

Following the Kinetics of Localised Corrosion on AA6111 Using SVET

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This paper describes use of the scanning vibrating electrode technique (SVET) as a means of following the kinetics of intergranular corrosion (IGC) and pitting corrosion as it affects AA6111 aluminium alloy under conditions similar to conventional salt spray testing. The AA6111 used contained approximately 0.77 wt% copper and was obtained in the T4 solutionized and naturally aged condition. AA6111 coupons were heat treated in air at 185°C for varying periods up to 4 days to produce samples in the underaged, peak-aged and overaged condition – as confirmed by hardness measurement. Post heat treatment samples were ground and polished. On immersion in dilute (1% w/w) neutral aqueous sodium chloride solution the SVET was used to map the dynamic evolution of localized anodic and cathodic currents associated with IGC and pitting corrosion activity. Area integration of SVET data allowed the instantaneous (localised) corrosion rate and its time dependence to be determined quantitatively. Integration with respect to time allows the estimation of total metal loss over the experimental period (24 hours). It is shown that a large portion of the corrosion current in neutral salt solution is macroscopically localised.

Keywords: AA6111, localized corrosion, intergranular, ageing, scanning vibrating electrode technique.

1. Introduction

1.1 AA6111

Aluminium sheet alloys of the AA6xxx series, Al-Mg,Si-(Cu), are finding increasing application in the automotive industry because of the need to increase fuel efficiency by lowering vehicle weight. In the USA the higher strength AA6111 alloy is preferred, whilst in Europe the lower strength and lower copper AA6016 predominates. Both possess a good combination of strength and formability. AA6xxx series alloys are precipitation hardenable due to the presence of their main alloying elements; magnesium, silicon and copper. AA6111 contains 0.76wt% magnesium and 0.64wt% silicon and a relatively large 0.77wt% of copper. When used to manufacture automotive body panels the sheet is pressed whilst still relatively formable before being hardened during the 'paint bake' process. This heat treatment is required to cure the paint that is applied to the formed body panel but it also takes advantage of the hardenability of the alloy to make the finished product more dent resistant. Paint baking is carried out at 180°C for approximately 30 minutes.

1.2 Precipitation Sequence

AA6111 is an Al-Mg-Si-Cu alloy, these AA6xxx series alloys undergo a complex precipitation sequence when they are aged. There are numerous possible intermediate phases depending on the amount of copper in the alloy and also the ratio of magnesium to silicon present. Initially clusters of silicon, magnesium or a combination of silicon and magnesium form, with further heating and diffusion these clusters develop into GP zones. At peak ageing β'' (Mg_2Si) is the dominant intermediate phase and this coexists with metastable versions of the Q phase ($Cu_2Mg_8Si_7Al_4$). When overaged the equilibrium incoherent Q phase forms [1].

1.3 Precipitation Hardening

Precipitation hardening occurs with ageing and the hardness is dependent on the size, spacing and coherence of the magnesium, silicon and aluminium containing precipitates that are present after heat treatment. Hardness is related to the ease with which dislocations are able to move through or around these precipitates.

1.4 Corrosion

The AA6xxx series alloys are relatively corrosion resistant but second phase precipitation can increase susceptibility to intergranular corrosion (IGC) [2,3,4,5,6]. In AA6111 aged at 180°C for between 0.5 and 11 hours there are two precipitating phases which coexist, monoclinic β'' and hexagonal Q [1]. Copper rich grain boundary precipitates are believed to behave as local cathodes and couple microgalvanically with adjacent Cu and Si depleted zones increasing IGC susceptibility [2,3,4]. The presence of these Cu rich Q phase precipitates at grain boundaries is dependent on the post ageing cooling rate and it has been shown that a more IGC resistant material results from water cooling as opposed to air cooling after ageing. It has recently been demonstrated that in the under-aged condition produced by paint bake simulation, a nearly continuous Cu-enriched film forms along grain boundaries and IGC susceptibility is maximized [6]. On further ageing this film breaks up, producing discrete Q phase particles and IGC susceptibility is reduced [5]. This study showed that a AA6xxxx series alloy containing 0.13% copper at peak hardness (T6 condition) will, after air cooling, become less susceptible to IGC as compared to the same material in the underaged condition [6]. The result of this study is in contradiction to others on a range of AA6xxx series alloys which show them to be most susceptible at this temper.

