

3D Visualisation of Corrosion Propagation in AA2024 Aluminium Alloy

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In the present study, in-situ optical microscopy and ex-situ scanning electron microscopy have been employed to monitor and examine the initiation and propagation of localized corrosion in AA2024-T3 aluminium alloy in 1.5 M sodium chloride solution. The combination of ultramicrotomy and low voltage scanning electron microscopy (LVSEM), with selective detection of backscattered electrons (BSE), significantly improved depth and lateral resolutions and atomic number contrast (Z-contrast) sensitivity, enabling high resolution tomography of localized corrosion. Such probing provides direct evidence that links the surface appearance, the alloy microstructure and the corrosion propagation path. It is evident that localized corrosion of the rolled AA2024-T3 aluminium alloy is generally initiated at intermetallic particles. Further, it is found that localized corrosion that remains active during the course of testing is associated with large clusters of intermetallic particles that are buried beneath, but connected to, the alloy surface. Propagating away from the initiation sites, corrosion develops preferentially along selected grain boundaries.

Keywords: Tomography; LVSEM; Corrosion; Aluminium Alloy.

1. Introduction

Interrogation by conventional two-dimensional methods often fails to provide a precise microstructural description of grain shape and alignment, as well as the nature and distribution of second phase particles, that dictate material properties and performance under service conditions. Thus, a three-dimensional (3D) description is essential in advancing the understanding of the microstructure/performance relationship, for example, local microstructural criteria for the initiation and development of localized corrosion. Recently, using X-ray based techniques, 3D characterization has been employed in order to establish the microstructural criteria for the initiation and development of localized corrosion [1,2]. Using zone plate lenses, X-ray tomography can achieve spatial resolution of 50 nm [3], although lensless methods only approach 1 µm [4,5], that is insufficient to resolve crucial features that define the corrosion pathways. In order to overcome such deficiencies, we show here the advances made from an innovative combination of low voltage scanning electron microscopy (LVSEM) and serial sectioning of metallic materials to provide tomographic reconstruction.

2. Experimental Procedure

Commercial, cold-rolled sheet AA 2024-T3 alloy (Mg 1.6 wt%, Fe 0.5 wt%, Si 0.5 wt%, Cu 4.8 wt%, Mn 0.5 wt%, Cr 0.1 wt%, Zn 0.24 wt%, Ti 0.15 wt%, Al rem.) was employed. Specimens, of dimensions of 20 x 20 x 1.5 mm, were mechanically polished using 1 µm diamond paste. The specimens were cleaned ultrasonically in an acetone bath and dried in cool air stream. Immersion testing was carried out in 1.5 M NaCl solution with the addition of droplets of hydrogen peroxide. An in-situ video system was employed to monitor the specimen surface during immersion testing. Specimens, before and after immersion testing, were examined using a Carl Zeiss ULTRA 55 SEM. Ultramicrotomy was employed for sequential cutting to generate suitable surfaces from the specimens for ex-situ tomography. Serial cross-sections were produced with a diamond knife on a

Leica Ultracut ultramicrotome, cutting through the volume of interest in 50 nm steps. Volumetric SEM images from a set of sequential ultramicrotomed serial surfaces were acquired at an operating beam energy of 1.5 keV, using an in-lens backscattered electron detector. This in-lens BSE detector produces a low voltage, short working distance, high-resolution compositionally weighted image signal with minimal topographic contrast, which is suitable for high resolution SEM tomography.

Successively acquired 2D images were aligned, after correction for stage drift and tilt, using cross-correlation of reference markers; the image data were processed to perform 3D volumetric reconstructions, with the images being segmented into specific features based on grayscale, i.e. atomic number contrast. Once the features are segmented, the individual 3D volumetric reconstruction is generated, such that each feature uniquely occupies its own space within the 3D reconstructions. Individual features are assigned a false colour to represent its chemical composition, and the features may be displayed as a solid, semitransparent, or transparent object.

3. Results and Discussion

Using the in-situ video system during immersion, hydrogen gas evolution was observed at local sites on the alloy surface where electrochemical reactions were taking place, indicating localized corrosion. The link between hydrogen gas evolution and localized corrosion was confirmed by ex-situ SEM examination. The sites where gas evolution persists during the course of testing represent continuous localized corrosion, and the sites where gas evolution ceases during the course of testing are considered to represent discontinuous localized corrosion. Fig. 1 displays a scanning electron micrograph of an AA2024 T3 aluminium alloy after immersion testing for 45 min, showing sites of continuous and discontinuous localized corrosion. It is clearly evident that clusters of intermetallic particles are present at the centre of all localized corrosion sites.

