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Guo, Liya; Street, Steven R.; Mohammed-Ali, Haval B.; Ghahari, Majid; Mi, Na; Glanvill, Sarah; Du Plessis, Andrew; Reinhard, Christina; Rayment, Trevor; Davenport, Alison J.

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# The Effect of Relative Humidity Change on Atmospheric Pitting Corrosion of Stainless Steel 304L

Liya Guo <sup>\*1,2</sup>, Steven R. Street<sup>1</sup>, Haval B. Mohammed-Ali<sup>1,3</sup>, Majid Ghahari<sup>1</sup>, Na Mi<sup>1</sup>, Sarah Glanvill<sup>1</sup>, Andrew Du Plessis<sup>1</sup>, Christina Reinhard<sup>4</sup>, Trevor Rayment<sup>4</sup>, and Alison J. Davenport<sup>\*1</sup>

<sup>1</sup>*School of Metallurgy and Materials, University of Birmingham, B15 2TT, UK*

<sup>2</sup>*Department of Materials, Imperial College London, SW7 2AZ, UK*

<sup>3</sup>*Physics Department, University of Zakho, Iraq*

<sup>4</sup>*Diamond Light Source Ltd., OX11 0DE, UK*

*\*Corresponding author. Email address: [liya.guo@imperial.ac.uk](mailto:liya.guo@imperial.ac.uk), [a.davenport@bham.ac.uk](mailto:a.davenport@bham.ac.uk)*

## **Abstract**

Relative humidity fluctuations tend to influence atmospheric corrosion under natural exposure conditions. In this study, the effect of change in relative humidity on pitting corrosion of stainless steel under MgCl<sub>2</sub> droplets is investigated with *in situ* X-ray microtomography and optical microscopy. Relative humidity fluctuations (between 33% RH and 85% RH or between 33% RH and 12% RH) tend to lead to nucleation of many small pits whereas continuous exposure at constant 33% RH leads to growth of a single pit. This indicates that natural fluctuations in relative humidity might be beneficial for preventing the growth of a large penetrating pit.

*Keywords: Atmospheric pitting corrosion, Wet-dry cycling, Stainless steel, X-ray microtomography*

## 1 Introduction

In the UK, stainless steel containers (304L or 316L) are used for storing intermediate level nuclear waste (ILW). The containers are intended to be disposed in a geological disposal facility (GDF), but such a facility is not available yet. In the meantime, the ILW containers will be placed above ground for a number of decades. The integrity of the containers must therefore be ensured [1-4]. However, atmospheric pitting corrosion can take place on these containers when there is aerosol deposition of salt particles on the metal surface and the relative humidity (RH) reaches the deliquescence point of the salt [5]. These pits can then lead to atmospherically-induced stress corrosion cracking, which could lead to structural failure when the containers are moved to their final storage site [6].  $MgCl_2$  is commonly used in lab-based atmospheric corrosion tests of stainless steel [7] [8] [9] [10] as it is a common constituent in marine aerosols with a low deliquescence relative humidity (DRH, 33%), making it more likely to cause pitting than NaCl droplets (high DRH, 75%).

Measurements of temperature and RH in a typical store over 2 years indicated that the RH generally fluctuates between 30% RH and 90% RH, and the temperature varies between 0 and 30 °C [1]. However, research on atmospheric pitting corrosion of stainless steel has generally focused on constant conditions of RH [2] [9, 11] [12] [10] [13]. Studies on the effect of RH variations have been limited to corrosion current or potential monitoring [7, 14-18] [19]. However, the current or potential response only gives the overall corrosion behaviour of the sample tested. It does not indicate whether the response is caused by growth of individual pits or initiation of new pits during RH fluctuations. Growth of a single pit means that large pits can form, which might be more likely to lead to atmospherically-induced stress corrosion cracking, while new pit initiation is of much less concern since a large population of small pits is less likely to lead to cracks [20]. The critical RH for pit repassivation of 304 was reported to be 70-75% [14] and 56%-70% [19]. Hence stable pits

grown at an aggressive condition were expected to repassivate when RH was changed to a high value, greater than 75%. Traditionally, pits were expected to repassivate when the exposure RH was far below the deliquescence point of the corresponding salts.

Dehumidification system might be used to avoid localized corrosion in the storage of ILW containers [5]. However, Schindelholz and et al. [21] [22] recently showed that corrosion of carbon steel was observed under  $\text{MgCl}_2$  at 11% RH and under NaCl deposits at 33% RH.

In this study, atmospheric pitting corrosion under droplets of  $\text{MgCl}_2$  was observed with the use of *in situ* optical microscopy on lab-based experiments and *in situ* synchrotron X-ray microtomography to study the effect of RH fluctuations.

## 2 Experimental Method

### 2.1 Material and sample preparation

For studies in lab-based tests, 304L stainless steel sheets (3 mm in thickness, provided by Aperam) were cut into slices and the end grain surface was exposed. The sample, in the dimension of 3 mm  $\times$  2 cm, was then cold mounted. For studies in tomography tests, pin samples with 2 mm diameter were machined from the 304L sheet, with the rolling direction of the sheet parallel to the pin axis so that the top surface was the end grain of the sheet (Figure 1 [23]). The compositions of the 304L sheet is 18-19.5 wt% Cr, 8-10.5 wt% Ni, 2 wt% Mn, 0.75 wt% Si, 0.1 wt% N, 0.045 wt% P, 0.03 wt% C, 0.015 wt% S and Fe balance (provided by the supplier). The sheet had been cold rolled, solution treated (1040-1100 °C) and then cooled by forced air.

### 2.2 Droplet deposition

In both lab-based and tomography tests, specimens were ground with SiC papers to 600 grit and washed with de-ionised water (Millipore, > 15 M $\Omega$ .cm) and methanol. A droplet with volume of 1.1  $\mu\text{L}$  of 0.4 M  $\text{MgCl}_2$  was deposited on the end grain metal surface. In lab-based

tests, the droplet diameter was 1.9 to 2.1 mm, giving a chloride deposition density (CDD) of 900 to 1100  $\mu\text{g}/\text{cm}^2$ . In tomography tests, the droplet diameter was 2 mm, giving a CDD of 1000  $\mu\text{g}/\text{cm}^2$ . The CDD value is higher than the store environment: up to  $\sim 100 \mu\text{g}/\text{cm}^2$  [5]. This was to provide an aggressive environment to study the effect of RH fluctuations.

### *2.3 Relative humidity and temperature control*

For lab-based tests, after deposition of droplets, plates were put in a transparent desiccator, which contained saturated salt solutions and corresponding salts (Table 1 [24]) for RH control. 12% RH, 33% RH and 85% RH represent “dry”, “wet” and “wetter” conditions respectively. For tomography tests, silicone tubes were slipped over the pin where droplets were deposited. Filter paper soaked with saturated salt solutions was fitted into a silicone tube [20], and the sample was then sealed by an aluminium cap. The lab-based tests were carried out at  $22 \pm 2 \text{ }^\circ\text{C}$  and synchrotron tomography tests were carried out at  $21 \pm 1 \text{ }^\circ\text{C}$ . OMEGA OM-EL-USB-2-LCD and OMEGA OM-73 data loggers were used to monitor the RH and temperature in lab-based experiments.

### *2.4 In situ lab-based corrosion tests*

#### *Constant relative humidity at 33% RH*

In lab-based tests, specimens were exposed at constant 33% RH for 11 days as a controlled condition.

#### *One RH cycle*

Typically, samples were left at 33% RH (“wet”) for one day for pit initiation. Then the RH was changed either to 85% (“wetter”) or 12% (“dry”) for one day. Finally, the RH was changed to 33% for nine days to check whether re-growth of original pits or new pit initiation was favoured. To study the effect of pit size on the corrosion behaviour, specimens were

exposed at 33% RH for 21 days to initially grow a deep pit in the first period of a “wetter-wetter-wet cycle”.

### *Multiple RH cycles*

To study the effect of a number of cycles on atmospheric pitting corrosion, tests of multiple RH cycles were carried out. The initial condition was 33% RH (“wet”), and this was followed by five cycles to either the “dry” or “wetter” condition for one day and then back to the “wet” condition for one day.

