

## Electrochemical Activation of Surface Deformed Layers on Aluminium Alloys and Pure Aluminium

H. N. McMurray<sup>1</sup> Adam E. Holder,<sup>1</sup> G. Williams,<sup>1</sup> G. Scamans,<sup>2</sup>

<sup>1</sup>School of Engineering, Swansea University, UK

<sup>2</sup>Innoval Technology Ltd., Oxfordshire, UK

Surface damage by abrasion is well known to create near surface deformed layers (NSDLs) on a wide range of aluminium alloys. These thin (usually < 2 micron) NSDLs exhibit a grain size very much smaller (often sub-micron) than that of the bulk. It is also known that NSDLs can become electrochemically active compared to the bulk material. When the alloy is used in an organically coated form activation can give rise to a rapid, superficial (surface-active) form of filiform corrosion (FFC) The widely accepted cause of activation is the thermally promoted precipitation of discrete second phase particles at grain boundaries in the NSDL. This paper uses Scanning Kelvin probe (SKP) potentiometry to show that that on AA6000 series alloys anodic activation in the NSDL can occur without heat treatment and, therefore, without thermally-promoted intergranular precipitation. It is similarly shown that introducing an NSDL (without heating) produces open circuit potential drops of *ca* 0.6V on AA1000 series ( $\geq 99$  wt.% Al) alloys and *ca* 0.15V on pure aluminium ( $\geq 99.999$  wt.% Al). However, anodic activation in the NSDL is not enough (in isolation) to produce surface-active FFC. A feasible cathode must also be present. In the case of pure aluminum this can be provided by introducing a  $\text{Cu}^{2+}$  cation exchange pigment into the lacquer. Thus it is shown that although second phase particles are not necessary to anodically activate the NSDL they probably do play an important role in facilitating FFC by providing a good oxygen cathode.

**Keywords:** *Filiform Corrosion, Surface Activation, Near Surface Deformed Layer*

### 1. Introduction

In painted 6000 series panels structural failure through bulk IGC is unlikely to occur but serious cosmetic failure may result from filiform corrosion (FFC) [1,2]. It is now well known that shear deformation of the surface of thermomechanically processed aluminium alloys can produce a local microstructure very different from the bulk [3,4,5,6,7,8,9,10,11,12,13]. The near surface deformed layer (NSDL) is typically a few microns thick, characterized by a very fine, submicron, grain size and contains second phase particles which prevent recrystallization. Furthermore, a strong correlation has been demonstrated between the presence of a NSDL, the thermally-promoted precipitation of intermetallic phases within the NSDL, and FFC susceptibility [5,6,7,8,9,10,11,12,13,14,15]. For these reasons AA6000 sheet is typically etched (using an alkaline or an acidic cleaner) to remove any NSDL produced by rolling. However, automotive manufacturers frequently rectify surface defects in press-formed external closure panels by mechanical grinding immediately prior to pre-treatment and painting [14,15]. Surface abrasion during grinding reintroduces a NSDL and reactivates the surface with respect to FFC [14,15,16,17].

In a recent study, the rectification of AA6111 sheet was simulated by abrasion with silicon carbide (SiC) paper and the abraded samples used to investigate microstructure and corrosion morphology in the NSDL so produced [13]. In the current paper we follow the procedures described in [13] to generate an NSDL on AA6111, AA1050 and pure aluminium. We use Scanning Kelvin Probe (SKP) potentiometry to investigate the effect of the NSDL on open-circuit potential in humid air. We also

