The Role of CO₂ in the Oxidation-Protection of Mg-Containing Aluminum Alloys

CATHRINE KYUNG WON SOLEM, PER ERIK VULLUM, MAHSA EBADI, GABRIELLA TRANELL, and RAGNHILD E. AUNE

TEM EDS–EELS and XPS have been performed on disc samples of Al alloys 5182 (AlMg4.5Mn0.4) and 6016 (AlSi1.2Mg0.4) heat treated in an oxidizing atmosphere of 76 pct synthetic air, 20 pct Ar, and 4 pct CO₂. For both alloys, an amorphous C–C bonded layer on top of a nanocrystalline MgO layer was observed, which is believed to inhibit further oxidation of Mg for the 5182 alloy and breakaway oxidation for the 6016 alloy.

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SMALL additions (≥ 4 pct) of CO₂ in an oxidizing atmosphere have proven to have an immediate significant inhibiting effect on the rate of oxidation of the Al alloys 5182 (AlMg4.5Mn0.4) and 6016 (AlSi1.2Mg0.4), in regard to mass gain and oxide layer thickness.[1–3] The mechanism in which CO₂ inhibits the oxidation rate is, however, still unclear and under investigation.

Previous research[3] has established, through transmission electron microscopy (TEM) analyses, that after being exposed to small amounts of CO₂ at 750 °C, the Al alloy 5182 exhibited an amorphous carbon (C) layer with a thickness of 40 to 100 nm on top of a 200- to 400-nm-thick MgO layer, formed during heating of the alloy, according to Eq. [1].[3] The amount of C originating from the sample could easily be distinguished from the C deposited during sample preparation due to a Pt–Pd (80:20) electrically conducting layer between the two C layers. The Pt–Pd coating was originally applied due to poor conductivity caused by the dense, continuous nanocrystalline MgO oxide layer. It was concluded that further breakaway oxidation (see Eq. [2]) had been inhibited by the presence of a C layer, retarding further oxidation of the Mg and MgAl₂O₄ (spinel) formation.

A similar inhibiting effect has also been observed in earlier research by the present authors for low Mg-containing Al alloys.[1] Further investigations of the Al alloy 6016 (with 0.4 wt pct Mg) were hence carried out with the aim to identify if a small amount of CO₂ in the atmosphere even in this case enables the formation of an amorphous C layer protecting the alloy from further oxidation.

\[
\begin{align*}
2\text{Mg} + \text{O}_2 & = 2\text{MgO} \quad \Delta G_{750°C}^0 = -981.64 \text{ kJ} \\
\frac{2}{3}\text{MgO} + \frac{4}{3}\text{Al} + \text{O}_2 & = \frac{2}{3}\text{MgAl}_2\text{O}_4 \\
\Delta G_{750°C}^0 & = -925.66 \text{ kJ}
\end{align*}
\]

The Al alloy 6016 was examined by TEM using a double spherical aberration-corrected cold FEG JEOL ARM200FC microscope (JEOL Ltd., Tokyo, Japan), operated at 200 kV. No Pt–Pd coating was applied. The TEM lamellae were prepared by a Helios G4 UX FIB (FEI, Hillsboro, OR), and further investigations were carried out by a high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) combined with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) to secure that all elements of interest were mapped in the same way as in the previous study by the present authors.[3]

A Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer (Kratos Analytical Ltd., UK) was applied to analyze the oxidized discs of Al alloys 5182 and 6016. The depth profiling was performed by \(\text{Ar}^+\) clusters of ions at 4 kV. X-ray photoelectron spectroscopy (XPS) was performed with a monochromatic AlKz X-ray source operating at 11 mA and 11 kV (121 W). A pass energy of 160 eV was applied for the survey scans investigating an area of approximately \(700 \times 300 \mu\text{m}\), and 20 eV for the high-resolution peaks. CasaXPS (Casa Software Ltd, Japan), version 2.3.24 was used to analyze the data.

