

## Significance of Trace Element Segregation in Corrosion of Aluminum Alloys

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Recent advances in investigating the near surface nanostructure of aluminum alloys are discussed along with the developing understanding of the relationship between the surface chemistry, topography, nanostructure, electrochemistry, and corrosion behavior. Low melting point trace elements in Group IIIA-VA, in particular, Pb and Sn, are given attention in relation to increasing recycling and significance of certain of these elements to electrochemical and corrosion properties of commercial aluminum alloys. These elements, which have low solid solution solubilities in aluminum, segregate to the surface above their respective melting points, causing significant anodic activation. Tin becomes homogenized in the aluminum matrix with increasing annealing temperature, losing its activating capability at trace element concentration levels in the matrix. Thermal segregation of Pb, if present in the alloy, at high annealing temperatures (600°C) is the dominating cause of activation since Pb is not soluble in aluminum. The presence of nobler alloying elements, such as Cu, Mn, Si, and Fe in solid solution counteracts anodic activation. Crystalline oxide growing during heat treatment traps segregating liquid phase Pb into semi-continuous nanofilm at the oxide-aluminum matrix interface, which wets a large area of aluminum surface, causing increased activation. An attempt is made to explain the low-temperature activation of the commercial alloy AA8006 by use of the experience gained from the study of simpler model solid-solution alloys.

**Keywords:** Trace elements, recycling, heat treatment, segregation, oxidation.

### 1. Introduction

As an increasing fraction of aluminum used in practice becomes recycled, the type and amount of trace elements present in the commercial alloys increase. Although the effect of these elements on the mechanical properties may not be significant at the levels they are present in the alloy, their impact on the surface properties, such as electrochemical, corrosion, tribological and optical properties, is often easily observable. While certain modifications of the surface properties can be utilized in a positive manner, such as in the development of sacrificial anodes [1], anodes for aluminum-air batteries [2], and electrolytic capacitors [3], their effect in more conventional applications, such as architectural, packaging and automotive, are often undesirable, *e.g.*, because of increased corrosion susceptibility [4]. This work is concerned about the trace elements in Group IIIA-VA metals, in particular Pb and Sn, which are characterized by low melting points and low solid solution solubilities in aluminum. These two properties in combination may lead to significant enrichment of the elements at the grain boundaries and surface of aluminum alloys by heat treatment, with unexpected changes in corrosion and surface properties.

The electrochemical polarization behavior of an active commercial aluminum alloy (AA8006-T0) in chloride environment is shown in Fig. 1. As compared to the etched surface, which behaved very similar to pure aluminum, the active, as-received surface was characterized by a significant decrease in the pitting potential and a significant increase in the anodic current output in the potential region, where the surface is normally expected to be passive. In this temper, the painted alloy was susceptible to filiform corrosion. Etching eliminated surface activation and filiform corrosion. Annealing the etched material for 1 h at 600°C restored activation and susceptibility to filiform corrosion. Surface characterization [5] and comparison of the electrochemical behavior of model binary AlPb

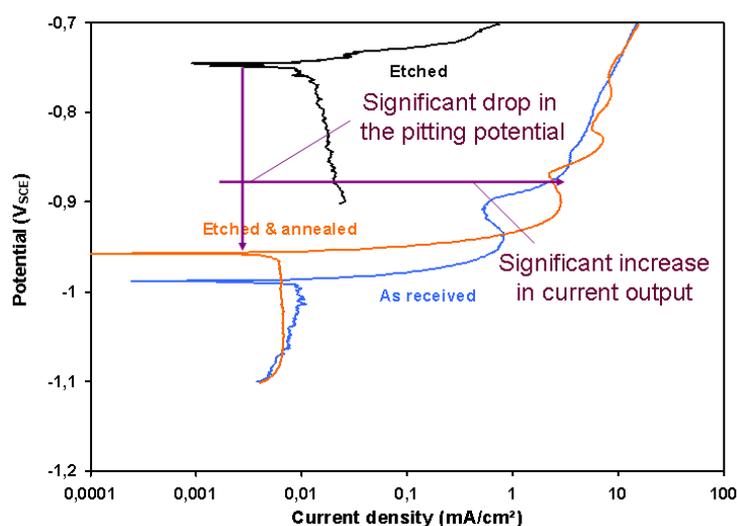


Figure 1. Polarization curve for aluminium alloy AA8006-T0 in 5% NaCl solution at 25°C in as-received, etched, and etched-and-annealed conditions [5].

