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Short Communication

Challenges to electrochemical evaluation of nanometric sandwiched thin specimens using liquid cells designed for application in liquid-phase TEM corrosion studies

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ABSTRACT

Liquid-phase transmission electron microscopy (LP-TEM) has provided corrosion scientists with a unique opportunity to directly correlate nanoscopic morphological and compositional evolutions to the corresponding electrochemical response of corroding thin TEM specimens. Electrochemical liquid cell designs are key components of a LP-TEM study towards an implementation which is representative for realistic exposure conditions of bulk samples. However, the application of commercially available liquid cells in corrosion studies brings along an important shortcoming of galvanic coupling effects due to the inevitable connection of the TEM specimens with Pt patterned electrodes. Here, we introduce an approach of fabricating electrochemical liquid cells to alleviate the current cell design challenge for corrosion studies. Besides, we present a protocol for preparing thin specimens to be electrochemically investigated with our home-made electrochemical liquid cell. We finally confirm the effectiveness of this methodology by electrochemically evaluating thin specimens of AA2024-T3 in an open-cell configuration through open circuit potential and potentiodynamic polarisation measurements.

1. Introduction

Electrochemical liquid phase-transmission electron microscopy (LP-TEM) has recently emerged as an unparalleled opportunity to explore corrosion phenomena in situ and at the nanoscale [1,2]. Thanks to the developed liquid cells, it is possible to polarise (bias) electrochemical reactions taking place at the specimen/electrolyte interface while the corresponding morphological and compositional changes are captured [3–7]. However, this significant prospect in relation to the approach and its application in corrosion science studies comes with inherent experimental challenges and concerns [8–13]. This mainly includes the demanding and delicate preparation and transfer operations of thin specimens of alloys [14], in particular when simultaneous electrochemical and morphological investigations are planned [15].

Contemporary liquid cells are typically composed of a top and bottom silicon-based chip assembly by which the specimen and its liquid surrounding are isolated from the ultra-high vacuum TEM column [16].

In addition, electrodes including working (WE), reference (RE) and counter electrodes (CE) are patterned on one of the chips mostly for batteries, catalysts and electrodeposition applications [6,17]. They are normally made of Pt in order to facilitate the micromechanical fabrication process [16]. In the case of corrosion studies, the thin alloy specimens have to be electrically connected to the Pt WE electrode in order to conduct electrochemical measurements [15]. Since Pt is electrochemically active and highly noble with respect to many metals and alloys, this can result in extensive galvanic corrosion of the TEM specimens once in contact with the electrolyte. It should be mentioned that Pt WE electrodes on the electrochemical chips have a significantly higher surface area than the prepared thin specimens. This phenomenon particularly causes a considerably accelerated corrosion of the thin specimens, in particular when reactive materials such as common aluminium, zinc and magnesium engineering alloys are of interest. This challenge, which can potentially limit applicability and reliability of the electrochemical measurements, has not been considered in the design of

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the currently available commercial electrochemical TEM liquid cells if intended for corrosion studies. Moreover, electrochemical liquid-phase TEM studies of corrosion face several experimental considerations in relation to intricate sample preparation to be representative for realistic conditions of bulk samples. For instance, selective masking of the TEM specimen can be used to restrict the surface area involved in the electrochemical process, enabling top- or cross-sectional studies of corroding thin specimens [18].

The current work deals with these practical challenges in order to design and develop electrochemical chips and to present sample preparation protocols towards reliable LP-TEM studies of corrosion. We first introduce our approach in manufacturing home-made electrochemical chips to deal with galvanic coupling and background current impact. In addition, we present a protocol in order to prepare thin specimens for electrochemical LP-TEM studies of corrosion. Then, we apply this methodology in electrochemically investigating thin specimens of AA2024-T3 in an open-cell configuration through open circuit potential (OCP) and potentiodynamic polarisation measurements. Besides, the specimens are evaluated morphologically before and after the tests using scanning electron microscopy (SEM).