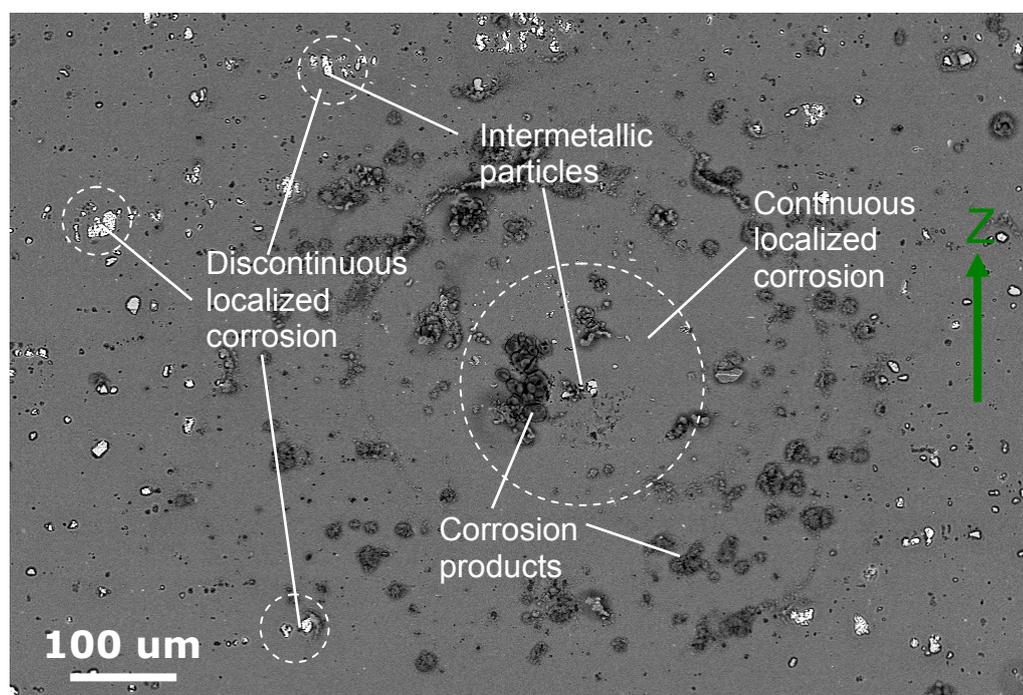


Fig. 1 Scanning electron micrograph of an AA2024 T3 aluminium alloy after immersion testing in 1.5 M NaCl for 45 min, showing sites of continuous and discontinuous localized corrosion.

EDX analysis of the intermetallic particles within the cluster revealed copper- and copper/magnesium- containing particles, suggesting that the cluster is comprised of CuAl_2 and CuMgAl_2 . At the site where continuous localized corrosion proceeded, corrosion products are evident. For the site where discontinuous localized corrosion occurred, little corrosion product is present, although trenching in a zone of influence of the intermetallic particles is clearly evident.

However, based on the surface plan view of Fig. 1, it is difficult to determine how localized corrosion developed. In order to gain further insight into the propagation mechanism, cross sections of the localized corrosion sites were examined by SEM. Fig. 2 shows a scanning electron micrograph of a discontinuous localized corrosion site, displaying both the surface appearance of the localized corrosion site and its cross section. It is clearly revealed that the whole cluster of intermetallic particles is exposed to the testing solution and the matrix in the vicinity of intermetallic particles was attacked. A number of similar discontinuous localized corrosion sites were examined. All such sites exhibit shallow attack of the matrix in the vicinity of individual or clusters of intermetallics, without any significant penetration.

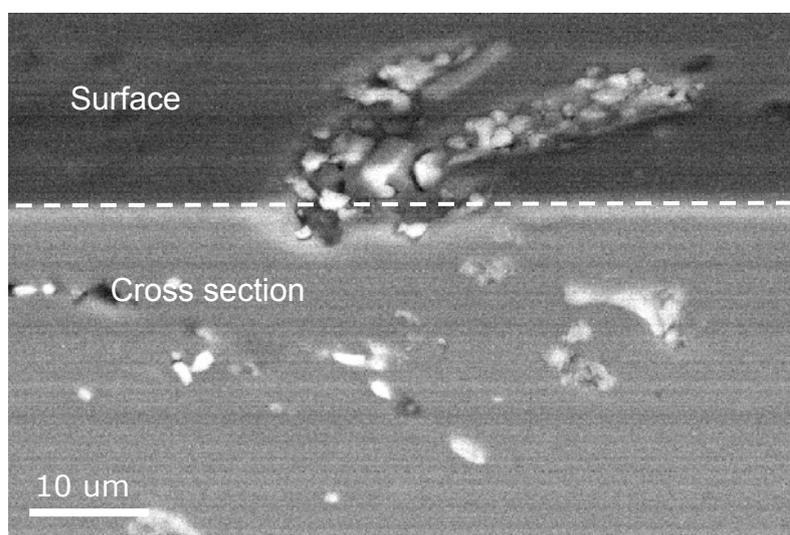


Fig. 2 Backscattered electron image of cross section of a discontinuous localized corrosion site.