the hot-rolled alloys AA3005 (1.12 wt% Mn, 0.39 wt% Fe, 0.12 wt% Si, 0.55 wt% Mg, 0.01 wt% Zn, 0.008 wt% Cu) [7,8] and AA8006 (0.4 wt% Mn, 0.02 wt% Mg, 1.5 wt% Fe, 0.16 wt% Si, 0.02 wt% Zn, 0.02 wt% Cu) (Fig. 1) [5] showed activation by heat treatment for the same period of time at 350°C. As indicated earlier, Pb was present as a trace element from the primary source in all alloys. Glow discharge optical emission spectroscopy (GDOES) and recent glow discharge mass spectrometer (GDMS) analyses of alloy 8006 indicated also the presence of trace elements Sn and Ga at of the order 10 and 100 ppm concentrations and originating from recycling and primary source, respectively. The effect of Ga is not discussed any further because larger amounts of Ga (above 500 ppm) are needed to obtain significant activation [2].

A study of corrosion morphology on alloy 8006 was investigated after deep caustic etching of the

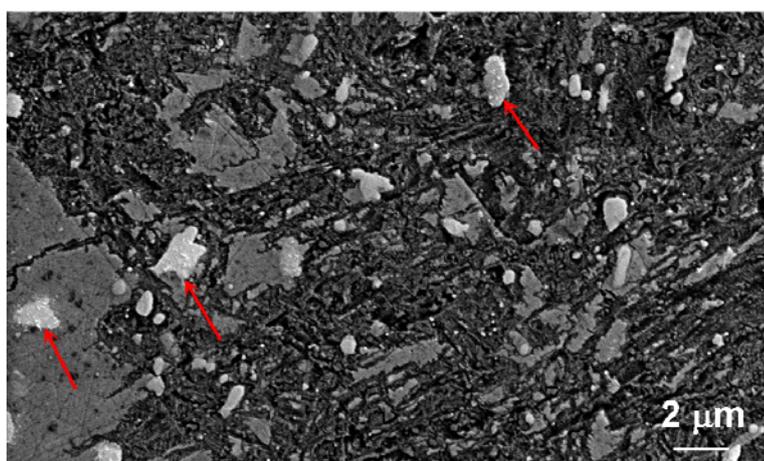


Figure 2. Corrosion morphology on alloy AA8006 by potentiodynamic polarization up to  $-0.85 V_{SCE}$  in 5% NaCl solution. The sample was etched in alkaline solution and then heat treated for 1 h at 450°C and quenched in water before the polarization test. Red arrows show a few of the intermetallic phases discussed in the text.

alloys [[6]] revealed the cause of activation as the surface enrichment of the trace element Pb. However, a number of commercial alloys can be activated by heat treatment at lower temperatures (e.g., at 300°C for 1 h), while certain other cannot be activated, although they contain Pb, as will be reviewed further below. Therefore, the role of other trace elements, such as Sn, had to be also considered along with other alloying and trace elements, in particular Mg, Si, and the transition elements Cu, Fe, and Mn.