2. Design of electrochemical liquid cell for corrosion studies

Fig. 1 shows the schematics and also the SEM image of the newly

designed electrochemical chip. As can be seen in Fig. 1a, there are four Pt electrodes integrated into the chips which can be reached by four connection pads. The two electrodes patterned at the sides of the chip (patterns coloured in blue) are approx. 300–500 nm tall. In the case of doing electrochemical measurements, one of each can serve either as the reference electrode (RE) or the counter electrode (CE). Moreover, these side electrodes function as spacers and can actually define and confine the channel through which the electrolyte can pass; it is 250 μm wide around the membrane (Fig. 1b). Unlike the side electrodes, the middle Pt patterns are covered by 30-nm Si_xN_y . This can be implemented by initial deposition of the middle Pt electrodes followed by their coverage by the Si_xN_y layer [16]. The side Pt electrodes are deposited at the next stage of the chip manufacturing process. The Pt electrodes patterned in the middle (coloured in blue) can be used as the electrical connection path to attach the thin TEM specimens (lamellae) for applying an external bias. However, in order to achieve the electrical connection, the Si_xN_y cover has to be removed locally; this process will be explained later. It should be noted that covering the middle Pt electrodes with TEOS using the FIB/SEM microscope is not possible because the scale of the Pt electrodes is too large for such a microscope to handle; hence, local removal of an externally and earlier applied Si_xN_y cover is more practical than later coverage within the microscope. Besides, an on-chip inlet and outlet are integrated in the cell design through which the electrolyte can run into and out of the liquid cell, allowing to establish an