At least seven droplets were studied at each condition.

Droplets were examined with a Leica DFC 420 light optical microscope (OM) after the first 33% RH exposure and at the end of the cycle. In this study, the width of a pit refers to the diameter of a circle which has the same area as the pit area. The depth of a pit refers to the greatest depth found among different parts of a pit and it was measured by OM by using the depth of focus. Note that the depth measured by OM might be under-estimation if some part of the pit is underneath overhanging metal.

### *2.5 In situ synchrotron X-ray microtomography tests*

The design of the cell for synchrotron X-ray microtomography tests has been detailed previously [20] [25] and will not be repeated here. Samples were scanned regularly during RH cycles. The synchrotron tomography tests using monochromatic 70 keV X-rays were performed on the Beamline I12 at Diamond Light Source [26]. The pin sample was rotated and projections were collected at intervals  $0.1^\circ$  per step through  $180^\circ$ . The exposure time per projection used was 1.0 s with a pixel size of  $1.8 \mu\text{m}$ . The total scan time per sample was 40-45 minutes. Filtered back-projections algorithm was used during reconstruction. The tomography data was analysed by Fiji [27] for 2D visualization and characterisation of the pit, and Avizo software for 3D characterisation of the pit [25]. The area of the top surface of the

pit is defined as pit area in tomography. Pit width was calculated from the pit area, using the same definition mentioned above. The depth of the pit was measured from the pit mouth to the pit bottom.

### **3 Results and discussion**

#### *3.1 Number of pits after one day exposure at 33% RH*

In lab-based tests, after exposure of droplets on a 304L surface at 33% RH for one day, varying number of pits have been observed in each droplet. Figure 2(a) shows a typical droplet containing (b) one pit and Figure 2(c) shows another droplet containing (d) multiple pits after one day of exposure at 33% RH. Multiple pits (usually two or three) in lab-based experiments tend to be in clusters. This is consistent with previous work: after exposure at 33% RH, one single pit and a shallow dish region surrounded by satellite pits have both been reported in literature [9] [10] [13]. The difference in the pit number and morphology might be due to the difference in CDD, surface finish and microstructure of the specimens studied [25].

In *in situ* X-ray microtomography experiments, single or multiple pits could both be observed after one day of exposure at 33% RH. However, the multiple pits were not close to each other, unlike the clusters of the multiple pits in lab-based experiments (Figure 2(d)). The random position of the multiple pits raised a concern that there may be a beam damage effect [28] [29] [30].

The number of pits under a droplet after exposure at 33% RH for one day is summarised in Table 2. In lab-based experiments, one single pit was the most frequent observation. It was also possible to observe multiple pits in clusters. In a few cases, there were no pits under one droplet. In no situation were there two or more pits occurring at a large distance from each other under the droplet. For tomography tests, multiple pits with random position were more frequently observed.

### 3.2 Corrosion behaviour at constant relative humidity at 33% RH

If there is only one single pit under a droplet after one day of exposure at 33% RH, after 11 days of exposure at 33% RH, the width of the pit can be greater. Figure 3 shows an example, where the width of the pit increased after exposure for 6 days and 11 days. There was no obvious change in the top part of the pit. It is likely that the top part has already repassivated. However, the bottom part was getting wider and wider with the increasing exposure time. Partial repassivation of the pit due to limited cathodic current available in atmospheric conditions has been observed by Street *et al.* [13] and Maier and Frankel [10]. If there was growth of the width of the single pit under a droplet, growth of the pit on only one side was generally observed.

For droplets containing multiple pits after one day of exposure at 33% RH, growth of one of the multiple pits was frequently observed, as shown in Figure 4. Two pits were observed under the droplet after one day of exposure. There was no width change for the upper pit (highlighted with black dashed square) after 11 days of exposure. However, the width of the lower pit (highlighted with red dashed square) increased gradually during the exposure. Three droplets containing multiple pits under a droplet were examined part way through the exposure at 33% RH for 11 days. It was found that after six days of exposure, there was increase in the width of two pits. However, only one of the pits under each droplet showed further width change after 11 days of exposure. This observation might be due to the limited cathodic current available to support the anodic dissolution under droplets in atmospheric conditions [10] [13] [31]. Pits are only stable when the maximum cathodic current is greater than the minimum anodic current required to support pit growth. In atmospheric conditions, the maximum cathodic current is limited due to a limited droplet size. Therefore, there is a competition among the pits and only one tends to grow eventually. In immersed conditions in



dilute solutions, it has been reported that multiple pits initiate under potentiostatic conditions while only one or two pits survive under galvanostatic control [32].

Table 3 gives a summary of the corrosion behaviour of the droplets exposed at constant 33% RH in lab-based experiments. Although the number of pits under each droplet varied, growth of an original pit is most frequently observed and it is very uncommon to observe new pit initiation. For some droplets, there is neither obvious width change of the pit nor new pit initiation from one day of exposure to 11 days of exposure. The original pit may have re-passivated or kept growing in depth. However, it is impossible to measure the depth of the pit in lab-based experiments. Therefore, pit growth is counted only when there is a width change.

### 3.3 Corrosion behaviour under “wet-wetter-wet cycles” (33% + 85% + 33%)

Figure 5 shows the typical behaviour of a droplet in which only one pit was found after exposure at 33% RH for one day. When the RH was increased to 85% for one day and then returned to 33% for nine days, one new pit was formed while there was no obvious width change in the original pit. Three droplets that contained one or more pits after one day exposure at 33% RH were examined after 85% RH exposure. For these three droplets, there were no newly initiated pits when RH was increased to 85%. However, there were always new pits when the RH was changed back to 33%. Furthermore, during the cycling, there was no obvious width change in the original pit that initiated after the first 33% RH exposure. This suggests that the original pit re-passivated when the RH was increased to 85% RH and did not re-initiate when the RH was changed to 33%. This observation was consistent with previous literature: the RH for re-passivation of a pit was reported to be 70% to 75% for 304 (with a surface finish of 2000 grit) [14] and 56%-70% (surface polished with a 0.25  $\mu\text{m}$  diamond suspension) [19].

Mi [28] and Street [13] observed that for 304, the breakdown potential for pit initiation decreases with increasing chloride concentration in 0.05-5 M MgCl<sub>2</sub>. At room temperature, 2 M MgCl<sub>2</sub> is equivalent to 83% RH and 5 M MgCl<sub>2</sub> is equivalent to 33% RH [33]. Therefore, new pit initiation was always observed when RH changed from 85% to 33% since the breakdown potential is more easily reached in concentrated solutions. Beom [15] observed that the current was greatest during the drying stage from 90% RH and 50 °C to 30% RH and 60 °C in a study of stainless steel 409 and stainless steel 439 under CaCl<sub>2</sub> electrolyte layers, although it couldn't be determined whether the increase in current was caused by pit growth or new pit initiation. Tsutsumi [34] also reported pit initiation of 304 under MgCl<sub>2</sub> solutions when RH changed from 95% to 25%.

In lab-based tests, some samples were left at the initial 33% RH for 21 days, followed by exposure at 85% RH for one day and then exposure at 33% RH for seven days. New pit initiation could be observed at the end of the cycle. In addition, side growth of the original pit after a “wet-wetter-wet cycle” could be observed among some droplets. In Figure 6, after exposure at 33% RH for 21 days, one pit was observed. When the RH was increased to 85% for one day, there were no new pits and no obvious change in the original pit. After the final exposure at 33% RH for seven days, there was still no new pit initiation, but slight side growth of the original pit (highlighted with the red dashed square) could be observed. The pit was initially exposed at 33% RH for 21 days; therefore, the pit was expected to be deeper and wider [25] than the pit which was initially exposed at 33% RH for one day. It seems that the deep and wide pit may not have completely repassivated at 85% RH. For repassivation to take place, concentrations of metal ions inside the pit need to be lower than a critical value [35-37]. Compared with a shallow pit, a deep pit would require more time for metal ions to diffuse from the pit bottom to the pit mouth according to Fick's 2<sup>nd</sup> Law. Furthermore, pit covers have been reported on top of long-time-exposure pits [25] [20], and can be observed

as a white layer above the pit (vertical sections in Figure 7). The covers would provide effective diffusion barriers to limit the escape of metal ions from the pit. Therefore, repassivation of a deep pit was more difficult than a shallow pit.