## 2. Commercial Alloys

The extruded alloy AA3102 (0.42 wt% Fe, 0.21 wt% Mn, 0.07 wt% Si) was activated by 1 h heat treatment at 600°C as a result of surface segregation of lead [6], while the hot-rolled alloys AA3005 (1.12 wt% Mn, 0.39 wt% Fe, 0.12 wt% Si, 0.55 wt% Mg, 0.01 wt% Zn, 0.008 wt% Cu) [7,8] and AA8006 (0.4 wt% Mn, 0.02 wt% Mg, 1.5 wt% Fe, 0.16 wt% Si, 0.02 wt% Zn, 0.02 wt% Cu) (Fig. 1) [5] showed activation by heat treatment for the same period of time at 350°C. As indicated earlier, Pb was present as a trace element from the primary source in all alloys. Glow discharge optical emission spectroscopy (GDOES) and recent glow discharge mass spectrometer (GDMS) analyses of alloy 8006 indicated also the presence of trace elements Sn and Ga at of the order 10 and 100 ppm concentrations and originating from recycling and primary source, respectively. The effect of Ga is not discussed any further because larger amounts of Ga (above 500 ppm) are needed to obtain significant activation [2].

A study of corrosion morphology on alloy 8006 was investigated after deep caustic etching of the samples to remove the nanocrystalline layer, heat treating for 1 h at 450°C and quenching in water and subsequently polarizing potentiodynamically in 5% NaCl solution up to selected potentials on the polarization curve. Figure 2 shows the corrosion morphology on a sample polarized up to  $-0.85 V_{SCE}$ . Bright intermetallic particles of sizes up to 1 µm, clearly seen in Fig. 2, decorated the surface of the 8006 alloy samples. These particles were identified in earlier work as intermetallic phases  $\alpha$ -Al(Mn,Fe)Si and  $(Al,Mn)_6Fe$  [9]. Darker gray areas on the figure are uncorroded, and the darkest areas are corroded superficially (etched) under the thermally formed oxide film, which is still attached to the surface. The superficial layers of corrosion appeared

to occur on the aluminum matrix, independent of the location of the intermetallic phases. This behavior focused interest on the role of trace and alloying elements in solid solution with the aluminum matrix and, consequently, initiation of work on solid solution model alloys containing the trace and alloying elements in selected combinations.

### 3. Lead

The instability of Pb in Al at temperatures above the melting point of Pb is well known, leading to the segregation of the metal readily to the grain boundaries [10] and further to the surface [11]. While the amount of Pb segregation required at the surface, to obtain the degree of activation shown in Fig. 1, occurs relatively fast at 600°C, the time required to obtain the necessary segregation increases significantly with decreasing temperature, *e.g.*, to 24 h at 500°C [11]. However, the amount of segregation required to obtain the maximum activation possible is very small, and further activation is not possible by increasing amount of Pb segregation to the surface [12]. Thus, the amount of activation obtained by heat treatment for 1 h at 600°C is the same for binary AlPb alloys containing 5 and 50 ppm Pb.

The cause for the behavior of Pb has been shown to be the formation of a nearly continuous Pb-rich film of a few nanometers thickness at the metal-oxide interface by heat treatment, as verified by energy dispersive X-ray diffraction analysis of cross-sectional TEM foils [13]. The film is formed by entrapment of Pb segregating from the surface grains of the aluminum metal and inwardly

