Effect of grain size on corrosion of high purity aluminium

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\begin{abstract}
A complete understanding of how grain refinement, grain size, and processing affect the corrosion resistance of different alloys has not yet been fully developed. Determining a definitive 'grain size--corrosion resistance' relationship, if one exists, is inherently complex as the processing needed to achieve grain refinement also imparts other changes to the microstructure (such as texture, internal stress, and impurity segregation). This work evaluates how variation in grain size and processing impact the corrosion resistance of high purity aluminium. Aluminium samples with a range of grain sizes, from $\sim 100\ \mu$m to $\sim 2000\ \mu$m, were produced using different processing routes, including cold rolling, cryo rolling, equal channel angular pressing, and surface mechanical attrition treatment. Evaluation of all the samples studied revealed a tendency for corrosion rate to decrease as grain size decreases. This suggests that a Hall--Petch type relationship may exist for corrosion rate and grain size. This phenomenon, discussed in the context of grain refinement and processing, reveals several interesting and fundamental relationships.
\end{abstract}

\section{Introduction}
Grain boundaries have distinct properties relative to bulk material in terms of atomic coordination, reactivity, and diffusion rates. The proportion of atoms that lie at inter-crystalline regions as a total of surface area can become significant as grain size decreases [1,2]. Consequently, it is not unreasonable to expect surfaces with relatively high grain boundary densities to exhibit different electrochemical behaviour from coarser-grained surfaces with low grain boundary densities. 'Grain boundary engineering' through grain refinement and various severe plastic deformation (SPD) techniques has been shown to be an effective way to improve mechanical properties such as strength and wear resistance [3--11]. Additionally, manipulation of grain boundary character has been used to enhance corrosion resistance of some materials. A classic example is improved intergranular corrosion resistance of Alloy 600 tubing, used in nuclear power production, through development of an increased quantity of low $\Sigma$ coincident site lattice boundaries [7,12]. Furthermore, different thermo-mechanical processing routes are known to have an important effect on the corrosion response of a material [13--17]. Despite these studies, which show that both mechanical and corrosion properties can simultaneously be altered through grain boundary modification and processing route, few (if any) efforts have been made to improve corrosion rates through grain size adjustment. Typically, improvements in corrosion resistance are achieved through bulk alloying or the use of various claddings and or coatings. As such, working towards materials with maximum corrosion resistance strictly by alteration of surface reactivity through grain size variation is somewhat novel. While alloying fundamentally changes the bulk material chemistry and coatings and claddings are prone to defects, grain size adjustments could be used to improve corrosion resistance without fundamentally altering the bulk composition (perhaps leading to decreased material costs).

The Hall--Petch relation reveals that yield strength is inversely proportional to grain size. However, an analogous relationship, if one exists, between grain size and corrosion rate has yet to be identified and is an area worthy of exploratory work. There have been a number of studies on different materials that involve grain size variation and corrosion performance, but as detailed in a recent review there is little consensus as to an all-encompassing effect applicable across different materials or even within similar alloy classes [17]. For instance, relatively little has been published directly or indirectly on the effect grain size variation has on the corrosion of aluminium (Al) and Al alloys [5,6,18--22]. Of studies that consider grain size and Al or Al alloys, the majority suggest that as grain size decreases corrosion resistance improves. Improved resistance generally is attributed to an ability of high grain boundary...
density surfaces to passivate more readily or to the physical breakdown of second phase intermetallic particles [5,6,20,21]. However, fine-grained Al has also been reported to be more susceptible to corrosion than coarser-grained control specimens [18,19]. Generally, a consensus within the literature does not exist which is not altogether surprising for a number of reasons. First, studies of grain size effects on corrosion are inherently difficult because any processing and/or alloy additions used to achieve grain refinement may impart physical or chemical changes to the material in addition to the intentional grain size modification. Such secondary consequences from thermo-mechanical processing include the development of texture, internal stresses, and segregation of alloying additions to grain boundaries, each which may have an impact on electrochemical response. As a result, general interpretation of the literature is complicated as the effect of grain refinement is difficult to decouple from other processing induced effects. More generally, the relationship between grain size and corrosion resistance is likely environment specific thus studies in different electrolytes may produce opposing results. However, within more specific groupings of materials, processing routes, and environmental families, the existence of such relations seems plausible.