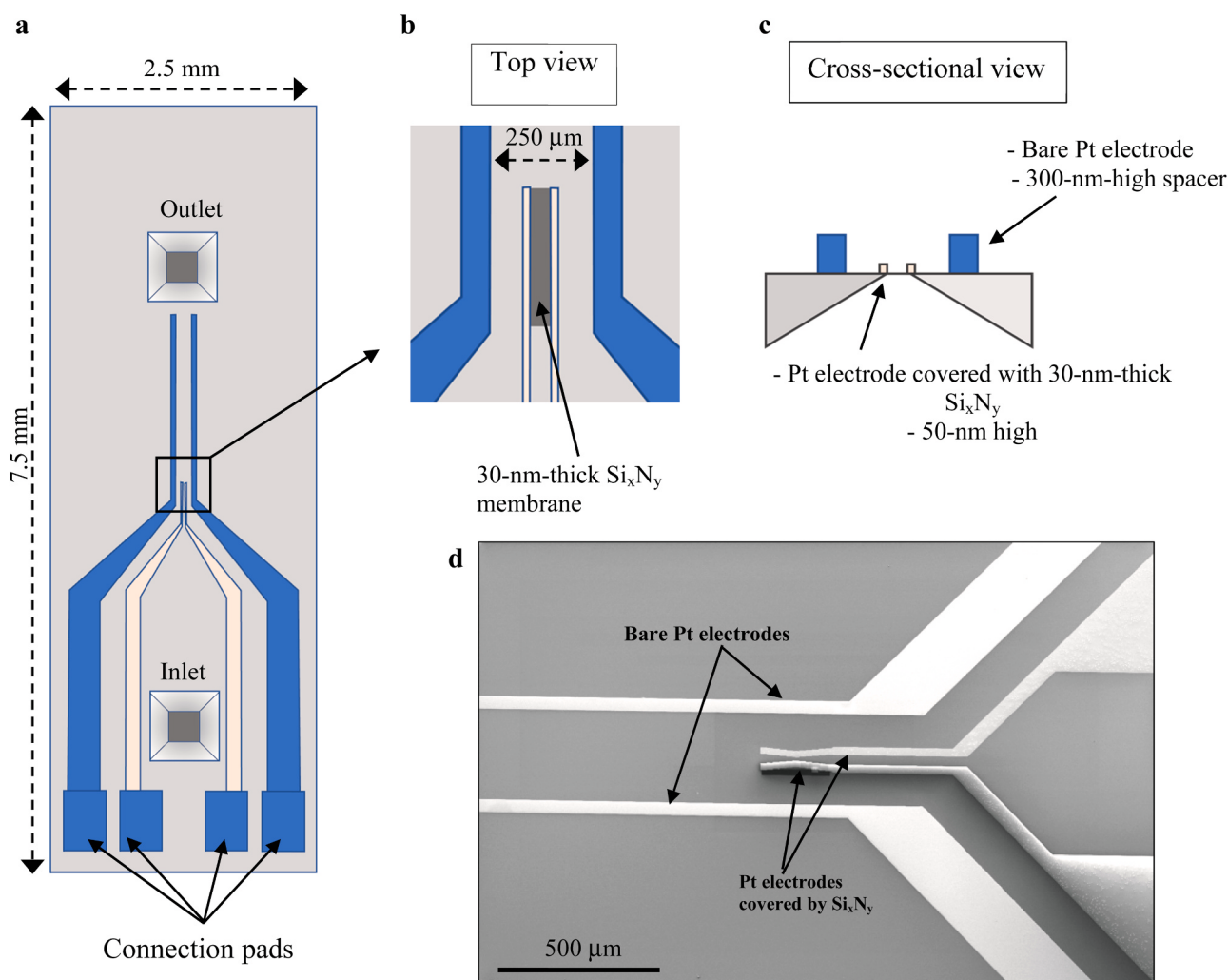


Fig. 1. MEMS chip specifically designed for corrosion studies. (a) Schematic representation of the bottom chip. Note that a liquid cell is composed of a top and bottom chip. The top chip includes no specific features except a Si_xN_y membrane. (b) Top and (c) cross-sectional view of the chip around the membrane. (d) SEM image of the central region of the bottom chip as fabricated.

electrolyte flow through the specimen area of the cell. Note that a liquid cell is composed of a top and bottom chip; the top chip, which includes no specific features except a 50 μm -wide Si_xN_y electron transparent membrane, is presented elsewhere in a prior work of the authors [18].

3. TEM specimen preparation procedure for corrosion studies

Prior to loading a TEM specimen into the bottom chip, several preparation stages that are shown in Fig. 2 have to be carried out. Here, we perform sandwiching the lamellae to control the oxidation direction, allowing cross-sectional observations of local corrosion. We have recently used this form of specimen preparation for studying local corrosion phenomena in freely-corroding AA2024-T3 samples (not biased) [18]. As shown in Fig. 2a, a lamella is sandwiched by applying two thin layers of tetraethyl orthosilicate (TEOS) (approx. 30 nm) on the sides of the specimen via the 2-keV electron beam. TEOS is electrochemically inert and does not disturb the system through galvanic coupling. We have demonstrated that TEOS with a thickness of 30–40 nm can resist even severe alkaline environments, protecting TEM specimens when sandwiched between two layers of TEOS [19]. To get an electrical connection between the specimen and chip, the Si_xN_y layer has to be removed locally before positioning the lamella. Fig. 2b shows a region of $5 \mu\text{m} \times 20 \mu\text{m}$ at which the Si_xN_y layer has been removed by Ga ion milling. The Ga ion milling should be performed for approx. 30 s (30 keV, 30 pA) to make certain of the Si_xN_y removal. As is evident in Fig. 2b, the bare region shows a brighter contrast compared to the covered regions. The next stage is to transfer the prepared lamella to the chip and position it at the membrane where the Si_xN_y is removed (Fig. 2c). The electrical connection can be obtained by ion-beam Pt deposition as shown in Fig. 2d. Thus, care should be taken during this process in order to avoid potential Ga ion-beam damage and Pt contaminations. In practice, it is usually preferable to perform Pt ion

deposition at a relatively low ion-beam current (smaller ion beam size), allowing deposition to occur just on the region of interest. Afterwards, three edges are covered by TEOS layers of 200- or 300-nm thick to leave the clean edge bare and interacting with the electrolyte. All the processes here were performed with a Thermo Fisher Helios G4 focused ion beam (FIB); the further details related to the sample preparation and transfer process as well as the deposition parameters are reported elsewhere [18].

In this work, two sandwiched specimens from AA2024-T3 are loaded on the designed chips and studied by open circuit potential (OCP) and anodic potentiodynamic polarisation (scan rate 2 mV/s) measurements. Fig. 3 shows the open-cell setup for electrochemical evaluation of nanometric sandwiched thin specimens. The chips were initially oxygen plasma-cleaned for 1 min in order to make them hydrophilic [8]. As shown, the experiments were performed ex-situ by putting the bottom chip on a home-made holder connected to an Ivium potentiostat. Then, a tiny droplet (a couple of μl) of 0.01 M NaCl solution (open to air) was dropped in the central region of the chip before conducting electrochemical measurements.

