

Investigations of the Role of Cl on Pit Initiation in Aluminum Using STEM-EDS Spectral Imaging

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Motivation—Although it is well known that the presence of chloride in an electrolyte can initiate pitting in passive metals, the precise mechanisms responsible for pit initiation are still under debate. The local Cl concentration, the critical location either at the surface, within the oxide or at the metal-oxide interface, and the nature of the bonding between Cl and the passive film are all thought to be important for pit initiation. In order to distinguish between these factors, ion implantation has been used to control the concentration, location and source of Cl in the aluminum thin film system, and Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy (STEM-EDS) spectral imaging has allowed the discovery of the resulting Cl-rich nanostructures that influence corrosion pitting.

Accomplishment—Samples were implanted at ambient temperature using 35 keV Cl^+ ions with fluences ranging from $1 - 7 \times 10^{16}$ ions/cm². When the films are polarized in a halogen-free electrolyte, an increase in pitting probability is observed with increasing implanted Cl concentration. STEM-EDS was performed on cross-sections prepared with a focused ion beam and on conventional plan-view specimens. The Cl distributions were measured using a spectral imaging analysis technique developed at Sandia. At each 2 nm pixel, the x-ray spectrum excited by the electron beam is collected and a multivariate statistical analysis is performed to correlate pixels with the same spectrum. Each pixel can be coded according to its spectrum in order to create a map that shows the spatial distribution for each spectrum. Figure 1 shows

the bright field image (plan view) and the Cl distribution observed for the samples implanted with a fluence of 1×10^{16} /cm² (a), and 5×10^{16} /cm² (b), where the intensity of the Cl-containing spectrum increases as the color scale goes from blue to red. These results show that when the Cl fluence is high enough such that the pitting probability increases substantially, the Cl distribution changes from relatively uniform and homogeneous (Fig. 1a) to heterogeneous nanostructures (Fig. 1b). The larger ~ 10 nm Cl-rich nanostructures have a preference for forming along the grain boundaries in the films where the pitting probability is high. Diffraction patterns obtained from the films implanted with a Cl fluence of 5×10^{16} /cm² show lattice spacings consistent with AlCl_3 in addition to the Al lattice. If these nanostructures occur close enough to the passive oxide layer, they could be responsible for stabilizing pitting corrosion.

Significance—Pitting corrosion in passive metals occurs in the presence of aggressive halogens such as Cl. This work shows that in order to stabilize pitting in a halogen-free electrolyte, a critical Cl concentration, accompanied by the formation of high Cl-content nanostructures is required. Further work is underway to determine whether the observed distribution is stable as the films are polarized towards pitting. The ability to measure local changes in Cl concentration with the high spatial resolution attainable using this technique is expected to lead to further understanding of the role of Cl in pit initiation.

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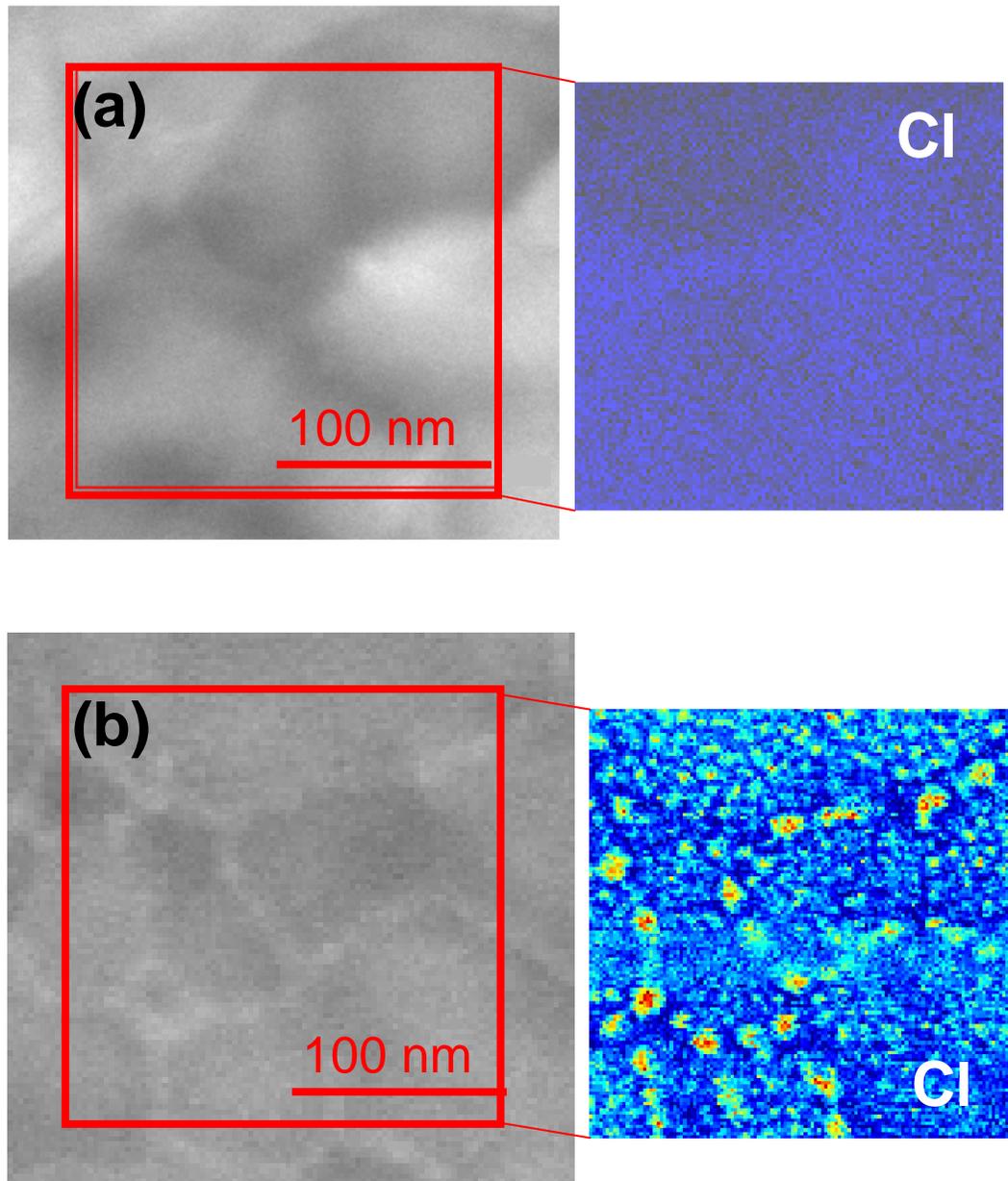


Figure 1. (a) Bright field TEM image of Al thin film implanted with a Cl fluence of $1 \times 10^{16}/\text{cm}^2$, the spectral image for the homogeneous Cl-rich component is shown to the right (b) Bright field TEM image of Al thin film implanted with a Cl fluence of $5 \times 10^{16}/\text{cm}^2$, the spectral image for the Cl-rich component on the right shows evidence of nano-cluster formation, with the largest clusters along the grain boundaries.