2. Experimental Procedure

2.1 Material

AA6111 sheet of 1.1mm thickness was provided by Innoval in the solutionised (at 620°C) and naturally aged T4 temper (composition by weight Al, Mg 0.76%, Fe 0.24%, Si 0.64%, Cu 0.77%, Mn 0.20%). The AA6111 sheet had been hot and cold rolled and alkali cleaned on-line to remove any resulting surface deformed layer. As-received AA6111-T4 was cut into 40 x 40mm coupons and degreased using acetone. When not in use the coupons were stored at -18°C to prevent any unwanted natural ageing.

2.2 Heat Treatments

The samples were heat treated in air at 185°C for times up to 96 hours and naturally cooled in air at room temperature.

2.3 Grinding and Polishing

In order to provide a clean and uniform surface for SVET experiments and to remove any oxide that may have formed during heat treatment, all samples were ground and polished. Grinding was carried out by hand using silicon carbide paper and then a polishing wheel was used with 1 μ m diamond paste.

2.4 Hardness Measurements

Vickers hardness measurements were carried out before and after heat treatment to measure the precipitation hardening effect and to identify the underaged, peak aged and overaged samples. All samples were hardness tested a third time, 1000 hours after they were heat treated to confirm that the material had not aged further during storage. Each measurement was repeated and the stated value is in fact the average of three measurements all taken using 1kgf.

2.5 Corrosion Experiments

Teflon tape was used to mask off all but a 10mm by 10mm square on the polished side of each sample. Samples were then attached to a stage and immersed in an electrolyte of 1% w/w NaCl in distilled water. SVET measurements were carried out using a probe consisting of a platinum wire 125 μm in diameter surrounded by a glass sheath and vibrating at a frequency of 140Hz with a peak to peak vibration amplitude of 30 \pm 5 μm . The probe was scanned 100 μm above the sample. Scans over the 10mm by 10mm area were carried out every 30 minutes for 24 hours. Measurements were taken every 0.2mm in both x and y directions.

3 Results and Discussion

3.1 Hardness

Hardness measurements show that the initial hardness of AA6111 in the solutionised and naturally aged T4 condition is 83HV1 and that heat treatment of the material at 185 $^{\circ}\text{C}$ increases hardness for times up to 5.56 hours when the peak hardness of 121HV1 is obtained. When longer heat treatments are applied at this temperature the material becomes overaged and hardness gradually falls. The complete age hardening curve is shown in fig. 3.1.

