

The effect of mechanical surface patterning on filiform growth characteristics

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The effect of surface patterning on filiform corrosion characteristics has been studied using both as-rolled material and re-worked AA2024 material and following the filament dimensions and spatial density as a function of time. It was shown that the direction of the filiforms corresponds with the directions of the deepest micro-trenches. Both chemistry-based and geometry-based mechanisms are presented to explain the preference of the direction of propagation. The tendency to filiform corrosion has been quantified by the site density and the average filament length. The lower growth rate on the as-rolled material was attributed to stronger mechanical anchoring of the coating. The option of imposing macro surface patterns to confine filiform corrosion attack has been explored successfully. © 2002 Kluwer Academic Publishers

1. Introduction

The filiform corrosion susceptibility of aluminium alloys subjected to a mechanical grinding procedure has gained technological interest in automotive applications as grinding is commonly used as part of an assembly and repair service prior to pre-treatment for painting [1, 2]. From earlier research work it is already known that the actual propagation direction of the filaments is influenced by the surface topology. Filaments typically follow the rolling direction [1, 3–7] or scratch lines on a ground surface [1, 3, 8]. If a pronounced topography is removed either by mechanical polishing, etching, anodising or sandblasting [1, 3, 4], the directionality is lost and a more random filiform corrosion growth direction takes over. It is reported that mechanical grinding of aluminium surfaces prior to coating give no improvement of the filiform corrosion susceptibility compared to degreasing [1, 3, 6, 8, 9]. It is even reported that dry sanding of aluminium alloy surfaces increased the filiform corrosion susceptibility significantly, attributed to the presence of embedded impurities at the substrate surface after sanding [2]. The detrimental effects of sanding could be reduced by proper lubrication during sanding. An acid or alkaline etching procedure to remove the mechanically affected surface layer or a reactive pre-treatment is necessary to remove the disturbed surface layer and render the surface highly resistant to filiform corrosion [1, 3]. In addition, mechanically polished surfaces were shown to be less filiform corrosion susceptible than as-rolled or ground surfaces [1].

Although effects of grinding or re-working may be due to indirect chemical effects, the effect on the growth direction may also be attributed to geometrical effects. The effect of rolling and grinding marks on growth direction is studied in this work in more detail, both for

the as-rolled material and material which had received a subsequent polishing and re-working treatment. The results are interpreted qualitatively on the basis of a chemical or geometry based model. Furthermore, specific macro-surface patterns have been designed with the aim of prematurely blocking filiform growth, and their effectiveness has been examined.

2. Experimental

The material used in this investigation was commercial AA2024-T351 aluminium sheet metal with a thickness 1.2 mm. The sheet metal, in its original foil protected state, was cut into samples measuring 150 by 80 mm with the rolling direction parallel to the long side of the sample. Two surface states were examined: the as-rolled state and a chemically polished/mechanically re-worked state. All tests were performed in duplicate.

The surface roughness of the as-rolled material was measured using AFM and was found to be 0.29 μm . The periodicity in the rolling marks was of the order of 0.6 μm . The polished/re-worked state was obtained by immersing the material for 10 minutes in a solution of 93% H_3PO_4 (85%, $M = 98.0 \text{ g/l}$) and 7% HNO_3 (65%, $M = 63.0 \text{ g/l}$) kept at 80°C, rinsing in water and unidirectional grinding the dried samples with P4000 SiC grinding paper in a direction perpendicular to the rolling direction. The re-worked surface was lightly polished multi-axially using 3 μm diamond paste to remove the highest asperities. The surface roughness of the polished/re-worked material was 0.12 μm .

