

# Screen-printed platinum electrodes for measuring crevice corrosion: Nickel aluminium bronze as an example

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**Abstract:** Screen-printed platinum electrodes were used to monitor crevice corrosion processes. The electrodes, printed on an inert alumina substrate, formed the bottom of an artificial crevice when mechanically clamped to a rectangular block of nickel-aluminium bronze (NAB). Cyclic differential pulse voltammetry was used to detect corrosion products over time whilst the assembly was immersed in a 3.5% by weight aqueous solution of sodium chloride. Cupric ( $Cu^{2+}$ ), ferric ( $Fe^{3+}$ ) and ferrous ( $Fe^{2+}$ ) ions were detected with evolution profiles indicative of selective phase corrosion.

**1 Introduction:** Rectangular platinum electrodes (Heraeus Silica and Metals, RP10001-145B) were screen-printed on inert 96% alumina substrates (Coors Ceramics, ADS-96R) using standard thick-film processing techniques. An insulating glass dielectric paste (ElectroScience Laboratories, 4905CH) was then printed over the electrodes with patterned windows defining the active electrode areas (4.0 x 2.0 mm for the counter electrode and 3.0 x 1.5 mm for the working electrode). A silver-palladium thick-film paste (ESL, 9635) was printed over the free end of each electrode to provide a solderable connection.

The electrodes were mechanically clamped to a 20 x 17mm block of nickel aluminium bronze (NAB; CuAl9Ni5Fe4Mn) using a parallel acrylic clamp with nylon bolts, as shown in Fig. 1. The NAB sample had previously been polished using silicon carbide paper and cleaned with acetone and de-ionised water. Between the surfaces of the metal block and electrode assembly an artificial crevice is formed due to their surface roughness. Silicone sealant

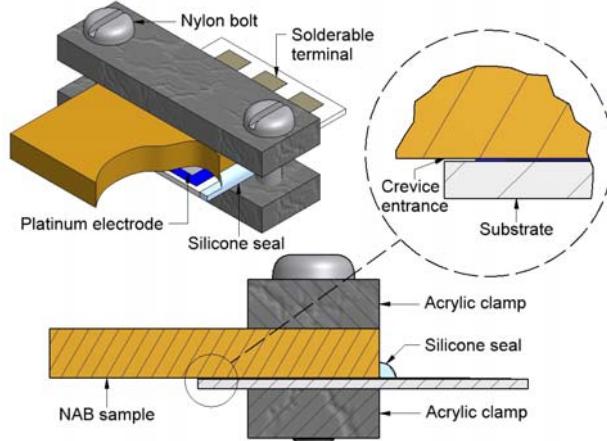


Fig. 1. Cut-away illustration of crevice sensor.

was applied around three sides of the NAB block to produce an occluded crevice and over the electrical connections to provide insulation.

The crevice assembly was placed in aqueous solution of 3.5% by weight sodium chloride (VWR, AnalaR, Normapur, >99.5%). At regular intervals, cyclic differential pulse voltammetry was performed using an Autolab PGSTAT302N potentiostat (EcoChemie) with potential waveforms set with respect to an Ag/AgCl (3.5 M KCl) reference electrode (VWR, GelPlas). Waveform parameters were: step size  $\pm 2$  mV; interval time 100 ms; modulation amplitude  $\pm 20$  mV; modulation time 40 ms and effective scan rate of 20 mV/s. Potentials were swept from +800 mV down to -800 mV and back to +800 mV. From voltammograms produced, corrosion products were identified by the potentials at which current peaks occurred, whilst their relative concentrations were inferred from magnitudes of current peaks.

