Characterization of Lead Enrichment on Electrochemically Active AlPb Model Alloy

Oystein Sævik,a Yingda Yu,a Jan Halvor Nordlien,b and Kemal Nisancioglu³,a,b,c,

aDepartment of Materials Technology, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
bHydro Aluminium Research and Development Materials Technology, N-4256 Håvik, Norway
cE-mail: kemaln@material.ntnu.no

Certain commercial aluminum alloys can become electrochemically activated by heat-treatment as a result of enrichment of the trace element Pb at the surface. For a better understanding of the nature of activation, Pb enrichment resulting from annealing for 1-24 h at 300-600°C in air, followed by quenching in water, was investigated on an AlPb binary model alloy, by use of electrochemical polarization, electron optical techniques, and glow discharge optical emission spectroscopy. Most of the enriched Pb was found to be near the oxide film-aluminum matrix interface, probably in solid solution with aluminum. The surface concentration reached an apparent saturation level of 0.8 wt % at 600°C, up from 20 ppm in the bulk. In addition, segregated metallic Pb particles were detected at an increasing density and size with increasing time of annealing at 600°C. However, segregation of Pb particles did not have an appreciable effect on activation. It is suggested, therefore, that the electrochemical activation is related to reduced passivity of the overlying oxide by Pb enriched in solid solution at the metal surface and ensuing pitting potential depression in the combined presence of aggressive chloride ions in the test solution.

Electrochemical activation of various commercial aluminum alloys resulting from high-temperature heat-treatment has been a subject of attention for the past several years because of its importance in galvanic and filiform corrosion. The phenomenon is observed by heat-treatment at temperatures above 350°C. It is characterized by deep corrosion potential transients with characteristic arrests in slightly acidified chloride solutions, starting from highly negative potentials in relation to the usual pitting or corrosion potential of about −0.75 V SCE. In addition, anodic polarization in neutral chloride solutions gives high anodic current output with oxidation peaks corresponding to the potential arrests.

Recent work on commercial AA8000 and 3000 series alloys related the cause of activation to the enrichment of a metallic near surface layer by lead, which was present in the material as a trace element only at the parts per million level. This layer, which existed in the metal phase right under the metal-oxide interface, was a fraction of a micrometer thick on the average on these rolled materials, but the thickness varied significantly locally from nearly zero to about 1 μm. We refer to this layer as the subsurface layer throughout this paper.

In continuing work by use of model binary AlPb alloys, the concentration of enriched Pb in the subsurface layer was found to reach the order of 1 wt % independent of the bulk Pb content in the test range of 5-50 ppm, as revealed by quantitative glow discharge-optical emission spectroscopy (GD-OES). The maximum enrichment seemed to correspond to the metal-oxide interface. Mechanical polishing or caustic etching appeared to remove most of the lead from the surface. However, the etched surface of the commercial alloys was enriched again with lead as a result of reannealing at temperatures above 350°C. Annealing temperatures higher than 500°C were required for the binary model alloys.

Transmission electron microscopy (TEM) work on heat-treated (1 h at 600°C) model binary AlPb alloy containing 50 ppm Pb indicated apparent enrichment of Pb at the metal-oxide interface and at the grain boundaries near the surface. No phase segregation was observed, and the exact locations of enrichment could not be determined. However, no Pb enrichment was detected along the grain boundaries and the grain bodies in the bulk of the material, starting at a distance of about 0.5 μm from the oxide-metal interface. Based on these results and with reference to the work of Gabrisch et al., Pb was postulated to diffuse from the bulk of grains to the lower energy grain boundaries and further to the metal-oxide interface as a result of heat-treatment.

A number of issues remain to be clarified for better understanding of the activation of aluminum alloys by surface enrichment of Pb. These include the effect of heat-treatment, the gas environment used during heat-treatment, especially the partial pressure of oxygen, the nature of segregation and/or enrichment at the surface as a result of heat-treatment, and subsequent anodic polarization in chloride solution, the role of chloride ions in the solution, and the activation mechanism itself. As part of a research program launched to understand these factors, the present work aims to obtain additional microstructural information about the nature of Pb enrichment resulting from heat-treatment, specifically, the location and state of Pb, by use of electron optical techniques, in particular, high-resolution transmission electron microscopy (HRTEM) and GD-OES. The present study is restricted to ambient air as the heat-treatment environment.