Figure 7(a) shows horizontal and vertical sections of a tomogram of a pin sample. The left images show the pit found on the pin sample after exposure at 33% RH for 21 days, followed by exposure at 85% RH for one day. The pin sample was then exposed at 33% RH for one day, shown in the right images. The main part of the pit appeared to grow slightly in both width and depth. Figure 7(b) is a summary of the size change of the main part of the pit (excluding the deep fissure), during cycling. The deep fissure was related to the presence of ferrite in the studied samples [38]. It can be observed that there was a slight increase in the pit width and pit depth. Compared with exposure at 85% RH for one day, the pit volume has increased by ~30% of its volume at the end of the test.

Table 4 is a summary of the corrosion behaviour of droplets after one “wet-wetter-wet cycle” in lab-based tests. It shows that if there were pits after exposure at 33% RH for one day, after one “wet-wetter-wet” cycle, the original pits did not show any growth while there was always new pit initiation. If the pits have been exposed at 33% RH for 21 days, after one cycle, growth of the original pit can be observed.

#### *3.4 Corrosion behaviour under “wet-dry-wet cycles” (33% + 12% + 33%)*

After a “wet-dry-wet cycle”, growth of the original pit could be observed at the end of the test (Figure 8). There was no obvious width change of the original pit after exposure at 33% RH and 12% RH. When the RH was changed back to 33% RH for nine days, there was a side growth of the original pit. This indicated that a pit might be able to survive at 12% RH, the dry condition. One reason why repassivation is difficult at 12% RH might be due to the low efflorescence relative humidity (ERH) of  $\text{MgCl}_2$  and  $\text{FeCl}_3$ . Below ERH, water evaporates

from the salt solutions. The crystals on the metal surface at 12% RH (Figure 8) indicated that efflorescence process had started. The crystals can still be observed when the RH was changed to 33%. At room temperature, incomplete efflorescence of  $\text{MgCl}_2$  has been reported to be lower than 2% [39, 40]. Corrosion could be inhibited if there is insufficient water available to solvate metal ions [31]. However, since water might still be retained in the droplet at 12% RH due to the low ERH of  $\text{MgCl}_2$ , pitting corrosion might not be inhibited completely. Incomplete repassivation of pits due to imperfect drying has been observed by Cruz [18] after immersion of a stainless steel sample in NaCl solutions and then drying at 67% RH (ERH of NaCl has been reported ~41 to 51% RH [40-45]). Another reason might be due to lack of sufficient water to form the passive film. At 85% RH, there is plenty of water available to form the oxide film. Thereby, compared with 85% RH, it would be more difficult for the pit to repassivate at 12%.

After a “wet-dry-wet cycle”, initiation of one or two new pits could be observed for some droplets. Initiation of new pits was observed when the RH was increased from 12% to 33% for the three droplets which were checked after 12% RH. This indicated the importance of water. Increased water activity will enable solvation of metal ions with increasing RH from 12% to 33% and therefore the increase in RH increases the dissolution of the metal.

Consequently, new pits were commonly observed at 33% RH rather than 12% RH.

Figure 9(a) shows a pit (imaged with tomography) which was exposed at 33% for 21 days, followed by a “wet-dry-wet cycle”. Compared with the size of the pit after exposure at 33% RH for 21 days, there was no obvious width and depth change of the pit after exposure at 12% RH for one day. However, when the RH was increased to 33% for one day, the depth and width of the pit both increased. Figure 9(b) is a summary of the size change of the pit shown in (a). After cycling, the volume of the pit has increased by ~15% of its size after exposure at 33% RH for 21 days. In tomography tests, new pit initiation and growth of the original pit

can take place at the same time. Since these two behaviours were rarely observed at the same time in lab-based experiments, this may indicate a radiation damage effect. The interaction between an X-ray beam and water might affect the electrochemical processes and induce pit initiation [28] [30] [29]. Therefore, the tomography results should be analysed with caution, and need to be compared with *ex situ* observations. Nevertheless, the tomography results provide useful information on pit morphology in a 3D view and pit growth kinetics.

Table 5 is a summary of the corrosion behaviour of the droplets after the “wet-dry-wet cycle”. In lab-based tests, growth of the original pit and new pit initiation could both be observed. However, in very few cases, growth of the original pit and new pit initiation were observed to take place under the same droplet. New pit initiation is more likely to take place under the droplets which contained one single pit after exposure at 33% RH for a day while growth of the original pit is more likely to take place under the droplets which contained multiple pits.

### 3.5 Effect of number of cycles

Figure 10 shows a typical droplet that was exposed at 33% RH for one day, followed by change of RH from 85% to 33% five times. The droplet was exposed at each RH for one day. During the cycling, there was no width change of the original pit (black dashed square) that initiated after the initial exposure at 33% RH. After five cycles, four new pits (red dashed square) were observed.

In lab-based experiments, if there was only one pit under the droplet after the initial 33% RH exposure, no newly initiated pit was found to be both wider and deeper than the original pit. This might be due to the formation of corrosion products. Visible rust was observed after the tests. Corrosion products could increase the approach resistance of the droplet. Due to the ohmic losses, a smaller cathodic current would be available to support the growth of new pits

[31]. Thereby, the newly initiated pit appeared to be either smaller or shallower than the original pit.

For the studied droplets, after five cycles, usually two to six new pits could be found and there was no width change of the original pit that initiated after the first day of exposure at 33% RH.

Similar multiple-cycle experiments were also carried out for the “wet-dry-wet cycles” and usually three to eight newly initiated pits could be observed after five cycles. Similar to the “wetter” cycle, the newly initiated pits were not both wider and deeper than the original pit.

Table 6 is a summary of the droplets exposed for different RH sequences. The table shows that the possibility of initiation of new pits increases with increasing number of cycles.

### *3.6 General discussion on atmospheric pitting corrosion*

It is well established that the controlling factor in pit stability is the need to sustain a sufficiently aggressive solution (concentrated acidic metal chloride) within the pit so that metal dissolution can continue. If the solution in any part of the pit is too dilute, then local passive film growth is favoured over metal dissolution. The criterion for pit stability is that the rate of metal ion production (metal dissolution rate) should be at least as great as the rate of metal ion escape from the pit via diffusion [46] [47] [48] [49]. Where the bulk solution is dilute, the solution concentration within the pit may be sufficiently dilute for local repassivation to take place, leading to the formation of pits in stainless steel with “lacy” covers [50] [51] [52] [53] [54] [55].

In the present work, at 85% RH, the bulk solution is dilute enough (equivalent to 1.9 M MgCl<sub>2</sub>) for stainless steel to passivate at the corrosion potential within the droplet. However at 33% RH, the corrosive bulk solution is concentrated enough (equivalent to 5 M

MgCl<sub>2</sub>) for stainless steel to pit (Figure 3 and Figure 4). This is consistent with previous work that the pitting potential decreased with increasing chloride [46] [56] [57] [13].

After a “wet-wetter-wet” cycle, there was no width increase of the original pit that had initiated after the first 1-day 33% RH exposure (Figure 5), indicating that it had probably re-passivated. During the 1-day of exposure at 85% RH (“wetter”), it is likely that the metal ions could diffuse away rapidly from the bottom of the relatively small pit, which could then fully re-passivate. This is consistent with the observation that such pits did not grow further when the RH was reduced to 33%, but instead, new pits initiated. However, a pit that had grown initially at 33% RH for 21 days (rather than 1 day) would be much deeper. In this case, after increasing the RH to 85%, diffusion of metal ions out of the pit would take place more slowly than for a 1-day pit because of the greater pit depth. Thus a sufficiently concentrated solution could be maintained at the bottom of the deeper pit, which could continue growing throughout the 1 day at 85% RH, even though there may have been re-passivation around the pit mouth. These pits could therefore continue to grow after the RH was reduced to 33% (Figure 6).