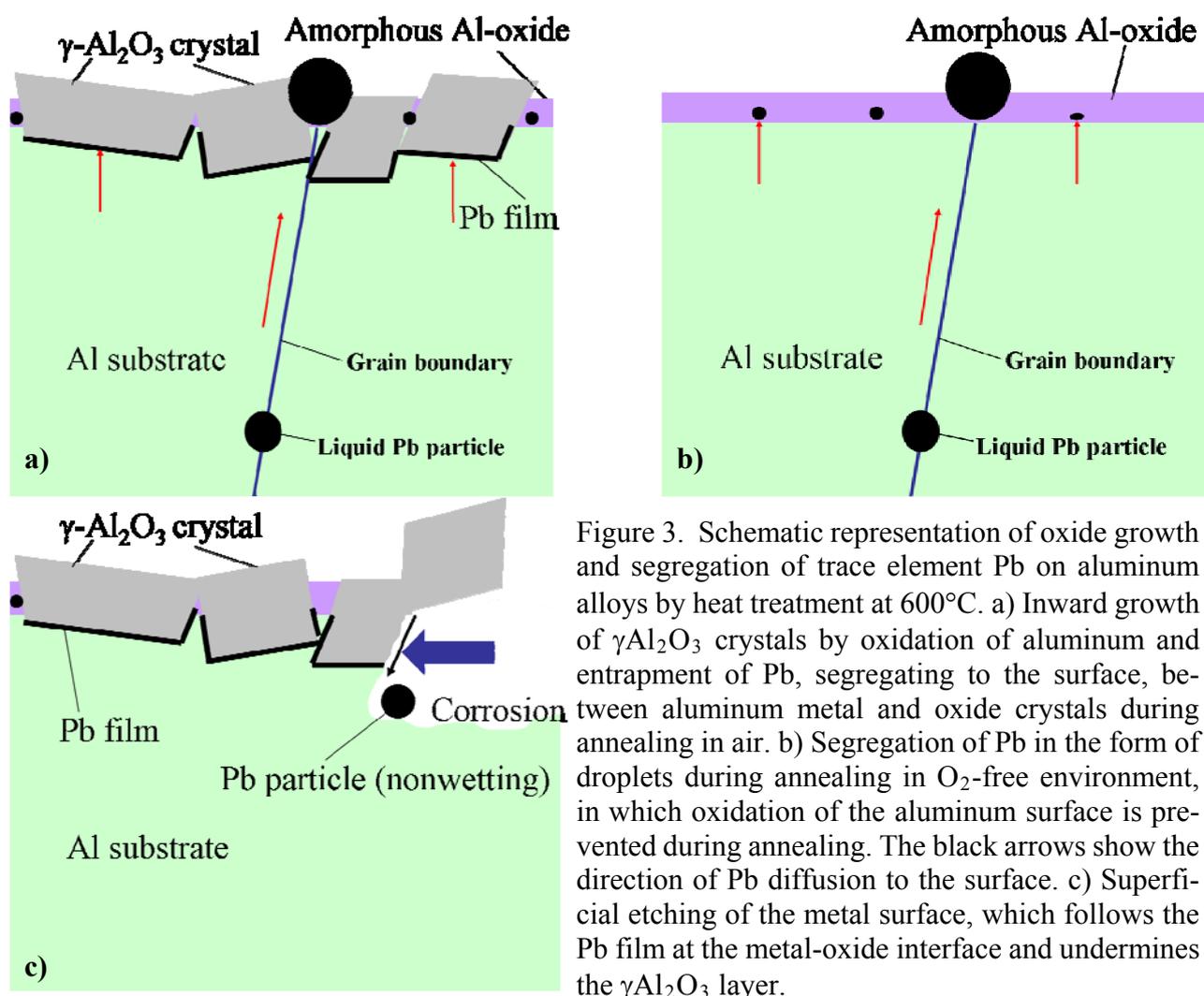


Figure 3. Schematic representation of oxide growth and segregation of trace element Pb on aluminum alloys by heat treatment at 600°C. a) Inward growth of  $\gamma\text{-Al}_2\text{O}_3$  crystals by oxidation of aluminum and entrapment of Pb, segregating to the surface, between aluminum metal and oxide crystals during annealing in air. b) Segregation of Pb in the form of droplets during annealing in  $\text{O}_2$ -free environment, in which oxidation of the aluminum surface is prevented during annealing. The black arrows show the direction of Pb diffusion to the surface. c) Superficial etching of the metal surface, which follows the Pb film at the metal-oxide interface and undermines the  $\gamma\text{-Al}_2\text{O}_3$  layer.

