**TEM Characterization of Segregated Lead on Annealed Aluminum**

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It has recently been discovered that the surface enrichment of trace element lead as a result of heat treatment above 300° C leads to electrochemical activation of certain aluminum alloys in chloride solution (1). Segregation of up to 0.8 wt% was detected by glow discharge optical emission spectroscopy (GD-OES) at the metal-oxide interface of certain commercial alloys, which nominally contained only a few ppm of Pb as a trace element (2). However, the morphology, microstructure and the chemical state of the segregation could not be ascertained. 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 (3) rather than the metal-oxide interface. The objective of the present work is to provide further evidence about the nature of Pb segregation by high resolution TEM (HRTEM) investigation of a model binary AlPb alloy

The Al-50ppm Pb rolled samples, prepared from the pure components, were heat-treated at 600° C in an air circulation furnace for 1 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. TEM cross-sectional specimens of the oxide-covered surfaces were prepared by gluing the oxidized surfaces of two strips with epoxy and following with conventional TEM sample preparation method of polishing, dimpling, and ion milling.

TEM bright-field micrograph in Fig. 1 shows marked Pb particles at the metal-oxide interface, as expected in the light of earlier GD-OES results (1, 2). The particle size was around 5-10 nm. Nanoprobe (nominally 6 nm lateral resolution) EDS analysis of the particles revealed higher Pb peak intensities than those reported in the earlier paper from analysis of metal-oxide interface regions without being able to visualize the Pb particles (4). The flat bottom surfaces on the aluminum side of otherwise rounded particles indicate that the particles wetted the aluminum metal surface. Particles, which were detached from the aluminum surface, were also observed embedded in the oxide. These preserved the flatness of their surface facing the aluminum metal.

The lattice distance of the segregations could be measured in one dimension from HRTEM images as shown in Fig. 2, which exhibits a Pb particle embedded in the thermally-formed crystalline $\gamma$-$Al_2O_3$ oxide layer. The particle lattice distance was determined as 0.286 nm by using the $\gamma$-$Al_2O_3$ (d (111) = 0.453 nm) as the internal reference. This value corresponds exactly to the lattice distance of cubic Pb (111), indicating that the particles were metallic Pb rather than an oxidized species.

Some of these particles were unstable under the TEM electron beam probably caused by the low melting point of the segregated Pb particles. Nanosize particles are known to exhibit significant melting point depression with decreasing size (5). In connection, the possibility of melting of the wetting nanoparticles, as a result localized passage of high current densities during anodic polarization in chloride media is under consideration as a possible step in the mechanism of activation of aluminum by Pb.

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**References**

1. Y. W. Keuong, J. H. Nordlien, S. Ono, and K. Nisancioglu, in *Corrosion and Corrosion Protection*, J. D. Sinclair, R. P. Frankenthal, E. Kalman, and W. Plieth, eds., Proceedings vol. 2001-22, p. 876, The Electrochemical Society, Pennington, NJ (2001).
2. J. T. B. Gundersen, S. Ono, J. H. Nordlien and K. Nisancioglu, *Proc. 15th Int. Corr. Congress*, Granada, Spain, 22-27 September 2002.
3. H. Tsubakino, A. Nogami and T. Yamanoi, *Appl. Surf. Sci*., **185,** 298 (2002).
4. Y.-D. Yu, Ø. Sævik, J. T. B. Gundersen, J. H. Nordlien, and K. Nisancioglu, *Extended Abstracts 202nd ECS Meeting*, Abstract No. **273**, The Electrochemical Society, Pennington, NJ (2002).
5. R.S. Berry, *Nature* **393**, 212 (1998).

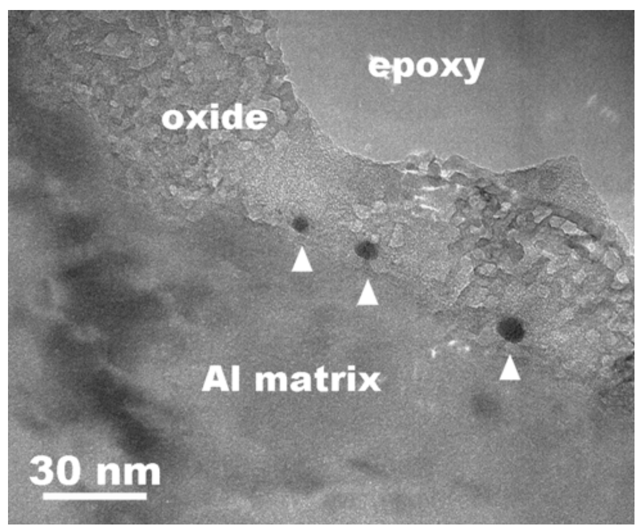


Fig.1. TEM bright-field micrograph of 2 h annealed cross-section specimen with segregated Pb nanoparticles as marked by arrows.

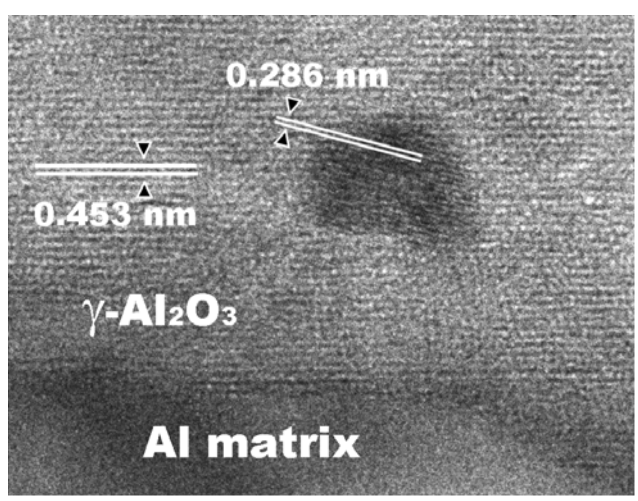


Fig. 2. HRTEM image of Pb particle embedded in the crystallized $\gamma$-$Al_2O_3$ oxide layer.