At 12% RH (“dry”), much below the DRH of MgCl<sub>2</sub>, there was insufficient water in the bulk solution to form the passive film to re-passivate the pit. Meanwhile, due to the low ERH and the likely presence of iron chlorides, the pit may remain wet and is able to grow further when the RH is increased to 33% (Figure 8 and Figure 9). However, some pits may dry out, leading to formation of new pits during cycling (Table 5).

### *3.7 Implications for storage conditions for intermediate level nuclear waste containers*

The RH generally fluctuates between 30% and 90% in realistic conditions for the storage of ILW [1] while lab-based tests are usually performed under constant RH e.g. [9] [10] [13]. In the current study, it was found that a pit could keep growing throughout the 11-day constant

33% RH exposure while a shallow pit repassivated at 85% RH. Therefore, this indicates that the experiments carried out at constant RH probably represent a worse case than would be expected in waste stores. In addition, these results show that an increased number of RH fluctuations either to high RH or low RH leads to an increased number of small pits. This suggests that natural fluctuations are beneficial in that they lead to initiation of a larger population of small pits rather than growth of a large deep penetrating pit that might develop into a site for atmospherically-assisted stress corrosion cracking.

It was also observed that a pit might survive exposure to 12% RH and keep growing when RH changed back to 33% RH. Therefore, dehumidification methods may not be effective in preventing localized corrosion as a pit might not repassivate completely even when RH was decreased to 12%.

#### **4 Conclusions**

The effect of fluctuations in relative humidity on atmospheric pitting corrosion of 304L under MgCl<sub>2</sub> droplets was investigated.

- It was found that after one day of exposure at 33% RH, generally either one pit or a cluster of pits are observed. After further exposure at a constant 33% RH for 10 days, growth of the original pit is generally observed. If a cluster of pits is present, only one of the pits is observed to grow continuously throughout the test.
- A pit that has grown at 33% RH for one day will tend to repassivate when the RH is increased to 85% and a new pit will commonly be observed at a different site when the RH is returned to 33%. However, pits grown at 33% RH for 21 days may not repassivate at 85% RH and can continue to grow when RH is returned to 33%.



- A pit that has grown at 33% RH for one day or 21 days can continue to grow after one day at 12% RH if the RH is returned to 33%. Initiation of new pits can be observed when the RH changes from 12% to 33%.
- Multiple RH fluctuations tend to lead to nucleation of many small pits whereas continuous exposure at constant 33% RH leads to growth of a single pit.
- Natural fluctuations in RH might be beneficial in favouring initiation of a large population of small pits rather than leading to growth of a large penetrating pit. Tests carried out at constant RH in lab might lead to larger pits than would be expected in realistic conditions where there are RH fluctuations.

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## Figures

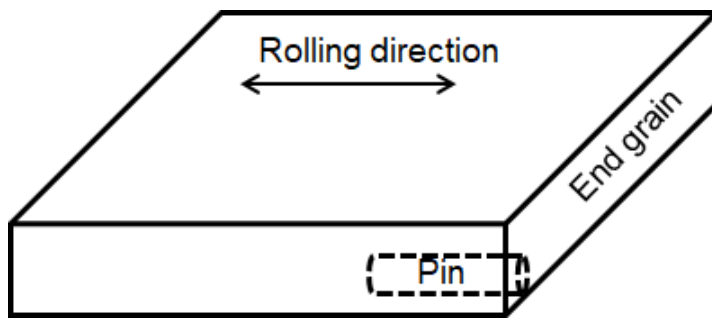


Figure 1 Schematic diagram showing the orientation of the pin sample [23].

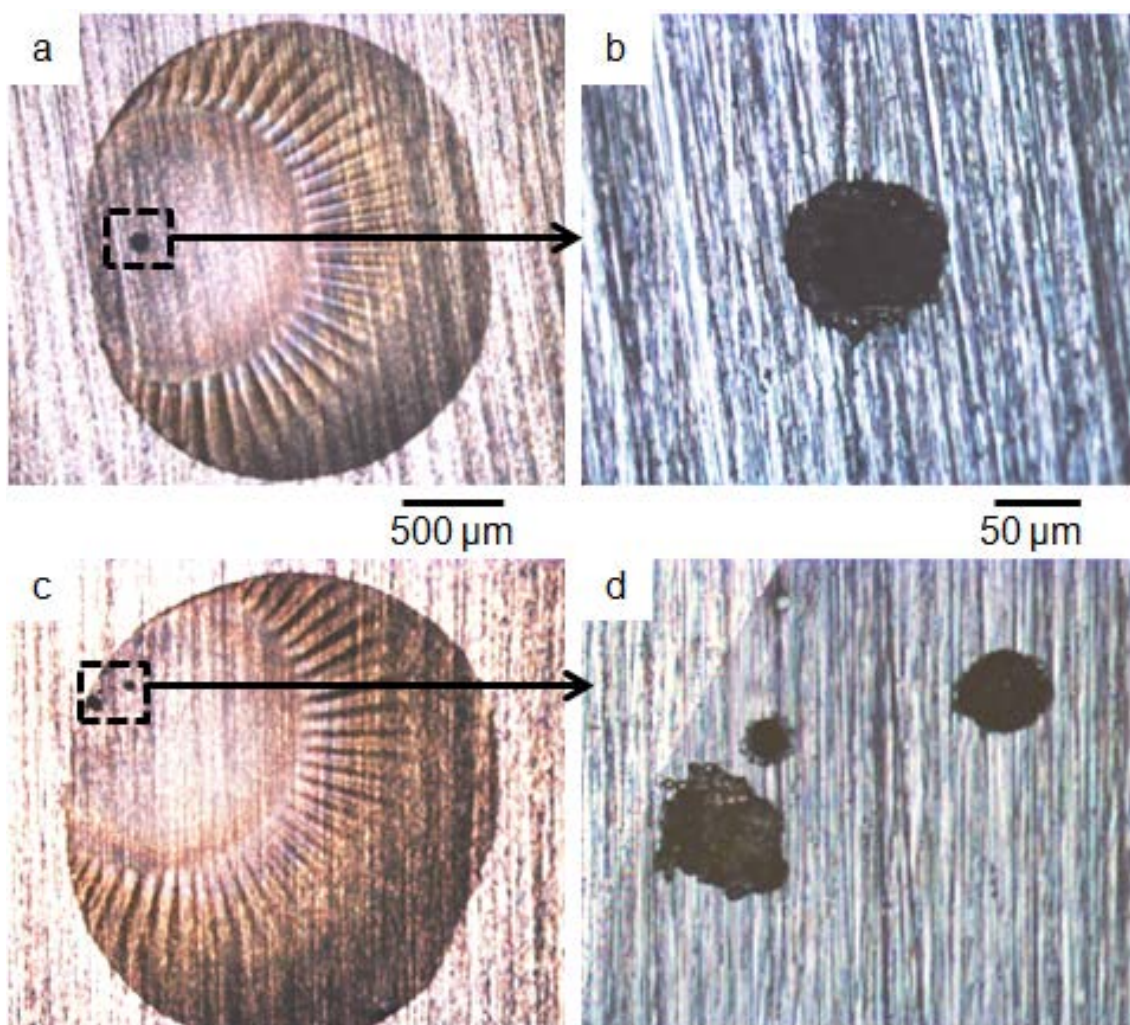


Figure 2 OM images of 304L (a) and (c) under  $\text{MgCl}_2$  droplets with a chloride deposition density (CDD) of  $1000 \pm 100 \mu\text{g}/\text{cm}^2$  containing (b) one single pit and (d) multiple pits in clusters after exposure at  $33 \pm 2\%$  RH and  $22 \pm 2^\circ\text{C}$  for one day.