Experimental

The binary AlPb alloys used in this work, containing 20 and 50 ppm Pb, were prepared from high-purity aluminum (99.98%; Si main impurity) and lead (99.99%). These materials are designated as AlPb20 and AlPb50, respectively. The alloys were cast as 20 mm thick plates and subsequently scalped and cold rolled to a final thickness of about 2 mm. Samples were metallographically polished through 1 μm diamond paste. This was followed by heat-treatment at 300-600°C in an air circulation furnace for 1, 2, 4, and 24 h and subsequently quenching in distilled water at room temperature. The fact that the samples were quenched in water immediately after heat-treatment, instead of slow cooling, e.g., in ambient air, should be emphasized.

All samples were acetone degreased prior to electrochemical measurements, which were performed in a chloride-containing electrolyte exposed to ambient air at 25±1°C and stirred by a mechanical stirrer at a fixed rate. The cell geometry, including the container size, electrode holders, and locations, the stirrer geometry and location were identical in all electrochemical runs to obtain identical hydrodynamic conditions in the test solution.

Electrochemical characterization included measurement of the corrosion potential as a function of time in acidified synthetic sea water solution according to ASTM G85, Annex 3. The solution pH was 3. These measurements gave potential transients resulting from the slow dissolution of the activated metallic subsurface layer, if present. Polarization measurements were also performed both potentiostatically at selected potentials and potentially dynamically at a...
potential sweep rate of 0.1 mV/s in neutral 5 wt % NaCl solution. The sweep rate was in the positive direction starting from an initial value, which was 50 mV more negative than the corrosion potential recorded immediately after immersion of the sample in the test solution. Further details about the experimental apparatus and procedure for the electrochemical tests are given in Ref. 7 and 9.

TEM cross-sectional specimens were prepared by gluing the oxidized surfaces of two strips with epoxy and curing at 100°C and then naturally cooling to room temperature. The glued sample was then cut into 0.5 mm thick slices perpendicular to the oxidized surfaces, mechanically ground to about 120 μm thickness, and then further thinned using a dimple grinder, yielding a sample thickness of about 30 μm at the oxidized surface region. Finally, the electron transparency was achieved by using a Gatan precision ion polishing system at an ion-milling angle of 3.5° with beam energy of 3.5 kV.

The stripped surface oxide specimen was prepared by immersing an annealed sample into a mercuric chloride-methanol solution to remove the thermal oxide film from the aluminum substrate, followed by cleaning in distilled water and retrieving onto TEM sample grid.

TEM observations were carried out using a Philips CM30 microscope with a point-to-point resolution of 0.23 nm. The microscope was equipped with an energy-dispersive X-ray spectroscopic (EDS) detector, operated at an accelerating voltage of 300 kV. Field emission gun-scanning electron microscope (FEG-SEM) studies were performed on a Hitachi S-4300SE instrument also equipped with EDS capability. Quantitative depth profiling was performed by using a LECO GDS-750A optical emission spectrometer (GD-OES) in the dc mode.

Results

Corrosion potential.—Corrosion potential of heat-treated AlPb20 samples exhibited deep transients relative to the corrosion potential of the polished sample in the acidified synthetic seawater, as shown in Fig. 1. The corrosion potential of the heat-treated samples was a couple hundred millivolts more negative than the polished sample at the outset, and it increased in a typical wavy pattern as a function of immersion time, as the activating material was slowly etched away from the metallic subsurface layer. In contrast, the corrosion potential of the polished sample remained nearly constant at −0.76 mV_{SCE}, well-known pitting potential of aluminum in chloride environment. The initial potential of about −0.93 mV_{SCE} can be related to cathodic control resulting from lack of active cathodes on a passive surface or conversely, an active oxidation process. Subsequent increase of the corrosion potential can be a result of anodic passivation, followed by the onset of a new active oxidation process at the peak potential of −0.88 mV_{SCE}. The increase in the noise associated with the phenomenon and subsequent drop in the potential to a minimum indicated a localized oxidation process. After the minimum, the corrosion potential increased continuously toward the potential of the polished surface. The transients for samples annealed for 1 and 24 h were nearly identical. A mixed potential transient can be interpreted in different ways, and the interpretation given here is based on the a priori knowledge of the polarization data to be discussed next.

