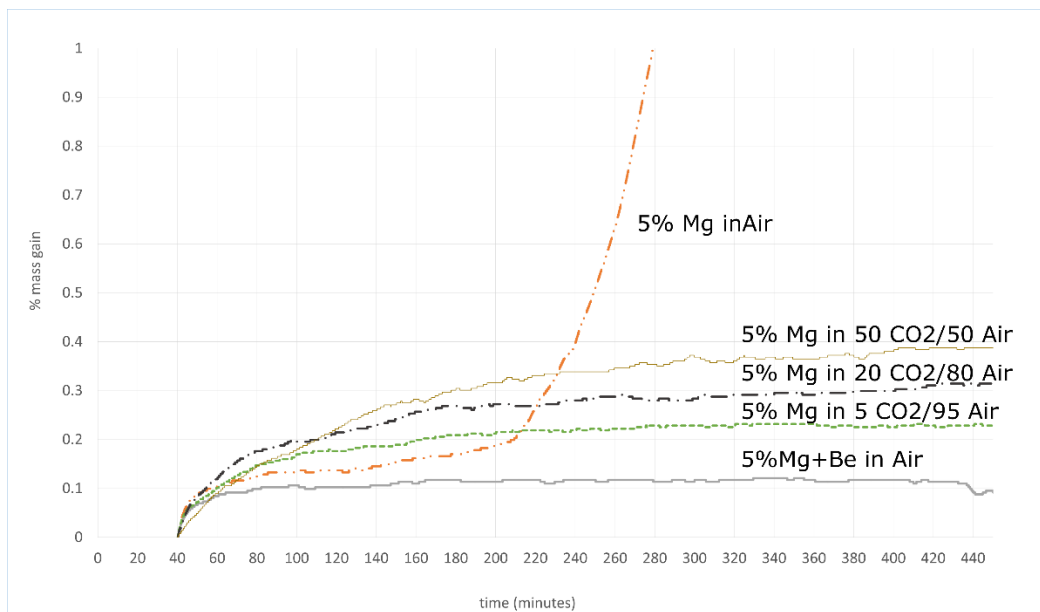


Figure 1 TGA curve showing the effects of CO₂ on the oxidation at 750 °C.

Morphology and composition

Examination of the generated oxide layer in the FIB showed an oxide layer with a uniform thickness of 300-400 nm that was composed of small grains of MgO as confirmed by the diffraction pattern and EDS scan in the TEM. The grains averaged 35 nm across as shown in Figure 2-Figure 3. This oxide layer is similar to what was found on the beryllium containing samples from previous work (1).

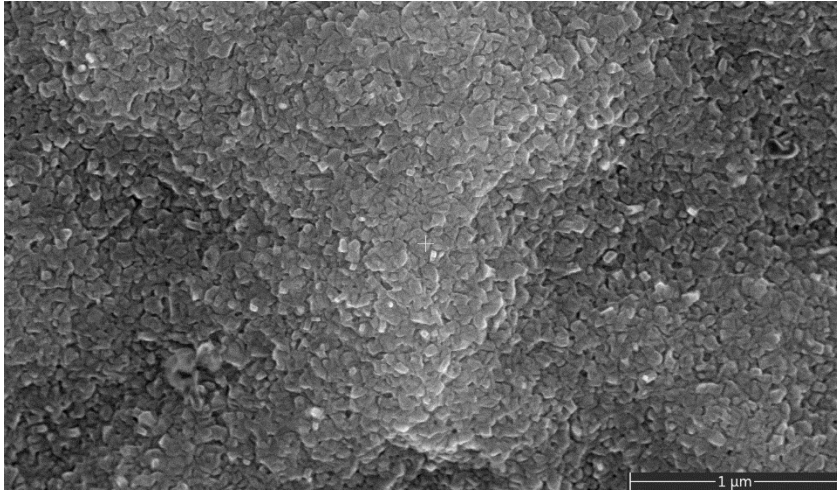


Figure 2 Top surface of sample oxidized in 20CO₂/80 Air for 7 hours at 750 °C showing small grains of MgO.