Scanning electron micrographs of cross sections of a continuous localized corrosion site are illustrated in Fig.3. The atomic number contrast of the BSE images clearly revealed regions of different composition. EDX analysis and morphological examination of the contrasting regions suggest the presence of aluminium matrix, S phase, S phase remnants after possible dealloying and aluminium hydroxide, as indicated in Figure 3. For the cross section taken from the centre of the continuous localized corrosion site, it is evident that a large cluster of intermetallic particles, approximately $10\ \mu\text{m}$ length and $5\ \mu\text{m}$ thickness, is buried beneath the alloy surface, and intersects the alloy surface, as shown in Fig.3 a). The matrix, in the vicinity of intermetallic particles was attacked during immersion. A cross section prepared from a location approximately $5\ \mu\text{m}$ away from the centre of the continuous localized corrosion site, Fig. 3 b), reveals severe grain boundary attack which developed to depths up to $10\ \mu\text{m}$.

However, based on the individual 2D cross-sectional views of the localized corrosion site, it remains difficult to understand the relationship between the surface appearance, the alloy microstructure and the corrosion propagation path. For instance, it is difficult to explain the observation, as indicated by the arrow in Fig. 3 b), that a grain boundary that does not appear to be

connected to the aggressive NaCl solution is attacked. Thus, 3D volumetric reconstruction is necessary to determine the corrosion propagation path precisely and to link the microstructural features to the corrosion propagation path. Serial cross-sections were produced using ultramicrotomy, cutting through a localized corrosion site in 50 nm steps. Volumetric images from the sequentially ultramicrotomed serial cross-sections were acquired. 3D volumetric reconstruction was generated, as shown in Fig 4, with selective transparency applied to the aluminium matrix, and blue, red and yellow applied to the S phase, the S phase remnant after dealloying and the aluminium hydroxide respectively. Further, Figure 5 shows a representative view through a specific series of cutting planes.