Different processing paths that can be used to achieve grain-refined microstructures include rolling operations and SPD techniques such as surface mechanical attrition (SMAT) and equal channel angular pressing (ECAP) [8,9,23]. SMAT is a multi-directional peening process which induces SPD and grain refinement in a thin surface layer [9,10]. The ECAP process involves pressing a billet of material through a sharp bend in a die which induces SPD and grain refinement [8,11]; a detailed description of ECAP in the context of Al can be found in [8]. The ECAP process itself has been noted to both increase [3–5,13,14,22,24,25] and decrease [26–28] corrosion resistance. Conversely, SMAT has been reported to accelerate corrosion, posited to be from the introduction of internal stresses and defects at which attack may initiate [13,14,29].

The aim of this work is to investigate the role different processing routes play in corrosion performance, and to compare the relative effect from grain refinement to that of processing. More specifically, this is done explicitly for high purity Al with the long-term view to develop a fundamental understanding of the principles underpinning the relation for Al alloys.

2. Experimental

2.1. Specimen preparation

Pure Al samples with a range of grain sizes were produced using different processing routes in combination with post-processing heat treatments. The parent material for all processed specimens was a single cast ingot of ultra high purity Al (99.9999, Alpha Aesar) with grains on the order of 1 cm in diameter. An Al wire (99.999, Alpha Aesar) was also evaluated for comparison. High purity Al was chosen for study to help minimize secondary processing effects (such as segregation of solute to grain boundaries) that could complicate interpretation. The use of ultra high purity Al limits the lowest grain size that can be produced, however this is a trade-off for using such pure material. Four different SPD processes were used for grain refinement, including ECAP, SMAT, cold rolling, and cryo rolling. ECAP specimens were produced at room temperature from cylindrical billets of Al with an initial diameter of 0.995 cm. Separate billets were passed 1, 4, and 8 times (denoted herein as ECAP 1, ECAP 4, and ECAP 8, respectively) using route BC (billets were rotated 90° and in the same direction between passes) and not exceeding 20 tons of pressing pressure. ECAPed samples were cut to expose a face perpendicular to the pressing direction for optical imaging, grain size determination and corrosion testing. SMAT processing was carried out for approximately 15 min in a SNC-II surface nanocrystallization-testing machine in vacuum at room temperature using stainless steel milling media. Cold-rolled (room temperature) and cryo-rolled (conditioned in liquid N₂) samples were passed multiple times for a total reduction in thickness of greater than 90%. To create a wider dispersion of grain sizes some samples were subsequently heat treated at 200°C in an oil bath for 10, 30, and 60 min.

2.2. Grain size and materials characterisation

Specimens were prepared for metallography by grinding to 1 μm using diamond paste and electro-etched to reveal the grain structure. A Struers Lectro-pol 5 was used to electro-etch samples in Barker's reagent (2–4% HBF₄ in 200 mL H₂O) for 60 s at 20.0 V. Grain sizes were determined manually from optical images, using manual counting and the line intercept method. Electron backscattered diffraction (EBSD) was carried out on limited number of finely polished (0.05 μm alumina suspension) samples using a FEI Quanta 3D FEG equipped with a Pegasus Hikari EBSD system using TSL software. Elemental depth profiling was collected using a Leco GDS850 glow discharge optical spectrometer (GDOES).

2.3. Electrochemical evaluation

Potentiodynamic polarisation experiments were carried out in aerated 0.1 M NaCl on samples ground to 1200 grit and were repeated in triplicate at a minimum. Each sample (same grain size) was used for multiple experiments. A 3-electrode flat cell setup, consisting of a saturated calomel electrode (SCE) reference and platinum counter electrode mesh, in conjunction with a Biologic VMP3 potentiostat, was used for all experiments. Polarisations were initiated at −100 mV vs. open circuit potential (OCP) after 5 min of stabilisation and were scanned upward at a rate of 1 mV/s until current densities of 1 mA/cm² were reached. Corrosion current densities (jcorr) and corrosion potentials (Ecorr) were determined via software (EC-Lab®) assisted Tafel-type extrapolation, and passive current densities (jpass) were taken as the average of current densities at −0.7 V_SCE and −1.0 V_SCE. Anodic polarisation experiments were also conducted in 0.1 M NaCl solutions of assorted pH to determine if and how corrosion rates of ‘fine’ and ‘coarse’ grained Al varied as a function of pH. The pH of solutions was adjusted using additions of HNO₃ and NaOH to achieve approximate pH values of 2.0, 4.5, 10.8, 11.9, and 13.1, respectively.