Electrochemical polarization.—Figure 2 shows typical anodic polarization curves for pure aluminum and alloy AlPb20 in 5% NaCl solution. The figure includes also polarization data for alloy AlPb20 in 5% Na2SO4 solution. The data for polished AlPb20 are without heat-treatment, whereas all other curves represent heat-treated samples. In chloride solution, pure Al and non-heat-treated AlPb20 exhibited similar polarization behavior identical as anodic behavior above the pitting potential (≥ −0.75 V_{SCE}) of pure aluminum is concerned. However, the AlPb alloy had a much higher apparent passive current than the pure Al in the range −0.9 to −0.7 V_{SCE}. Observation of the surface under an optical microscope (not shown) revealed slight pitting in this range, indicating that the surface was slightly activated anodically. Thus, the polished sample appeared to exhibit two pitting potentials, the lower one at about −0.9 V_{SCE} corresponding to the active surface and the higher one at about −0.75 V_{SCE} to the bulk.

In the heat-treated condition the pitting potential, which was identical to the corrosion potential, was shifted in the negative direction relative to the pitting potentials of pure Al and non-heat-treated AlPb. The heat-treated AlPb sample exhibited a high oxidation current at the potential range where the other specimens, indicating a significantly active surface relative to both the non-heat-treated state and pure Al. The polarization curve for the heat-treated AlPb20 in Fig. 2 demonstrates the role of chloride in activation, verifying an earlier more detailed study on the effect of chloride, Pb enrichment was not possible in chloride-free solutions of neutral pH, as demonstrated here by the sulfate solution. In this solution, no pitting was observed on the heat-treated AlPb20 alloy. Similar results obtained by polarization in other types of neutral-pH solutions were reported in the earlier paper.

Figure 3 shows that activation of alloy AlPb20 increased with increasing annealing temperature. Increasing heat-treatment time above 1 h at 600°C did not affect the polarization curve significantly. The effect of annealing time, shown in Fig. 4, was more visible at the lower annealing temperature of 500°C, i.e., 24 h of annealing at this temperature approached the degree of activation corresponding to 1 h annealing at 600°C. The results were not significantly different for Pb concentration in the range 5-50 ppm investigated in the binary model alloy system, although the data shown here are limited to the AlPb20 alloy. The oxidation peaks observed at −0.93 and −0.88 V_{SCE} corresponded well with the phenomena indicated by the corrosion potential data, i.e., the initial
potential (the first potential arrest) and the maximum potential (the second potential arrest) observed in Fig. 1. The polarization data presented so far thus confirm that the low corrosion potential transient of the heat-treated AlPb sample shown previously (Fig. 1) was controlled by anodic activation and subsequent passivation of the surface as the active layer was removed.

More detailed studies of the electrochemical behavior of various commercial and laboratory-made alloys can be found in Ref. 1-7 and Ref. 9. The present data verify the earlier results.

In addition to the foregoing, the importance of the chloride ion and the transient nature of the activation phenomenon should be reiterated. The oxidation peaks became larger with increasing chloride concentration in the solution. The surface furthermore passivated as the active layer was etched away from the surface, as indicated clearly by the potentiostatic data shown in Fig. 5. The current density for the samples annealed at 600°C was high at the outset at the applied potential of −0.88 V SCE, and it decreased with time as the active layer was etched by at least two subsequent mechanisms, decaying finally to nearly zero. Integration of the curve for 1 h-annealed sample showed that 0.89 C/cm² of charge was required to remove the active subsurface layer and passivate the freshly exposed metal surface. This corresponds to an apparent active aluminum subsurface layer thickness of 0.3 μm. The curves for samples annealed for 1 and 24 h were nearly identical; the charge passed by the 24 h sample was slightly larger. The amount of charge passed for the samples annealed at 500°C was smaller at the same applied potential, as expected. The annealing time also became a significant parameter at the lower annealing temperatures.

The surface became superficially etched as a result of potentiostatic polarization, as shown in Fig. 6 for the 1 h sample. Initiation was in the form of pits localized to the grain boundaries. The pits propagated superficially, giving the surface the etched appearance.

![Figure 3](image3.png)  
**Figure 3.** Effect of heat-treatment temperature on the polarization behavior of alloy AlPb20 in 5 wt % NaCl solution.

![Figure 4](image4.png)  
**Figure 4.** Effect of heat-treatment time at 500 and 600°C on the polarization behavior of alloy AlPb20 in 5 wt % NaCl solution.

