ABSTRACT

The technique of mapping pairs of parameters is described as a method for the evaluation of the ability of those parameters to discriminate the type and rate of corrosion. The standard deviations of potential and current are able to achieve this discrimination for the dataset studied. Skew and kurtosis do not provide useful discrimination.

Keywords: Electrochemical noise; standard deviation; skew; kurtosis; map

INTRODUCTION

A number of approaches have been proposed for the identification of the type and rate of corrosion from electrochemical noise (EN) data. These have been reviewed elsewhere, and a number of studies have attempted to assess the reliability of the various methods that have been proposed (although there is a need for more such work covering a wider range of corrosion systems). In this paper we are concerned with techniques that can be used in practical corrosion monitoring applications. In this context monitoring methods must produce relatively simple outputs, such that interpretation does not require expert knowledge (more sophisticated techniques may well have application when there are indications of a corrosion problem and further investigation is required). For this reason this paper focuses on the simpler statistical analysis techniques, and proposes a data analysis method that appears to offer the required simplicity and clarity.
BACKGROUND

At best (because the standard error increases rapidly for parameters of higher order) four independent statistical parameters can be derived from an EN time record. These can be expressed in various ways, with the purest expression being as the first four statistical moments. However, it is more normal to use the following set:

- Mean
- Standard deviation
- Skew or skewness
- Kurtosis or normalized kurtosis

It may be necessary or desirable to perform trend removal, filtering or other operations before determining these parameters, but these operations do not fundamentally change the nature of the parameters, and they will not be considered further here. The mean potential is clearly a material dependent value, while the mean current has an expected value of zero, so these are not considered further here. Each of the remaining parameters can be derived for both potential and current noise, leading to a total of six parameters.

Having obtained these six parameters the problem is then to decide how to extract useful information about the type and rate of corrosion. Previous work has discussed this problem, and a number of approaches have been proposed by various authors (see reference 1 for a review). The rate of corrosion is generally accepted to be given reasonably reliably by the electrochemical noise resistance, the standard deviation of potential divided by the standard deviation of current.

PARAMETER MAPPING

Various parameters have been proposed to provide information about the type of corrosion, including:

- The coefficient of variation (the standard deviation of current divided by the mean current)
- The localization index (the standard deviation of current divided by the rms current)
- The pitting factor (the standard deviation of current divided by an estimate of $i_{\text{corr}}$)
- The characteristic charge (the charge in each event, assuming a shot noise process)
- The characteristic frequency (the frequency of events, assuming a shot noise process)
- The skewness of current
- The skewness of potential

A more general approach to the problem would be to produce a multi-dimensional map of the type of corrosion as a function of the six measurable parameters. This approach leads to the concept of using neural network methods to translate from the statistical parameters to indicators of the type of corrosion. Unfortunately there are not really sufficient well-defined data sets available to train such networks. Furthermore, it is hard to place reliance on a modeling process that is difficult to visualize. For this reason a slightly simpler approach is examined here, whereby pairs of parameters are correlated by means of a 2-dimensional map. Every data point available is plotted on the map at an x-y location corresponding to the values of two of the available parameters. By color coding the points according to the type of corrosion, is it then easy to see how well the particular pair of parameters discriminate between the types of corrosion (in the printed version of this paper it has been necessary to black and
white graphs, which has restricted the clarity of the discrimination, but the file on CD-ROM should display some color, which may make the discrimination clearer)

The data set used is that produced by Al-Mazeedi, based on steel in two systems, nitrite / chloride and CO₂ / NaCl / thioacetamide. The details of the experimental method are given elsewhere², which also presented the parameter map for the derived parameters \( R_n \) and \( f_n \). The latter is reproduced in Figure 1 for comparison purposes. By adding or removing the inhibitive species (nitrite or thioacetamide) the corrosion behavior was varied between uniform (shown as pink/gray squares) and localized (shown as black crosses) and inhibition (shown as blue/dark gray triangles).

RESULTS

Figures 2 to 12 present the parameter maps for some of the 15 possible combinations of the six statistical parameters (combinations that are not plotted have been examined, and show no indication of any discrimination ability).

It can be seen that only the maps involving the standard deviations of potential and current show any indication of discrimination between the different types of corrosion, with the map of the two standard deviations giving a relatively good separation of the various corrosion types. Thus it can be concluded that, at least for these data sets, the skew and kurtosis do not contain significant information on the type of corrosion.

Considering the map of standard deviation of potential and standard deviation of current, it can be seen that it appears similar in discrimination ability to that for \( R_n \) vs \( f_n \). This is because the two maps (when plotted on log-log scales) are simple transformations of each other. Thus the map of \( R_n \) vs \( f_n \) can be considered as a method of representing the standard deviation data with axes that have a rather more meaningful interpretation.

CONCLUSIONS

Parameter maps provide an effective method of looking for pairs of electrochemical noise parameters that permit the discrimination of the type or rate of corrosion.

Of the basic statistical parameters (the standard deviation, skew and kurtosis of the potential and current noise), only the standard deviations provide useful discrimination for the datasets studied.

Owing to the convertibility of the standard deviation parameter pair and the \( R_n / f_n \) pair, the two maps contain essentially the same information, and it is a matter of preference as to which map to use.

REFERENCES

FIGURES

FIGURE 1 Parameter Map – Electrochemical Noise Resistance, $R_n$, vs Characteristic Frequency, $f_n$ [in this and subsequent figures pink/light gray squares correspond to uniform corrosion, black crosses correspond to pitting corrosion and blue/dark gray triangles correspond to inhibition/passivation]
FIGURE 2 Parameter Map – Standard Deviation of Potential vs Standard Deviation of Current

FIGURE 3 Parameter Map – Skew of Current vs Standard Deviation of Current
FIGURE 4 Parameter Map – Kurtosis of Current vs Standard Deviation of Current

FIGURE 5 Parameter Map – Kurtosis of Potential vs Standard Deviation of Current
FIGURE 6 Parameter Map – Skew of Current vs Standard Deviation of Potential

FIGURE 7 Parameter Map – Kurtosis of Current vs Standard Deviation of Potential
FIGURE 8 Parameter Map – Kurtosis of Potential vs Standard Deviation of Potential

FIGURE 9 Parameter Map – Skew of Potential vs Standard Deviation of Potential
FIGURE 10 Parameter Map – Kurtosis of Potential vs Skew of Current

FIGURE 11 Parameter Map – Skew of Potential vs Skew of Current
FIGURE 12 Parameter Map – Kurtosis of Potential vs Kurtosis of Current