4. Results and discussion

Fig. 4 shows the SEM morphological and electrochemical evaluations of the sandwiched 400-nm-thin specimens. As can be seen in Fig. 4a, the first lamella contains several grains indicated by the white dashed lines while the second specimen (Fig. 4b) contains three large Al_2CuMg (S-phase) intermetallic particles. The specimens are covered at three edges leaving a clean edge bare to the electrolyte (indicated by the white arrows). It should be mentioned that S-phase is highly reactive to the aqueous environments undergoing dealloying due to preferential dissolution of aluminium and magnesium [18,20].

The OCP values were being recorded versus one of the side Pt

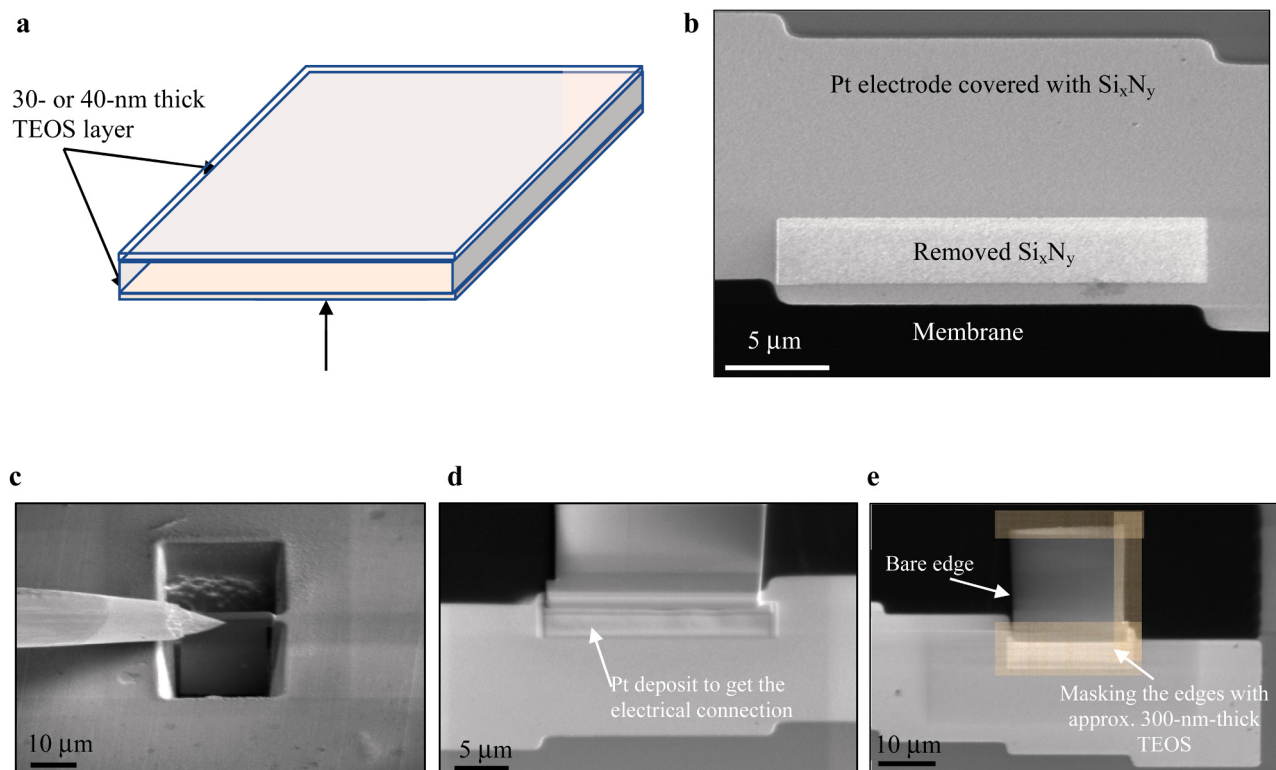


Fig. 2. Different stages of loading the chip with a lamella electrically connected. (a) Schematic of an AA2024-T3 sandwiched thin specimen of (approx. $12 \mu\text{m} \times 20 \mu\text{m}$). (b) Local removal of Si_xN_y on the Pt WE. (c) Transfer of the prepared specimen to chips using the nano-manipulator. (d) Ion-beam Pt deposition to connect the specimen to the Pt WE. (e) Coverage of the three edges shown in yellow with TEOS and leaving the clean edge bare for electrochemical experiments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