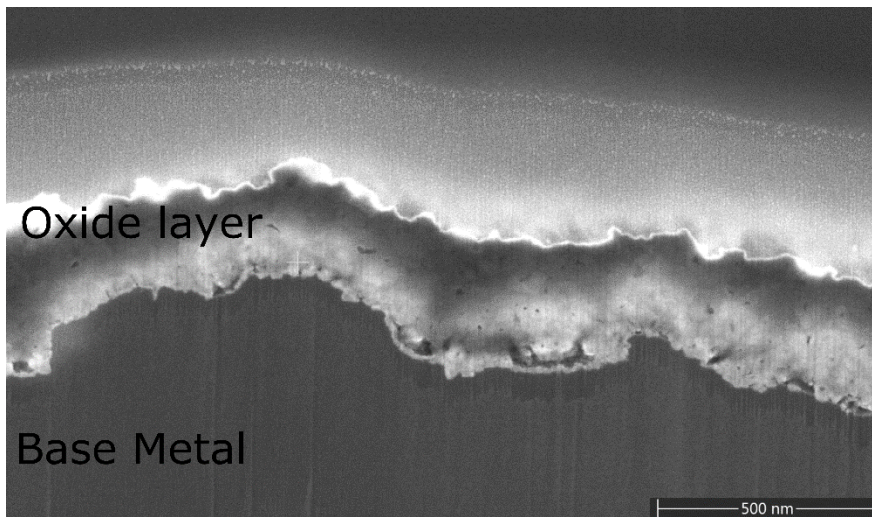


Figure 3 Cross-section of oxide layer on sample oxidized at 750 °C in 20CO₂/80 Air for 7 hours.

Yttrium addition

TGA curves

The summarized results for yttrium samples that were oxidized to completion (oxidation of all Mg to MgAl₂O₄) are given in Table 1 with the mass gain curves shown in Figure 4. For comparison the results of a baseline containing a 5 % magnesium alloy is also included. The time for breakaway oxidation to begin after the isothermal period had been reached was calculated to determine the effectiveness compared to a 5 % Mg alloy that was free of yttrium. A sample with 100 ppm of beryllium and 5 % magnesium was tested to the same procedure as the yttrium containing samples, and it did not break away after 16 hours of oxidation.

Yttrium additions on average had a limited impact on the oxidation compared to a 5 % Mg alloy, however, significant variation was found amongst the samples as shown in Figure 4 with breakaway times varying from 170 to 328 minutes. The total sample mass gain is determined by the magnesium content as the oxidation will essentially stop once all the magnesium is oxidized to MgAl₂O₄. As the total percent mass

gain for Y3 was less than Y1 and Y2 it would indicate the magnesium content in the samples varied. However, this did not seem to affect the breakaway time for this alloy significantly as Y1 had a higher Mg content than Y3, yet it broke away later as can be seen in Table 1.

Table 1 Mass gain and breakaway time for oxidation tests for yttrium samples that were oxidized to completion.

Test	Mass gain (mg)	% Mass gain	Breakaway time (min)
Y1	43.7	15.6	328
Y2	42.2	15.6	186
Y3	31.2	12.9	170
5% Mg reference	30.5	13.6	209

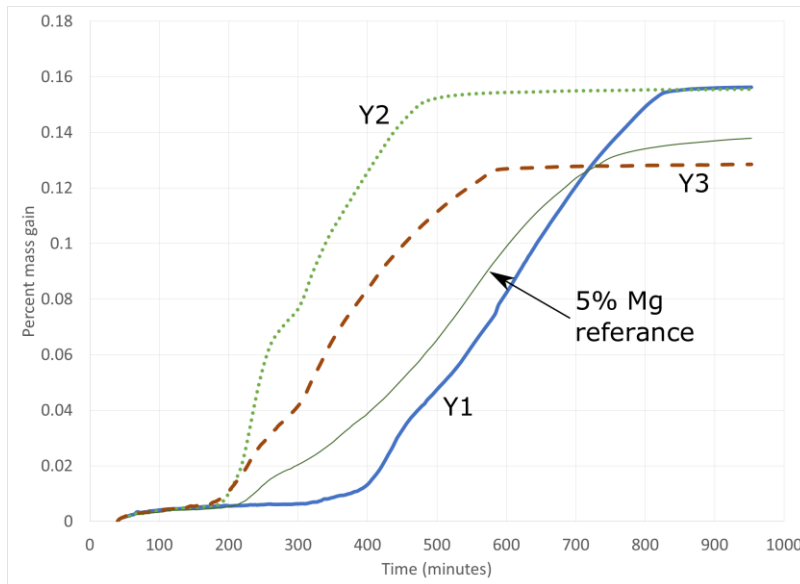


Figure 4 TGA curves for yttrium containing alloy oxidized in air at 750 showing a large variation between breakaway times in comparison to a 5% magnesium reference that did not contain yttrium.