growing  $\gamma\text{Al}_2\text{O}_3$  crystals by oxidation of the same grains during heat treatment in air, as sketched in Fig. 3a [13]. Formation of the film may partly be caused by dealloying of the aluminum surface during high temperature oxidation. Larger quantities of Pb than needed for film formation during heat treatment segregate along the grain boundaries to the surface through the pores between the  $\gamma\text{Al}_2\text{O}_3$  crystals. However, particulate segregations of Pb do not participate as significantly as the film segregation in the activation process because nearly spherical particles provide small contact area with the aluminum substrate. Heat treating AlPb samples in oxygen-free environment prevents oxidation of the surface and formation of the  $\gamma\text{Al}_2\text{O}_3$  layer. As a result, a Pb-rich film cannot be formed, and Pb can segregate only in the form of nearly spherical particles, giving insignificant activation due to a very small contact area formed between the segregated Pb particles and the aluminum surface, as sketched in Fig. 3b. This mechanism explains the small amount of Pb needed to activate and independence of activation on the amount of Pb present in aluminum. In chloride solution, anodic polarization of AlPb alloys leads to superficial etching of a very thin layer of metal following the segregated Pb film, as sketched in Fig. 3c, by undermining of the thermally-formed  $\gamma\text{Al}_2\text{O}_3$  layer [14,15].

#### 4. Effect of Alloying Elements on Activation by Lead

Certain commercial alloys containing Pb as a trace element, were observed to show resistance to activation, especially those containing an appreciable amount of Cu as an alloying element. Electrochemical polarization data of ternary model alloys containing Al, 20 ppm Pb and a third alloying element, which is nobler than aluminum, shown in Fig. 4, indicated that the third element in the selected concentration in the alloy reduced the activation of aluminum caused by Pb in the binary AlPb alloy [16]. The effect of Cu was then investigated in more detail because of its more pronounced passivation effect in relation to the other elements tested.

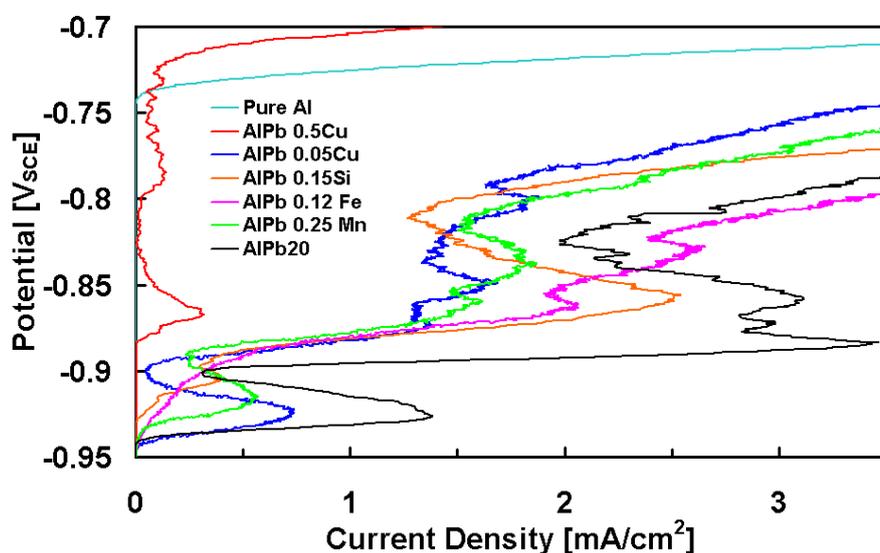


Figure 4. Polarization curves for Al-20ppm Pb alloys containing a third element, whose concentration is specified in the figure legend in wt%. All samples were heat treated for 1 h at 600°C and quenched in water [16].

Extensive electron-optical and electron-spectroscopic investigation and GD-OES depth profiling did not show any specific physical or chemical interaction between Cu and the segregated Pb at or close to the surface of AlPbCu specimens. The nature of Pb segregation resulting from heat treatment at 600°C was nearly identical to Pb segregation in the binary AlPb alloy, as described in the previous section. Copper did not become enriched at the oxide-metal interface as a result of heat treatment. Copper enrichment occurred as a result of corrosion by dealloying. It was concluded that the passivating effect of Cu was a result of ennoblement of the alloy surface by firstly the presence of Cu in solid solution and secondly by enrichment of Cu at the surface caused by anodic segregation during corrosion.