The chemical composition of the surface layer of the two sample types was analysed using XRF. The results are shown in Table I. The data indicate that the Mg and Si-concentrations are significantly influenced by the polishing/re-working procedure, the largest effect

TABLE I XRF-analysis of the chemical composition of the substrate surface in the as-rolled, and chemically polished/mechanically re-worked state (in wt%)

| Element | As-rolled | Chemically polished and mechanically re-worked |
|---------|-----------|--|
| Cu | 4.51 | 4.62 |
| Mg | 2.28 | 1.50 |
| Mn | 0.66 | 0.66 |
| Fe | 0.15 | 0.16 |
| Si | 0.13 | 0.19 |
| Other | 0.22 | 0.23 |
| Al | Balance | Balance |

being due to the chemical polishing procedure, with the preferential removal of Mg and Si. More specifically, the Si-concentration decreased from 0.13 to 0.08 wt% due to chemical polishing and increased again to 0.19 wt% after the re-working treatments, probably related to incorporation of some SiC-particles in the surface layer during grinding. The Fe-concentration showed a constant level of 0.14–0.16 wt%, while the Mn-concentration was stable at 0.66 wt%.

Prior to coating a chromate phosphate conversion coating was applied according to the following procedure. First, degreasing by immersion for 20 seconds in AD Chemicals Cleaner Z19S at 56°C, followed by a cold water rinse in running tap water for 1 minute. Application of the chromate phosphate conversion coating by immersion for 20 seconds in a 'Unicon 87' solution at 43°C in accordance with product data sheets, followed by a treatment for 15 seconds in an air furnace at a peak material temperature of 160°C. It is important to realize that this conversion coatings was neither selected nor optimized nor tested for its effectiveness in preventing filiform corrosion from developing. To coat the sample with an organic coating enabling easy detection of filiform corrosion, a clear polyester coating was applied with a wire bar. The coated sample was cured at a peak material temperature during 55 seconds at 240°C. The mean dry coating thickness in this case is $\sim 20 \mu\text{m}$. The reverse side of the panels was protected by an air-drying polyester coating with a layer thickness of $\sim 21 \mu\text{m}$.

The coating defects required for filiform corrosion testing were applied by mechanically scribing through the organic coating using a fresh scalpel blade, just before the initiation procedure. The filiform corrosion tests were carried out according to specification DIN65472 [10], i.e., at a temperature of 40°C and a relative humidity of 82%. The initiation time above hydrochloric acid vapour was one hour. The total exposure time was 1000 hours. The degree of filiform corrosion after 168, 500 and 1000 hours was determined using optical microscopy (at glancing incidence) for quantifying the density and average length of the filaments. A manual procedure was used to determine the characteristic data but good care was taken in standardising the evaluation. The tendency to filiform corrosion initiation was quantified by the site density, i.e., the number of filaments per millimetre scratch length. The filiform growth rate was quantified by recording the av-

erage filament length per sample at the various times of examination. The sensitivity to filiform corrosion is quantified by the corrosion number, which is defined as the product of the site density and the average filament length.

In addition to this investigation into the effect of micro surface topology on filiform growth characteristics, macro surface patterns have been designed and with the aim of prematurely blocking filiform growth. These experiments have been performed using as-rolled material only. Fig. 1a shows the position of these macro-surface patterns in relation to the position of the artificial line-shaped coating defects on the samples. Several patterns have been applied either as single or a double blocking barrier: examples are presented in Fig. 1b to 1d. The patterns were applied by a hardened steel scribing needle attached to an engraving unit and had a surface penetration depth of about $10 \mu\text{m}$, i.e., a depth significantly larger than the depth of the natural rolling marks. Prior to coating the samples were chromated according to the following procedure. First, degreasing by immersion for 10 minutes in Gardobond VP10036 at 60°C, followed by a cold water rinse in running tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. Then, deoxidation by immersion for 10 minutes in Oakite 60-FC-25 at room temperature, followed by a cold water rinse in tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. Finally, application of the chromate conversion coating by immersion for 15 seconds in a 'Alodine 1200' solution at room temperature in accordance with product data sheets, followed by a cold water rinse in running tap water for 30 seconds and a final rinse in de-ionised water for 30 seconds. Following the pretreatment, a white polyester powdercoating was deposited with an approximate post-curing coating thickness of $62 \mu\text{m}$ (standard deviation $5 \mu\text{m}$). The same powdercoating was deposited on the reverse side of the panels. The coating was cured at 200°C during 20 minutes.