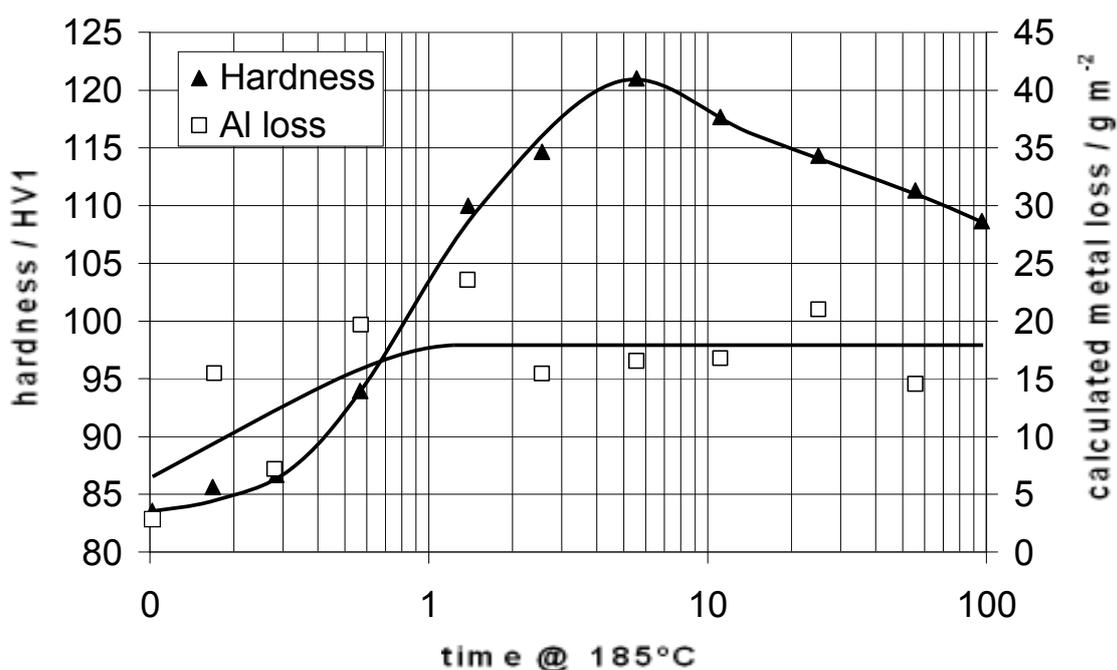


Fig. 3.1 Hardness and calculated metal loss of AA6111 samples heat treated for times up to 96h.

3.2 Corrosion

Spots and rings of corrosion product of a range of sizes and shapes gradually appeared on all samples while they were immersed in the electrolyte, this suggests that pitting corrosion was occurring. Fig. 3.2 is a group of photographs of samples in the T4 (0h @ 185°C), underaged (0.57h @ 185°C), peak aged (5.56h @ 185°C) and overaged (55.56h @ 185°C) conditions after 24h immersion in the electrolyte. On looking at these and the other samples it was not apparent that there was a systemic change in corrosion appearance as a result of the degree of ageing.

SVET current density maps in fig. 3.3 indicate that the spots and rings of corrosion were as a result of points of anodic activity. There is a clear correspondence between these points of anodic activity and the pattern of corrosion products seen on the samples after immersion. It can also be seen that the larger and more irregularly shaped areas of corrosion product are in fact the result of multiple anodes in that area. The remainder of the surface of the samples acted as the cathode with the cathodic area being larger than the anodic.

Fig. 3.3 shows that a large portion of the corrosion current is macroscopically localised, anodes are relatively large and well spaced with a background of homogeneous cathodic current density. In this case macro, rather than micro-galvanic coupling seems to be more favourable.

The calculated metal loss values shown in fig. 3.1 show that minimum metal loss occurred on the sample that was in the unaged T4 condition, for samples heat treated for a significant length of time metal loss appeared to be quite constant at around 15 to 20 g m⁻². Research on another AA6xxx series alloy where the same heat treatment temperature was applied showed the material to be susceptible to intergranular corrosion in the unaged and underaged conditions, resistant to localised corrosion at near peak ageing and susceptible to pitting when overaged [6] The alloy used in this study contained less copper than AA6111 and so susceptibility to corrosion may have been more ageing dependent.

Recent work has shown that the rate of filiform corrosion on AA6111 increases with increasing age hardening up to a point before decreasing [7]. It was shown that filiform corrosion rate is more dependent on ageing than pitting corrosion appears to be in this study. The rate of filiform corrosion on coated AA6111 is likely to be determined by the availability of copper precipitates and so it is logical that microstructural changes as a result of heat treatment would have more of an effect. The rate of localised corrosion on the AA6111 SVET samples used in this study is much more likely to be determined by the mass transport of oxygen because the samples are not coated and so there is an abundance of copper in contact with the electrolyte for the cathodic reaction.

Anode lifetimes varied greatly with some appearing on only one of the half hourly scans and others appearing early in the experiment and then persisting for the remainder of the 24 hours. Fig. 3.4 shows the SVET-measured current density for two anodes on the peak aged (5.56h @ 185°C), one remained active for much longer than the other but both show a similar profile. The current density increases from approximately zero to a peak value then falls and plateaus at a value above zero. Both peak and plateau current density values are higher for the long lived anode than the short lived anode. The point at which the short lived anode formed was slightly cathodic before switching to anodic when the pit initiated.