Other elements, which are more noble than aluminum in chloride solution, show a similar effect based on their nobleness and concentration in solid solution with aluminum, as can be inferred from Fig. 4. In particular, reduction caused in activation by Fe is small because of its small solubility (0.04% at 600°C) in aluminum. Manganese and Si, because of their higher solid solution solubilities, increase the nobleness of aluminum with increased concentration of these elements in the alloy and thereby counteract the activation caused by Pb to an appreciable degree, as shown in Fig. 4.

In contrast to the foregoing, the presence of the more active Mg gives increased activation to the AlPb alloy [17]. However, this occurs at a lower annealing temperature of 450°C. With increasing temperature, the activation reduced by the presence of Mg in relation to the binary AlPb alloy. The effect of Mg on the activation of alloy AlPb surface was attributed to the ease by which the spinel  $MgAl_2O_4$  can be formed on the Mg containing alloy in addition to the usual  $\gamma Al_2O_3$ . The low temperature activation was attributed to increased surface enrichment of Pb as a result of increased selective oxidation of the surface during heat treatment in the presence of Mg and possible Pb-rich film formation as a result of entrapment by the spinel. Recent TEM work on alloy 8006 verifies film formation by this mechanism, with the additional information that the film also contains Sn [18]. Reduction in the activation with increased annealing temperature is attributed to Sn dissolving back into the aluminum matrix, such that the activation becomes dominated by Pb alone, as discussed in the previous section.

## 5. Tin

Indium and Sn were reported to activate aluminum by heat treatment at temperatures significantly lower (300°C) than that required for Pb (600°C) [3]. Recent work on model binary AlSn alloys, containing Sn in the range 30-1000 ppm [19], confirmed activation by Sn segregation by low temperature annealing (300°C). Activation by heat treatment at this temperature is caused by thermal segregation of Sn since its solid solution solubility in aluminum is very low. Activation is temporary; the surface passivates by removal of segregated Sn by undermining during corrosion. Equivalently, removal of the segregated Sn by mechanical polishing passivates the surface. This behavior is similar to that of Pb as summarized above with the exception of the significant difference in the heat treatment temperature required for thermal segregation to occur.

In contrast to the behavior of Pb, however, Sn becomes homogenized in solid solution with aluminum with increasing annealing temperature, thereby reducing the effect of activation. However, this depends on the amount of Sn in the metal. While activation is insignificant for 30 ppm Sn content, it becomes relatively significant for 1000 ppm Sn at 600°C. In this case activation occurs by anodic segregation, *i.e.*, enrichment of Sn by selective corrosion of the more active Al component, in amounts sufficient to cause activation. Entire material volume is then susceptible to this type of activation since Sn is homogenized in the bulk solid solution with aluminum.

These results agree with the GD-OES depth profiles for this alloy, indicating significant Sn segregation to the surface by annealing at 300°C. On sample annealed at 600°C followed by quenching in water, most of Sn was homogenized in the bulk of the AlSn30 alloy, albeit tendency for little enrichment of Sn at the surface, which was about three times smaller than that for the 300°C-annealed sample. Al-1000 ppm Sn alloys developed a thick amorphous oxide layer as a result of quenching, which was not observed on the AlPb alloys, indicating the high activity of the surface.

## 6. Trace Elements in Combination

The results summarized so far, especially the similarity of the polarization curves and STEM observation of Pb-rich nanofilm at the metal-oxide interface for model and commercial alloy specimens heat treated at 600°C indicated that the dominating cause of activation resulting from high temperature annealing of all commercial alloys studied was the thermal segregation of Pb. The causes of

activation of certain commercial alloys by annealing at significantly lower temperatures could not be identified. In a preliminary effort to explain the low-temperature activation of the commercial alloy AA8006 [18], the anodic polarization behavior of model aluminum alloys containing combinations of trace elements Pb and Sn and the alloying element Mg, which were selected based on the data summarized above, was investigated.