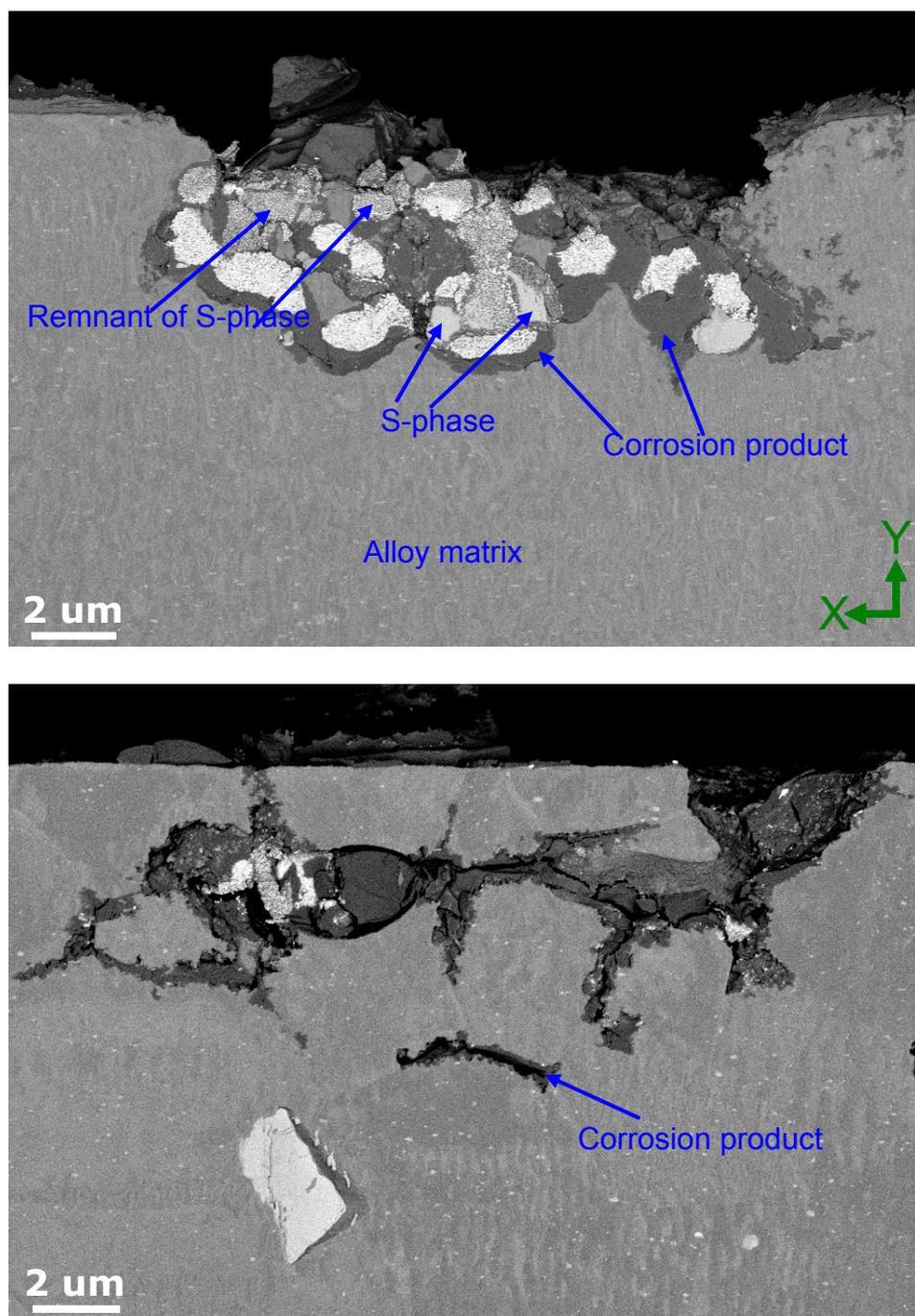


Fig. 3 Backscattered electron images of cross sections of a continuous localized corrosion site: a) the centre of localized corrosion site; and b) 5 μm away from the centre.

It is evident that the localized corrosion is associated with a cluster of S-phase particles, which is buried beneath the alloy surface and intersects the alloy surface at the position where the centre of the localized corrosion site is located. The remnant S-phase particles after anodic dissolution and dealloying show cathodic nature, forming a galvanic couple with the adjacent matrix, leading to preferential attack of the latter. Further, the 3D volumetric reconstruction clearly reveals the corrosion propagation path that displays the connection between the corrosion front located deeply in the bulk alloy and the alloy surface, i.e. the testing solution. Propagating away from the initiation sites, corrosion develops preferentially along selected grain boundaries. The understanding of such phenomenon will be further advanced by the complementary information from the authors' current work on the relationship between the intergranular corrosion susceptibility and grain boundary structure and composition using 3D electron backscatter diffraction (EBSD) and 3D EDX mapping.

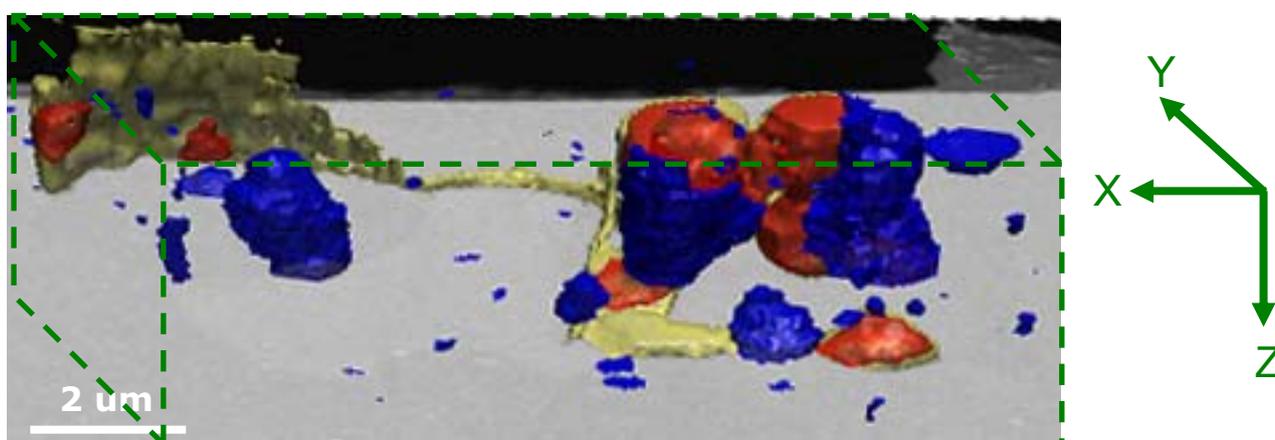


Fig. 4 3D volumetric reconstruction with selective transparency applied to aluminium matrix, and blue, red and yellow applied to S phase, S phase remnant after dealloying and aluminium hydroxide respectively.