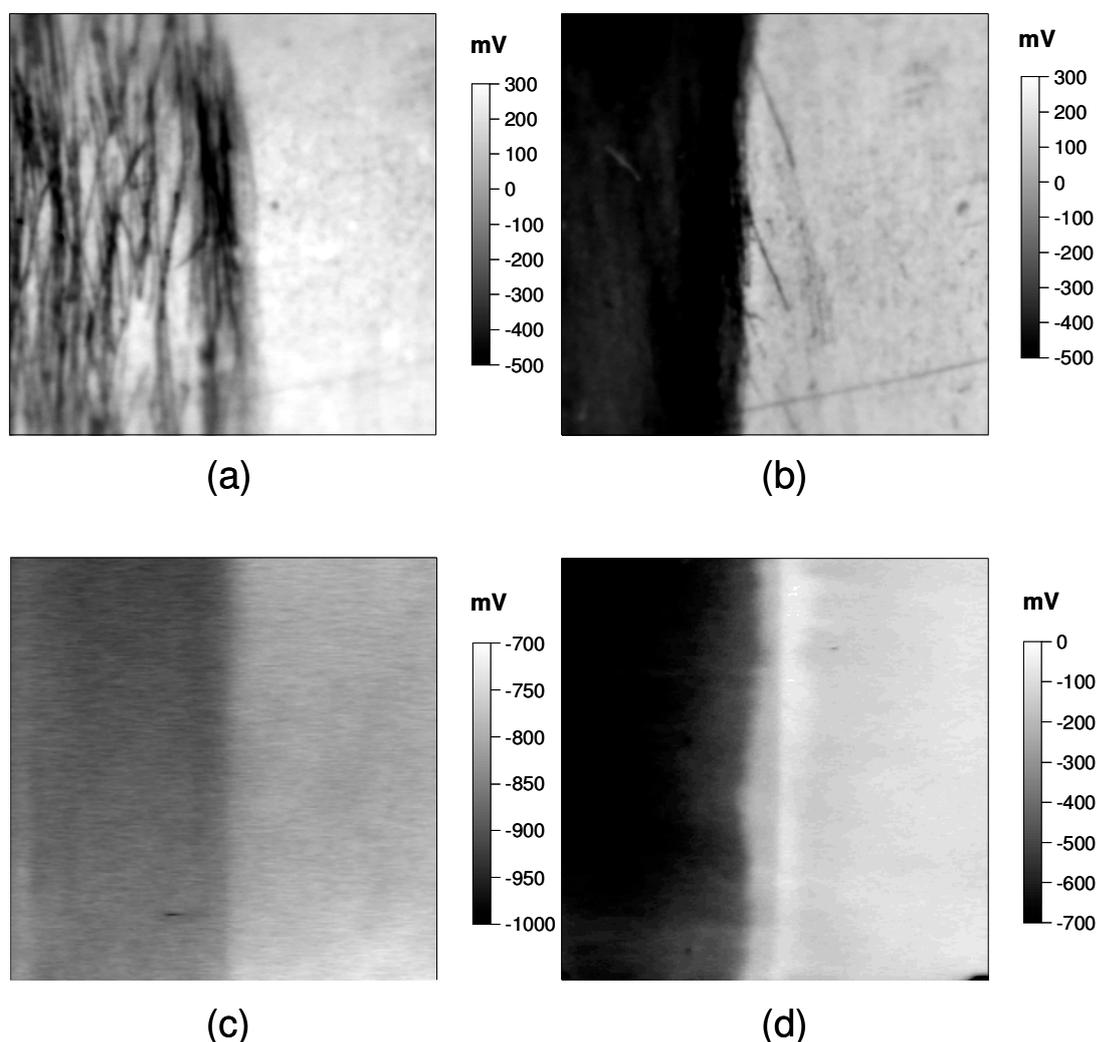
use SKP to follow the kinetics of chloride-induced FFC on organic coated metals and to determine characteristic potentials associated with the FFC localized corrosion cell. In so doing we show that thermally promoted precipitation of second phase particles (by post-abrasion heat treatment) is not necessary for electrochemical activation of the NSDL or the promotion of FFC. The SKP technique does not require the presence of a bulk electrolyte and is capable of measuring localized free corrosion potentials ( $E_{corr}$ ) beneath humidity films and/or intact polymer layers [18,19,20,21].