3. Results and discussion

Firstly, a qualitative discussion of the general appearance of the filiform corrosion pattern is presented. Fig. 2 shows the typical filiform corrosion patterns on the as-rolled and polished/re-worked samples. The figure shows that the filiform corrosion propagation direction for the as-rolled surfaces is preferentially in the rolling direction. For the polished/re-worked substrate the preferential filiform corrosion propagation direction is in the direction of the re-working direction, perpendicular to the original rolling direction. As the re-working is parallel to the main scratch from which the defects were initiated, the filiforms were on average parallel to the main scratch and the region of filiform corrosion did not extend very far in the direction perpendicular to the initiating scratch. Such dependencies have also been reported in the literature [3, 4, 6, 7]. However, the origin of the phenomenon is not clear as grinding or working of the substrate surface not only changes the surface topology but also can have an indirect chemical effect. The chemical effect of rolling, grinding and re-working is attributed to the alignment of particles

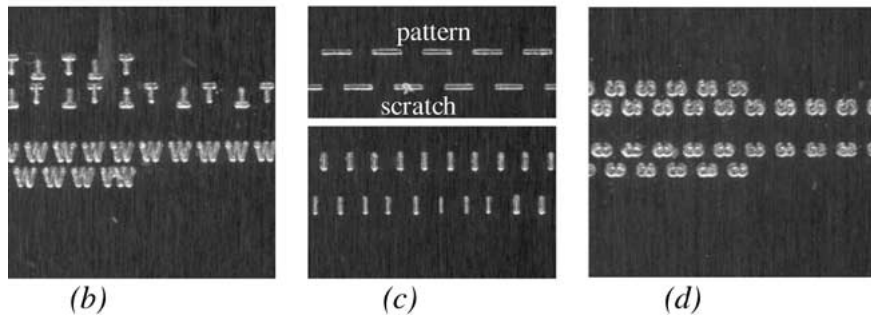
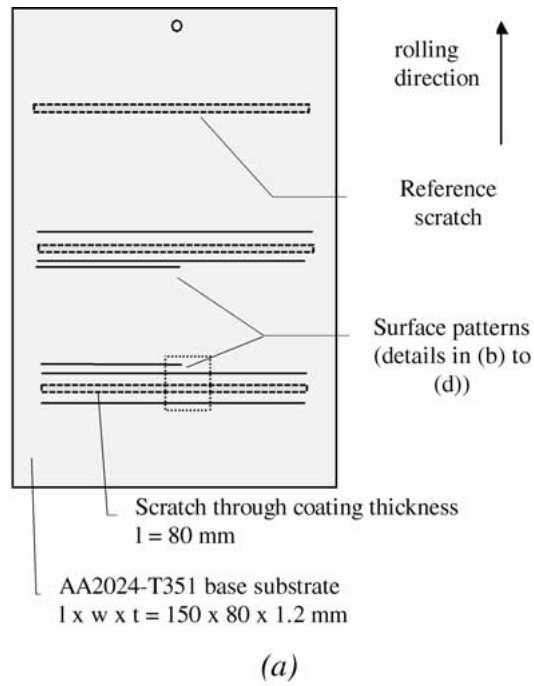


Figure 1 Schematic representation of the sample geometry, indicating the positions of the coating defects and the macro surface patterns (a). (b) to (d) show some examples of the surface patterns in more detail.

