Corrosion of pure aluminium and aluminium alloy: a comparative study using a slow positron beam

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Abstract. Corrosion-related defects in pure Al and AA 2037 Al alloy have been investigated by positron beam-based Doppler broadening energy spectroscopy. Defect profiles have been analyzed by measuring the $S$ parameter as a function of incident positron energy up to 30 keV. When pure Al samples are immersed in 1M NaOH for various times, a significant increase in the $S$ parameter near the surface is observed. This implies that the corrosion process involves the creation of defects and nanometer voids. In contrast, a significant decrease in the $S$ parameter is observed after the corrosion of water-quenched Al alloy by the same method, which is interpreted as being a result of Cu enrichment near the metal-oxide interface layer.

1. Introduction
Positron annihilation spectroscopy (PAS) has been widely used as a probe for defect studies at the atomic dimension in solids, such as vacancies, vacancy clusters, dislocations, and nanometer-scale voids. The use of variable energy positron beams allows one to probe the depth profile of solids, and is particularly suitable for analysis of surface and near-surface defects [1]. PAS investigations of corrosion-related defects in aluminium have been reported [2, 3]. Significant numbers of vacancy-type (open volume) defects were found near the metal-oxide film interface, and it was concluded that the number of defects and size increased due to corrosion in NaOH or aqueous phosphoric acid solution. Furthermore, these investigations suggested that the cavities were interfacial voids which were revealed by AFM after dissolution of the overlying oxide. Wu et al. reported on corrosion-related defects in iron and AISI 304 and 316 stainless steels studied by Doppler broadening energy spectroscopy (DBES) during corrosion processes [3, 4]. The significant increase in $S$-parameter after corrosion in iron was interpreted as due to the formation of defects and voids. However, a decrease of the $S$-parameter in AISI 304 and 316 stainless steels after corrosion was interpreted as dissolution of the passive oxide film. In this paper, we report the results of the investigation of corrosion-related microstructure and defects during corrosion processes in pure Al and AA 2037 Al alloy using the slow positron beam technique.

2. Experiment
Pure Al foils were purchased from Goodfellow Corporation (Berwyn, PA). Pure Al samples were about 300 μm thick with 99.999% purity, and were cut into 20mmx20mm for DBES measurements. These samples were annealed at 450°C for 30min and served as defect-free
reference samples, having only a very small vacancy concentration in the bulk. AA 2037 Al alloys were produced by continuous casting (CC) in the Aleris International factory, USA. The main chemical compositions in the samples are 1.48%Cu, 0.45%Mg and 0.24%Mn. Hot bands were cut into 20mmx20mmx2mm pieces for DBES measurements. The as-quenched samples were annealed at 500ºC for 3 hours and then quenched to room temperature in water.

The 1M NaOH immersion solution was prepared from reagent-grade chemicals and deionized water. Corrosion of samples was carried out for different time at room temperature. The DBES experiments were performed using the slow positron beam at the University of Bath. The DBES spectra, recorded using a high-purity Ge solid-state detector, were obtained as a function of positron energy from 0.25 to 30 keV at room temperature. The total count for DBES spectra was 106 with a counting rate of 1000 cps near the 511 keV peak.

3. Results and Discussion

3.1. S-energy profiles

Figure 1 shows the $S$ parameter as a function of positron incident energy (i.e. S-energy profiles) for pure Al and 2037 Al alloy after different dissolution times in 1M NaOH solution. The data points are $S$ parameters calculated from individual annihilation spectra measured at particular beam energy. The top x-axis is the mean depth of the implanted positrons from the surface at each incident energy as calculated by a well-known equation [1]. The solid lines in the figures are the results of a simulation, to be discussed below. The estimated accuracy of the $S$ value is within 0.001. The $S$ values in this paper are normalized by dividing by the bulk $S$ parameter, which in figure 1(a) is approached as a plateau at energies greater than 15keV. A normalized $S$ value larger than one indicates the presence either of a phase having an $S$ parameter larger than Al, or of open volume defects.

![Figure 1](image)

Figure 1 S-energy profiles for pure Al (a) and water-quenched 2037 Al alloy (b) after different dissolution times in 1M NaOH solution. Data points are measured values, and solid lines are results of fitting with simulation.

From the data in figure 1, we observe a different effect between pure Al and Al alloy due to corrosion. When the pure Al samples were immersed in 1MNaOH for 5-20min, a significant increase in the $S$ parameter near the surface is observed. The non-monotonic variation of $S$ with beam energy indicates that a near-surface defect layer is present having annihilation characteristics different from either the surface or the bulk metal. This general peaked shape of the $S$ profiles suggests the presence of open-volume defects such as voids.

However, for water-quenched Al alloy samples, a significant decrease in the $S$ parameter is observed after corrosion by the same method. A monotonic variation of $S$ with beam energy is
observed in NaOH treated samples for times increasing from 3-10min, which will be discussed below.

