

Studies on localized corrosion in aluminium alloys using *in situ* transmission electron microscopy

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Environmental transmission electron microscopy (ETEM) is becoming an increasingly important field of study as it is possible to investigate the material-environment interactions on a nanoscale, the scale at which most of these interactions initiate. In a TEM, this is achieved by one of the following approaches: the opened type, using a differentially pumped vacuum system where the reactive gases are spread around the specimen area of the TEM; and the closed type, using a windowed environmental cell. Here, we present an environmental cell based approach to investigate gas-material interactions *in situ* [1]. For this a functional MEMS device known as the nanoreactor was developed in house. The nanoreactor consists of two facing dies made with thin-film technology on a silicon substrate, Fig.1(a). A Pt wire is embedded in the bottom die of the nanoreactor to allow localized resistive heating. When assembled together with the top die, Fig.1(b), it is possible to study the gas-material interactions from room temperature to 700°C and pressures as high as 4.5 bar, which is nearly impossible to achieve using the opened type approach [2,3]. In the current study, we use the nanoreactor and analytical TEM techniques to investigate the localized corrosion in aluminium alloys in a gas-liquid environment at 1 bar pressure. The nanoreactor is introduced into the TEM using a specially designed specimen holder [2], for the present study equipped with an exchangeable gas tubing made of Pt to allow reactive gases.

Aluminium alloys consist of several intermetallic precipitates, dispersoids, and segregated regions like precipitate free zones etc. which exhibit distinctly different electrochemical characteristics compared to the surrounding microstructure. As a result, there are numerous galvanic couples which are of the order of a few nanometres, which make these alloys susceptible to localized electrochemical attack. The *in situ* TEM studies were carried out in 2024-T3 and 7075-T76 alloy systems, which find wide applications in the aerospace industry due to their exceptional mechanical properties yet susceptible to localized corrosion. The specimens for TEM studies were thin cross sectional lamellae prepared using a Ga Focused Ion Beam (FIB). Pt deposition before cutting the lamellae to protect the surface was avoided as Pt can form a strong galvanic couple with Al. The FIB lamellae were then transferred to the bottom half of the nanoreactor and the two halves were aligned and glued to assemble a nanoreactor. Once the nanoreactor is leak tight, it is then interfaced with two exterior tubes in a custom made TEM specimen holder.

The *in situ* corrosion experiments were carried out at room temperature in an environment of oxygen bubbled through aqueous HCl of pH = 3 at 1 bar pressure. Fig.2 shows the preliminary results from the *in situ* corrosion studies on a 2024-T3 specimen, which were carried out for a duration of nearly 8hrs. Movies were recorded during the experiment using a CCD camera at 3 fps. Initially, changes at the top layer and the re-deposited material were observed. After an exposure to the reactive environment for 5hrs, the contrast of the grain boundary precipitate at location 1 appeared to diminish along with the formation of dark features surrounding the precipitate. This change was more prominent after 7hrs exposure to the reactive environment. This was interpreted as the re-distribution of elements as a result of de-alloying of the precipitate, indicating an anodic behaviour of the precipitate. At location 2, after exposure to the reactive environment for 7 hours, a lighter area around the precipitate and dark features surrounding this region shows up. These phenomena are interpreted as a result of a corrosive attack of the specimen surface of the matrix (lighter contrast) and the formation of corrosion products (darker contrast). This has to be confirmed from elemental analysis and these studies are in progress. As a prerequisite to the *in situ* corrosion studies, quasi *in situ*

corrosion studies were carried out in similar specimen-environment conditions. From these studies, it was observed that the copper rich grain-boundary precipitates undergo de-alloying, identified from the EELS Cu L_{2,3}-edge [4]. Further studies to understand the mechanism of de-alloying in both 2024 and 7075 alloy systems are in progress.