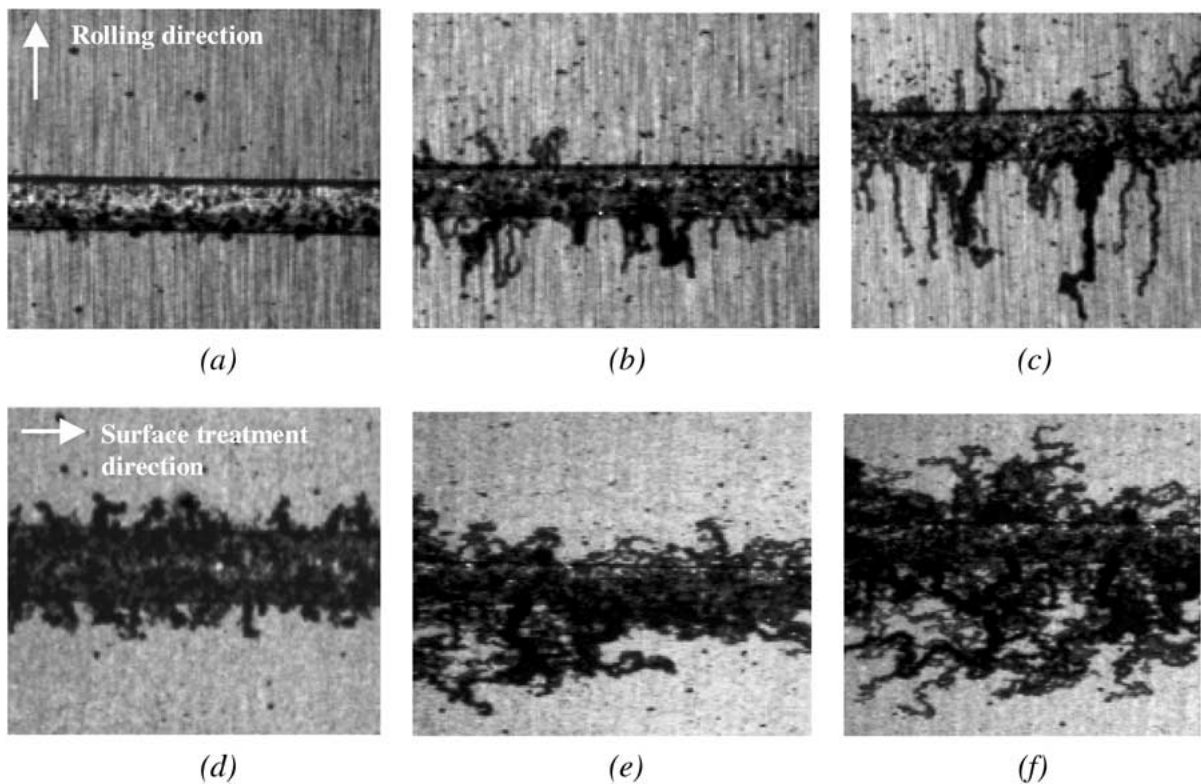


Figure 2 Optical macro-graph of the filiform corrosion attack on as-rolled ((a) to (c)) and mechanically polished ((d) to (f)) material, after 48 hours (a) and (d), 400 hours (b) and (e) and 1000 hours (c) and (f) of accelerated testing. Width of each micrograph 2.5 mm.

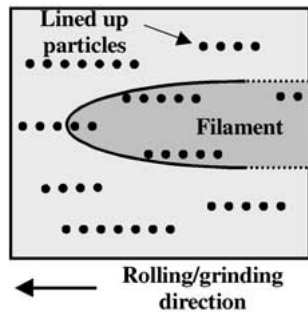


Figure 3 Schematic representation of the indirect chemical effect of rolling on the preferential filiform corrosion propagation direction.

(i.e., precipitates, dispersoids and constituent particles) in the direction of rolling, grinding or working [11]. By rolling, or more general mechanically re-working the particles will line up in the direction of the surface treatment process and a higher concentration and/or finer distribution of particles will be present in this direction, as shown schematically in Fig. 3. For a high concentration and/or fine distribution of particles it is likely that other 'fresh' cathodic particles are more rapidly reached by the corroded zone around active particles, which in turn will participate in the substrate matrix dissolution. The increased cathodic area would lead to a rapid growth of the corrosion front in this direction and thus a high filiform corrosion propagation rate relative to the other directions. A more extensive description of the effect of the chemistry of the aluminium surface, and in particular the effect of second phase particles, on filiform corrosion has been presented elsewhere [4, 5, 12–18].