3. Results and discussion

3.1. Processing to create a dispersion of grain sizes

Fig. 1 shows sample optical micrographs of grain structures from an ingot in the as-received condition and after ECAP, SMAT, cold rolling, and cryo rolling operations. All processing methods were found to induce grain refinement relative to the as-cast condition, which had grains sizes on the order of 1 cm, although the degree of refinement and shape of grains varied. After 1 ECAP pass the microstructure was observed to have undergone some refinement, particularly near the edge of the specimen, and consisted of a wide range of irregularly shaped small and large grains. After 4 and 8 ECAP passes the entire microstructure was considerably more refined with an approximately equiaxed structure with average grain sizes of 132 μm and 115 μm, respectively. SMAT samples were observed to have equiaxed grains of average sizes between approximately 113 μm to 142 μm. In general, multi-pass ECAP and SMAT lead to microstructures with grain sizes tightly distributed around an average grain size value. In contrast, the 1-pass ECAP and
Fig. 1. Sample optical micrographs of high purity aluminium after different processing routes and heat treatment times in 200 °C oil: (a) as-cast 0 min, (b) ECAP 1-pass 0 min, (c) ECAP 4-pass 0 min, (d) ECAP 8-pass 0 min, (e) SMAT 0 min, (f) SMAT 10 min, (g) SMAT 60 min, (h) cold-rolled 0 min, (i) cryo-rolled 0 min, and (j) Al wire 10 min. In all cases the scale bar is 200 μm.

both cold and cryo rolling appeared to have microstructures consisting of a wide distribution of sizes. For both rolling operations the microstructure consisted of banded regions in which either relatively small or large grains would predominate. This phenomenon is seen in Fig. 1i, which shows the transition from a region containing 'large' grains in the centre-left of the micrograph to one containing 'small' grains on the right. The heat treatment of samples generally had little effect on altering grain size, but did allow some coarsening. As such, a reasonable distribution of grain sizes ranging in sizes from ~100 μm to ~2000 μm was created for this study. Grain sizes smaller than 100 μm were not achieved on account of the extremely high purity of the starting material. SPD techniques are capable of producing much greater refinement (viz. 100 nm) in less pure materials.
Fig. 2. (a) Sample polarisation curves in 0.1 M NaCl for high purity Al processed in a number of different ways to achieve grain refinement, (b) a GDOES composition profile up to depths of 30 μm from the surface of Al processed through SMAT. At depths of less than 5 μm, peak Fe and Mg concentrations of approximately 42 wt.% and 1.3 wt.% were observed, respectively, and detectable levels of Fe and Mg enrichment persist up to depths of 20 μm. The Fe and Mg come from the use of stainless steel milling media, which in this case had previously been used to SMAT Mg surfaces.

3.2. The effect of grain size on electrochemical behaviour

Anodic polarisation experiments in 0.1 M NaCl were used to compare the electrochemical response of high purity Al processed via different methods. Fig. 2a contains representative curves for different processing routes. Processing had a dramatic impact on polarisation behaviour with different routes causing variation in \( j_{\text{corr}} \), \( E_{\text{corr}} \), and reaction kinetics. In general, the ECAP and wire specimens had the lowest \( j_{\text{corr}} \) values. SMAT specimens generally had high rates of anodic and cathodic kinetics and consequently high \( j_{\text{corr}} \) values. This phenomenon was actually somewhat uncharacteristic in that \( j_{\text{corr}} \) rates being an order of magnitude higher warranted further investigation. Whilst this aspect will not be the focus of this study it was found that SMAT specimens had significant surface contamination as a result of processing. The contamination was identified as iron (Fe) and the corresponding GDOES spectrum is seen in Fig. 2b. As a result, SMAT specimens will not be discussed further in this study with respect to mechanisms at play.

Additionally, a number of the ECAPed specimens displayed a peculiar passive behaviour in which no apparent breakdown was evident. Specimens that exhibited this type of behaviour could be polarised to potentials as high as 2 V_SCE with no obvious breakdown—however in such cases, the current densities were measured in excess of what would be considered passive (noting that no crevice corrosion was observed). Such an occurrence has also been noted by Song et al. [27], however to date, no rational explanation exists for this phenomenon which will require future work.