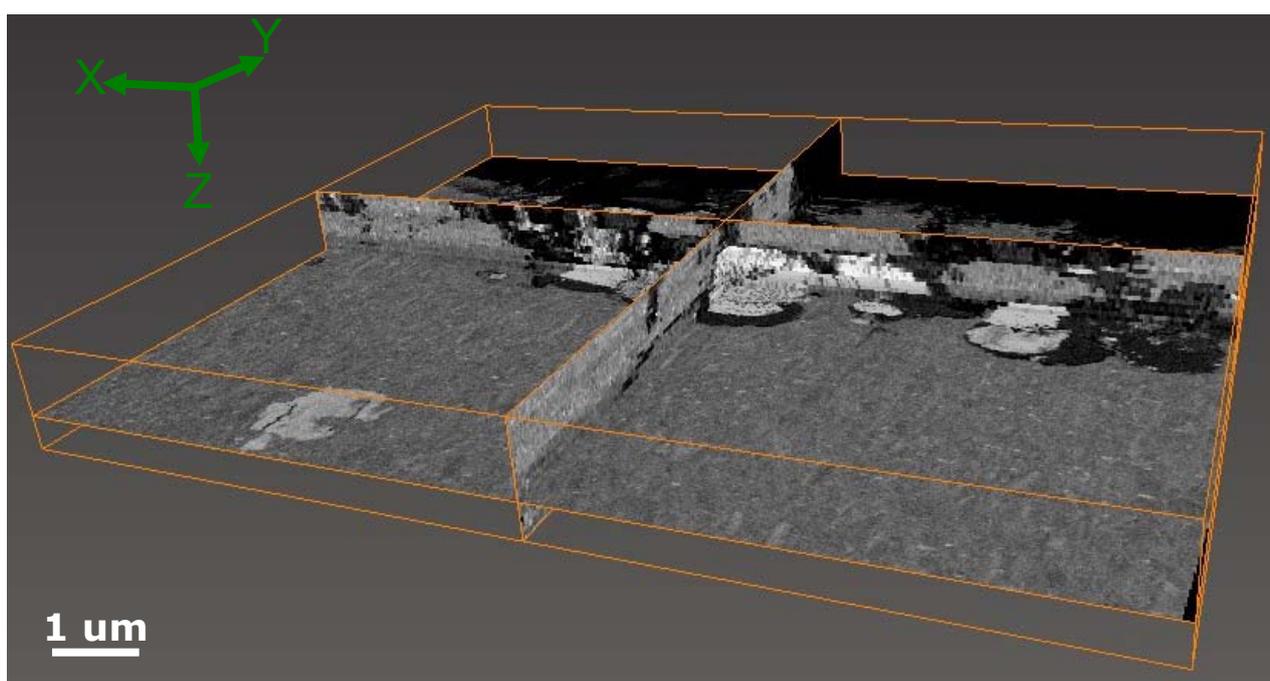


Fig. 5 Representative view of the animated sequences through a specific serial of cutting planes.

Aluminium oxidation at the corrosion front produces aluminium ions; their rapid hydrolysis results in acidification of the solution within the propagating front region, which is also chloride-enriched. The previous are necessary condition to maintain active localized corrosion. Clearly, the geometry of the continuous localized corrosion sites is different from that of the discontinuous localized corrosion sites. The former has a relatively large reaction volume beneath the alloy surface with a small area of connection at the alloy surface to the testing solution, restricting diffusion between the local region and the bulk solution and, therefore, maintaining the necessary acidity of the solution within the corrosion front region for continuous corrosion propagation. The latter has a relatively shallow reaction volume that is openly connected to the testing solution, resulting in ready access of bulk solution to the local region and pH increase.

4. Conclusions

High resolution 3D visualisation of localized corrosion propagation is achieved by the innovative combination of ultramicrotomy and low voltage scanning electron microscopy. 3D tomography provides direct evidence that links the surface appearance, the alloy microstructure and the corrosion propagation path, therefore, revealing the role of intermetallic particles and the transition to intergranular corrosion. Localized corrosion of the rolled AA2024-T3 aluminium alloy is generally initiated at intermetallic particles. Localized corrosion that remains active during the course of testing is associated with a large cluster of S phase particles that is buried beneath the alloy surface and also associated with severe grain boundary attack.

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