Morphology and composition

After oxidation for 16 hours the samples were found to be significantly distorted from their original disk shape and were covered with a black oxide layer. Cross-sectional images from the SEM are shown in Figure 5-Figure 6, with the dashed rectangle showing the outline of the original sample shape (10 mm diameter x 1.25 mm). EDS scans showed that the samples were covered in a layer of $MgAl_2O_4$ spinel with no traces of yttrium in the oxide layer. The presence of the spinel phase was determined from the Mg:O ratio, where a 1:1 ratio indicated MgO and a 1:4 ratio indicated $MgAl_2O_4$. Towards the center of the sample, un-oxidized aluminum was found. An yttrium containing phase was found in the aluminum metal where the yttrium had segregated out into a second phase where the primary component was aluminum. This phase existed as discrete particles spread throughout the aluminum. The exact composition of the yttrium phase was not determined as the particle size is less than the analysis volume of the EDS. The measured yttrium content was found to be between 3-5 atomic percent. Given that the yttrium content in the second phase was less

than 5 atomic percent it is likely that it was the Al_3Y phase as this is the intermetallic phase with the lowest yttrium content.

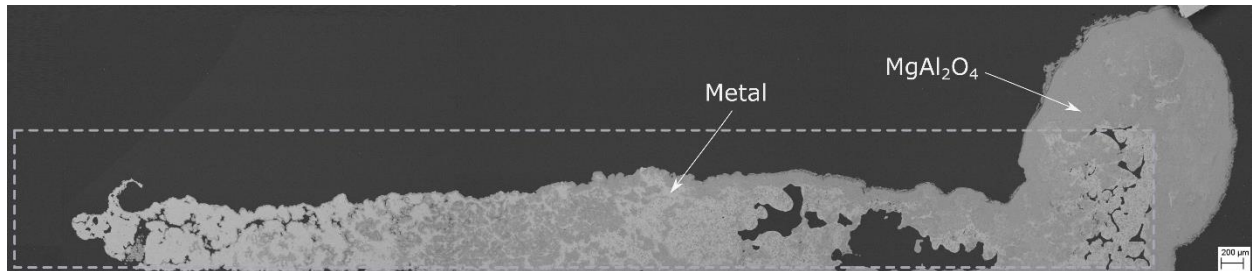


Figure 5 Cross-section of 5 % Mg sample oxidized at 750 °C for 16 hours in air with the dotted line representing the original sample shape.

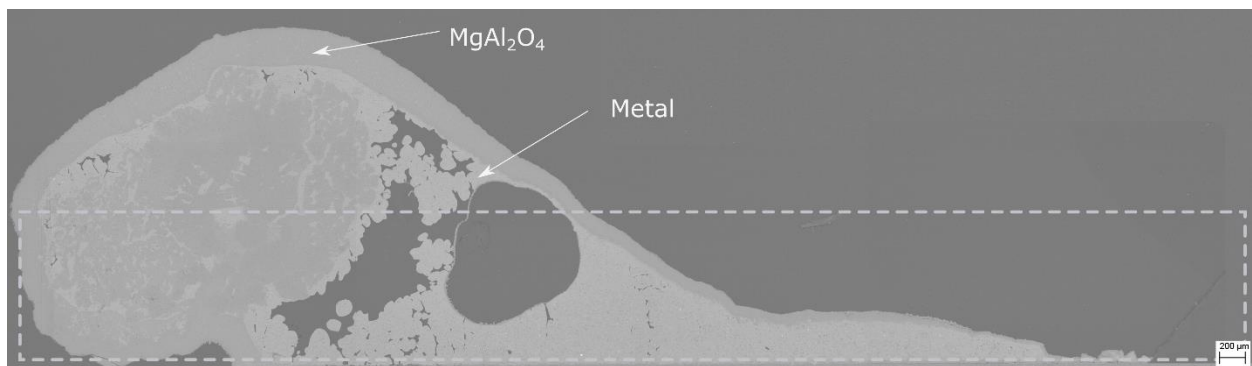


Figure 6 Cross-section of 5 % Mg +Y sample oxidized at 750 °C for 16 hours in air with the dotted line representing the original sample shape.