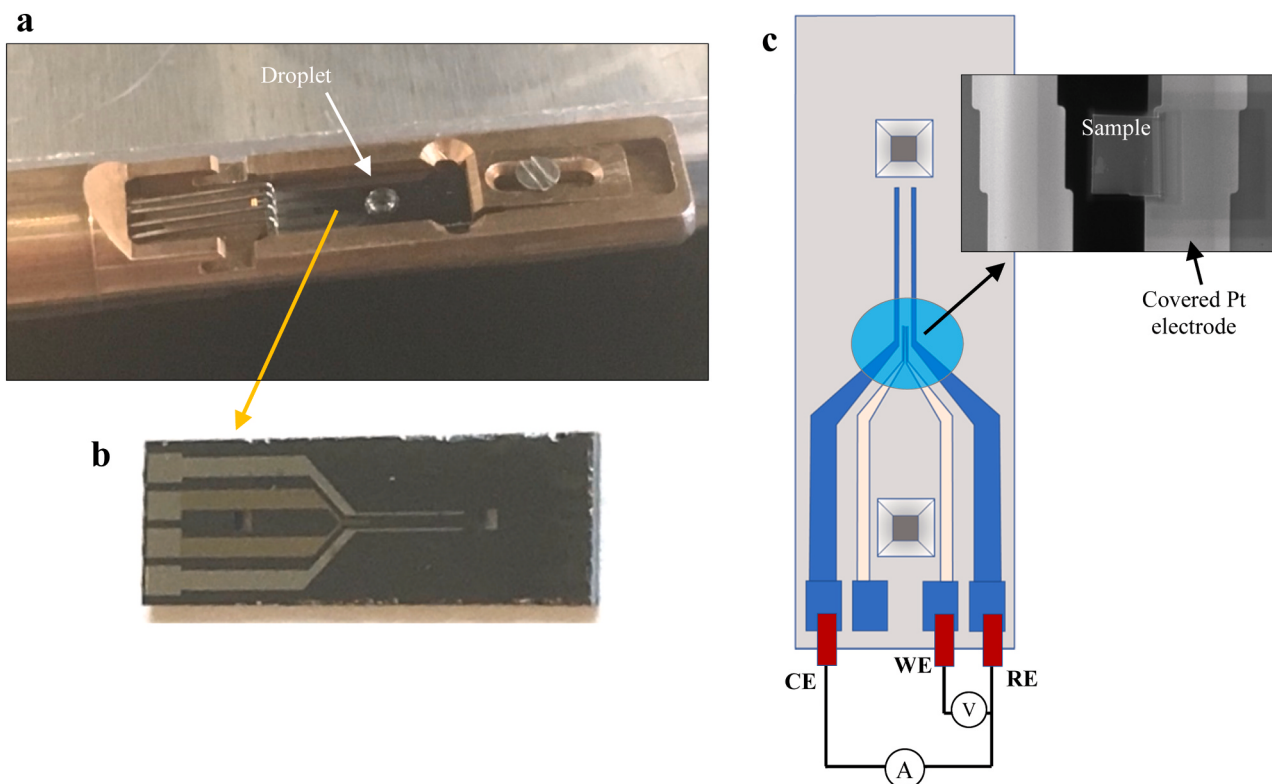


Fig. 3. Open-cell setup for electrochemical evaluations of nanometric sandwiched thin specimens. (a) Macrograph of the tip of the home-made TEM holder. (b) Macrographs the developed chip loaded on the holder. (c) Schematic of the chip and the configuration of the electrodes when connected to a potentiostat. As shown, a droplet of 0.01 M NaCl solution is used as the electrolyte. The inset shows the SEM image of the specimen connected to one of the covered Pt electrodes.