The geometrical effect of rolling and re-working can be explained best with the aid of Fig. 4. When analysing the longitudinal section in Fig. 4b it can be seen that the (schematic) incident angle of the very tip of the filament is relatively small compared to the angle of incidence for the situation (angle of incidence on Face I) represented in the cross-sectional view of Fig. 4c. For surface faces with the orientation according to Face I it can be seen that the angle between the filament tip front and the substrate surface can be represented by a relatively blunt notch, while the notch for the longitudinal section is relatively sharp and constant. From classical crack tip propagation theory it follows that the filament tip is likely to open and propagate in the direction of

the sharp notch (small angle of incidence) and thus in the direction of rolling or re-working.

In practice, surfaces are not ideally perfect and surface textures different from those represented in Fig. 4 can be encountered. For this reason occasionally also propagation directions different from the rolling and re-working direction can be observed, as shown in Fig. 2. In general, these deflections from the preferential direction are characterised by discrete steps and the propagation direction after the deflection usually is in rolling or re-working direction again. These discrete steps can be caused by discrete substrate surface imperfections and also a sudden and discrete propagation direction change can be encountered when the angle of incidence as shown in Fig. 4c is on faces with orientations according to Face II. In these cases a very low angle of incidence and thus a sharp notch can cause discrete propagation direction changes opposite or perpendicular to the rolling, grinding or working direction. Gradual and steady propagation of filaments in directions other than the rolling, grinding or working direction is seldomly observed. The theory of the geometrical effect on preferential propagation direction is implicitly supported by observations in the literature that if a pronounced topography is removed either by very fine mechanical polishing, etching, anodising or sandblasting [3, 4, 6], the directionality is lost and a random filiform corrosion growth behaviour takes over. However, the relative contributions of the chemical effect and the geometrical effects on filiform corrosion however are hard to quantify and further work in this field is required.

Quantitative analysis of the experimental observations on the filiform corrosion kinetics as a function of the exposure time is presented in Fig. 5. The values for the site density in Fig. 5a show that after 1000 hours of accelerated exposure the number of initiations along the scratch is relatively independent of the substrate surface condition, either as-rolled (1.13) or re-worked (1.20). However, the initiation rate for the re-worked samples seems higher than that for the as-rolled surfaces: after 168 hours the site density for the re-worked samples is 1.04 mm^{-1} while for the as rolled surfaces a site density of 0.80 mm^{-1} is reached at that point. Fig. 5a also shows that most of the filaments initiated during the first 168 hours of the test, both for the as-rolled ($\sim 71\%$) and surface treated ($\sim 87\%$) surfaces. After 500 hours

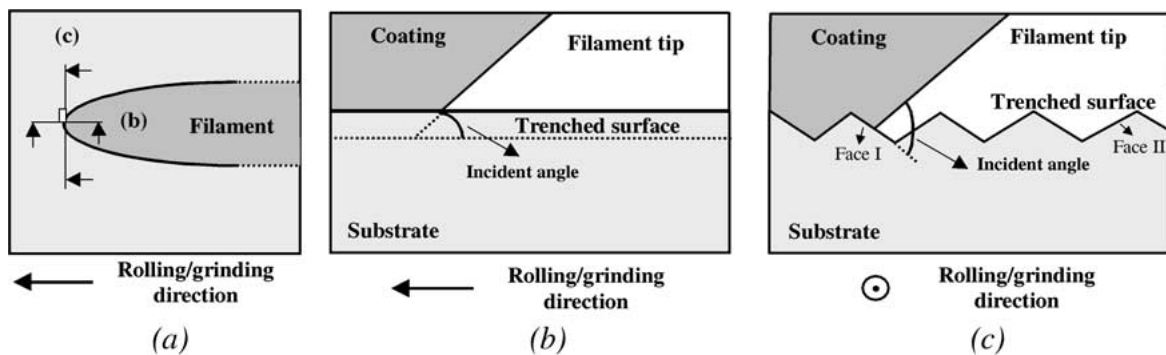


Figure 4 Schematic representation of the geometrical explanation for a sample with grinding marks. (a) shows a top view of a filament on a rolled/ground surface. (b) and (c) are schematic representations of a longitudinal and cross-sectional view of the filament tip on the trenched surface respectively.