## 2. Experimental

Polyvinylbutyral-*co*-vinylalcohol-*co*-vinylacetate (PVB), molecular weight 70,000 – 100,000 was obtained from the Aldrich Chemical Company. All other chemicals were obtained from Aldrich in analytical grade purity. AA6111 sheet of 1 mm thickness was provided by Innoval in the solutionised (at 620°C) and naturally aged T4 temper. AA1050 was supplied by Novelis as 0.3mm thick coupons. Both alloys had been cleaned on-line to remove any rolling-induced surface deformed layer. Pure aluminium (99.999% pure) was supplied by Goodfellow Cambridge Limited as 1mm thick coupons. As-received material was cut into 40 x 40 mm coupons and degreased using acetone. The as-received surface was removed and a near surface deformed layer (NSDL) introduced by 2 minutes of vigorous manual abrasion with 180 grit silicon carbide (SiC) paper. When required, coupons were bar coated with a 15.5% w/w ethanolic PVB solution to produce an air-dried PVB coating thickness of  $30 \pm 5$   $\mu\text{m}$ , as determined using a micrometer screw gauge. 10mm defects 13mm apart, running normal to the substrate rolling direction, were scribed through the PVB layer on each coupon using a scalpel. When required, FFC was initiated by introducing 1 $\mu\text{l}$  of 2 Molar aqueous HCl into each defect using a glass micro-capillary. Following initiation, samples were held initially in room air (approximately 20°C and 50% RH) for 30 mins. - then transferred to the SKP environment chamber at 60% RH. Potentiometric measurements under atmospheric corrosion conditions were carried out using SKP instrumentation described in detail elsewhere [22,23]. Unless stated otherwise, the SKP reference probe was a 125  $\mu\text{m}$  diameter gold wire vibrated normal to the sample surface at 280 Hz, with a 40  $\mu\text{m}$  peak-to-peak amplitude, and mid-amplitude probe-sample distance of 120  $\mu\text{m}$ .