![Figure 5](image5.png)  
**Figure 5.** Effect of heat-treatment temperature and time on the potentiostatic behavior of alloy AlPb20 at an applied potential of −0.88 V SCE in 5 wt % NaCl solution.

![Figure 6](image6.png)  
**Figure 6.** Surface morphology of an AlPb20 specimen, heat-treated for 1 h at 600°C, after potentiostatic polarization at −0.88 V SCE in 5 wt % NaCl solution. Micrographs were obtained at a grain boundary at (a) low and (b) high magnification.
The crystallographic etching varied with the grain orientation, as expected, resulting in a needle-like morphology, as shown in Fig. 6b. Post mortem electron optical investigations did not reveal any evidence of Pb segregation in the corroded areas.

**GD-OES data.**—Elemental depth profiles obtained for the annealed AlPb20 alloy also verify earlier data insofar as significant Pb enrichment of the surface, including the oxide, oxide-metal interface, and the metallic subsurface layer, as shown in Fig. 7. The data shown were obtained from two samples which were heat-treated at the same temperature for different periods of time. While the Al profiles were nearly identical for the two samples, the O profiles indicated slightly thicker or denser oxide on the sample annealed for 4 h than on the sample annealed for 1 h at 600°C. Judging further from the shape of Al and O profiles, the Pb enrichment is thought to be at a maximum at the metal-oxide interface, and the enriched subsurface region extended a certain distance into the metal. The thickness of the enriched subsurface layer calculated from the integration of the potentiostatic current-time data in Fig. 5 for the same type of sample. The only change detectable between 1 and 4 h of annealing was the increase in the thickness of the Pb-enriched region in the metal phase with the time of annealing. The peak concentration did not appear to increase significantly with annealing time.

The wider Pb peak on the 4 h-annealed sample can be attributed to segregated Pb-containing particles or nonuniform sputtering during depth profiling as indicated by the sputtered surface morphologies of the two samples in Fig. 8. It is clear from the figure that different grains were sputter-etched at different rates. The nonuniformity was larger for the 4 h-annealed sample resulting from larger grains. Although the depth profiles may be distorted by a nonuniform sputtering rate, the area under the curves must still give the correct amount of Pb enriched in the subsurface region. The amount of Pb enriched in the subsurface region, calculated in this manner from GD-OES data, is shown in Table I as a function of annealing temperature and time. The amount of Pb enriched in the subsurface region increased both with increasing annealing temperature and annealing time, as expected.

**FEG-SEM data.**—The secondary electron images obtained at an accelerating voltage of 15 kV indicated a porous oxide structure on sample AlPb20 heat-treated at 600°C, as shown in Fig. 9. The porous topography was typical for all samples heat-treated at high temperatures, including pure aluminum. The porous structure resulted from the gaps between the γ-Al2O3 crystals, which contained amorphous aluminum oxide, as is well known from earlier studies of thermally grown oxides on aluminum.12,13 Lead was not visible by FEG-SEM on the 1 h-annealed specimen, as shown in the backscattered electron image in Fig. 9b. On the 24 h-annealed specimen, however, the Pb particles filling the pores were readily visible, as shown in Fig. 10a and b.

<table>
<thead>
<tr>
<th>Heat-treatment time and temperature</th>
<th>1 h at 300°C</th>
<th>1 h at 400°C</th>
<th>1 h at 500°C</th>
<th>1 h at 600°C</th>
<th>4 h at 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface concentration (mg/m²)</td>
<td>0.20</td>
<td>0.23</td>
<td>0.38</td>
<td>1.65</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Table I. Effect of heat-treatment conditions on the total amount of Pb enriched at the surface of alloy AlPb20.
TEM data.—Observations of the cross-sectional specimens in Fig. 11 revealed that the oxide film thickness did not increase significantly in the range 1-4 h of annealing at 600°C and remained at about 50 nm, in good agreement with the earlier results. The oxide film probably achieved a terminal thickness at a much earlier stage than the minimum 1 h annealing time used in the present work. The crystals in the thermally grown oxide, shown in Fig. 12, were characterized as γ-Al$_2$O$_3$, as can be seen from the HRTEM projection in the inserted image. No metallic or oxidized Pb particles could be identified either at the metal-oxide interface or in the bulk oxide film at this sample location.