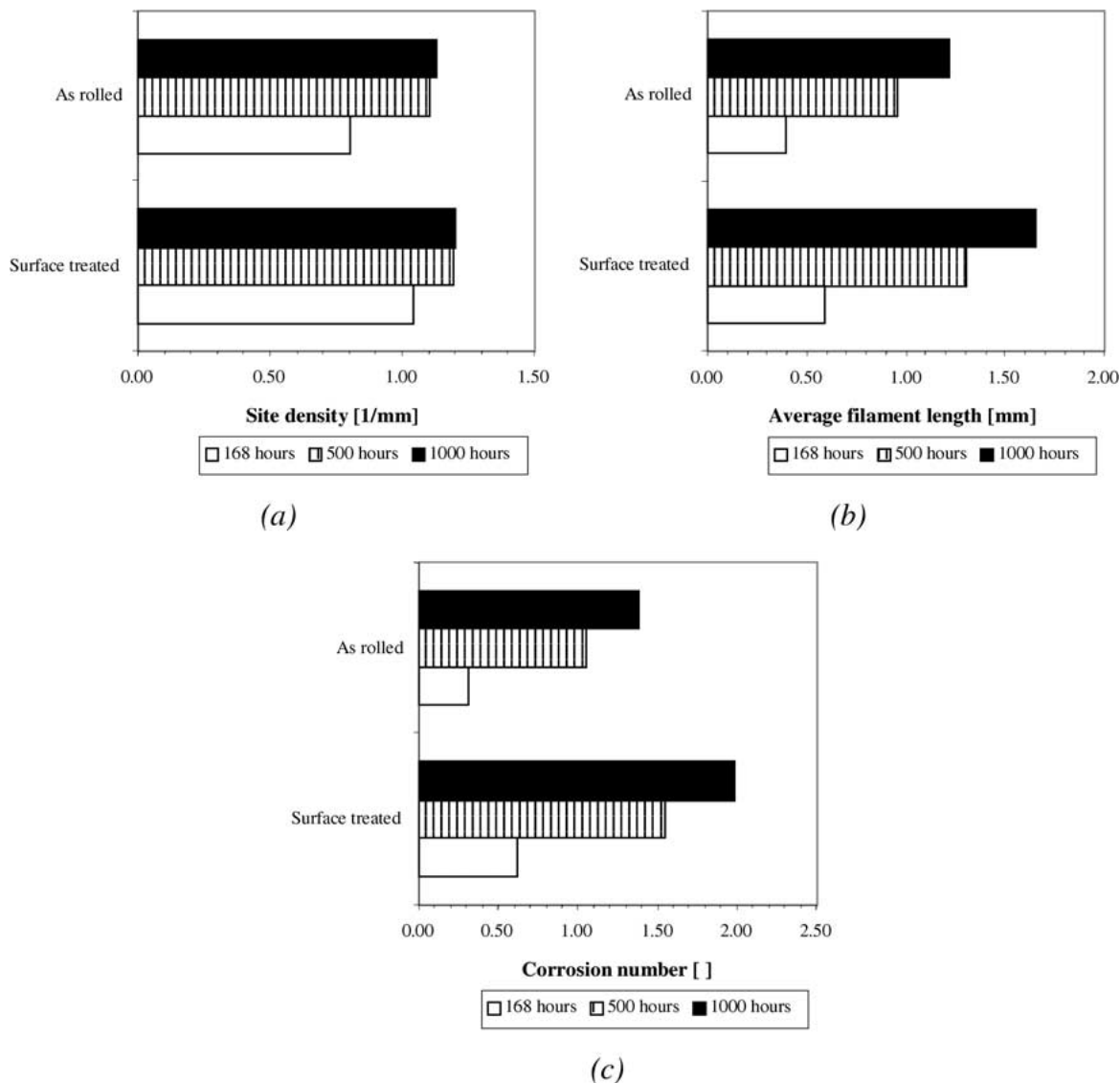


Figure 5 Site density (a) [number of filaments per scratch length], (b) average filament lengths [mm] and (c) corrosion number for the as-rolled and re-worked sample.

virtually all filaments are present. As the final filament site density is such that the entire length of the scratch is occupied, the observed decrease in filiform initiation rate with exposure time is unavoidable and does not necessarily reflect the true initiation kinetics.