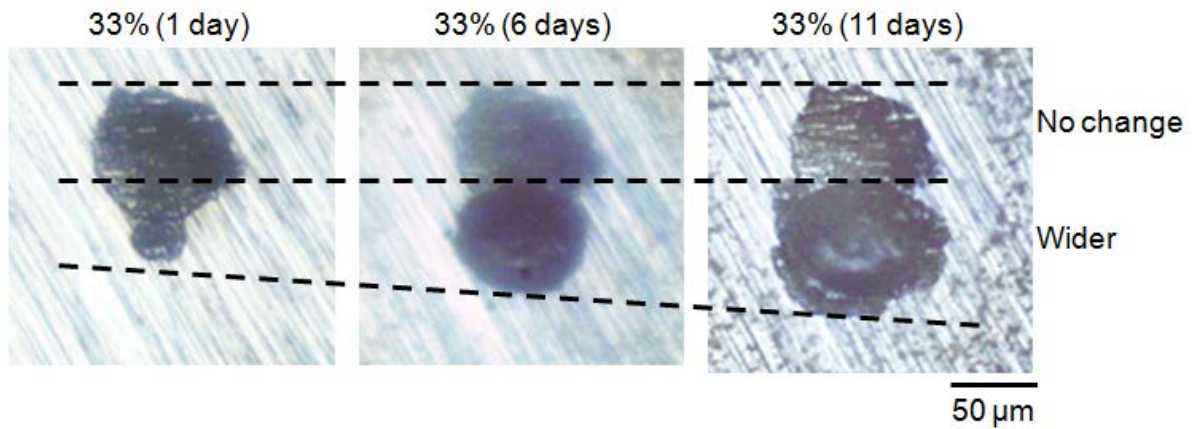


Figure 3 In situ OM images of a pit formed on a 304L under a  $\text{MgCl}_2$  droplet (CDD:  $1000 \pm 100 \mu\text{g}/\text{cm}^2$ ) after exposure at  $33 \pm 2\%$  RH and  $22 \pm 2^\circ\text{C}$  for 1 day, 6 days and 11 days. Only one single pit was found under that droplet.

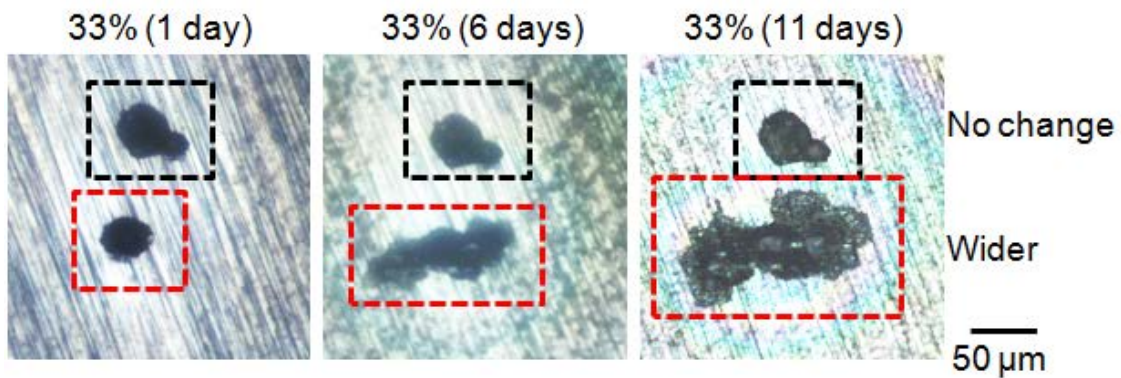


Figure 4 In situ OM images of 304L under a  $\text{MgCl}_2$  droplet (CDD:  $1000 \pm 100 \mu\text{g}/\text{cm}^2$ ) containing two pits after exposure at  $33 \pm 2\%$  RH and  $22 \pm 2^\circ\text{C}$  for 1 day, 6 days and 11 days.



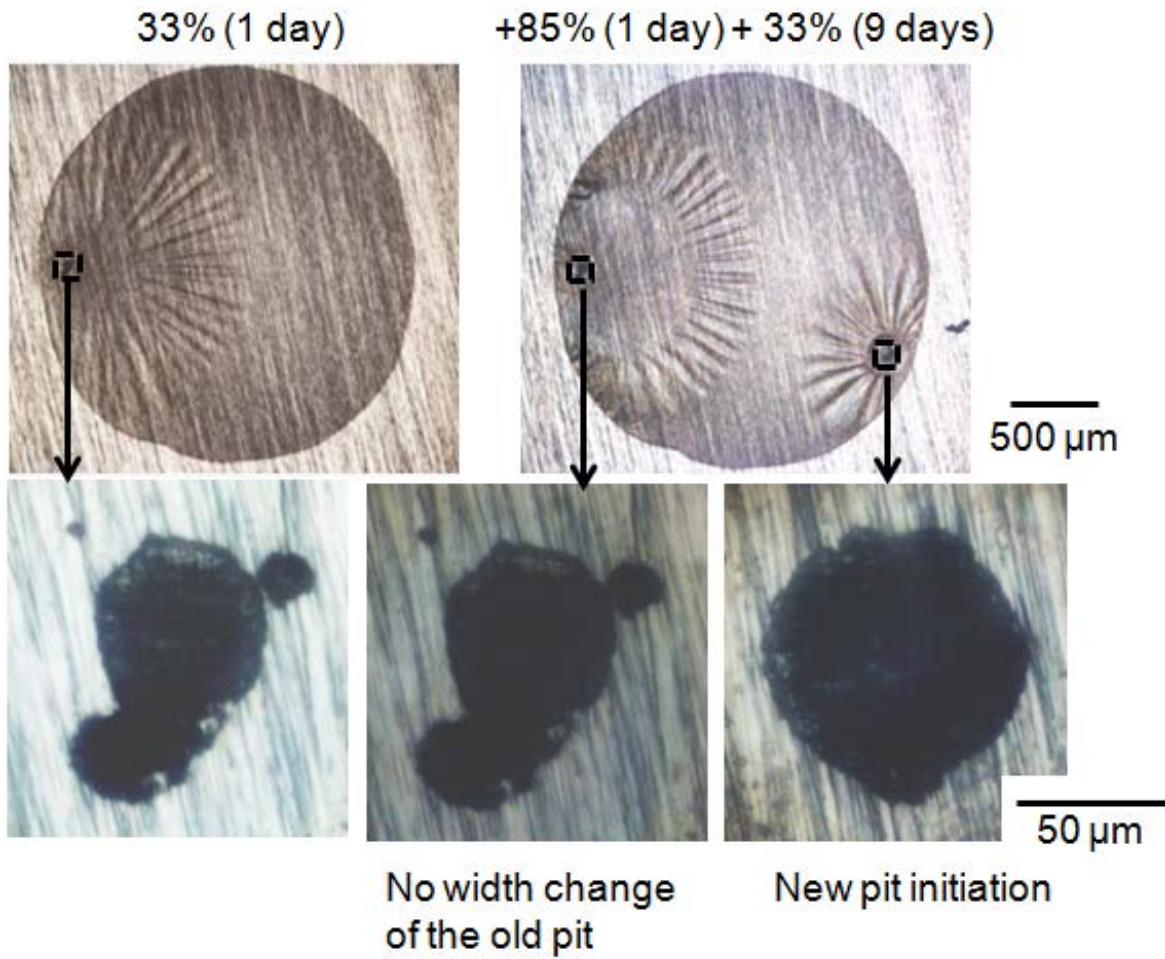


Figure 5 In situ OM images of 304L under  $\text{MgCl}_2$  droplets with a CDD of  $1000 \pm 100 \mu\text{g}/\text{cm}^2$  and the corresponding pit after exposure at 33% RH for one day, followed by exposure at 85% RH for one day and exposure at 33% RH for nine days at  $22 \pm 2 \text{ }^\circ\text{C}$ .