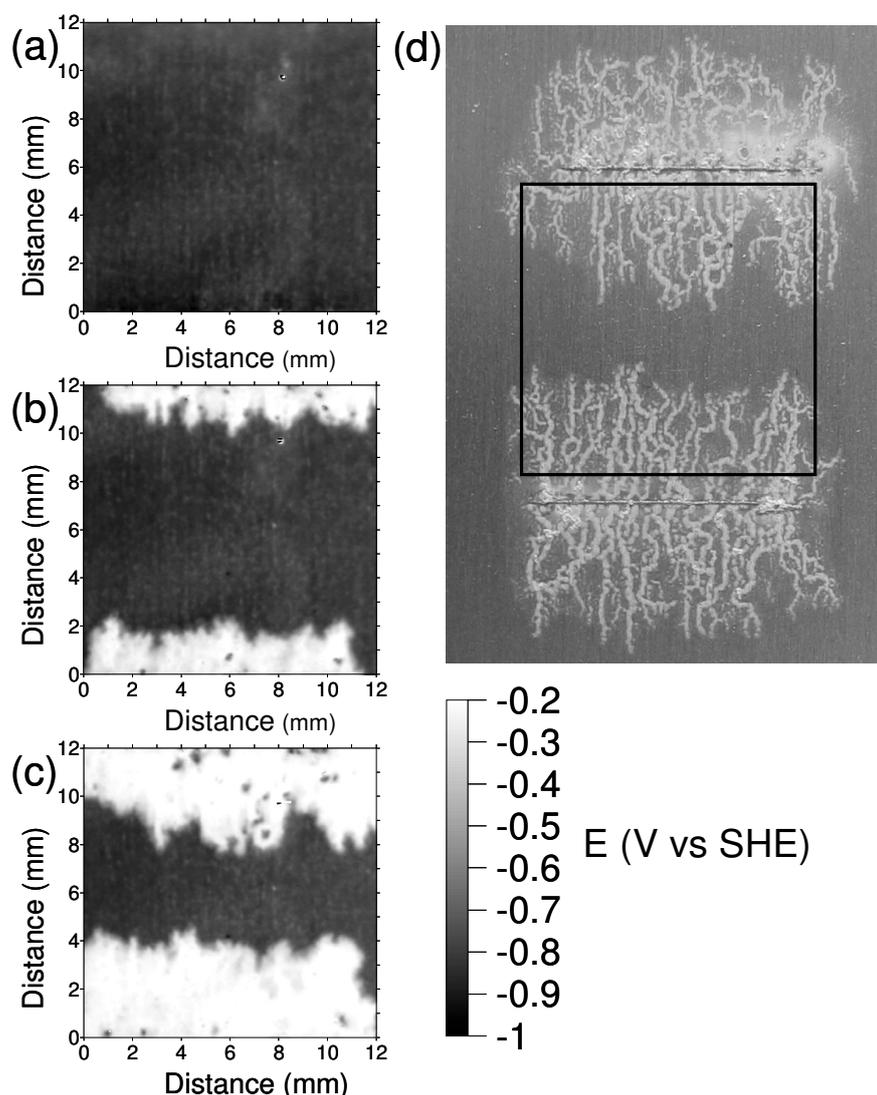
## 3. Results and Discussion

When samples of AA6111, AA1050 and pure aluminium were partially abraded with SiC paper – such that half of the sample surface was abraded and the other half was not – then SKP revealed a characteristic depression in surface potential in the abraded portion of the sample attributable to the development of an abrasion-induced NSDL. Fig. 1 shows a series of interpolated greyscale maps illustrating the distribution of (SKP-derived) free corrosion potential ( $E_{corr}$ ) values over a series of partially abraded bare (uncoated) aluminium samples in air at 50% RH. In each case, the area scanned was 12mm by 12mm and the abraded portion of the sample corresponds to the left half of the image. Fig. 1 (a) shows data obtained from AA1050, in which the left side of the sample had been gently scratched with SiC paper. The regions of lower potential associated with NSDL present in the scratches are visible as a series of dark vertical features. In Fig. 1 (b) the same AA1050 has been completely abraded on the left side. In this case the region of lower potential associated with NSDL is visible as a dark rectangle corresponding to. In Fig. 1 (c) a sample of pure aluminium has been completely abraded on the left side. As in Fig 1 (b) the abraded area exhibits a lower potential but, for pure aluminium, the potential contrast with the non-abraded surface is less marked. In Fig. 1 (d) a slightly different approach has been used. Here AA6111 has been abraded all over using SiC paper the resulting NSDL removed from the right side by caustic etching and desmutting in NaOH. It may be seen that the potential contrast developed between the right and left sides of the sample is similar in Figs. 1 (b) and (d).



**Fig 1.** Interpolated greyscale maps showing the distribution of  $E_{corr}$  (mV vs. SHE) over a 12mm by 12mm area in air at 50% RH. Key: (a) AA1050 left side gently scratched with SiC paper (b) AA1050 left side abraded with SiC paper (c) 99.999% Pure aluminium, left side abraded with SiC paper (d) AA6111 abraded using SiC paper then resulting NSDL removed from the right side by caustic etching in NaOH and desmutting in nitric acid.

None of the samples in 1 had been subject to post-abrasion heat treatment and the thermally promoted precipitation of second phase particles can not, therefore, be responsible for the potential changes observed. In Fig 1(a) the non-abraded AA1050 exhibits an  $E_{corr}$  of approximately 0.2 V vs. SHE. However, (on the LHS) individual scratches on the partially abraded AA1050 surface exhibited potentials as low as -0.5 V vs. SHE. It is also evident that the undamaged surface between the scratches also retains a high potential (approaching 0V). In Fig 1 (b), where the same AA1050 sample is completely abraded on the LHS, the potential is reduced to a fairly uniform -0.6 to -0.8 V vs. SHE. For pure aluminium Fig 1 (c) shows that potential depression caused by abrasion is limited to approx 0.15V. In Fig 1 (d) the potential of abraded AA6111 is approximately -0.7V by comparison with approx -0.1V for the etched (NSDL free) surface.