When analysing the average filament length as a function of time it can be seen that at all exposure times the value for the average filament length for the re-worked samples is typically 30% higher than that for the as-rolled surfaces. Fig. 5b also shows a decreasing propagation rate with time. The filament length increases approximately parabolic in time, but the number of inspection times is insufficient to determine the time dependence with any accuracy. Such a parabolic dependence has also been reported in literature [19, 20]. Some entrapment of chloride in the corrosion product filled filament tail and in pitting events along the filament tail [3, 4, 6, 21, 22] could contribute to a stagnation of filament growth rate after considerable exposure times, in addition to a decrease of oxygen concentration gradient with increasing filament lengths [19–21]. However both oxygen diffusion through the tail of the filament and chloride depletion is unlikely to be affected by the

precise surface topology, the differences in growth rate between both sets of samples observed here, suggest that other factors also influence the growth rate. Mechanical anchoring of the coating in the trenched as-rolled surface, and an increased critical fracture toughness for delamination, may be considered.

The susceptibility to filiform corrosion as reflected in the corrosion number, is significantly higher for the re-worked samples than for the as-rolled surfaces. This is mainly due to the apparent higher growth rate. Only for the short exposure time of 168 hours does an increased nucleation rate contribute to the observed increased filiform corrosion susceptibility.

Finally, Fig. 6 shows the effect of the presence of macro surface patterns in the vicinity of the coating defect on the propagation of filaments in filiform corrosion testing.

Fig. 6a shows a typical and frequently observed example of deflection of a filament at such a macro pattern in the substrate surface underneath the organic coating. As explained in the geometrical model for the directionality of the filament growth, the filament is less likely to cross such a relatively deep and discrete

