

## Localised corrosion in aluminium alloy 2024-T3 using *in situ* TEM†

Sairam Malladi,<sup>\*ab</sup> Chenggang Shen,<sup>b</sup> Qiang Xu,<sup>b</sup> Tom de Kruijff,<sup>b</sup>  
Emrah Yücelen,<sup>bc</sup> Frans Tichelaar<sup>b</sup> and Henny Zandbergen<sup>b</sup>

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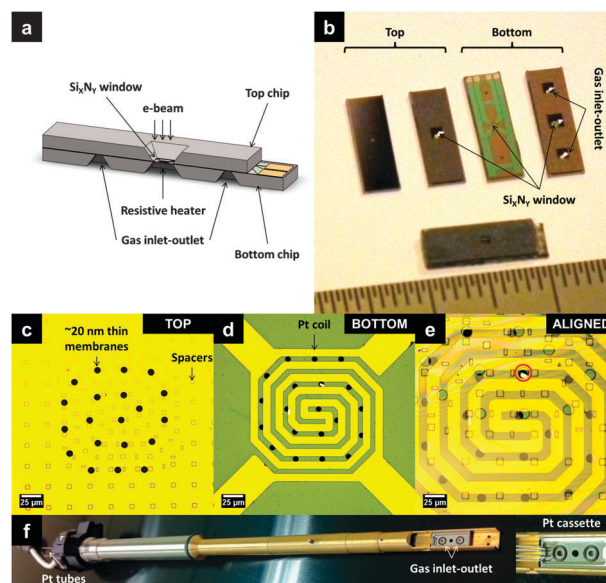
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An approach to carry out chemical reactions using aggressive gases *in situ* in a transmission electron microscope (TEM), at ambient pressures of 1.5 bar using a windowed environmental cell, called a nanoreactor, is presented here. The nanoreactor coupled with a specially developed holder with platinum tubing permits the usage of aggressive chemicals like hydrochloric acid (HCl).

Environmental transmission electron microscopy (ETEM) is becoming an increasingly important field of study as the ability to create a controlled atmosphere around a specimen makes it possible to study several specimen–environment interactions on the nano-scale.<sup>1</sup> In a TEM, which is usually operated under ultra-high vacuum, the controlled environment is achieved by one of the following approaches:<sup>2</sup> the open type, using a differentially pumped vacuum system in which the reactive gases are spread around the specimen area of the TEM; and the closed type, using a windowed environmental cell.<sup>3</sup> Over the years, the differentially pumped vacuum systems have proven to be very effective in achieving atomic resolution; however, the maximum achievable environmental pressures are in the order of 10–20 mbar. More recently, with the advancements in fabrication of microelectromechanical systems (MEMS) based devices, environmental cells based on Si chips with thin membranes of silicon nitride ( $\text{Si}_x\text{N}_y$ ) have shown some intriguing possibilities for *in situ* experimentation.<sup>3–7</sup>

We have adopted the closed environmental cell based approach to facilitate the *in situ* ETEM studies. A functional MEMS device known as a nanoreactor has been developed in-house for this purpose. The nanoreactor consists of two facing chips fabricated using thin-film technology on a silicon substrate, as illustrated in Fig. 1(a). A photograph showing both sides of the top and bottom chips as well as a glued nanoreactor is presented in Fig. 1(b). As seen in Fig. 1(b), the central area of the chip is etched to create a  $\sim 400$  nm thin  $\text{Si}_x\text{N}_y$



**Fig. 1** (a) Conceptual sketch of a nanoreactor; (b) photographs of the top and the bottom chip, with an  $\sim 400$  nm  $\text{Si}_x\text{N}_y$  window in  $800 \times 800 \mu\text{m}^2$  area; the inlet and the outlet for reactive gases in the bottom chip. Optical micrographs of the 400 nm  $\text{Si}_x\text{N}_y$  window showing (c) top and (d) bottom chips, respectively, with  $10 \mu\text{m}$  circular holes over spanned with  $\sim 20$  nm  $\text{Si}_x\text{N}_y$  membranes for electron transparency. The bottom chip is embedded with a Pt spiral for heating. The red encircled region in (e) shows aligned assembly. A glued nanoreactor is introduced into the TEM with the holder made, shown in (f). The holder has Pt tubing and the tip consists of a Pt cassette.

window which further consists of several  $\sim 20$  nm thin  $\text{Si}_x\text{N}_y$  membranes for electron transparency, as shown by the dark circles in the subsequent optical micrographs in Fig. 1(c–e). The top chip has  $\sim 200$  nm spacers to prevent the stiction of the opposite membranes while the bottom chip consists of an embedded Pt wire to allow localised resistive heating to temperatures as high as  $700^\circ\text{C}$ . After aligning and assembling the chips together, Fig. 1(e), it is possible to study a number of gas–material interactions by varying temperatures as well as pressures. Using this system, we have demonstrated that it is possible to study catalysis in TEM as well as in scanning transmission X-ray microscopy (STXM)<sup>5</sup> and (de)hydrogenation of hydrogen storage materials<sup>8</sup> *in situ*.