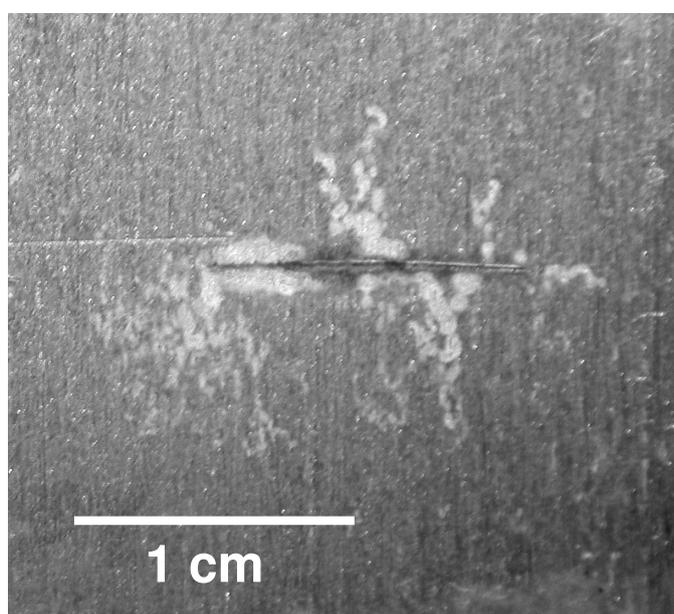


**Fig. 2** Interpolated greyscale maps showing  $E_{\text{corr}}$  distribution measured over PVB coated, NSDL-bearing AA6111-T4 ( $T_{\text{HT}} \leq 25^\circ\text{C}$ ) in air at 60% *r.h.* and  $40^\circ\text{C}$ . Time key: (a)  $t = 7$  hours (b)  $t = 54$  hours and (c)  $t = 108$  hours following FFC initiation. (d) is a photographic image of the sample at  $t = 108$  hours; the area scanned using SKP is indicated by a dashed line.

The AA6111 and AA1050 alloys both contain metallic additions which are capable of becoming precipitated in the form of intermetallic particles at grain boundaries. Thus it is possible that the presence of such intermetallics plays a role in the formation of, and electrochemical characteristics of, any NSDL formed on these alloys. However, this not true of pure aluminium and the abrasion-induced potential depression seen in Fig 1(c) must result from the intrinsic properties of aluminium in the NSDL.

On the basis of mixed potential theory, the potential depression associated with the presence of an abrasion-induced NSDL is consistent with either anodic activation or cathodic deactivation of the surface. However, it is now generally accepted that the presence of a NSDL makes the surface of aluminium alloys more susceptible to corrosion processes such as filiform corrosion (FFC) and, by implication, more reactive. I would therefore be reasonable to assume that anodic activation is the principle characteristic of the NSDL. Certainly, we found it possible to induce a fast, superficial form

of FFC on all the aluminium (alloy) samples described here once they had been abraded to induce an NSDL and coated with PCB . Fig. 2 shows representative grey-scale maps of  $E_{corr}$  distribution obtained (using SKP) at (a)  $t = 7$  hours (b)  $t = 54$  hours and (c)  $t = 108$  hours over a PVB coated NSDL-bearing AA6111 in the as-received T4 temper. Fig. 2(d) shows a photographic image of the same sample at the end of the experimental period. In parts (a) - (c) of Fig. 2 the value of  $E_{corr}$  in uncorroded portions of the surface ( $E_{intact}$ ) is approx.  $-0.85V$  vs SHE. Individual corrosion filaments cannot be separated. Surface-active FFC appears as an approximately continuous front propagating away from the coating defects and leaving in its wake an area of increased potential ( $E_{corr} =$  approx.  $-0.3V$  vs SHE.). FFC of the type and extent seen in Fig.2 was not observed in AA6111-T4 in the absence of prior abrasion to induce a NSDL.



**Fig. 3** Photographic image of a pure (99.999%) aluminium showing FFC. The sample had been abraded to induce a NSDL then coated with 30 microns of PVB containing 0.2 volume fraction of  $Cu^{2+}$  bentonite (a cation exchange clay). This image obtained 1 week after FFC initiation (then holding in air at 93%RH) and removal of the PVB coating.

Superficial FFC could even be induced on abraded pure aluminium, although for the FFC filaments to propagate at a reasonable rate  $Cu^{2+}$  cations had to be supplied to filament tail (using an in-coating cation exchanger) to provide (by becoming replated as Cu) a sufficiently active  $O_2$  cathode. The typical appearance of the corroded surface is shown in Fig. 3 above. It should be noted that FFC could not be induced on pure aluminium without prior abrasion, i.e. in the absence of an abrasion induce NSDL. This implies that anodic activation in the NSDL is necessary for this superficial (surface-active) form of FFC to occur. However it is not enough (in isolation) to produce surface-active FFC which propagates at any significant rate. A feasible cathode must also be present. In the case of pure aluminum this can be provided by introducing a  $Cu^{2+}$  cation exchange pigment into the lacquer. This further implies that although second phase (intermetallic) particles are not necessary to anodically activate the NSDL in aluminium alloys they probably do play an important role in facilitating FFC by providing a good oxygen cathode.