An abridged summary of average corrosion rate (\( j_{\text{corr}} \)) values is given in Fig. 3a. Each data point displayed in Fig. 3 (as well as those in Figs. 4 and 5) represents the average of at least three experiments and is indicative of a specific processing route–heat treatment combination. Fig. 3a reveals the Fe-influence on SMAT data, which is not presented in the remainder of the plots, and also shows little correlation between other parameters. Processing the data in Fig. 3a (disregarding the SMAT results) via the ladder of powers reveals that, in a Hall–Petch type manner, there is a trend when the grain size is raised to the power of \(-\frac{1}{2}\) (Fig. 3b). The trend is amenable to linear regression (via Origin 8) and yields a relationship suggesting that as grain size decreases, corrosion rate decreases. The linearization is intended to show a general relationship between grain size and corrosion across different processing methods and it is conceded that there are outliers in the data. The cause of the outliers is most likely due to the inherent difficulty (and manual aspect) of measuring true grain sizes from 2 dimensional images. Additionally, the influence of processing route, presumably through developed texture and stresses, on corrosion response is believed to
Fig. 4. (a) Average pitting potentials and (b) passive current density of high purity Al in 0.1 M NaCl as a function of grain size after various possessing routes.

contribute to data scatter evident in Fig. 3b. As shown, the linearization is effectively weighted towards specific processing methods thus exact fitting parameters are only strictly applicable to this set of data and not to aluminium alloys more generally. However, despite difficulty in determining accurate grain sizes and an inability to tightly control factors such as texture and internal stresses an overriding effect is still observed. Within some specific processing families, which in some respects might have similar stresses and or textures, a trend is more apparent.

Fig. 4a shows that grain refinement had little effect on average $E_{\text{pit}}$ values with the wire, cold rolling, cryo rolling, ECAP 4 and 8 specimens showing no discernable change relative to the as-cast ingot. Most values were observed to be between approximately $-0.675 \text{ V}_{\text{SCE}}$ and $-0.69 \text{ V}_{\text{SCE}}$ irrespective of grain size or processing route. However, some anomalous behaviour, as previously mentioned, was observed with the ECAP specimens that was manifest as an ennoblement of $E_{\text{pit}}$. This phenomenon seems to be difficult to understand on the basis that in all other cases, $E_{\text{pit}}$ remained unchanged. That $E_{\text{pit}}$ remains stable between specimens of varying grain size is in line with the present understanding that $E_{\text{pit}}$ represents a potential above which pits are stable, and this electrochemical driving force is essentially independent of the grain size, and more so is a function of the environment, material type, and sweep rate (all of which remained constant in this work) [30].

To our knowledge, such a relationship has not been previously reported. In part, this could be due to: (1) other authors using dissimilar ingots as the test materials, (2) the use of alloys which also undergo chemical distribution variations with grain size, and or (3) not analysing data which has been raised to the power of $-\frac{1}{2}$.

Fig. 4b shows that as grain size decreases, $j_{\text{pass}}$ values were observed to increase rather markedly. This trend was observed when plotting $j_{\text{pass}}$ vs. the grain size raised to $-\frac{1}{2}$. As with Fig. 3b, due to the inherent error in grain size determination and differences in processing route (variation in texture and internal stress) a large amount of data scatter exists and the linearization is only capable of illustrating a general trend. Specific fitting parameters are not provided, as they would only strictly be relevant to the set of data shown here within. We note that with the finest grain sizes studied, such passive current densities are comparatively high (in the realm of passivating metals). This phenomenon may not have been initially intuitive; with such a finding showing very clearly that the role of grain size on electrochemical kinetics can be rather marked. To understand the $j_{\text{pass}}$ vs. grain size phenomenon, we need to interpret the relationship in the context of other parameters; as a result, Fig. 5 shows the relationship between $E_{\text{corr}}$ and $j_{\text{corr}}$ of the various specimens, along with the relationship between $j_{\text{pass}}$ and $j_{\text{corr}}$, each of which is discussed separately below.
Fig. 5a shows that a trend exists whereby as corrosion rates increase, the $E_{corr}$ value becomes less noble. From offline inspection of the polarisation curves collected (excluding SMAT), it is apparent that this subtle shift is owing to a small decrease in the anodic reaction kinetics near $E_{corr}$. The net result is that $E_{corr}$ becomes ennobled as $j_{corr}$ drops, which is classic behaviour of a system under anodic control. If the reduction in $j_{corr}$ was related to cathodic reaction kinetics being slower, that would result in less noble $E_{corr}$ values, which is not the case herein. In contrast, as seen in Fig. 5b, as $j_{corr}$ decreases the corresponding $j_{pass}$ is increased. If the anodic reaction kinetics were unilaterally decreased with grain refinement, then the relationship between $j_{pass}$ and $j_{corr}$ would not have the correlation that is seen. Thence, from the data in Figs. 4 and 5, it is possible to present a hypothesis as to the role of grain refinement.