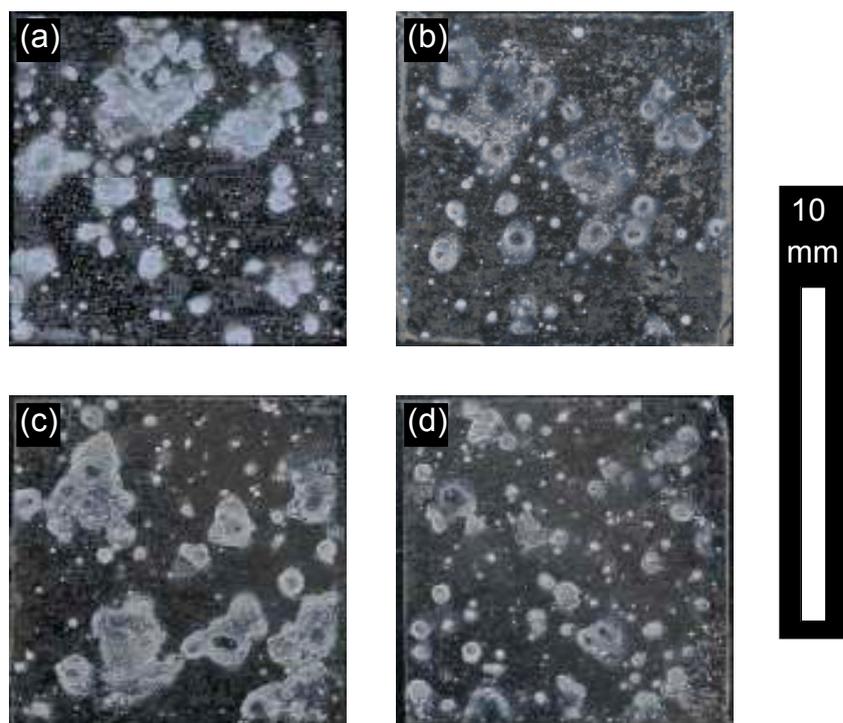


Fig. 3.2 Photographs of 10mm by 10mm exposed area of samples in the T4 (0h @ 185°C), underaged (0.57h @ 185°C), peak aged (5.56h @ 185°C) and overaged (55.56h @ 185°C) conditions after 24h immersion in 1% w/w aqueous NaCl solution.

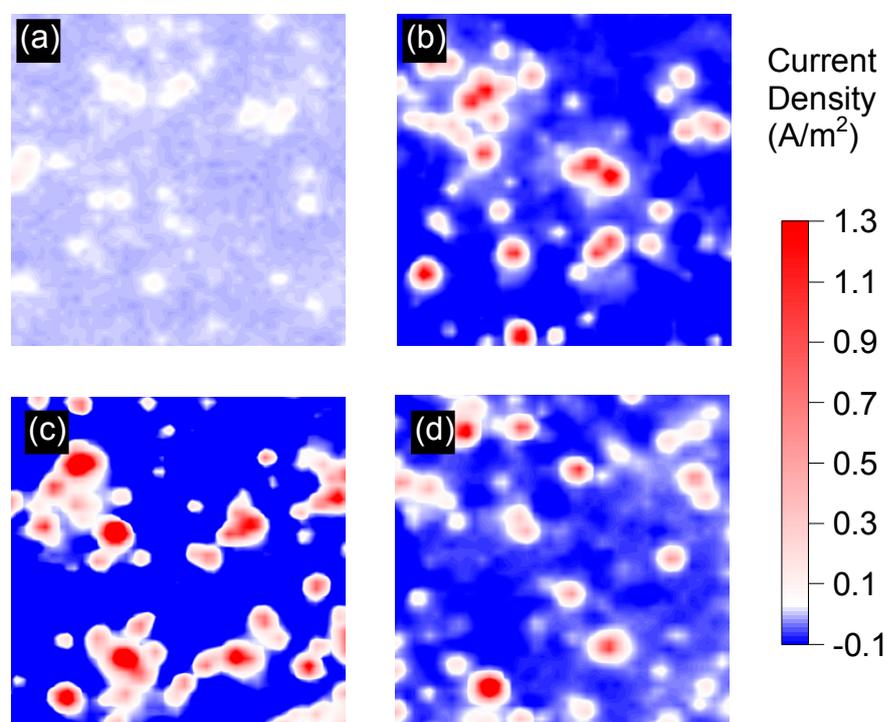


Fig. 3.3 SVET current density maps of 10mm by 10mm exposed area of samples in the T4 (0h @ 185°C), underaged (0.57h @ 185°C), peak aged (5.56h @ 185°C) and overaged (55.56h @ 185°C) conditions after 24h immersion in 1% w/w aqueous NaCl solution.

