OXIDATION OF COMMERCIAL PURITY ALUMINUM MELTS: AN EXPERIMENTAL STUDY

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Abstract

Oxidation and dross formation is an undesirable, but unavoidable part of the production of aluminum. Past efforts to minimise dross formation through improved melt processing practices have been hindered by uncertainty in the fundamental behavior of how oxides grow on molten aluminum. The growth of oxide films formed on pure aluminum melts held at various temperatures and exposed to ambient air is investigated. Growth rates (i.e. mass/area as a function of time) were determined by skimming oxide films from laboratory-scale melt surfaces after various exposure times and then processing these films to separate oxide from metal. Collected oxide films were characterized using transmission electron microscopy (TEM) and electron diffraction techniques. γ-Al_2O_3 appears to be the dominant oxide species and no breakaway oxidation was observed even at 850°C/14h. The microstructural evolution of the films is discussed in light of the results and behavior implications of this work for industrial cast house situations are discussed.

Introduction

Molten aluminum has a high affinity for oxygen and in an industrial cast house setting, melt losses associated with re-oxidation of molten metal (extracted from oxide in the electrolytic cells) and dross formation represent significant operating costs. A large portion of this is suggested to arise from molten metal transfer operations [1]. However, a medium-scale experimental and simulation study of pouring molten aluminum into a sow mold suggested that the amount of oxide generated in the actual transfer was quite small and that other factors are probably more important [2, 3].

As far as the oxidation literature is concerned, the oxide that forms on solid aluminum at room temperature is amorphous [4, 5], while at higher temperatures, crystalline γ-Al_2O_3 is the dominant oxide. It has been suggested that the γ-Al_2O_3 nucleates at the interface between the amorphous oxide and the metal.[5]

Microstructural studies of oxide films grown on molten aluminum have shown that the first oxide formed is crystalline γ-Al_2O_3 [6]. The few studies that have been done on molten, pure aluminum show that after an initial, rapid formation of an oxide layer, the oxidation rate slows down significantly. After some incubation time during which the oxidation rate is fairly stable, breakaway oxidation has been subsequently observed, where the oxidation rate increases dramatically before stabilizing again after further exposure times [6, 7]. Breakaway oxidation has been attributed to phase transformations (such as γ-Al_2O_3 to α-Al_2O_3) causing localized stresses and failure of the oxide layer and providing a short-circuit path for oxygen to contact the underlying metal [6, 8, 9, 10, 11].

Al oxidation is very sensitive to the presence and condition of residual oxide on the initial material [9, 10, 11, 12, 13] and also to the presence of even trace amounts of impurities [5]. Thus, there is significant variability in data between researchers (using various experimental techniques) and even within individual data sets. This uncertainty in the data has made it problematic to develop reliable oxidation models that can be used to optimize melt handling processes and minimize oxidation.

The present work describes preliminary aspects of an experimental study of the oxidation of commercial high purity aluminum melts exposed to ambient air, from both a kinetic and microstructural point-of-view.

Experimental Method

In order to study the oxidation behavior of the aluminum melts exposed to ambient air, a purpose-built oxidation apparatus was constructed, based on equipment and techniques partially described by Freti et al. [14]. The oxidation rig consisted of a melt vessel of refractory material (Pyrotek N17 fiber board) and is shown in Figure 1. The vessel contained 6 kg of molten commercial high purity aluminum (99.96% Al), with an exposed surface area of 270×190 mm and a depth of 55 mm. The high temperature stainless steel base of the vessel was heated from below via two LPG burners. The melt temperature was controlled via a thermocouple inserted into the melt through the side wall of the vessel, approximately 25 mm below the melt surface. Temperatures were controlled to within ±2°C of the target temperature.

Melts were held at temperatures ranging from 750 to 900°C and were exposed to ambient air for various times from 30 s to 21 h. Samples of the oxide film, referred to as "skims" were taken from the melt surface after various exposure times by skimming the entire melt surface and then quickly solidifying the skimmed material under flowing argon, to minimize further oxidation during solidification. In skimming the melt surface, molten aluminum was collected along with the oxide film: the oxide itself comprised less than 1 wt% of each skim. Figure 2 shows the typical skims collected during the experiments.