If grain boundaries are considered to be more ‘reactive’ than the grain interiors, then it may be possible that near $E_{corr}$, grain-refined specimens rapidly form an oxide, which judging by the data herein, is protective and capable of producing a lower $E_{corr}$ than coarse-grained counterparts. This characteristic of fine-grained materials being more ‘reactive’ then follows that as potential is raised, the rate of growth of oxide is accelerated and hence higher passive current densities are realised when moving away from $E_{corr}$. Finally, when $E_{pass}$ is reached, the critical driving force for stable dissolution has been met (in the environment) and the specimens break down independently of grain size or prior reaction rate. In essence, decreasing grain size tends to make the specimen more reactive; in a passivating environment/pH, that serves to decrease corrosion rate through faster growth of a protective oxide. Also apparent from this work however is that this enhanced reactivity, which is posited to allow for different rates of oxide growth, is confined to controlling the rate of anodic reactions. It seems as though grain refinement has little role in the rate at which cathodic reactions can be sustained (presumably because cathodic reactions rely on electronic more so than ionic conduction, with increased grain boundary density being important for the latter. This is in agreement with the detailed experiments of Lee and White [31] who elegantly revealed that small increases in oxide film ion conduction are associated with grain boundaries when comparing polycrystalline Al with single crystals. In the work herein, the lineal length of grain boundary covers several orders of magnitude from the largest to smallest grain size studied.

3.3. Electrochemical dependence on pH

Conventional thermodynamic predictions (E-pH diagrams) suggest that Al will corrode in both alkaline (>pH $\sim$8) and acidic (<pH $\sim$4) electrolytes. However, these predictions do not provide any indication of corrosion rate or account for changes in microstructure and surface reactivity that would accompany variation in grain size among otherwise compositionally similar materials. As such, corrosion rate as a function of pH was determined from experiments on as-cast (coarse grains $\sim$1400 $\mu$m) and ECAP 8-pass (fine grains $\sim$115 $\mu$m) Al specimens in 0.1 M NaCl solutions of varied pH values. Sample polarisation curves as a function of pH for both fine and coarse-grained surfaces are shown in Fig. 6. ECAP processing/fine-grained microstructures revealed a rather dramatic effect on polarisation response both at low and high pH values. Such vast differences were not observed at neutral pH, and reveal that for the same bulk material the grain structure alone can have rather significant role in the ultimate reaction rate.

Fig. 7 shows a summary of average $j_{corr}$ as a function of pH. It is observed that $j_{corr}$ is unilaterally lower across the pH range for the grain-refined specimen. Over the entire range of pH values, the ECAP specimen demonstrated less variation in $j_{corr}$ than the as-cast specimen. Corrosion current densities of both samples were within, or close to within, a standard deviation of each other in pH
4.48, 6, and 10.75 solutions. However, the ECAP specimen showed a relative decrease for \( j_{\text{corr}} \) in pH 2, 11.85, and 13.1 electrolytes.

In addition to Fig. 7, at each pH value the average \( E_{\text{corr}} \) of ECAPed specimens was observed to be nobler than the corresponding \( E_{\text{corr}} \) value of the as-cast sample. This would again suggest that the difference in response is under anodic control. It is also interesting that the fine grain specimen sustained lower dissolution currents at potentials separated from \( E_{\text{corr}} \). This would indicate that thermodynamically driven dissolution of the oxide occurs more readily on coarse-grained surfaces (viz. grain interiors) than on finer grained specimens. Further analysis of such phenomena is not pursued herein, however it suffices to show that different electrochemical responses are seen for the same bulk material with varying grain structure, and that the response is also tied in with the testing environment.

3.4. General discussion

In the general discussion of the results there are several factors that need consideration. The factors below represent both the assumptions and aspects that could also play a role in such studies. Firstly, it is important to mention that this study has found production of grain-refined structures using any SPD techniques creates a potential for surface contamination with possible implications for corrosion response. SPD places a sample in intimate contact with the materials and tooling used for deformation. A possible consequence of the heat and pressures involved with these processes is compositional alteration of the surface—especially true in the case of SMAT where high energy and long contact times exist.