#### 4. Conclusions

Using the Scanning Kelvin probe (SKP) it has been shown that that on AA6000 series alloys anodic activation in the NSDL can occur without heat treatment and, therefore, without thermally-promoted intergranular precipitation. It is similarly shown that introducing an NSDL (without heating) produces open circuit potential drops of *ca* 0.6V on AA1000 series ( $\geq 99$  wt.% Al) alloys and *ca* 0.15V on pure aluminium ( $\geq 99.999$  wt.% Al). However, anodic activation in the NSDL is not enough (in isolation) to produce surface-active FFC. A feasible cathode must also be present. In the case of pure aluminum this can be provided by introducing a  $\text{Cu}^{2+}$  cation exchange pigment into the lacquer. Thus it is shown that although second phase particles are not necessary to anodically activate the NSDL they probably do play an important role in facilitating FFC by providing a good oxygen cathode.

#### 5. References

- [1] R.T. Ruggieri, T.R. Beck, *Corrosion*, 39 (1983) 452.
- [2] A. Bauista, *Prog. Org. Coatings*, 28 (1996) 49.
- [3] G. M. Scamans, M. P. Amor, B. R. Ellard, J. A. Hunter, *Proceedings of ASST 1997* (1997) 229.
- [4] M. Fishkis, J. C. Lin, *Wear*, 206 (1997) 156.
- [5] H. Leth-Olsen, J. H. Nordlien, K. Nisancioglu, *Corros. Sci.*, 40 (1998) 2051.
- [6] H. Leth-Olsen, K. Nisancioglu, *Corros. Sci.*, 40 (1998) 1179.
- [7] G. M. Scamans, A. Afseth, G. E. Thompson, X. Zhou, *Mater. Sci. Forum*, 396-402 (2002) 146.
- [8] A. Afseth, J. H. Nordlien, G. M. Scamans, K. Nisancioglu, *Corros. Sci.*, 43 (2001) 2093.
- [9] A. Afseth, J. H. Nordlien, G. M. Scamans, K. Nisancioglu, *Corros. Sci.*, 43 (2001) 2359.
- [10] A. Afseth, J. H. Nordlien, G. M. Scamans, K. Nisancioglu, *Corros. Sci.*, 44 (2002) 145.
- [11] R. Ambat, A. J. Davenport, A. Afseth, G. Scamans, *J. Electrochem. Soc.*, 151 (2004) B53.
- [12] A. Afseth, J. H. Nordlien, G. M. Scamans, K. Nisancioglu, *Corros. Sci.*, 44 (2002) 2491.
- [13] Y. Liu, X. Zhou, G. E. Thompson, T. Hashimoto, G. M. Scamans, A. Afseth, *Acta Mater.*, 55 (2007) 353.
- [14] H. N. McMurray, A. J. Coleman, G. Williams, A. Afseth, G. M. Scamans, *J. Electrochem. Soc.*, 154 (2007) C339.
- [15] G. M. Scamans, A. Afseth, G. E. Thomson, Y. Liu, X. Zhou, *Mater. Sci. Forum*, 519-521 (2006) 647.
- [16] G. Svenningsen, M. Hurlen Larsen, J-E. Lein, J-H. Nordlien, K. Nisancioglu, 9th International Conference on Aluminium Alloys, *Aluminium Alloys their Physical and Mechanical Properties*, (2004) 818.[
- [17] H. N. McMurray, A. Coleman, G. Williams, A. Afseth, G. Scamans, *Mater. Sci. Forum*, 519-521 (2006) 679.
- [18] M. Stratmann, *Corrosion*, 61 (2005) 1115.
- [19] G. Grundmeier, M. Stratmann, *Ann. Rev. Mater. Res.*, 35 (2005) 571.
- [20] H. N. McMurray, G. Williams, *J. Appl. Physics*, 91 (2002) 1673.
- [21] A Leng. H. Streckel, M. Stratmann, *Corros. Sci.*, 41 (1999) 547.
- [22] G. Williams, H.N. McMurray, D.A. Worsley, *J. Forensic Sci.*, 46 (2001) 1085.
- [23] G. Williams and H. N. McMurray, *J. Electrochem. Soc.*, 148 (2001) B377.