Nanoprobe EDS analysis (nominally 6 nm lateral resolution) performed on similar metal-oxide interface regions for samples with different annealing times indicated Pb enrichment as shown in Fig. 13. These data were obtained by using the same nanoprobe spot size centralized at the metal-oxide interface with the spectrum collection time of 100 s. TEM CM30 pole-piece produced an unavoidable Cu K background peak. This peak was exploited to gain-normalize the EDS as an internal reference for comparing the Pb spectra acquired from different annealed sample metal-oxide interfaces regions. In the resulting spectra both Pb L and M peak intensities were clearly observed to increase with increasing annealing time from 1 to 4 h at 600°C. The same was true also for the O K peak, supporting the GD-OES data. However, because the cross-sectional micrographs indicated no significant oxide thickening from 1 to 4 h of annealing, the growth in the oxygen peak must be a result of increasing density of the oxide, probably as a result of formation of crystalline γ-Al$_2$O$_3$. The foregoing observations were typical for most of the cross-sectional TEM samples, which were annealed for 1 h. The Pb detected near the surface by EDS analysis of the cross-sectional foils was probably Pb in solid solution with the aluminum matrix in the subsurface region.

Lead segregation in the form of discrete particles was detectable only on a few samples as shown in Fig. 14. As can be discerned from the examples shown in the figure, particles of about 5-10 nm in size were segregated at the oxide-metal interface. Using the same acquisition condition as those in the above analyses, the EDS spectrum obtained for the particle in Fig. 14a is shown in Fig. 15. Sharp Pb peaks of higher intensity, relative to the near noise level detection in Fig. 13, could easily be seen, even though the size of this particle was only about 5 nm.

Segregated Pb-containing particles were further examined in HRTEM, as shown in Fig. 16, in order to explore their oxidation state. These particles were unstable under TEM electron-beam during HRTEM observation. As a result, the lattice image could be recorded only in one direction as shown in the figure. The lattice
plane value was determined accurately as 0.286 nm by using the (111) lattice plane (0.453 nm) of $\gamma$-Al$_2$O$_3$ crystals in the same image as internal reference, as illustrated in Fig. 17. This value agreed exactly with the (111) lattice plane of metallic Pb.

Inspection of Pb particles in Fig. 14 and 16 revealed that some were in contact with the aluminum metal, e.g., Fig. 14c, while some were detached from the metal surface with an oxide layer between the particle and the metal surface, e.g., Fig. 16a. Because the detached particles in almost all cases exhibited flat surfaces facing the aluminum metal, it is clear that they were in contact with the aluminum metal at a certain point during heat-treatment. As a result of oxide growth, which is well known to occur at the metal-oxide interface, some of these particles became detached from the aluminum surface and were incorporated in the aluminum oxide.

In contrast to the foregoing observation, no significant segregated Pb was detectable in the stripped oxide film, shown in Fig. 17, by EDS analysis. This may result from the general difficulty in observing the highly localized, nanosize particles which may also have been removed by the stripping treatment. This sample revealed the typical microstructure of thermally formed oxide on aluminum,
consisting of $\gamma$-Al$_2$O$_3$ crystals growing into the metal. The morphology correlated well with the porous structure observed in the FEG-SEM images in Fig. 9a.

**Discussion**

The purpose of the paper was to add new information to clarify the activation phenomenon related to the trace element lead, which has been under investigation for several years without realizing the role of Pb. The results demonstrated that metallic Pb can become enriched and segregated at the metal-oxide interface as a result of high-temperature heat-treatment in air, as demonstrated for the present model binary Al-50 ppm Pb alloy. These processes were further controlled by temperature and time-dependent diffusion. Independence of electrochemical activation on the bulk Pb concentration in the range 5-50 ppm for samples annealed at 600°C indicated that the metal surface was saturated with Pb in solid solution with aluminum in a metallic subsurface layer of a fraction of a micrometer thick on the average.

On most 1 h-annealed (600°C) samples, Pb enrichment could be verified by EDS analysis at the metal-oxide interface and at the grain boundaries near the metal-oxide interface, however, seldom observing any segregated Pb particles, except after prolonged heat-treatment at 600°C. The solid solution solubility of Pb in aluminum is 0.2 wt % at 659°C according to Ref. 14. It should be recalled that our samples were quenched in water after heat-treatment at 600°C. We therefore believe that the Pb detected in the subsurface was in most cases in solid solution with aluminum, although the GD-OES data indicated Pb concentrations above this level. This result may be due to the added presence of segregated Pb particles scattered over a large analysis area or supersaturation of Pb in the metallic subsurface layer.