Polarization curves for the model ternary alloy AlSnPb, containing nominally 20 ppm Sn and 20 ppm Pb, after heat treatment for 1 h at different temperatures are shown in Fig. 5a. The curve for 300°C indicates that thermally segregated Sn dominates the activation behavior, although GDOES data (not shown) indicate that both Sn and Pb are enriched at the surface. In contrast, the curve for 600°C indicates that segregated Pb film is the dominating factor in anodic activation (*cf.* Fig. 1 and 4). Tin is stable in solid solution with aluminum, and at such low concentration in solid solution it does not contribute to activation. Enrichment of Sn and Pb by heat treatment at 450°C is insufficient to cause activation commensurate with those observed at 300°C and 600°C, respectively.

Polarization curves for the model quaternary alloy, containing the same amount of Sn and Pb as for the ternary alloy and 200 ppm of Mg, are shown in Fig. 5b. The behavior of sample heat treated at 600°C is again controlled by segregated Pb. The presence of Mg appears to reduce activation by Sn at 300°C, while it enhances activation at 450°C. The cause of this behavior by combined presence of Sn, Pb and Mg in the model alloy is not clear, although the information summarized so far may suggest certain mechanisms, as will be discussed further below.

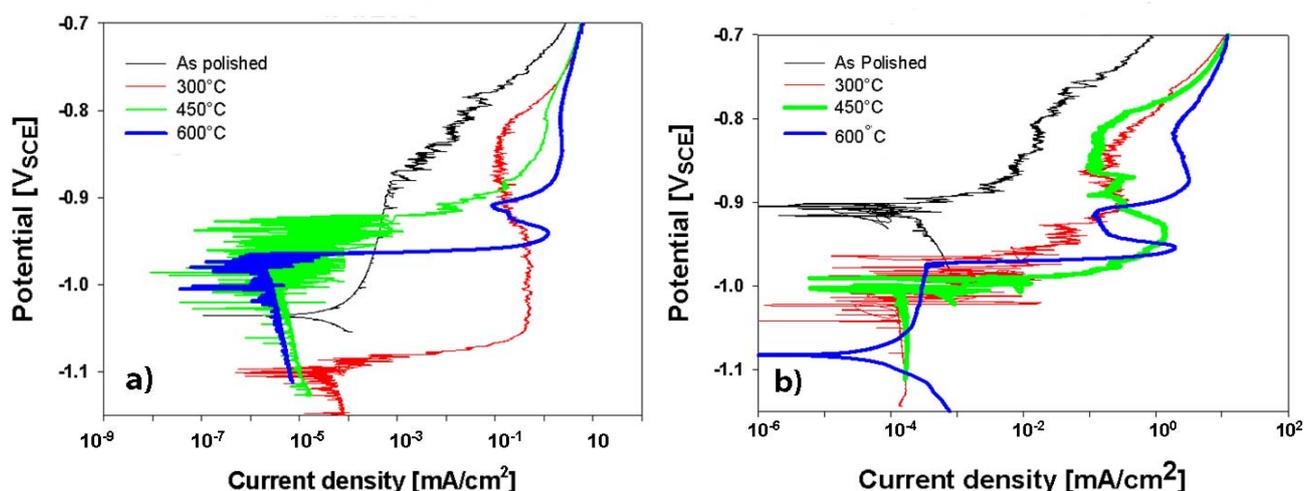


Figure 5. Polarization curves for Al-20ppm Pb alloys containing a) 20 ppm Sn and b) 20 ppm Sn and 200 ppm Mg. Heat treatment was performed for 1 h at the temperatures specified in figure legends, followed by quenching in water [18].

## 7. Discussion and Conclusions

The anodic behavior of alloys containing trace elements in Group IIIA-VA is controlled by segregation of these elements at the metal surface in contact with the aluminum alloy substrate, solid solution composition of the aluminum alloy and dealloying during corrosion. Unexpected synergistic effects caused by the combined presence of several trace and alloying elements render intuitive explanation of some of the results difficult. However, importance of distinguishing between thermal and anodic segregation of the activating element is clearly indicated. Lead in Al is not as activating as Sn *per se*. However, by becoming significantly enriched at the oxide-metal interface by heat treatment (thermal segregation), lead imparts appreciable activation to the aluminum surface. Anodic segregation is not an important mechanism for activation of aluminum by Pb.