Investigation of the yttrium containing sample oxidized for thirty minutes in the tube furnace showed that the yttrium had segregated to the oxide layer as discrete particles as shown in Figure 7. The oxide layer was found to be a thin layer of MgO measuring between 130-600 nm thick, but generally was 200-470 nm thick. Backscatter electron images show that the yttrium existed just below the oxide layer. No variation in the magnesium and oxygen EDS signal was seen between the regions containing yttrium and those without, but a variation in the aluminum signal was found, indicating that the yttrium was in the un-oxidized state just below the MgO oxide layer. After 90 minutes of oxidation, the yttrium phase was no longer visible with the backscatter detector due to a thickening of the MgO layer, but was still detectable with EDS.

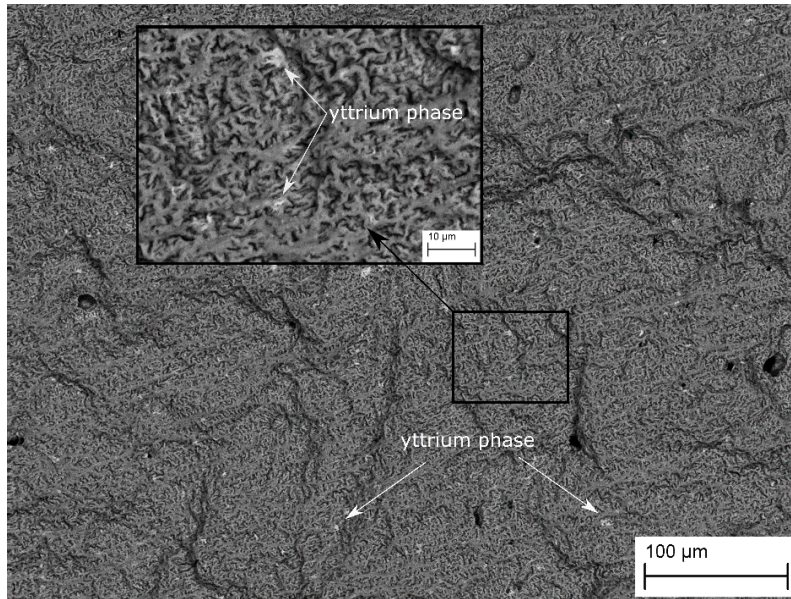


Figure 7 Surface of 100 ppm yttrium sample after 30 minutes of oxidation in air at 750 °C showing MgO layer with yttrium phase underneath.

Discussion

From a thermodynamic standpoint, the addition of limited amounts of CO₂ to an air atmosphere should have a no effect on the oxidation, as magnesium will react preferentially with oxygen. However, it is clear from the TGA results that this is not the case. The addition of CO₂ appeared to have a similar effect on the oxidation as beryllium additions, in that the growth of the granular oxide layer on top of the dense oxide layer was notably reduced. The granular oxide layer on top of a dense oxide layer was found after the oxidation of an AlMg alloy in air for time periods before the onset of breakaway oxidation. The addition of beryllium resulted in a loss of this granular layer. The loss of the granular layer was the result of reduced diffusion of magnesium vapor through the oxide layer caused by a BeO layer (1). This would indicate that the addition of CO₂ to the atmosphere modified the oxide layer, inhibiting the diffusion of magnesium out compared to an oxide layer formed in pure air. In an expanded explanation (8), it was concluded that a carbon-containing diffusion barrier is formed on top of/in the MgO layer, limiting the amount of magnesium vapor escaping from the alloy, resulting in a reduced oxidation rate.

The average effect of yttrium additions was limited with respect to the time breakaway oxidation began, with some samples showing an increase and some a decrease in time compared to a yttrium free 5% magnesium alloy. The formation of discrete Al₃Y particles near the oxide layer can be considered promising as it suggests that the segregation and nucleation conditions were sufficient to form a yttrium containing phase even with an initial concentration of only 100 ppm. However, these particles did not grow into a protective layer as was desired. The lack of a clear protective effect such as was seen in previous work on ignition proof magnesium alloys (7) is likely the result of having insufficient yttrium to form a protective layer. The Y:Mg ratio was only 1:500 as opposed to the 1:25 seen in the ignition proof magnesium alloy, therefore, it is possible that higher yttrium concentrations could inhibit oxidation.