3.2. S-W plots

Information about the types of defects could be revealed by plotting the \( W \) parameter as a function of the \( S \) parameter. The data for all the experiments for pure Al and Al alloy are in figure 2. \( S \) and \( W \) values for individual experiments fall on a common locus, which only consists of two straight-line segments connecting three vertices. The low energy \((S,W)\) state \((0.94, 1.30)\) represents annihilation of positrons trapped in the oxide film. The other \((S,W)\) states in the figure 2 represent defect-free bulk Al \((1.00,1.00)\) or quenched bulk Al alloy \((0.99, 1.10)\), and the open-volume defects near the surface at the metal-oxide interface \((S=1.06, W=0.85)\). The fairly straight line shown in figure 2 indicates that only two positron states contribute to annihilation – suggesting that only one type of (vacancy-type) defect is present in all the measurements, in the annealed sample as well as NaOH corroded pure Al samples. The curvature commonly seen near the maximum \( S \) is caused by the relatively small concentrations of this defect, so that all three states contribute to annihilation. Figure 2 also shows that only one type of defect is present in quenched Al alloy without NaOH dissolution, but that an additional effect acted on interfacial layer, which induced in a decrease of \( S \) parameter after NaOH dissolution.

![Figure 2](image)

**Figure 2** \( W \)-parameter as a function of the \( S \) parameter for pure Al (a) and water-quenched 2037 Al alloy (b) after different dissolution times in 1M NaOH solution. (\( S \) is from Fig 1 data.)

3.3. Fitting of S-energy profiles

The \( S \)-energy profiles in figure 1 were fitted by solving the positron diffusion-annihilation equation. The measured \( S \) parameters are fitted using a three-layer model (oxide film, interfacial defect layer and bulk) in the code VEPFIT and the results are plotted as solid lines in figure 1. For pure Al samples, the models used for fitting contained a surface defect layer and a bulk Al layer. Inclusion of a surface oxide layer was found to be unnecessary, as the oxide film thickness is so thin - found to be 5nm by Auger measurements - that the defect layer parameters obtained by the simulation are unaffected by its presence. Thus, the oxide film factors into the model as a surface boundary condition. The only input parameter for the fitting is the bulk Al diffusion length, which is set to 150nm \([2]\). For water-quenched Al alloy samples, and after dissolution in NaOH for 1min, the VEPFIT fitting model contained a surface defect layer and a bulk Al alloy layer similar to pure Al samples. However, thicker oxide films (about 20nm) are formed after dissolution in NaOH for 3-10min. Thus the VEPFIT models for the alloy contain an oxide film, an interfacial defect layer and the bulk. The fit values of the interfacial defect layer \( S \) (\( S_d \)), positron diffusion length (\( L_d \)), and thickness (\( B_d \)) are shown in table 1.

Table 1 shows that significant increase in the \( S \) parameter of the defect layer after dissolution mainly comes from the formation of defects and voids (a size of 0.1nm to several nm) near the surface during corrosion, which is consistent with previous results reported by Hebert et al. \([2,3]\). In our experiment, the defect layer thickness in pure Al is 114 nm in the annealed sample, compared with
about 30 nm after NaOH treatment. The dissolution rate in NaOH solution was measured and found to be 200 nm/min. The initial defect layer would then have dissolved during the 1 min treatment. It is clear that the defect layer after the treatment is dominated by new defects introduced by the immersion. Furthermore, Table 1 also shows that the $S$ parameter decreases with dissolution time in 2037 Al alloy, which differs from the increase due to the formation of significant numbers of open volume defects near the metal-oxide film interface induced by NaOH dissolution in pure Al samples. Many experiments [6,7] indicated that Cu has a strong influence on the corrosion of Al alloys, where it is present in matrix regions or as a constituent of secondary phases. In Cu-containing alloys, corrosion is promoted by reduction of oxygen at Cu-rich phases exposed at the alloy surface, with the associated pH rise resulting in alkaline corrosion of the adjacent matrix Cu-rich regions. Corrosion can also be generated from matrix material of low Cu content as a consequence of the growth of an amorphous oxide film. The enrichment of Cu has also been detected following various surface treatments of commercial Al alloys. Further, near-surface accumulation of impurities, including Cu, occurs during alkaline etching of Al [8]. The content of Cu in 2037 Al alloy is only 1.48%, and the annealed Cu has a low $S$ value of 0.83 due to presence of 3d-electrons. Therefore, Cu enrichment near the metal-oxide interface layer will induce a decrease of the $S$ parameter. The enrichment of Cu increases, and thus the $S$ parameter decreases, with dissolution time. The positron diffusion length increases with dissolution time, indicating a progressively lower defect/void concentration. Further investigations are in progress involving AFM, TEM and EDX experiments and will be reported in the future.

| Time (min) | $S_d$(nm) | $L_d$(nm) | $B_d$(nm) |
|------------|-----------|-----------|-----------|
| 0          | 1.034     | 2.1       | 114       |
| 5          | 1.048     | 2.6       | 38        |
| 10         | 1.045     | 2.8       | 32        |
| 20         | 1.049     | 2.7       | 29        |

| Time (min) | $S_d$(nm) | $L_d$(nm) | $B_d$(nm) |
|------------|-----------|-----------|-----------|
| 0          | 1.012     | 31        | 367       |
| 1          | 1.010     | 49        | 367       |
| 3          | 0.996     | 85        | 402       |
| 6          | 0.985     | 87        | 407       |
| 10         | 0.964     | 98        | 408       |

Table 1 Fitted parameters for the defect layer in pure Al and 2037 Al alloy.

4. Conclusions
When pure Al samples are treated in 1M NaOH for various dissolution times, a significant increase in the $S$ parameter near the surface is observed. This implies that the corrosion process involves the creation of defects and nanometer voids. A significant decrease in the $S$ parameter is observed after the corrosion of water-quenched Al alloy, which is interpreted as being a result of Cu enrichment near the metal-oxide interface layer.

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