

## Lead Segregation at Oxide-Covered Surface of Binary Al-Pb Model Alloy

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High temperature heat treatment above 300°C leads to electrochemical activation of certain aluminum alloys, as indicated by corrosion potential (1) and polarization measurements (2) in chloride solution. The activation was attributed to the enrichment of the trace element lead at the material surface, specifically at the metal-oxide interface, as determined by glow discharge optical emission spectroscopy (GD-OES) depth profiling (3). Lead segregation at the Al surface region has been investigated in the fabrication of electrolytic capacitors by etching (4). Recent microstructure characterization by use of transmission electron microscopy (TEM) suggested that Pb segregated in the amorphous oxide film formed during annealing in argon atmosphere (5) rather than the metal-oxide interface. In the present study, we investigate lead segregation on a binary model alloy after high temperature heat treatment in air.

The Al-50ppm Pb rolled samples were heat-treated at 600°C in an air circulation furnace for 1, 2 and 4 h. TEM observations were performed by using a Philips CM30 equipped with an energy dispersive X-ray spectroscopic (EDS) detector, operated at an accelerating voltage of 300 kV. Oxide film stripped from the annealed surfaces and cross-sectional specimens of the oxide-covered surfaces were prepared for TEM investigations.

TEM observations of the cross-sectional specimens revealed that the oxide film thickness of the annealed samples is about 100 nm, as shown in Fig. 1, independent of the annealing times used. However, Pb segregation at the metal-oxide interface increased with increasing annealing time between 1 to 4 h, as indicated by nano-probe (nominally 6 nm lateral resolution) EDS analysis shown in Fig. 2. No Pb containing particles were visible by means of high-resolution TEM (HRTEM) investigations in those regions where Pb was detectable by EDS. Crystallized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles were embedded in the amorphous oxide film as shown in the typical HRTEM image of a stripped film in Fig. 3. Moreover, Pb was not detectable in the stripped oxide film by EDS analysis, leading to the conclusion that Pb must be present only at the metal surface under the oxide film, in agreement with the GD-OES results.

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### References

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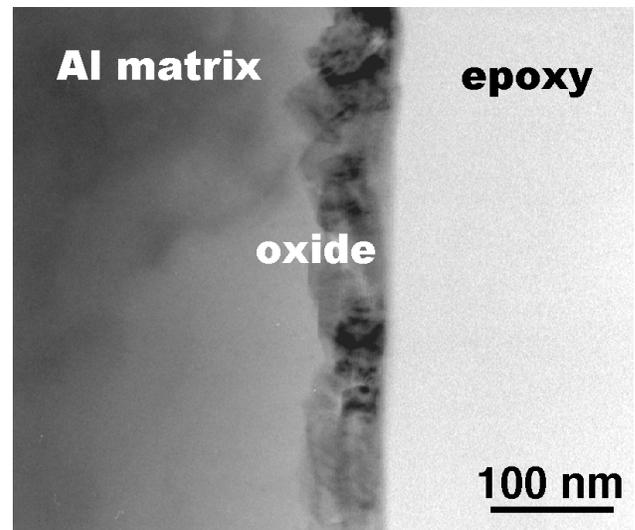


Fig. 1. TEM bright-field micrograph of 2 h annealed cross-section specimen with oxide thickness around 100 nm.

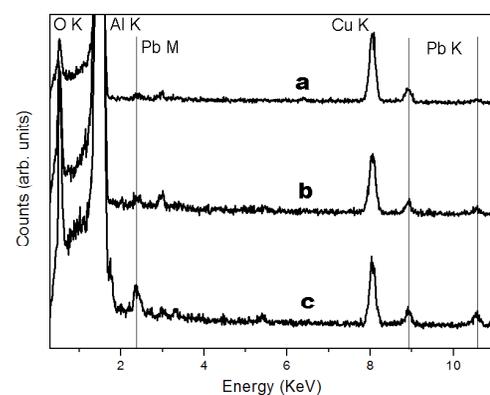


Fig. 2. EDS spectra of oxide-metal interface regions of TEM cross-section specimens, (a) 1 h, (b) 2 h and (c) 4 h annealing time. Cu peaks are from TEM pole piece and can be used as reference in comparing Pb peak intensities.

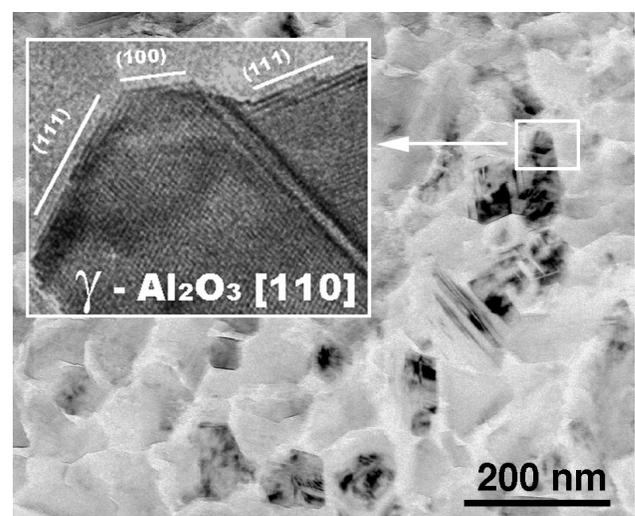


Fig. 3. TEM bright-field micrograph of the stripped oxide film from the 4 h annealed surface, and the enlarged HRTEM image of the crystallized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle embedded in the amorphous oxide as an insert.