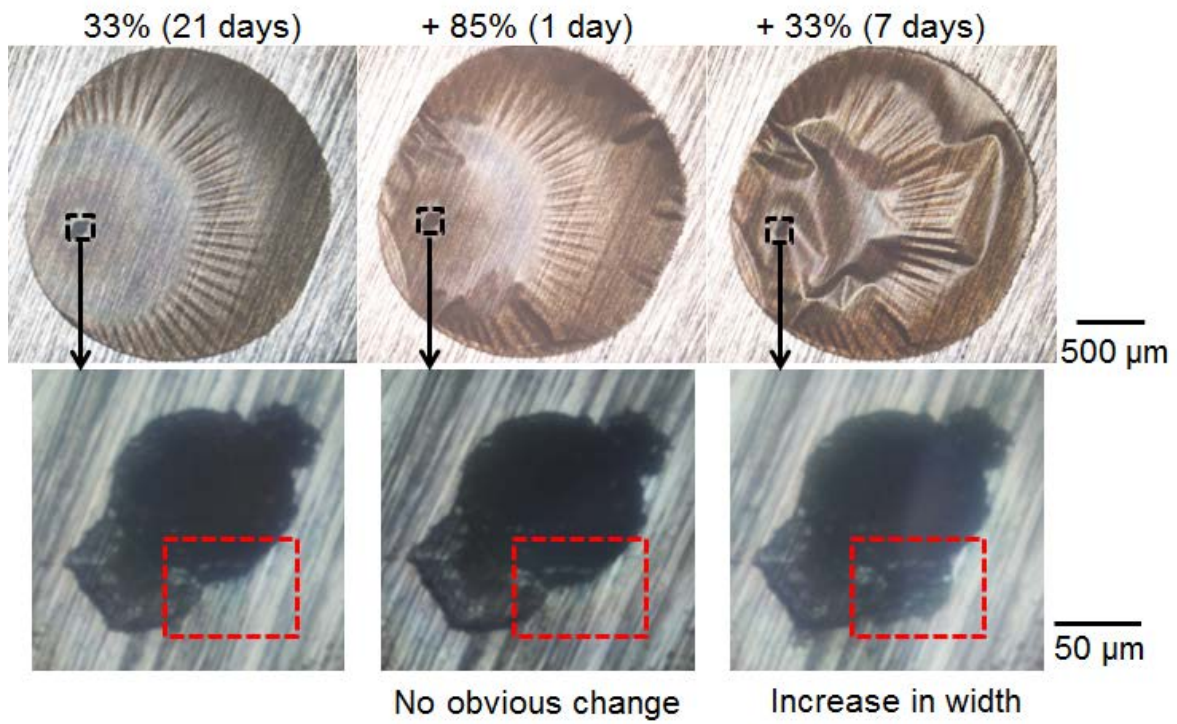


Figure 6 OM images of 304L under  $\text{MgCl}_2$  droplets with a CDD of  $1000 \pm 100 \mu\text{g}/\text{cm}^2$  and the corresponding pit after exposure at 33% RH for 21 days, followed by exposure at 85% RH for one day and exposure at 33% RH for seven days at  $22 \pm 2 \text{ }^\circ\text{C}$ .



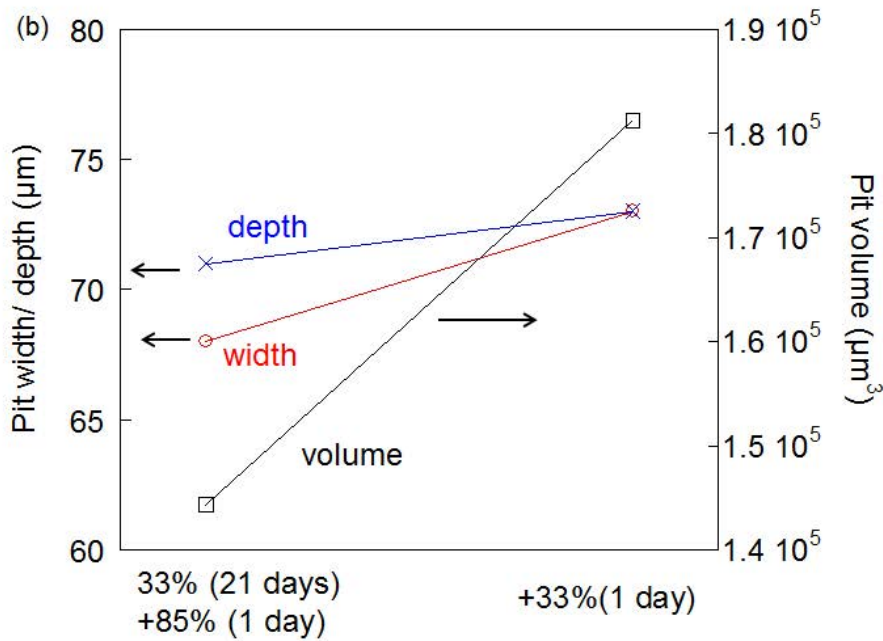
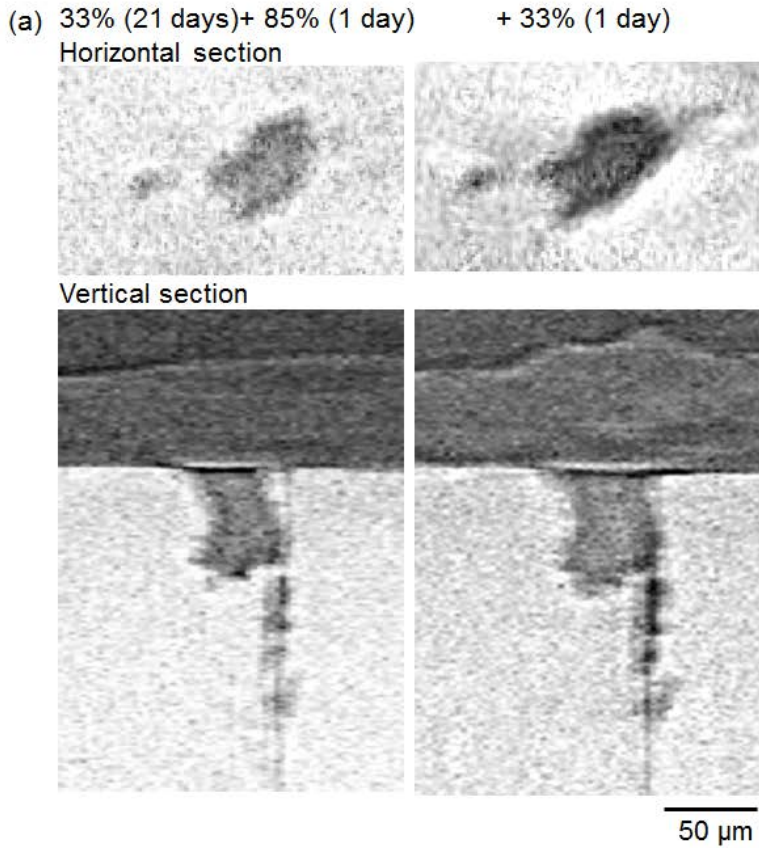


Figure 7 (a) Horizontal and vertical sections of a tomogram (in situ X-ray microtomography) of a 304L pin under a  $\text{MgCl}_2$  droplet with a CDD of  $1000 \mu\text{g}/\text{cm}^2$  after exposure at 33% RH for 21 days, 85% RH for one day and 33% RH for one day at  $21 \pm 1 \text{ }^\circ\text{C}$ . (b) Width, depth and volume of the pit shown in (a) during the “wet-wetter-wet cycle”.