**2 Results:** Typical voltammograms are reproduced in Fig. 2 which shows how they evolve with time indicating changes in ion concentrations. From calibration, individual

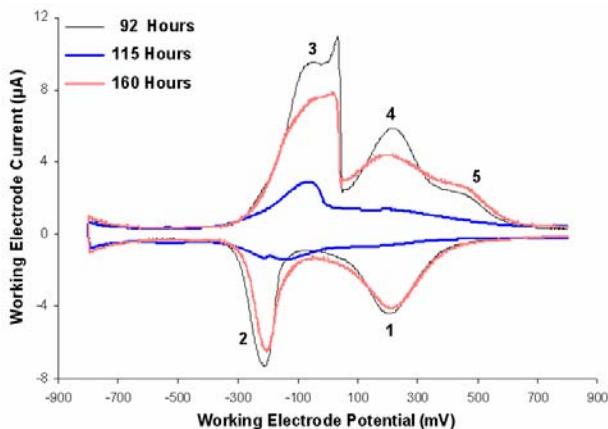


Fig. 2. Voltammograms at various times (hours).

current peaks have been identified: the  $\text{Cu}^{2+}/\text{Cu}$  redox couple (peaks 1 to 4) and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple (peak 5). The temporal change in the concentrations of  $\text{Cu}^{2+}$  (using peak 2 data) and  $\text{Fe}^{2+}$  are shown in Fig. 3. This indicates that there is a large increase in the concentrations of both ions within the crevice between 80 and 90 hours immersion, which gradually fall back to fairly constant levels over the following 20 hours. A second dramatic increase in both ions occurs after 140 hours. This time the  $\text{Fe}^{2+}$  concentration remains fairly constant for a period whilst the  $\text{Cu}^{2+}$  ion concentration drops to background levels. This is evidence of selective phase corrosion occurring within the crevice region and is in agreement with that reported in the literature [1].

**3 Discussion:** NAB is a complex alloy of nickel, aluminium, copper, iron and manganese and in terms of its microstructure has several distinct phases, the most abundant being a copper rich alpha phase. In an actively corroding crevice oxygen is rapidly depleted and diffusion from the bulk electrolyte is restricted due to the small crevice dimensions. Thus, two different chemical environments evolve inside and outside of the crevice causing a galvanic potential to be established across the metal. In the bulk environment outside the crevice, the NAB surface becomes cathodic, where the oxygen reduction reaction can readily take place, to the anodic crevice. Initially in the crevice region whilst the pH is still neutral, corrosion of the copper rich alpha phase is favoured and a rapid increase in  $\text{Cu}^{2+}$  ions

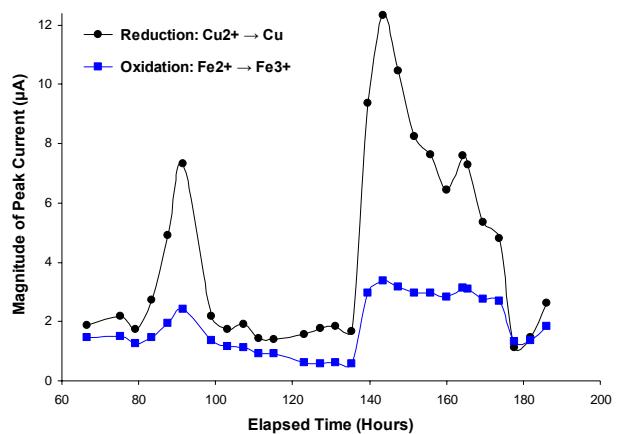


Fig. 3. Ion concentration profiles over time.

occurs. However, the crevice becomes increasingly anodic which initiates several corrosion reactions. Corroding metal ions in the crevice environment become hydrolysed to complex hydroxide groups with the liberation of excess protons ( $\text{H}^+$ ) which results in a localised drop in pH. This limits alpha phase corrosion and so the  $\text{Cu}^{2+}$  ion concentration no longer continues to increase. The increasingly acidic environment now favours corrosion of the kappa III phase (e.g. between 140 - 175 h), thus the relative concentrations of other metal ions (particularly iron and nickel) become gradually more prevalent in the crevice microenvironment. Throughout these processes, chloride ions from the bulk electrolyte migrate into the crevice to maintain electrical.

**4 Conclusions:** Screen-printed platinum electrodes have proved to be a useful analytical tool for monitoring crevice corrosion: measuring the time dependant concentration profiles of corrosion products will help to develop a model for how crevice corrosion processes initiate and evolve, which in turn will help in the development of appropriate remediation strategies.

#### Acknowledgements

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#### References

- [1] J.A. Wharton and K.R. Stokes, "Analysis of nickel-aluminium bronze crevice solution chemistry using capillary electrophoresis", *Electrochemistry Communications*, vol. 9, pp. 1035-1040, 2007.