References

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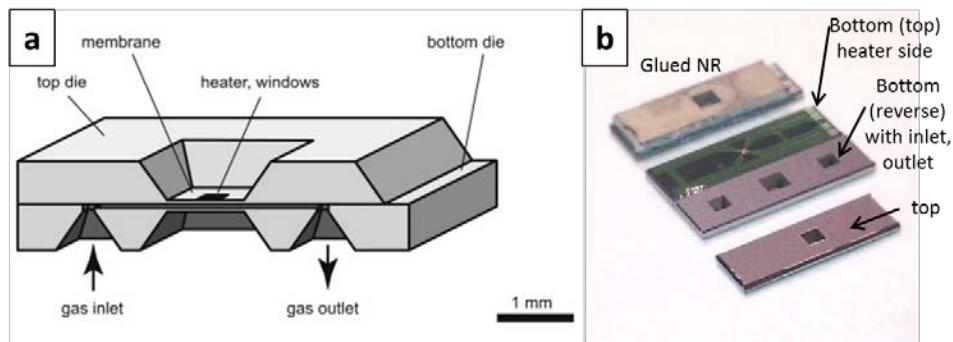


Figure 1. (a) Illustration showing the design of a nanoreactor; (b) photographs showing the bottom and top chips of the nanoreactor.

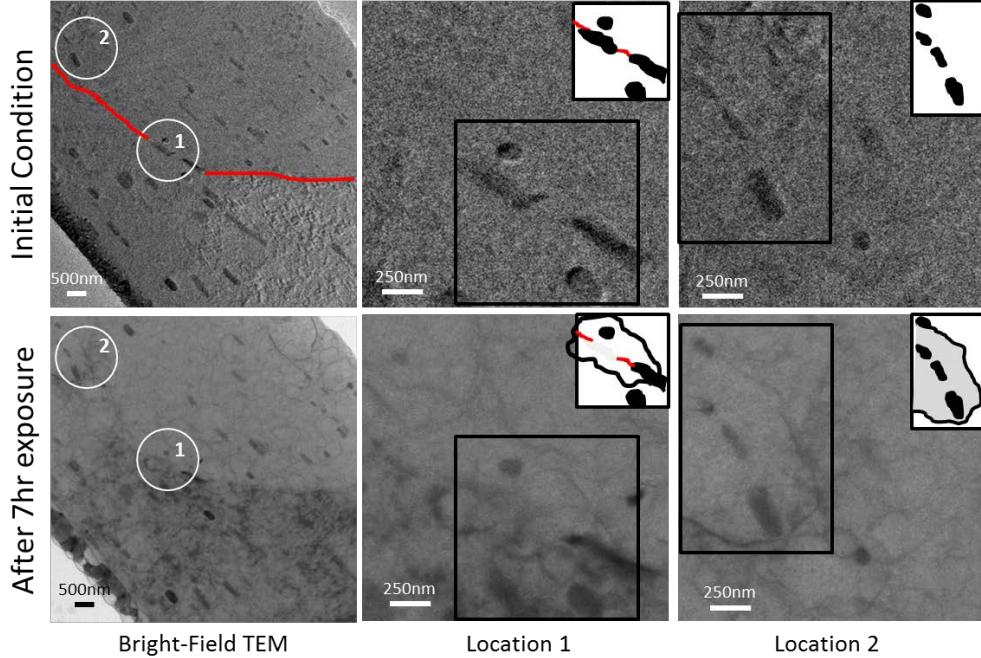


Figure 2. Bright-field TEM images showing the in situ corrosion attack at a grain boundary precipitate (location 1), and corrosion attack in the matrix around precipitates (location 2), before (top 3 images) and after (bottom 3 images) exposure to a reactive mixture of oxygen bubbled through aqueous HCl of pH = 3 at room temperature and 1 bar pressure. The grain boundary is highlighted by a red line in the figures. At location 1 a grain-boundary precipitate is removed by de-alloying while in location 2, the matrix surface is attacked. The black contours in the illustrations (bottom row) indicate possible corrosion products. The area shaded in grey is the region where the matrix is thinned.