Application Area: Corrosion

Coulometric Reduction as per ASTM B825

Keywords

Corrosion, ASTM B825, tarnish film, reduction current.

Introduction

The ASTM B825 is used to determine the corrosion and tarnish film on metal surfaces. This is achieved by using the so-called cathodic reduction method, which is a constant-current coulometric method [1].

Usually, the test is applied on control coupons, tarnished by gaseous environmental tests. A reduction current density of $-50\ \mu A\ cm^{-2}$ is applied, and the potential is recorded.

The horizontal potential steps in the voltage versus time plot correspond to different reduction potentials. The final potential step is due to the reduction of hydrogen ions in the solution, and it represents a limit beyond which no further reduction process can occur at higher potentials.

From the voltage versus time plot, the different corrosion processes that have taken place to produce the surface films can be detected. Furthermore, calculations can be made to get the amount of charge responsible of the reduction process at that particular voltage.

In this way, it is possible to detect the individual components of the total tarnish film. This allows comparing different corrosive properties of different environmental chambers, or different tests within the same chamber.

Experimental Setup

The sample under investigation was a double-sided tarnished copper specimen. The area was calculated as being $19\ cm^2$

As counter electrode, a platinum sheet electrode was employed. Finally, an Ag/AgCl 3 mol/L KCl reference electrode completed the cell.

An aqueous solution of 0.1 mol/L KCl solution was used as electrolyte.

A Metrohm Autolab PGSTAT302N together with a Metrohm Autolab 1 L corrosion cell were used for the measurement (Figure 1).

Figure 1 – The Metrohm Autolab 1 L corrosion cell.

For this experiment, the sample was placed inside the cell without the sample holder delivered with the 1 L corrosion cell.

To remove the oxygen dissolved in the electrolyte, nitrogen gas was bubbled into the solution for one hour during the preparation, and then the nitrogen flow was kept above the solution during the measurement.

After one hour of bubbling, the reduction current relative to the $-50\ \mu A\ cm^{-2}$ current density was calculated and applied to the cell. In this case, since the sample area was $19.2\ cm^2$, a current of $-960\ \mu A$ was applied.

A potential cutoff was added, to stop the measurement when the potential reaches the hydrogen evolution potential. If such potential was not reached, the procedures stopped when the reduction could proceed at a reasonable rate of not more than 4 to 6 h for the total reduction time.

Results and Discussion

In Figure 2, the potential versus time plot is shown.

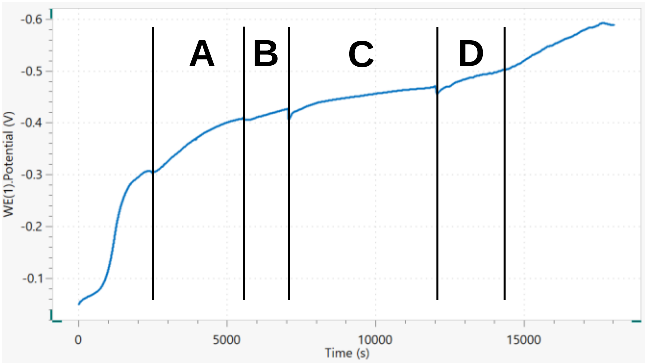

Figure 2 – The potential vs. time plot of a tarnished copper sample in KCl 0.1 mol/L, under nitrogen atmosphere. The letters refer to the plateaus.

Here, different plateaus can be seen. Each plateau is an indication of an oxidation product in the tarnish film.

The plateaus are from approx. 2500 s to 5500 s (A), from 5500 s to 7000 s (B), from 7000 s to 12000 s (C), and from 12000 to 14500 s (D).

The measurement stopped after 18000 s, i.e., 5 hours.

The quantity of charge reduced at the plateaus can be calculated according to the following Equation:

$$q = |it| \tag{1}$$

Where the charge $q\ (C)$ is calculated as the product of the current $i\ (A)$ and the time $t\ (s)$. Each value of calculated charge is related to the amount of the oxidation product, while the type of oxidation product is related to the potential at which the plateau occurs.

The following Table shows the charge values for each plateau.

Table 1 - Charge value for each plateau of Figure 2.

Plateau	Charge (C)
A	2.88
B	0.96
C	4.8
D	2.4

Also, the mass $W\ (\mu g)$ of a known substance can be calculated, as shown in Equation 2 below.

$$W = 10^3 it \frac{M}{NF} \tag{2}$$

Where $i\ (mA)$ is the current, $t\ (s)$ is the time to reduce the substance, $M\ (g\ mol^{-1})$ is the gram-molecular weight of the oxidation product (i.e., the weight of one mole of substance), N is the number of Faradays (equivalents) required to reduce one gram-molecular weight of the oxidation product, (M/N is the equivalent weight), and $F\ (= 96485\ C\ mol^{-1})$ is the Faraday constant.

The sample thickness $T\ (\text{Å})$ can be calculated (Equation 3):

$$T = it \frac{K}{a} \tag{3}$$

Where $i\ (mA)$ is the current, $t\ (s)$ is the time to reduce the substance, $a\ (cm^2)$ is the area, and $K\ (cm)$ is a conversion factor, given by Equation 4:

$$K = 10^5 \frac{M}{NFd} \tag{4}$$

Where $M\ (g\ mol^{-1})$ is the gram-molecular weight of the oxidation product, N is the number of Faradays required to reduce one gram-molecular weight of oxidation product, $F\ (= 96485\ C\ mol^{-1})$ is the Faraday constant, and $d\ (g\ cm^{-3})$ is the density of the substance being reduced.

Since the oxidation products forming the tarnish were not identified in the scope of this application note, the weight and thickness calculations could not be performed.

Conclusions

In this application note, a procedure to replicate the ASTM B825 is shown. The ASTM B825 is used to determine the corrosion and tarnish film on metal surfaces. A constant reduction current is applied to a tarnished metal sample, with the help of a Metrohm Autolab PGSTAT302N and a Metrohm Autolab 1 L corrosion cell.

The potential vs time plot shows the presence of four plateaus, which indicate four oxidation products being formed in the tarnish film.

With the help of the NOVA software, the charge relative to each plateaus is calculated, giving an indication of the amount of each oxidation product.

References

[1] ASTM B825-13, Standard Test Method for Coulometric Reduction of Surface Films on Metallic Test Samples, ASTM International, West Conshohocken, PA, 2016 www.astm.org.

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.