Figure 1 presents the SEM and TEM results of the low Mg-containing Al alloy 6016 disc oxidized in an...
atmosphere of 76 pct synthetic air, 20 pct Ar, and 4 pct CO₂ at 750 °C for 7 hours. As can be seen from Figures 1(a) and (b), a dense, continuous nanocrystalline MgO oxide layer with a thickness of 160 to 200 nm was identified to exist on top of a discontinuous spinel (MgAl₂O₄) layer consisting of large crystals in the range of 0.5 to 3 μm. From Figure 1(b) a weak contrast line above the MgO layer can be seen, and when tuning the contrast of the apparatus, a bright line 15 to 120 nm above the MgO layer was identified as shown in Figure 1(c) (marked with a white dashed line) confirming the presence of an adsorbed C layer.

From Figure 1 it can be observed that the Mg content in the alloy had an influence on the oxidation steps during heating at 750 °C, as breakaway oxidation clearly had occurred forming a discontinuous layer of MgAl₂O₄ particles separating the MgO layer and the Al bulk in the case of the low Mg-containing Al alloy 6016, but not for the high Mg-containing Al alloy 5182.[3] The presence of the spinel phase was confirmed by the quantification of the ratio between Mg, Al, and O (approximately 1:2:4) by EDS and EELS. It is therefore believed that the amorphous C layer inhibited not only the oxidation of Mg, but also the breakaway oxidation of MgO as the sample heat treated in synthetic air without the small additions of CO₂ revealed only the presence of MgAl₂O₄, and no MgO.[3] The thickness of the MgO layer was thinner for the Al alloy 6016 than for the Al alloy 5182, but the influence of adding 4 pct CO₂ to the oxidizing atmosphere still applies, however, to a lesser extent, for the low Mg-containing alloy.

The HAADF STEM image confirmed the observation of an amorphous C layer as shown in Figure 2(a). Moreover, the EDS–EELS analyses verified the presence of a continuous MgO layer, based on a combination of Mg (red), O (blue), and Al (green) is presented in Figure 2(h). In Figure 2(i), a combination of Mg (red), O (blue), and Al (green) is presented.
observed as blue/violet-colored MgAl$_2$O$_4$ crystals, strengthened the theory of inhibited breakaway oxidation.

Fe and Si were also mapped and confirmed earlier findings for Al alloys containing Mg and Si, where clusters of Si were found at grain boundaries and close to the surface.\cite{4}

Like in the case of the Al alloy 5182, the TEM analysis of the Al alloy 6016 confirmed that the C from the CO$_2$ had been adsorbed onto the sample surface, and the EDS–EELS analyses confirmed that it had been adsorbed onto a MgO surface. XPS analyses were subsequently carried out for both Al alloys in order to determine the bonding energies for C.

In Figure 3, the Mg1s, O1s, Al2p, and Mn2p peaks identified to be present in Al alloy 5182 are presented as a function of the binding energy for each sputtering time, and in Figure 4 the XPS spectra for Al alloy 6016, where Mg1s,
O1s, Al2p, and Si2p were identified to be present, are presented. The C1s peaks as a function of binding energy for the same sputtering times are presented for both alloys in Figure 5.

For Al alloy 5182 (4.5 wt. pct Mg), it was clear that the Mg had diffused towards the surface, as Mg1s was already recognized at values around 1304.0 eV after 50 seconds of etching (being very close to the top surface), having a concentration of 9.58 at. pct together with 32.12 at. pct for O1s. Very low concentrations of Al2p (< 3.53 at. pct) were observed by XPS after 1960 seconds (being closer to the bulk), strengthening the theory of no breakaway oxidation and thereby confirming the previous observations by TEM and EDS–EELS analyses (reported elsewhere [3]) as the Mg1s and O1s concentrations were identified to be 31.49 and 55.45 at. pct, respectively.

For Al alloy 6016, (0.4 wt. pct Mg), a concentration of 8.52 at. pct for O1s and 5.55 at. pct for Si2p were observed to be present at the very top surface of the Al sample. The XPS spectra of the Si2p strengthened the theory that Si clusters were present close to the Al disc sample surface, which thereby even in this case confirmed the previous observations by TEM and EDS–EELS analyses [4]. As for Al alloy 5182, the Al alloy 6016 revealed Mg1s identified for binding energies around 1304.5 eV after 350 and 750 seconds of etching, indicating the presence of MgO and carbonates [5]. A clear shift can, however, be seen in the Mg1s peak after 1960 seconds, as well as the appearance of an Al2p peak. The binding energies for these peaks correlate well, according to the performed TEM and EDS–EELS analyses, with the energies reported in the literature for MgAl2O4 [6] which here was only observed for the low Mg-containing Al alloy 6016.