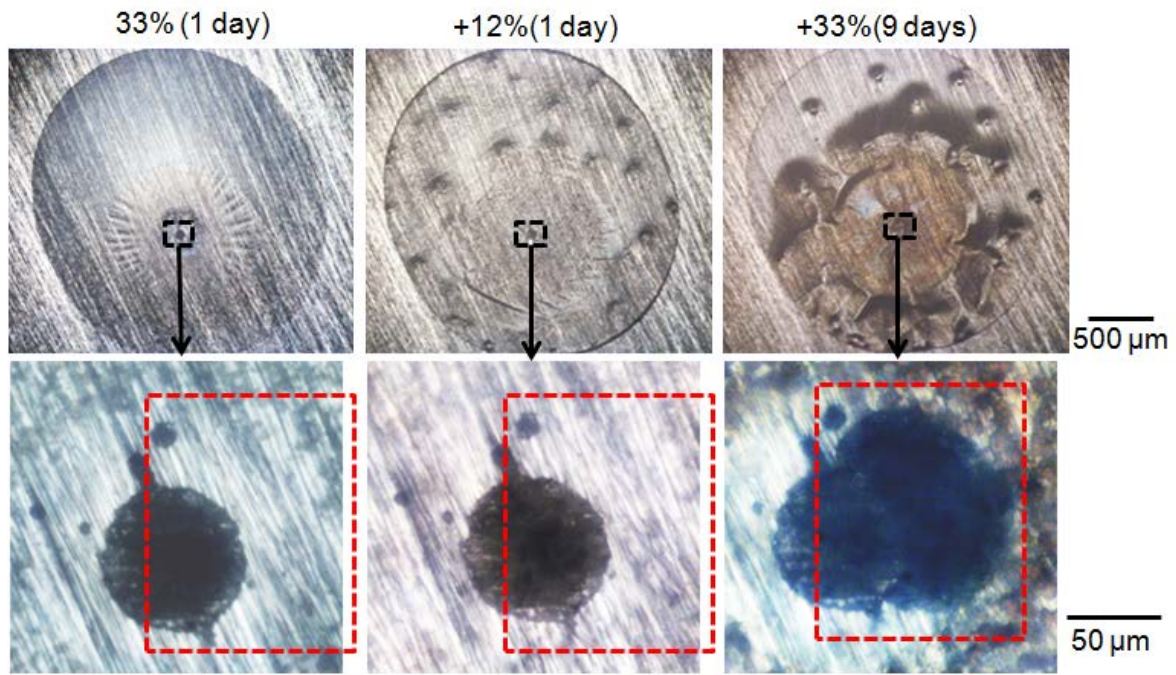


Figure 8 OM images of 304L under  $\text{MgCl}_2$  droplets (with a CDD of  $1000 \pm 100 \mu\text{g}/\text{cm}^2$ ) and the corresponding pit after exposure at 33% RH for one day, followed by exposure at 12% RH for one day and exposure at 33% RH for nine days at  $22 \pm 2 \text{ }^\circ\text{C}$ .

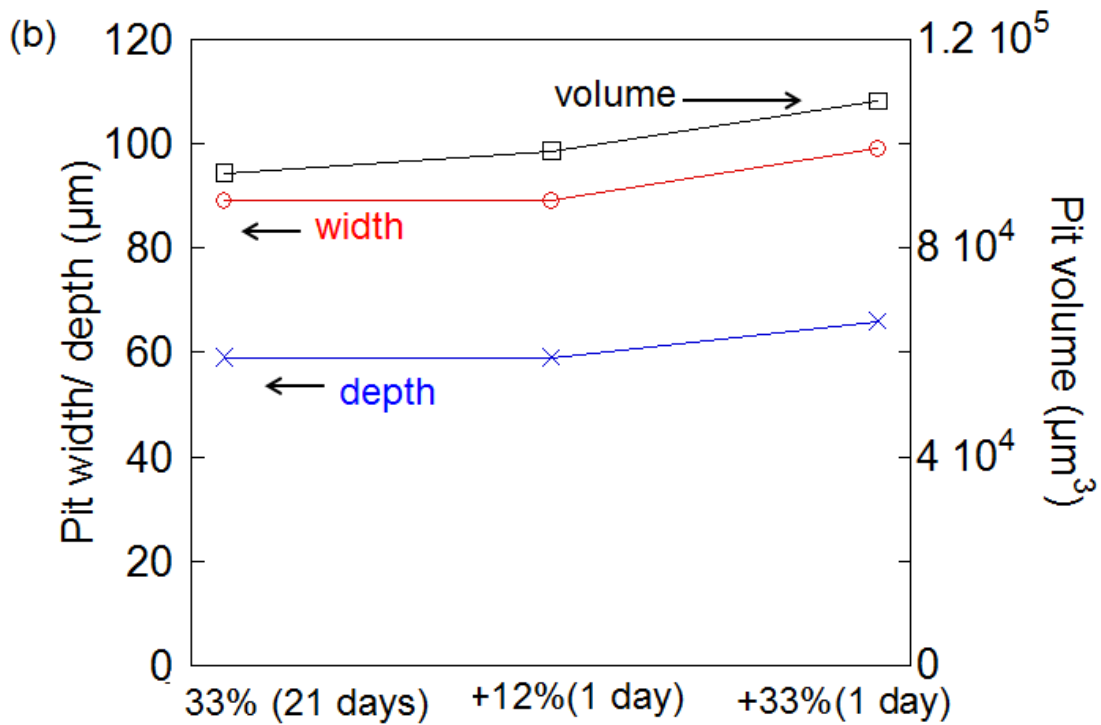
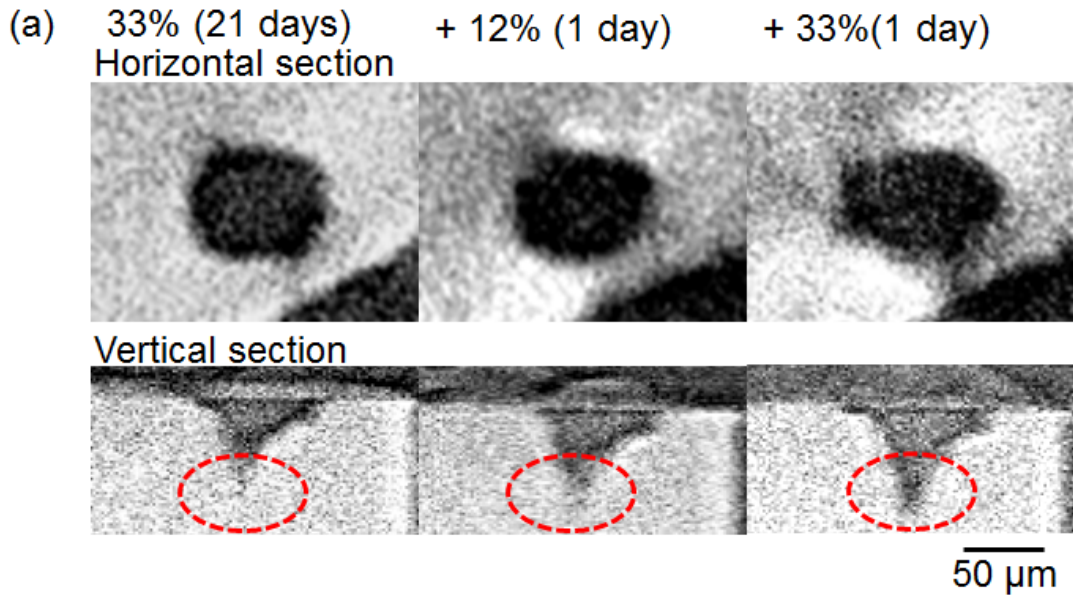


Figure 9 (a) Horizontal and vertical sections of a tomogram (in situ X-ray microtomography) of a 304L pin under a  $\text{MgCl}_2$  droplet (with a CDD of  $1000 \mu\text{g}/\text{cm}^2$ ) after exposure at 33% RH for 21 days, 12% RH for one day and 33% RH for one day at  $21 \pm 1 \text{ }^\circ\text{C}$ . (b) Width, depth and volume of the pit shown in (a) during the “wet-dry-wet cycle”.