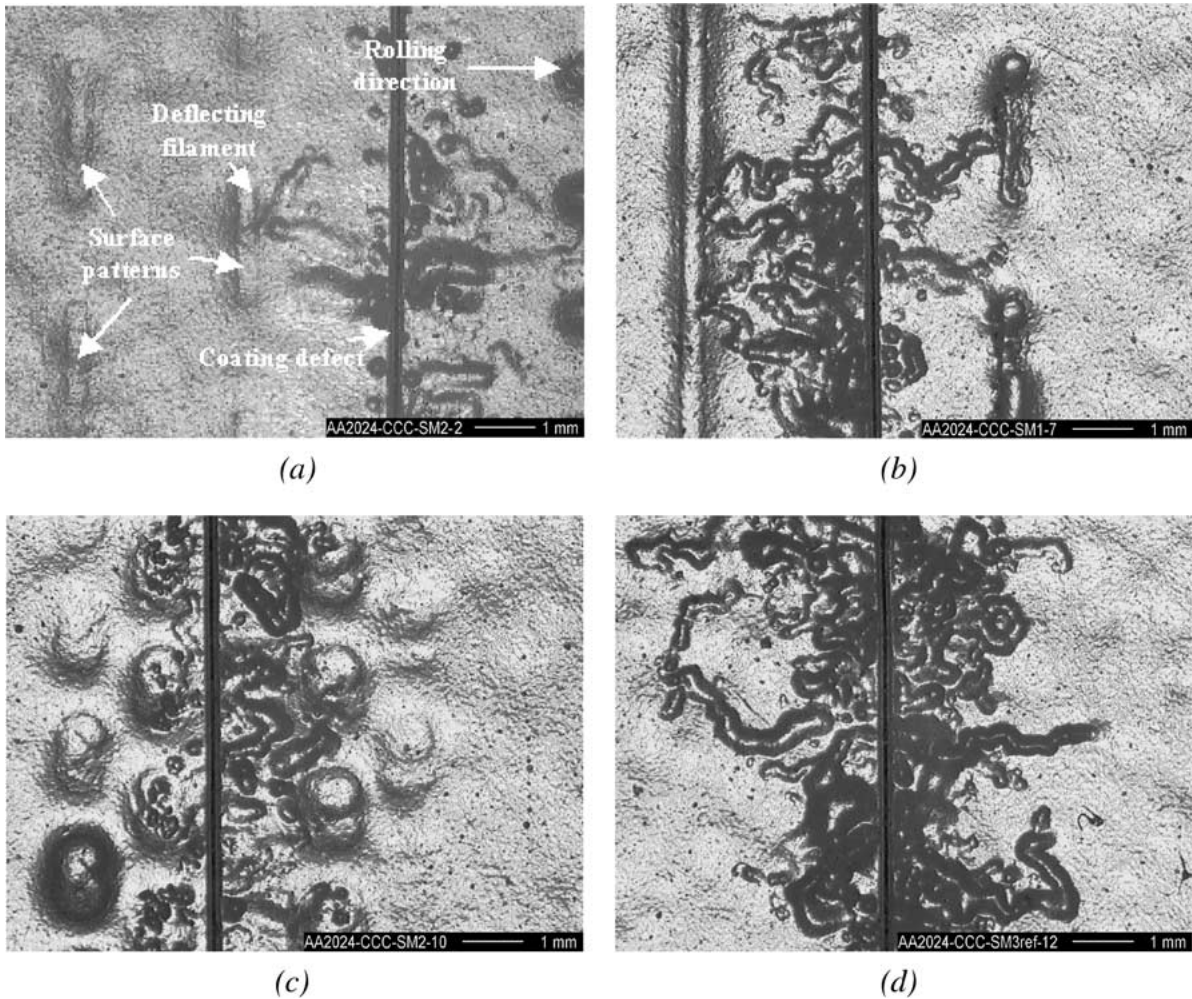


Figure 6 Optical micro-photographs of as-rolled filiform corrosion test substrates with macro surface patterns. (a) to (c) show the filiform corrosion attack for the patterned surfaces. Note the path deflection and reversal. (d) shows filiform corrosion on the as-rolled sample without macro-surface pattern.

surface mark and will preferentially deflect over the relatively less pronounced rolling marks and may grow in the reverse direction albeit on a different track. The observations support the hypothesis of the geometrical model for filament directionality above the chemical model discussed above. It should be pointed out that the macro patterns were made with a tool steel engraving needle, and deposition of foreign material, as occurs in the case of grinding with abrasives, did not apply here. Fig. 6b and c show the effectiveness of the surface patterning in confining the filiform corrosion between the coating defect and the first boundary of the macro-pattern. Fig. 6d shows the filament pattern on the as-rolled sample without macro-patterning. Filaments have grown over a considerably longer length away from the coating defect. The relative blocking performance of samples with different barrier configurations was found to be of similar level: no specific preferable surface pattern for blocking filiform corrosion propagation could be deduced from the present set of samples. This method of macro-patterning could possibly be used in practice to confine filament growth around accidental scratches formed during product use. To this aim, a gridded roll surface for the final rolling pass, imposing a grid of (several) micron-deep trenches in the sheet metal surface, could be employed. The minimum depth of the profile should be chosen such that

the grid pattern does not affect the optical appearance of the coating. The method of macro-patterning is likely to be successful in particular in confining filament growth from the edges of cut sheet metal, where the sheet metal is cut before the organic coating is applied. The cost of this additional mechanical treatment of the sheet material may however restrict its application to special cases, unless the linear pattern near and following the edge could be imposed during the sheet cutting process itself.

4. Conclusions

The present investigations on AA2024-T351 samples have shown that the filiform corrosion propagation direction for the as-rolled surfaces is preferentially in the rolling direction. For a mechanically re-worked substrate the preferential filiform corrosion propagation direction is in the direction of the final grinding, perpendicular to the original rolling direction. Both chemistry-based and geometry-based mechanisms are presented to explain the preference of the direction of propagation. Based on all observations, the latter explanation seems more likely. Mechanical anchoring could explain the lower growth rate in the as-rolled material. Application of specific macro surface patterns is shown to be a very effective way of confining filiform corrosion attack to the domain set by the surface pattern.

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