Based on the results of the tests with CO₂ and yttrium, further insights can be made into potential replacements for beryllium. Both beryllium and CO₂ reduced the oxidation by minimizing the diffusion of magnesium from the melt and out through the oxide layer. The diffusion of magnesium out through the oxide layer can then be taken as the rate controlling step in the oxidation process. Therefore, reducing the

diffusion of magnesium out from the bulk metal and/or oxygen in from the atmosphere to the reaction site is the ideal method to controlling the oxidation. In terms of a cover gas, CO₂ seems to be ideally suited for this as it readily available, relatively safe and effective. Any alternative cover gas would be required to react with the oxide surface to modify it in a way which prevents the diffusion of magnesium out. As it is not known exactly how the CO₂ modifies the existing layer, it is difficult to conclude which specific properties that would be required of a cover gas.

In terms of alternative alloying additions to beryllium, any alternative addition would be required to have the following properties at the very minimum:

- Strong tendency to segregate to the oxide-metal interface (surface active)
- Be stable in the melt/oxide layer (low vapor pressure)
- Ability to form a solid layer near the oxide metal interface

A strong segregation tendency is required as it will allow smaller quantities of the alloying element to be used. If the addition of a particular alloy element that is not specifically listed in the alloy designation is often restricted to a concentration as low as 0.5 % (500 ppm), this would be the absolute maximum limit any specific alternate would have (3). The high tendency of beryllium to segregate is a prime of example of this as only 2 ppm is required to protect a 5 % magnesium alloy, as after a short time the concentration near the oxide layer will be notably higher in beryllium than the bulk. A tendency to segregate will increase the effective concentration near the oxide layer and increase the likelihood of a diffusion barrier forming. Particular focus should, therefore, be placed on known surface active elements.

Any added element must be stable in the melt. If the element has a high vapor pressure any positive effects may be lost as the concentration will decrease with time and/or result in an increase in porosity of the oxide layer. The negative effects of elements with a high vapor pressure was noted by Thiele as translated by Drouzy and Mascré (9) (10).

Most importantly, the added alloying element must be able to react to form a solid layer at the oxide-metal interface that acts as a barrier to the diffusion of magnesium out and/or oxygen in. This layer could be within the oxide layer or just beneath the oxide layer. Given that the elements that have a higher preference for oxygen than magnesium do not appear to meet the other criteria listed above, it is unlikely that another oxide forming element, like beryllium, will be identified. Thus, the focus should be on finding an alloying element that forms a solid intermetallic phase at the oxide-metal interface.

Yttrium additions would appear to fulfill these requirements with the exception that it forms as discrete particles rather than as a layer at the oxide-metal interface. The formation of a second phase near the surface is promising, if the segregation to the surface can be further promoted the concentration may become sufficient to form a uniform layer as seen in beryllium containing alloys. If all the yttrium in the model alloy formed an Al₃Y layer at the surface the resultant layer would be 80 nm thick. A layer of this thickness could be sufficient to reduce magnesium diffusion through the oxide layer as it is two times thicker than the protective BeO layer found on the 100 ppm beryllium-5% magnesium alloy (1). This would indicate that sufficient amounts of yttrium existed in the melt, but it was not distributed in a manner that allows the desired results to be achieved.

Conclusion

The addition of CO₂ to an air atmosphere was shown to reduce the oxidation of an AlMg alloy to a similar extent as beryllium additions. It was proposed that the addition of CO₂ modified the surface of the oxide

layer in a way that reduced the transport of Mg out of the oxide layer resulting in a decrease in the oxidation and an increase in the time for breakaway oxidation to begin.

Yttrium additions were found to on average have little effect on the oxidation, but for individual experiments the time for breakaway oxidation to begin varied from 170 to 328 minutes compared to 209 minutes for an yttrium free alloy. Oxidation for shorter times showed that after 30 minutes of oxidation yttrium existed as a second un-oxidized phase of discrete Al_3Y particles just below the MgO oxide layer.

Based on the results of this work it was proposed three requirements for any future alternative alloying elements to beryllium must have. These are: tendency to segregate, stable in the melt, forms a solid layer at the oxide-metal interface.

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Figure 2 Top surface of sample oxidized in 20CO₂/80 Air for 7 hours at 750 °C showing small grains of MgO.

Figure 3 Cross-section of oxide layer on sample oxidized at 750 °C in 20CO₂/80Air for 7 hours.

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