electrodes while the other one was serving as the counter electrode. As can be seen in Fig. 4c, the Si_3N_4 -covered Pt electrode (no sample) shows a stable OCP values around 70 mV during a 3-min recording indicating its inherently high electrochemical inertness. Interestingly, the OCP shows very negative values when the specimens are loaded. The specimen without S-phase shows an initial OCP values of approx. -700 mV with several fluctuations down to -900 mV related to possible morphological and compositional evolutions within the specimen. And then the OCP increases and stabilises to approx. -550 mV. Comparatively, the specimen with S-phase particles shows lower initial OCP values around -1200 mV due to the presence of S-phase at the edge of the specimen [20]. Afterwards, the OCP rises to -700 mV possibly owing to the Cu-enrichment of the specimen as a consequence of selective dissolution of aluminium and magnesium (dealloying) [20]. The OCP remains almost stable over the next 60 s and again starts to increase to -600 mV after 150 s Fig. 4d compares anodic polarisation curves for the two specimens. As can be seen, the specimen with S-phase particles shows higher anodic activity than the one without the intermetallic particles, owing to the presence of S-phase particles. It should be noted that the sandwiched TEM specimens are merely representative for the electrochemical behaviour of only a very local region (i.e., a single intermetallic phase embedded in a relatively small alloy matrix region). In contrast, bulk sample experiments may reveal the electrochemical response of a broader, representative AA2024-T3 microstructure comprising all the matrix-embedded intermetallic particles of different sizes and chemical compositions. Thus, the potentiodynamic polarisation of a thin TEM specimen cannot be compared to that of bulk samples, in particular for the heterogeneous and complex alloy microstructure studied. Furthermore, the geometry of the TEM specimens (i.e., size, thickness, and here confinement between two TEOS layers) has a significant impact on the kinetics of electrochemical processes, as also evidenced by two recent liquid-phase TEM studies on the local corrosion mechanism [18] and the formation of lithium-based conversion layers

[19] in AA2024-T3. In fact, the main benefit of electrochemical liquid-phase TEM is the ability to directly correlate the electrochemical response of a thin TEM sample to the corresponding nanoscopic morphological and compositional evolutions.

The post-mortem SEM analysis shown in Fig. 4e and f reveals different corrosion-attack morphologies for the specimens after potentiodynamic polarisation testing. In the specimen without S-phase, some of the grains (Grain I and III) have been fully corroded while there are grains that are less attacked (Grain II). Furthermore, the grain boundaries are preferential pathways for propagation of corrosion. It can be postulated that the corrosion has initiated at the edge S-phase particle (indicated by the red arrow), after which it has further penetrated into the grain, reaching another S-phase particle partly located at the grain boundaries. Besides, we can observe that one of the grains in this specimen is completely dissolved. This can be attributed to the different electrochemical activities of the grains due to different crystal orientation [21]. However, the detailed mechanism related to the corrosion initiation in the presence of different phases and grains are to be obtained by complete electrochemical liquid cell TEM experiments. This study shows the importance of real-time electrochemical measurements by liquid-phase TEM to be able to correlate microstructural evolution to the electrochemical response of individual phases, which are to be executed in a follow-up study.

5. Conclusions

This study is a preliminary effort to develop the technique and circumstances for conducting electrochemical liquid-phase TEM investigations of corrosion. Here, we discussed the challenging limitations of the current commercial liquid cells for biased electrochemical response experiments in corrosion studies. As a remedy, we covered the Pt WE electrodes with Si_3N_4 to avoid galvanic coupling between the electrode and the specimens subjected to electrochemical