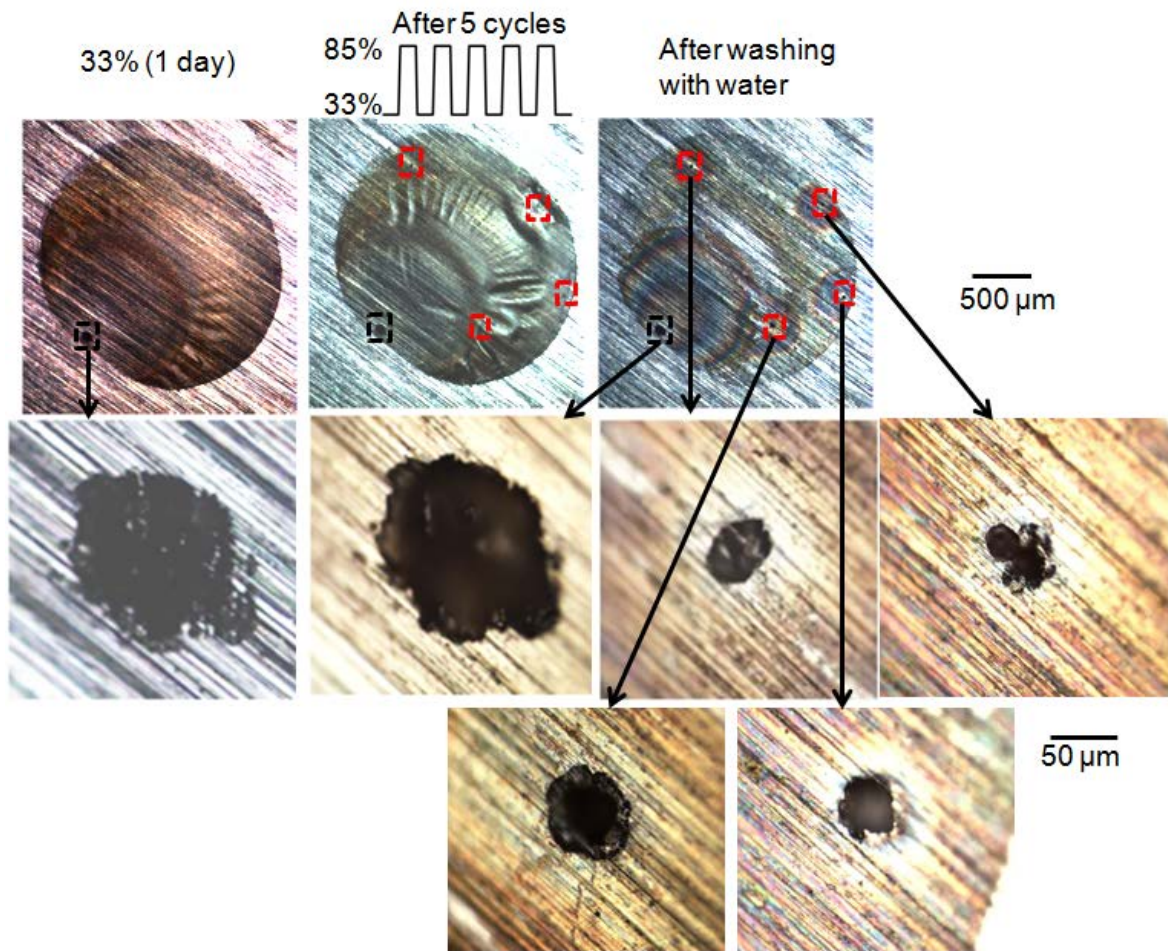


Figure 10 OM images of 304L and the corresponding pits under  $\text{MgCl}_2$  droplets (with a CDD of  $1000 \pm 100 \mu\text{g}/\text{cm}^2$ ) after exposure at 33% RH for one day, followed by the change of the RH from one day of exposure at 85% RH to one day of exposure at 33% RH for five times at  $22 \pm 2 \text{ }^\circ\text{C}$ .



## Tables

Table 1 Saturated salt solutions used to maintain a specific constant RH during corrosion tests at 20-25 °C [24].

Salt	LiCl	MgCl <sub>2</sub>	KCl
% RH	12	33	85
Label	“dry”	“wet”	“wetter”

Table 2 Number (percentage) of droplets with the corresponding corrosion behaviour (0 pit, 1 pit or multiple pits) found on 304L under MgCl<sub>2</sub> droplets (CDD: 1000±100 µg/cm<sup>2</sup>, ~2 mm in diameter) after exposure at 33±2% RH and 22±2 °C for one day.

\*Multiple pits in lab-based experiments were in clusters while the position of multiple pits in microtomography was random.

	Total no. of droplets	0 pit	1 pit	Multiple pits*
Lab-based	107 (100%)	11 (10%)	58 (54%)	38 (36%)
X-ray microtomography	6 (100%)	0 (0)	2 (33%)	4 (67%)

Table 3 Corrosion behaviour of 304L under MgCl<sub>2</sub> droplets (CDD of 1000±100 µg/cm<sup>2</sup>) after exposure at 33±2% RH for 1 day, and the number (percentage) of droplets showing the corresponding corrosion behaviour after exposure at 33±2% RH for 11 days in *in situ* lab-based experiments. The pits observed after initial exposure for 1 day were called as original pits.

After 1 day at 33% RH		After 11 days at 33% RH		
Corrosion behaviour	Total no. of droplets	Growth of the original pit	New pit initiation	No obvious growth and no new pits
0 pit	3 (100%)	0 (0)	2 (67%)	1 (33%)
1 pit	9 (100%)	5 (56%)	0 (0)	4 (44%)
≥2 pits	20 (100%)	15 (75%)	1 (5%)	4 (20%)

Table 4 Corrosion behaviour of 304L under MgCl<sub>2</sub> (CDD of 1000±100 µg/cm<sup>2</sup>) after exposure at 33% RH for 1 day/21 days, and the number (percentage) of droplets showing the corresponding corrosion behaviour after one “wet-wetter-wet cycle” in lab-based experiments.

Conditions	After 33% (1/21 days)		At the end of the test		
	Corrosion behaviour	Total no. of droplets	Growth of the original pit	New pit initiation	No change
33% (1 day) + 85% (1 day) + 33% (9 days)	0 pit	2 (100%)	0 (0)	1 (50%)	1 (50%)
	1 pit	6 (100%)	0 (0)	6 (100%)	0 (0)
	≥ 2 pits	4 (100%)	0 (0)	4 (100%)	0 (0)
33% (21 days) + 85% (1 day) + 33% (7 days)	0 pit	2 (100%)	0 (0)	0 (0)	2 (100%)
	1 pit	6 (100%)	2 (33%)	4 (67%)	0 (0)
	≥2 pits	7 (100%)	5 (72%)	1 (14%)	1 (14%)

Table 5 Corrosion behaviour of 304L under MgCl<sub>2</sub> droplets (CDD of 1000±100 µg/cm<sup>2</sup>) after exposure at 33±2% RH for one day, and the number (percentage) of droplets showing the corresponding corrosion behaviour after one “wet-dry-wet cycle” in lab-based experiments.

Condition	After 33% (1 day)		At the end of the test		
	Corrosion behaviour	Total no. of droplets	Growth of the original pit	New pit initiation	Growth of the original pit and new pit initiation
33% (1 day)+ 12% (1 day)+ 33% (9 days)	0 pit	2 (100%)	0 (0)	2 (100%)	0 (0)
	1 pit	7 (100%)	1 (14%)	6 (86%)	0 (0)
	≥ 2 pits	4 (100%)	3 (75%)	0 (0)	1 (25%)

Table 6 Corrosion behaviour of 304L under MgCl<sub>2</sub> droplets (CDD of 1000±100 µg/cm<sup>2</sup>) in lab-based experiments after exposure at constant RH, one “wet-wetter/dry-wet cycle”, five “wet-wetter/dry-wet cycles”. The number (percentage) in the table represents the number (percentage) of droplets studied under the same experimental condition which show the corresponding corrosion behaviour after exposure.

Conditions	Total no. of droplets	Growth of the original pit	New pit initiation	Growth of the original pit and new pit initiation	No change
33% (11 days)	32 (100%)	20 (63%)	3 (9%)	0	9 (28%)
33% (1 day) + 85%/12% (1 day) +33% (9 days)	25 (100%)	4 (16%)	19 (76%)	1 (4%)	1 (4%)
33% (1 day) + (85%/12% (1 day) + 33% (1 day)) × 5	15 (100%)	1(7%)	13 (86%)	0	1 (7%)