In order to separate the oxide from the metallic aluminum, the solid skims were immersed in a molten salt flux at 750°C, in an aluminum titanate crucible. The salt flux was essentially NaCl and KCl in a 1:1 molar ratio, with an addition of 2wt% NaF used to aid in separating the metal from the oxide and also to improve

coalescence of the molten aluminum [15, 16]. The oxide was retained in the salt flux, while the molten aluminum sunk to the bottom of crucible whereupon after cooling and solidifying, it could be recovered and weighed. The mass of oxide in the skims was determined by calculating the difference in mass between the recovered aluminum and the mass of the skim prior to the salt flux treatment.
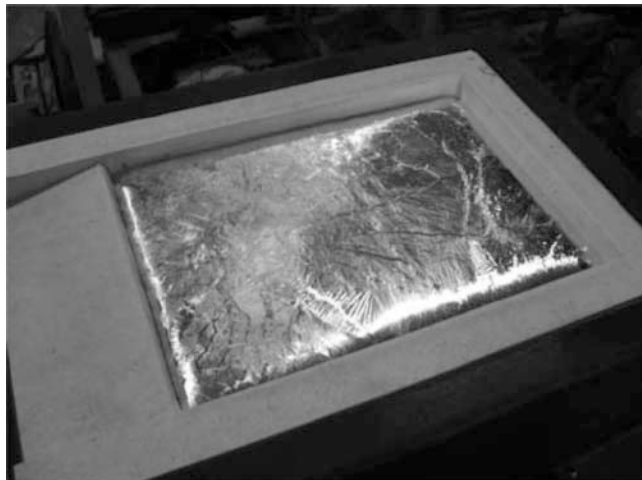

Figure 1. The LPG-fired oxidation rig containing 6 kg of molten high purity aluminum exposed to air. The exposed melt surface area is 270×190 mm, with a melt depth of 55 mm.
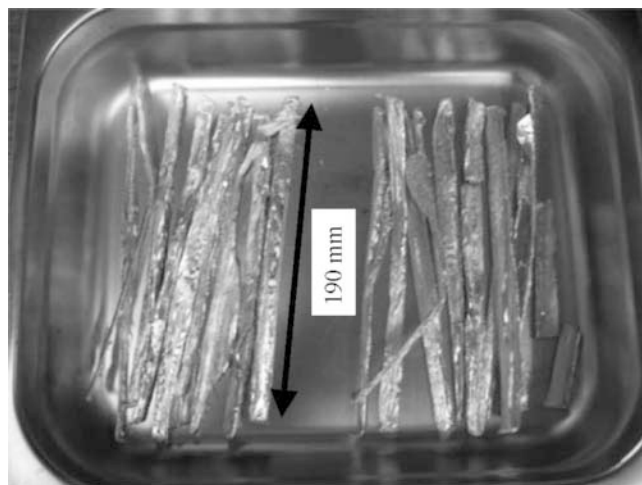

Figure 2. A collection of skims (190 mm in length) collected from the melt surface. The skims fold up during the sampling process; each skim represents the full surface area. The skims are predominantly metallic aluminum, with ~10-100 mg of oxide per skim.

For the purpose of microstructural study, additional oxide specimens were collected from the melts by inserting a blade made of N17 fiber board below the melt surface at an angle and then lifting it up, thereby collecting a thin foil of metal and oxide (in the order of a few hundred μm thick). 3 mm diameter discs were punched from these foils, and then observed in a JEOL JEM2100 transmission electron microscope (TEM). In these initial studies, no further specimen preparation was necessary as it was possible to observe the oxide film directly where it protruded out over natural fractures present in the foil.

Results and Discussion

Figure 3 shows that the amount of oxide that formed on the melt surface increased continuously over the holding times investigated (up to ~21 h). The same data is also presented as an average oxidation rate, i.e. mass of oxide formed per unit area per unit time, in Figure 4. This was calculated using the following equation:

$$R = m / A.t \ (g.m^{-2}.s^{-1}) \tag{1}$$

where R is the oxidation rate in $g.m^{-2}.s^{-1}$, m is the mass of oxide in g, A is the area of the melt surface in m^2, and t is the exposure time in seconds.
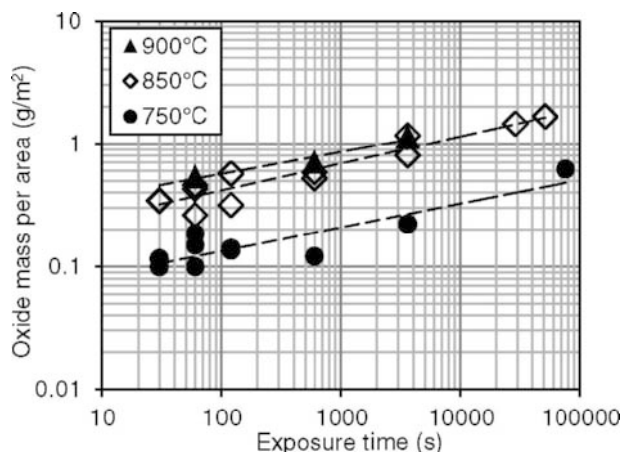