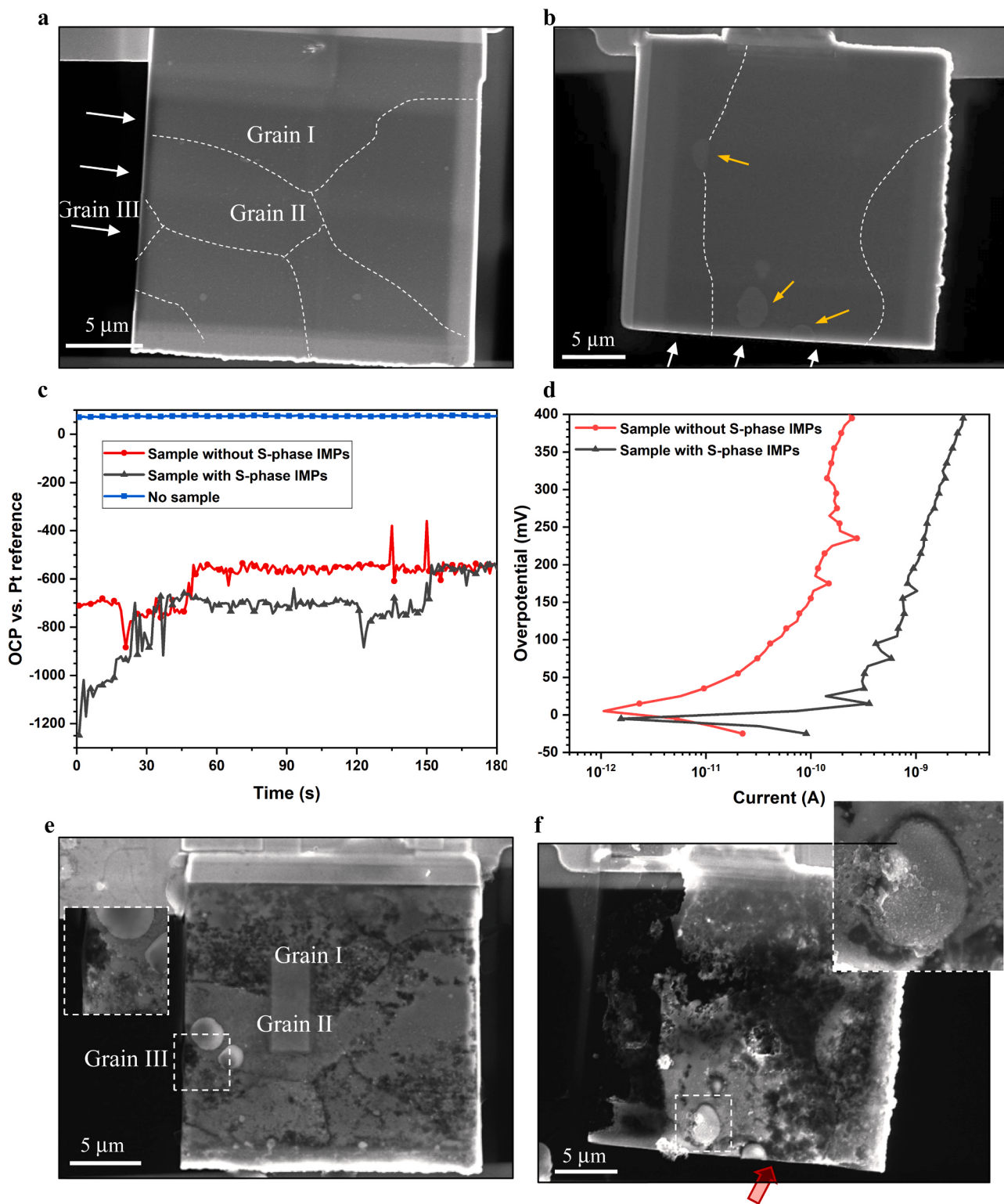


Fig. 4. SEM morphological and electrochemical evaluations of the sandwiched 400-nm-thin specimens. (a and b) SEM images of the specimens prior to the electrochemical measurements. (a) SEM image of the sandwiched specimen containing several grains and nanoscopic intermetallic particles and (b) the sandwiched specimen comprising coarse Al_2CuMg particles before exposure. The white arrows indicate the bare edge interacting with the electrolyte. (c) Open circuit potential (OCP) values of the different specimens recorded for 180 s (d) Potentiodynamic polarisation of the specimens – 25 mV up + 400 mV versus the OCP. The scan rate was 2 mV/s. (e and f) SEM images of the specimens subsequent to the electrochemical measurements. SEM image of (e) the corroded sandwiched specimen shown in Fig. 4a and (f) the sandwiched specimen shown in Fig. 4b. The insets are zoomed-in images of the corresponding rectangular regions.

measurements. We successfully used Si_xN_y covered Pt electrodes to study the electrochemical response of sandwiched thin AA2024-T3 specimens exposed to a corrosive aqueous NaCl solution. Sandwiched TEM specimens are recommended since they are able to guide the oxidation direction, mimicking cross-sectional propagation of corrosion. With the practical strategies taken here, the precise correlation of morphological evolutions to the electrochemical response of the corresponding corroding system are possible. Thus, the challenges should be well considered for the future corrosion studies with electrochemical LP-TEM.

CRedit authorship contribution statement

A. Kosari: Conceptualization, Methodology, Validation, Investigation, Writing – original draft. **H. Zandbergen:** Conceptualization, Methodology, Writing – review & editing, Supervision. **F. Tichelaar:** Conceptualization, Writing – review & editing. **P. Visser:** Conceptualization, Writing – review & editing. **H. Terry:** Conceptualization, Writing – review & editing, Supervision. **J.M.C. Mol:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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