<sup>a</sup> Materials Innovation Institute, Mekelweg 2, 2628CD, Delft, The Netherlands

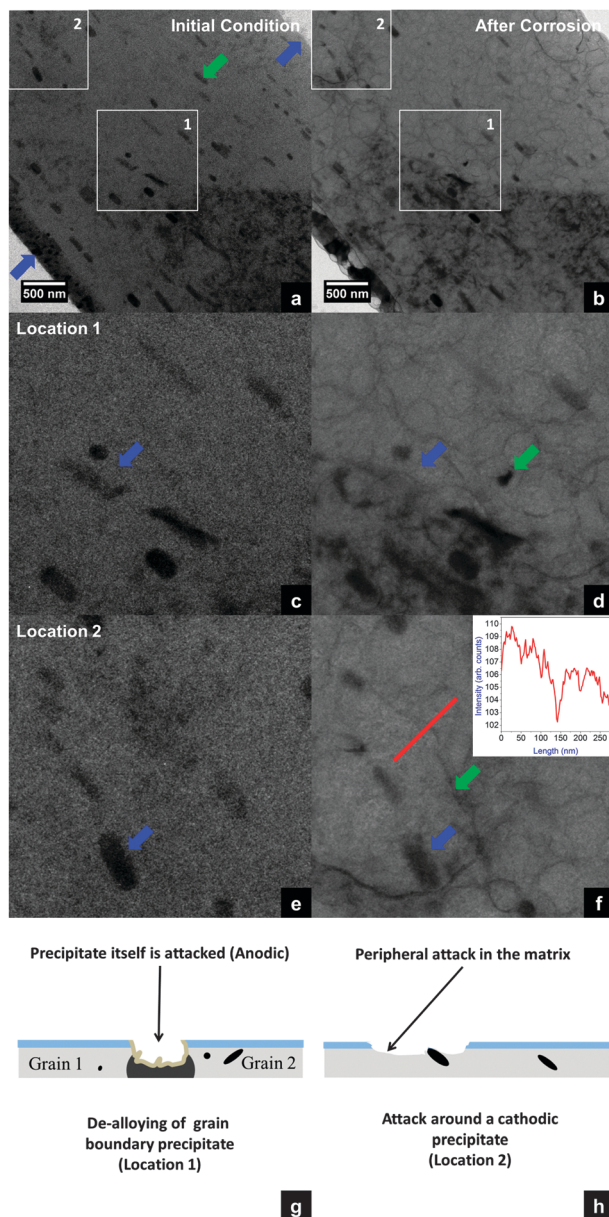
<sup>b</sup> Kavli Institute of Nanoscience, National Centre for HREM, Delft University of Technology, Lorentzweg 1, 2628 CJ, Delft, The Netherlands.  
E-mail: S.R.K.Malladi@tudelft.nl

<sup>c</sup> FEI Company, Europe NanoPort, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands

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**Fig. 3** (a and b) BF-TEM images obtained for the AA 2024-T3 FIB specimen before and after *in situ* corrosion at room temperature and 1.5 bar pressure. The artefacts during specimen preparation are indicated by blue arrows. (c and d) At location 1 a grain-boundary precipitate (shown by blue arrows) is removed by de-alloying. Also the appearance of a dark feature (green arrow) close to the grain boundary precipitate is observed. (e and f) At location 2, the matrix surface around one of the precipitates (blue arrows) is attacked. An intensity profile along a 275 nm line (red) across the attacked region shows a higher intensity close to the precipitate as compared to that of the matrix beyond the dark contour (shown by a green arrow). (g and h) Schematics illustrating the corrosive attack.

here is the influence of the electron beam. The electron beam could induce a negative charge on the aluminium specimen surface, an effect similar to cathodic polarization, which can cause a resistance to corrosive attack, on the other hand, it could also dissociate HCl to its respective ions, resulting in making aluminium susceptible to corrosion by  $\text{Cl}^-$  which is well documented.<sup>14</sup> These two counterbalancing effects under the electron beam cannot be distinguished in this particular study but call for more experiments in this direction.

Nonetheless, the corrosion attack observed here is consistent with localised corrosion studies in aluminium alloys<sup>13,14</sup> and based on these, conceptual sketches illustrating the corrosive attack around an anodic and a cathodic precipitate are presented in Fig. 3(g) and (h).

In this study, we have demonstrated an *in situ* approach to investigate corrosion reactions on a sub-micron scale. Although the exact 3D location of the precipitates across the cross-section is unclear from the BF-TEM images, as corrosion is a surface reaction, it is interpreted that the precipitates that have been attacked at locations 1 and 2 are closer to the surface. In future experiments this geometrical question can be answered by performing tomography before and after the *in situ* study. The silicon nitride membranes ( $\sim 20$  nm thick) of the nano-reactor withstand the pressures of  $\sim 1.5$  bar throughout the experiment for 5 hours of constant electron beam illumination and flow of highly reactive gas mixtures (combination of HCl,  $\text{H}_2\text{O}$  and  $\text{O}_2$ ), without any noticeable reaction or damage. Despite this stability, it is better to speed up the corrosion process to make a more efficient use of the TEM, which can be obtained by carrying out corrosion tests at higher temperatures using the heater. Also, it is possible to combine the morphological changes during heat treatment with the corrosion behaviour of aluminium alloys. In short, this approach opens up possibilities to investigate morphological changes during chemical reactions in various gas-liquid-material systems on the nanoscale.

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