Figure 3. The mass of oxide per unit area formed on high purity aluminum melts exposed to ambient air, at nominal melt temperatures of 750, 850 and 900°C. Note x and y axes are in logarithmic scale.
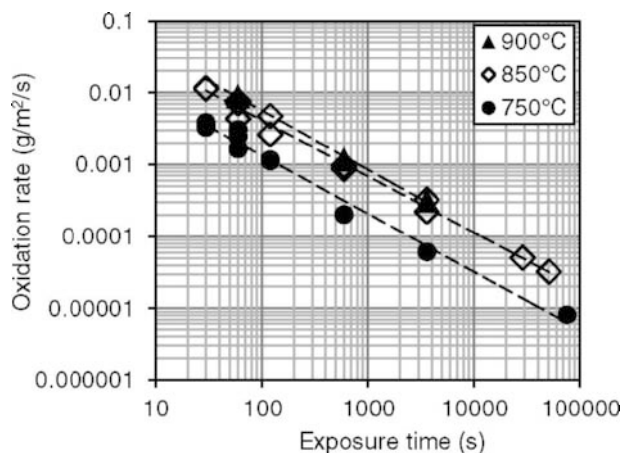

Figure 4. Average oxidation rates for oxide formed on high purity aluminum melts exposed to ambient air, at nominal melt temperatures of 750, 850 and 900°C. Note x and y axes are in logarithmic scale.

The mass of oxide that formed on the melts exposed to ambient air was found to increase continuously over the times investigated. The overall rate at which the oxide grew, however, decreased

continuously over the times investigated, with no observable breakaway oxidation events of the kind reported in other studies.

Overall, the amount of oxide that formed was very low, with under 2 g/m^2 of oxide forming at 850°C after ~14 h, and less than 1 g/m^2 of oxide forming at 750°C after ~ 21 h. This is less than has been reported elsewhere in controlled atmosphere studies [6, 7, 17, 18].

Increasing the nominal melt temperature from 750°C to 850°C resulted in an increase in the amount of oxidation, as can be seen in Figure 3. However, increasing the melt temperature further, up to 900°C, resulted in a negligible difference in oxidation behavior. This result was unexpected.

To further understand this apparent anomaly, a probe thermocouple was inserted into the melt, normal to the melt surface and in the centre of the exposed area, and a temperature profile was recorded as a function of depth into the melt. Figure 5 shows that the measured temperature profile of the melt varied with the set temperature of the melt.
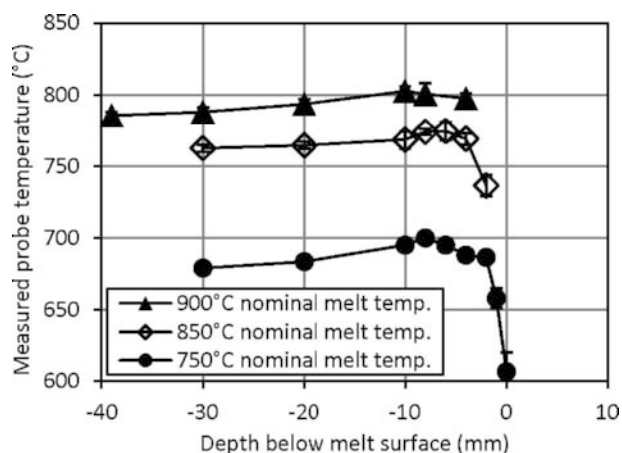

Figure 5. Temperature of the melt as a function of depth below the melt surface, when the nominal melt temperature was set to 750, 850 or 900°C.

There is clearly a temperature gradient through the melt depth, with the melt surface experiencing significant cooling due to being in contact with ambient air. This suggests that the melt surface temperature may be a significant factor in oxidation behavior, and may be a more useful metric than the nominal melt temperature. This has implications for industrial melt handling where oxidation can occur not just in a furnace (where the molten metal is exposed to air at elevated temperatures) but also in situations where the melt surface is exposed to ambient air, such as in launders and crucibles. It also may explain why this study produced significantly less oxide than in studies conducted by other researchers in controlled atmospheres under isothermal conditions.