Tin becomes segregated also thermally, but this occurs at a temperature (300°C), which is significantly lower than the temperature required for Pb. One reason is the difference in the melting points of the two elements. Thermal segregation occurs effectively at temperatures above the melting point of the activating element because diffusion of the liquid phase droplets to the surface occurs at a much faster rate than the diffusion rate in the solid state. Another reason is the low solubility of the element in aluminum at the respective temperatures. A third factor for activation by Pb is the formation of the Pb rich nanofilm at the metal-oxide interface, which gives a large area of metal surface wetted by essentially a very small amount of segregated Pb, such that concentration of Pb in the aluminum substrate is not important in determining the degree of activation. Thermal segregation is therefore an undesirable phenomenon in practice, allowing a very small concentration of a trace element giving a significant coverage of the metal surface by segregation and thereby giving significant activation. Since the phenomenon is restricted to the metal surface, removal of the active layer eliminates the activation problem, as long as the concentration of the trace element in the bulk is at the ppm level. The significance of bulk concentration applies particularly to Sn, as will be discussed further.

Activation by anodic segregation (dealloying) requires the presence of an appreciable concentration of the activating element in solid solution with aluminum, *i.e.*, an appreciable solid solution solubility of the element. Lead has virtually no solid solution solubility in aluminum at any annealing temperature of interest, and therefore, the element *per se* cannot cause activation by anodic segregation. Tin, however, shows relatively significant solubility with increasing temperature (0.1% at 600°C), and activation by anodic segregation becomes an important factor with increasing solid solution concentration of Sn. Furthermore the entire thickness of the specimen will show active behavior in contrast to the thermal segregation, which gives a thin surface layer, which is active. However, trace element levels in solid solution do not appear to cause activation. Possible synergistic effects in the presence of other activating elements are under investigation. Noble alloying elements, such as Cu, Mn, and Si with appreciable solid solution solubility in aluminum, counteract the effect of activating elements, whether they are segregated to the surface or are in solid solution.

While particulate segregates of Sn are sufficient to activate the aluminum surface, particulate Pb segregates do not give the same degree of activation. Pb has to become segregated in the form of a thin film as discussed above. The cause of this must be the wettability of the aluminum metal surface by the segregated element to cause the activation in accordance with the amalgamation theory. This is in turn related to the melting point of the element and the question whether a liquid phase alloy can be formed during anodic polarization by the heat generated locally by the exothermic oxidation process. This may be possible by the decreasing size of the segregated particles, which is known to cause significant melting point depression [20]. The decrease in the melting point by this mechanism may be sufficient for the Sn particles, whereas it is possible only for a Pb rich film, which is a few nanometers thick. Thus, this study shows the importance of film segregations of the activating elements as part of the activation mechanism.

An additional factor shown to be important, in relation to formation of the film segregation in the case of Pb, is the oxidation of the aluminum surface simultaneously with segregation of Pb during heat treatment. Entrapment of liquid droplets of Pb, segregating to the surface from the surface grains of the Al alloy, by inwardly growing oxide crystals is proposed as the governing mechanism of film formation. Segregation of Pb in the form of a film does not occur in the absence of significant film formation at the surface. A similar mechanism is probably involved in the low temperature activation of aluminum alloys containing Mg. Oxidation rate of the aluminum surface is not significant at 300°C. The rate of  $\gamma\text{Al}_2\text{O}_3$  is neither significant at 450°C, at which temperature, however, the degree of activation is optimal for the commercial alloys AA8006 and 3003 [5,7,8]. These alloys contain Mg as alloying element. The formation of the spinel oxide  $\text{Mg}_2\text{AlO}_4$  is believed to enhance film segregation of Pb also at this temperature. Pb rich film appears to form at this temperature on the commercial alloys, and work is in progress to verify the theory also for relevant model alloys.

## Acknowledgments

This work was supported by The Research Council of Norway and Hydro Aluminium.

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