The inhibition of the oxidation rate for both Al alloys can be further evaluated by looking at the XPS spectra for C1s in Figure 5. As can be seen from Figure 5(a), the C1s spectra for Al alloy 5182 revealed a sharp peak at the very top surface of the Al disc sample, having C–C, C–O, C=O, and carbonates binding energies, and an atomic concentration of 71.42 at. pct. This correlates well with the O1s peak observed in Figure 3(b) after 0 second of etching, as well as the amorphous C layer identified by TEM. The atomic concentration of C1s as shown in Figure 5(a) decreases, as a function of depth into the sample, to 56.23 at. pct after 50 seconds, and 26.59 at. pct after 350 seconds, with a changing distribution between C–C, C–O, C=O, and carbonates. This supports the results of Tosoni et al. [8] which found CO2 to be adsorbed onto MgO (100) surfaces as carbonates. Furthermore, the presence of the Metal–Carbon (M–C) bonding strengthens the previous observations made by XRD where Mg2C3 was confirmed to exist for the high Mg-containing Al alloy 5182 [3]. When reaching 350 seconds of etching there is a clear decrease in the atomic concentration of C1s (from 56.23 at. pct at 50 seconds to 26.59 at. pct at 350 seconds) as well as an increase in the case of Mg1s (from 9.58 at. pct at 50 seconds to 24.02 at. pct at 350 seconds) and O1s (32.12 at. pct at 50 seconds to 46.06 at. pct at 350 seconds). The changes in atomic concentration as a function of etching time and depth into the sample can be observed in Figure 6(a).

A similar observation was not seen at the very top surface in the case of the Al alloy 6016 at 0 second of etching. However, a decrease in the atomic concentration of C1s (from 97.58 at. pct at 50 seconds to 81.26 at. pct at 350 seconds) was observed at the same time as significant changes were observed in the XPS spectra for Mg1s and O1s (see Figures 4(a) and (b)). This observation corresponds well with the observation made previously for the high Mg-containing Al alloy 5182 (Figure 5). When looking at the distribution of the atomic concentrations based on the XPS spectra observed in Figure 6(b) an
increase of the Mg 1s (blue graph) and O 1s (orange graph) concentrations can clearly be seen past 350 seconds of etching time, as well as a decrease of the C 1s (gray graph). The significant increase of Al 2p (green graph) after 1960 seconds was also confirmed (from 3.71 at. pct at 750 seconds to 12.32 at. pct 1960 seconds), strengthening the theory of breakaway oxidation.

As a result of the stability of MgO at 750 °C (see Eq. [1]), it is believed that Mg vapor may have diffused through cracks in the nanocrystalline MgO layer,[9] allowing it to react with the adsorbed CO₂ forming MgO and elemental, amorphous C (see Eq. [3]).[10] The elemental C formed on the inherent MgO surface as shown in Figure I is then believed to hinder further oxidation, as the amorphous C layer prevents O₂ to react with any Mg or Al thermodynamically, this scenario is supported by the highly negative ΔG°_{\text{750°C}} value of Eq. [3]. It is, however, necessary with further thermodynamic calculations as well as investigating the mechanism of the formation of the C layer to establish the stability of this layer.

\[
\text{CO}_2(g) + 2\text{Mg}(g) = 2\text{MgO} + \text{C} \\
\Delta G°_{\text{750°C}} = -650.86 \text{ kJ}
\]

In summary, based on the results presently secured through TEM EDS–EELS and XPS, it is established that CO₂ has an important role in the view of inhibiting the oxidation rate of AlMg alloys. The CO₂ in the oxidizing atmosphere is believed to react with Mg (g), forming an amorphous C–C bonded layer on top of a nanocrystalline MgO layer in the case of both the Al alloys 5182 and 6016 which is considered to inhibit further oxidation of Mg and thereby breakaway oxidation of MgO. The presence of Metal–Carbon bonding energies also strengthens the previously reported observations made in view of the presence of Mg₂C₃ for the high Mg-containing Al alloy 5182 and clusters of Si on the very top surface for the low Mg-containing Al alloy 6016.

Future work will include thermodynamic calculations and further evaluations of the observed amorphous C layer establishing the mechanism behind the formation of the layer.

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