Grain refinement can cause increases in dislocation density and dislocation structure owing to the fact that grain refinement (in most cases) arises from plastic deformation of the metal. As a result, dislocation structures, and indeed the associated residual stress, may also impact corrosion rate. It is difficult to measure residual stress, particularly of a free surface, so in this instance a rough check for residual stress was done using Vickers microhardness testing of all specimens (not presented) in an aim to detect any anomalous and significant hardening between specimens. There was no evidence of any phenomena, and it is assumed for the materials tested herein, the level of residual stress is low, and in fact negligible for the free surface on which electrochemical testing was performed.

Another aspect that may influence the electrochemical response of a material is crystallographic orientation/texture. The image contrast in Fig. 1 gives some clue to the varying texture in these materials, however it is very much the case that with grain refinement, in particular between different refinement techniques, differences in texture arise. Based on the electrochemical results the wire, ECAP 1 and ECAP 8 specimens were identified as having low corrosion rates. Fig. 8 shows the pole figures (Fig. 8a) and number fraction of grain boundaries as a function of misorientation angle (Fig. 8b) of the wire, ECAP 1 and ECAP 8 samples. From the pole figures it is apparent that the texture of the wire is a typical \( \langle 001 \rangle \) 'wire texture' for cubic material, whilst the texture for ECAP specimens evolves towards a strong \( \langle 101 \rangle \) texture for the ECAP 8 specimen. Additionally, when comparing the number fraction for the grain boundary misorientation angles, the ECAP specimens display a higher number fraction of high angle grain boundaries relative to the wire; with the ECAP 8 specimen showing a slightly higher number fraction than the ECAP 1 specimen (Fig. 8b). In all, the texture of the specimens studied herein essentially covers the range of what may be expected in Al, however this did not completely mask the relevant trends observed. Texture variation may be part of the reason why there is significant scatter in the trends however. Future work will need to consider such factors, since it
is conceivable that the atomic packing – which varies for different crystallographic orientations – will impact reaction rates (at least for the crystalline grain interior), but the relevance to the role of orientation to the level of disorder in grain boundaries remains unclear. In a recent study on the role of ECAP on corrosion of Mg, it was noted that an increase in high angle boundaries was beneficial [25]. On reprocessing of the data in that paper, it is also obvious that the corrosion rate varies with grain size $\approx \frac{1}{2}$ in a similar fashion as shown for pure Al in this manuscript.

In general, grain refinement of pure Al (even for the range studied herein) appears to decrease corrosion rates by approximately half compared to the as-cast ingot sample. With increasingly complicated alloy factors other factors may dominate this behaviour - since chemical effects will dominate structural effects. Additionally, based on this study and review of the literature it seems likely that the relationship between grain size and corrosion rate changes depending on specific material and environment combinations. For example, within the context of this work grain refinement of pure Al appears to offer significant gains in corrosion resistance in acidic and alkaline NaCl environments whilst having lesser, but noticeable, impact in near neutral electrolytes. This illustrates that within specific material and environment combinations, grain refinement or grain coarsening may be an effective way to maximize corrosion resistance. As such, grain size tuning offers an engineer latitude in tailoring microstructures for enhanced corrosion resistance or designing materials with the same bulk chemistry to have varied corrosion rates.

4. Conclusions

- Various processing routes were able to produce a distribution of grain sizes for specimens cut from the same starting ingot.
- In neutral NaCl solutions, it was shown that the corrosion rate tended to decrease with decreasing grain size. This relationship has not been previously reported explicitly, and is of great significance if the relationship is generally applicable outside the realm of the system studied herein.
- Decreasing grain size resulted in an enhancement of $E_{corr}$ and decreased $j_{corr}$. This suggests that the reduction in $j_{corr}$ is under anodic control. Reduction in grain size was also concomitant with an increase in $j_{pass}$. The combination of results was rationalised on fine grain structures having more reactive surfaces with respect to oxide formation and film ion conduction.
- Pitting potential of pure Al generally does not appear to vary with grain size or processing route, with the exception of some anomalous behaviour from the ECAP specimens.
- Surface contamination is an important consideration in the understanding of materials processed via any plastic deformation techniques.
- The ability to tune electrochemical response as a result of grain structure modification alone has important implications for rational alloy design.

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References