After prolonged heat-treatment, i.e., 24 h, significant Pb segregation was observed. However, the electrochemical data did not indicate increased surface activation as a result of Pb segregation in the form of particles. This is additional evidence to the effect that Pb in solid solution with the Al metal in the metallic subsurface region, and not the segregated Pb particles, was responsible for activation. Annealing for 1 or 24 h at 600°C did not affect the anodic polarization curves because the subsurface concentration of Pb, which controlled activation, was at the same saturation level in both cases. Annealing at lower temperatures, which gave lower subsurface solid-solution concentrations of Pb, correspondingly lead to lower anodic activation levels.

The role of chloride here must be similar to its significance in localized corrosion. It takes part in further destruction of the oxide film, whose passivating properties were reduced by the presence of underlying solid-solution Pb, giving rise to the enhanced dissolution of aluminum. The surface was passivated again after the Pb-rich subsurface layer was corroded. Anodic activation of the surface, therefore, occurred in the form of a reduction in the pitting potential.
although there were significant differences in the pitting morphology of the active surface and the bulk of the specimen. Although a pitting type of mechanism because of the important role of chloride, corrosion of the active sublayer was clearly controlled by Pb distribution on the surface. Pitting initiated at the grain boundaries, because the oxide was probably weakest and Pb was apparently most concentrated at the grain boundaries as these were the diffusion paths to the surface, as discussed further below. Once the active subsurface was removed the surface was passivated similar to pure aluminum. A more localized, conventional type of pitting could be initiated again by only increasing the potential above the pitting potential of pure aluminum (−0.76 V\text{SCE}).

Segregation of metallic Pb in the liquid state along the low-energy grain boundaries of Al-Pb alloys as a result of heat-treatment above the melting point of Pb metal has been demonstrated by in situ TEM studies of alloys containing much higher Pb than the present sample. Based on this information, it is possible to envisage mobile Pb atoms to diffuse along the grain boundaries further toward the lower energy metal-oxide interface during heat-treatment and further spread along this interface. The temperature and time dependence of the enrichment process further supports such a mechanism. Pb can accumulate at the surface in the form of a persaturated solid solution subsurface layer. Qian et al.\textsuperscript{15} claim that surface activator atoms increase the dissolution probability of adjacent aluminum atoms by breaking the Al-O-Al bonds and formation of …Al(OH)\textsubscript{3} chains, which can easily dissolve. One activator atom can thus catalyze the dissolution of many aluminum atoms as it moves around on the surface. This process must clearly be enhanced by the presence of chloride ions in the solution. With the accumulation of Pb at the metal-oxide interface by prolonged heat-treatment, Pb segregates in the form of metallic Pb particles, similar to the mechanism described for the grain boundary segregation.\textsuperscript{16} Because the surface Pb loses its mobility in this manner, the Pb particles cannot be as effective in taking part in the activation process.

With reference to the controversy about the state and location of segregated Pb at the surface,\textsuperscript{10,16,17} the present TEM images give concrete evidence that the Pb particles are segregated at the metal-oxide interface while in contact with the aluminum-metal surface before they become incorporated in the thermal oxide as a result of continuing oxidation during heat-treatment. As long as the Pb particles are in metallic contact with the aluminum surface, it is thermodynamically impossible for the particles to become oxidized during heat-treatment. Nevertheless, the present data indicate that the detached particles, which are embedded in the oxide, are also metallic Pb.

### Conclusions

Enrichment of the oxide-aluminum interface by lead as a result of high-temperature heat-treatment was demonstrated. Lead enrichment at the metal surface occurred both in solid solution with the aluminum matrix in a metallic subsurface layer and in the form of segregated metallic Pb nanoparticles, which were unambiguously identified by high-resolution TEM. The segregated particles were detected both at the metal-oxide interface in metallic contact with aluminum and in detached form incorporated in the oxide layer. Pb in solid solution with aluminum in the metallic subsurface layer is responsible for surface activation and not the segregated Pb particles. The subsurface concentration of the activating Pb reaches a saturation level determined by the temperature of annealing. The degree of anodic activation is therefore independent of bulk Pb concentration and annealing time. Segregation of Pb particles as a result of excess Pb accumulation occurs in contact with the aluminum metal at the metal-oxide interface. Lead particles, still in metallic form, may become detached and embedded in the oxide during heat-treatment.

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