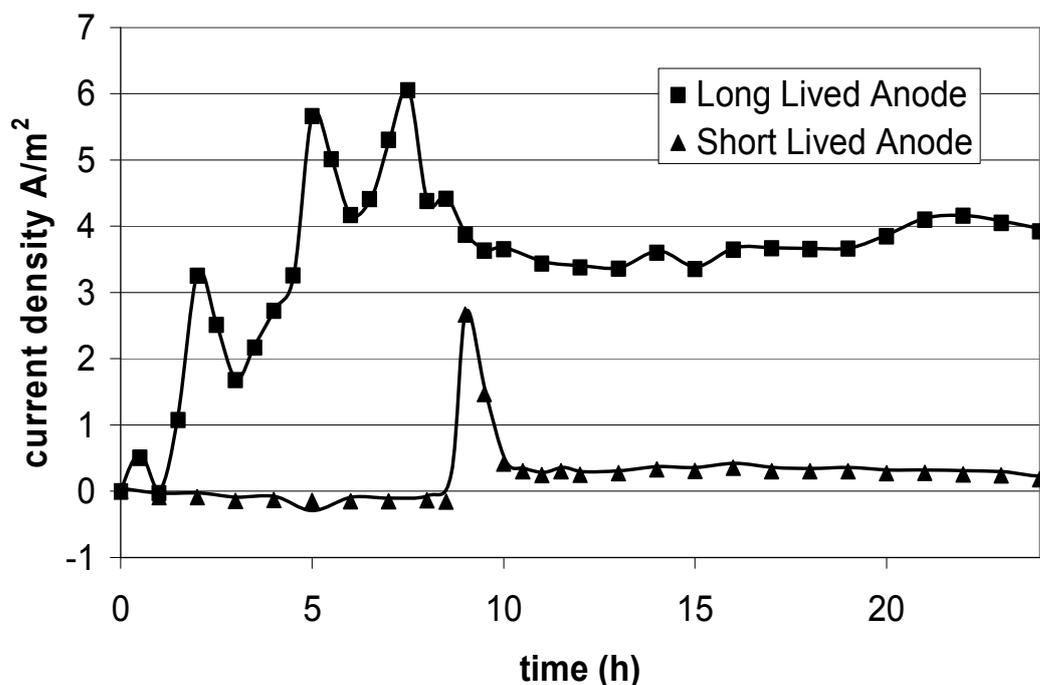


Fig. 3.4 SVET current density profiles of two anodes on peak aged (5.56h @ 185°C) AA6111 during 24h immersion in 1% w/w aqueous NaCl solution.

References

- [1] Y. Liu, X. Zhou, G.E. Thompson, T. Hashimoto, G.M. Scamans, and A. Afseth, "Precipitation in an AA6111 aluminium alloy and cosmetic corrosion," *Acta Materialia*, vol. 55, 2007, pp. 353-360.
- [2] G. Svenningsen, M.H. Larsen, J.H. Nordlien, and K. Nisancioglu, "Effect of thermomechanical history on intergranular corrosion of extruded AlMgSi(Cu) model alloy," *Corrosion Science*, vol. 48, 2006, pp. 3969-3987.
- [3] G. Svenningsen, M.H. Larsen, J.H. Nordlien, and K. Nisancioglu, "Effect of high temperature heat treatment on intergranular corrosion of AlMgSi(Cu) model alloy," *Corrosion*, vol. 48, 2006, pp. 258-272.
- [4] G. Svenningsen, J.E. Lein, A. Bjørgum, J.H. Nordlien, Y. Yu, and K. Nisancioglu, "Effect of low copper content and heat treatment on intergranular corrosion of model AlMgSi alloys, *Corros.*" *Sci. (in press)*, p. 101016/jcorsci200411025.
- [5] M.H. Larsen, J.C. Walmsley, O. Lunder, R.H. Mathiesen, and K. Nisancioglu, "Intergranular Corrosion of Copper-Containing AA6xxx AlMgSi Aluminum Alloys," *Society*, 2008, pp. 550-556.
- [6] G. Svenningsen, M.H. Larsen, J.C. Walmsley, J.H. Nordlien, and K. Nisancioglu, "Effect of artificial aging on intergranular corrosion of extruded AlMgSi alloy with small Cu content," *Corrosion*, vol. 48, 2006, pp. 1528-1543.
- [7] H.N. McMurray, A. Holder, G. Williams, A. Coleman, and G. Scamans, "Accepted Article: The Kinetics and Mechanisms of Filiform Corrosion on AA6111," *Electrochimica Acta*.