This also has implications for the analysis of the oxidation kinetics. That is, the temperature of the melt surface (and thus, the metal/oxide interface) needs to be taken into account when investigating the kinetics and mechanism of oxidation at that interface. The detailed kinetic analysis will be discussed in another paper.

The absence of any observed breakaway oxidation events in this study suggests that the oxide films did not experience any microstructural phase transformations during exposure to ambient air. It is therefore expected that the oxide structure should be fairly similar over the times and temperatures investigated.

Figure 6 shows a TEM micrograph of a typical oxide film collected at a melt temperature of 750°C after being exposed to ambient air for ~2 minutes. Two distinct features have been observed in the oxide films. There are readily-visible angular crystallites, ranging in size from a few tens of nm up 100-200 nm in size, distributed through a finer-scale matrix phase. The distribution of the crystallites is non-uniform and their orientations appear to be random. It is unclear at this stage whether these angular crystallites lie within the oxide film or are at the metal/oxide or oxide/air interface. Closer inspection of the oxide film (Fig. 7) shows that the matrix phase is much finer in scale than the angular crystallites and is polycrystalline rather than amorphous.
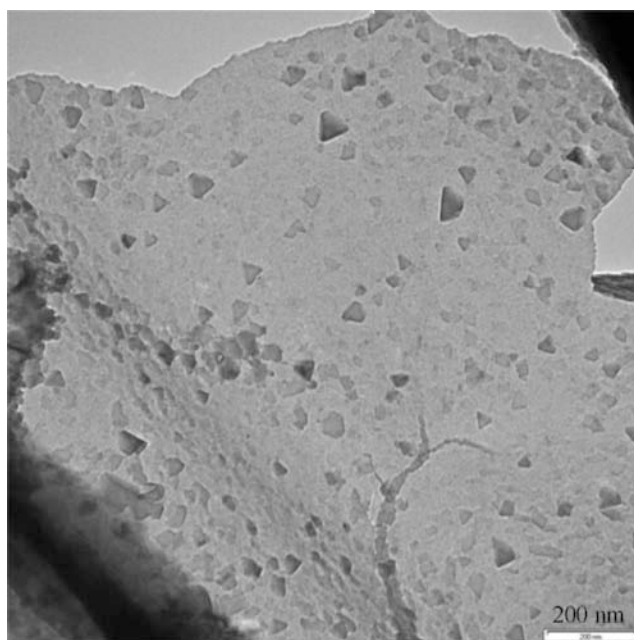

Figure 6. TEM micrograph of oxide film sampled at a melt temperature of 750°C after being exposed to ambient air for ~2 min. Scale bar is 200 nm.

To date, TEM observations of the microstructures of specimens sampled at all three temperatures for exposure times up to 1 h have shown very similar microstructures, and electron diffraction analyses confirm this. Figures 8 and 9 show electron diffraction patterns of specimens taken at 750°C after 10 minutes, and 850°C for 1 h, respectively. The patterns are essentially the same and have been indexed to γ-Al_2O_3. To date, no other oxide species have been observed in any sample, indicating that both the larger angular crystallites and the finer poly-crystalline matrix phase are comprised of γ-Al_2O_3.
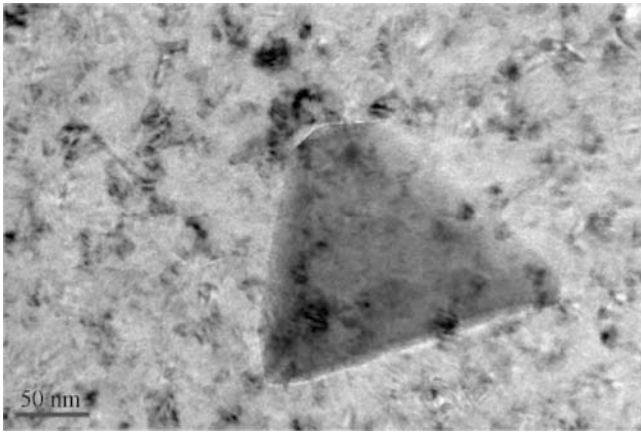
Figure 7. Detail of one of the larger, angular crystallites (specimen sampled after a 10 min exposure time at 850°C), showing the finer scale of the polycrystalline matrix phase. Scale bar is 50 nm.

The electron diffraction patterns of oxide films are ring-type patterns, indicating that the oxide is polycrystalline, consistent with the TEM observations. The diffraction rings are broken into discrete arcs, indicating that crystals are actually not randomly oriented but are aligned in some preferred orientation(s). It is not yet clear what causes this crystallographic texture in the growing oxide films.
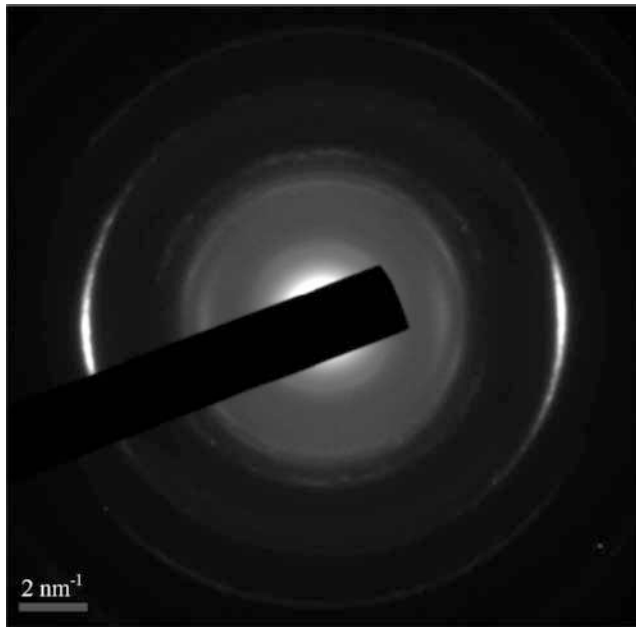

Figure 8. Typical electron diffraction pattern of oxide films formed on molten aluminum at 750°C after an exposure time of 10 minutes.
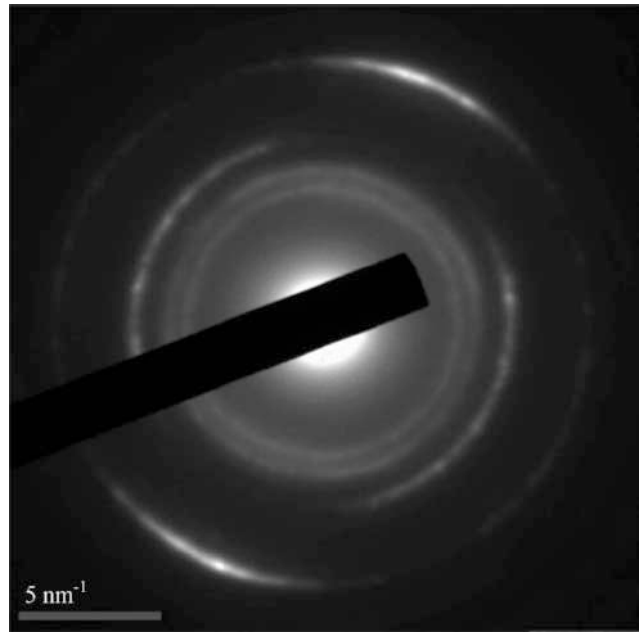

Figure 9. Typical electron diffraction pattern of oxide films formed on molten aluminum at 850°C after an exposure time of 1 h.

Preliminary Conclusions and Future Directions

When left undisturbed, high purity aluminum melts do not oxidize appreciably when exposed to ambient air, even at very long time scales up to ~21 h and at holding temperatures up to 900°C.

It has been demonstrated that exposing high purity aluminum melts to air is not, in and of itself, sufficient to account for the significant oxidation and dross formation that occurs in an industrial setting. Clearly there must be other significant factors/preconditions in the cast house that need to be met in order for this to occur.

It is likely that the low oxidation levels observed in this study are due (at least partially) to the thermal convection of the air reducing the actual melt surface temperature, with respect to the nominal melt temperature. Thus air temperature appears to be a significant factor in regards to the extent of oxidation, and has implications for melt handling processes in an industrial setting.

Microstructural characterization of oxide films formed after exposure times up to 1 h have shown that there are two "phases" present: larger angular crystallites and a finer poly-crystalline matrix phase. At this stage it is unclear if the larger crystallites are within the matrix phase or at one of its interfaces, but observation of cross-sectional specimens will resolve this uncertainty. Both of the "phases" appear to be γ-Al_2O_3. No other oxide species have yet been observed.

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