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The estimation of the charge transfer resistance by graphical analysis of inclined semicircular complex impedance diagrams

L. LEMAITRE, M. MOORS, A. P. VAN PETEGHEM

Laboratorium voor Non-Ferrometallurgie, Rijksuniversiteit te Gent, B-9000 Gent, Belgium

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Recently a graphical method for the determination of the charge transfer resistance, obtained from impedance measurements, was developed. The original method was limited to perfect, semicircular Nyquist plots. Extension to inclined or depressed semicircular arcs is made possible by a few simple mathematical and graphical manipulations.

1. Introduction

Impedance techniques are increasingly applied in the evaluation of the corrosion behaviour of metals and alloys. Determination of the corrosion behaviour is possible only after measuring the impedance over a wide range of frequencies. The results are often plotted in the complex plane. The variation of the impedance with frequency is conventionally displayed as a Nyquist diagram. For very simple systems the plot results in a semicircle, the centre of which is lying on the real axis. Such a complex plane plot is shown in Fig. 1, together with its equivalent circuit. This circuit consists of two resistances, R_e and R_t, and a capacitance C_d.

As we are considering very simple cases, R_e represents the resistance of the electrolyte, R_t is the charge transfer resistance and C_d is the electrochemical double layer capacitance. Hladky and co-workers [1] developed a monitor which determines R_t from the maximum value of the phase angle, ϕ_{max}, and the corresponding value of the magnitude of the impedance, $|Z|$. The charge transfer resistance is determined using (Fig. 2).

$$R_t = 2|Z| \tan \phi_{max}. \quad (1)$$

For many corroding metals, such as iron in aqueous sulphuric acid, experimental impedance data do not conform to semicircles which have their centres on the real axis [2]. In these cases the centres are below the real axis according to the argument developed by Cole and Cole [3]. The determination of R_t can then no longer be carried out by application of the 'tangential impedance technique'.

2. Mathematical and graphical procedure

The extension of the above method to inclined semicircles follows from a consideration of Fig. 3. The value of R'_t corresponds to the diameter of the inclined semicircle; R_t is given by the chord of the semicircle [4]. Consideration of Fig. 3 yields:

$$R'_t = 2\,(|\overline{FE}| + |\overline{EC}|) \quad (2)$$

$$|\overline{FE}| + |\overline{EC}| = |\overline{DB}| + |\overline{BC}| \quad (3)$$

$$|\overline{BC}| = |\overline{EC}| \cos \phi_{max} \quad (4)$$

$$|\overline{FE}| = |Z| \tan \phi_{max}. \quad (5)$$

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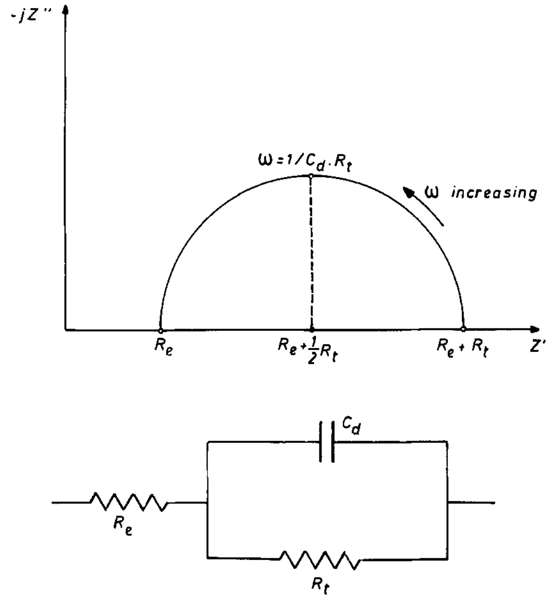

Fig. 1. Complex plane plot and equivalent circuit for systems exhibiting a very simple corrosion behaviour.

Substitution of Equations 4 and 5 in Equation 3 gives:

$$|\overline{EC}| = \frac{|\overline{DB}| - |Z| \tan \phi_{max}}{1 - \cos \phi_{max}}. \tag{6}$$

Substitution of Equations 5 and 6 in Equation 2 gives:

$$R_t' = \frac{2(|\overline{DB}| - |Z| \sin \phi_{max})}{1 - \cos \phi_{max}}. \tag{7}$$

As in the original method, developed by Hladky and co-workers, R_t' is a function of the parameters $|Z|$ and ϕ_{max}. Moreover the value of $|\overline{DB}|$ has to be known in order to determine R_t'. $|\overline{DB}|$ corresponds to the maximum value of the imaginary component of the impedance, Z''_{max}. Equation 7 can be written as

$$R_t' = \frac{2(Z''_{max} - |Z| \sin \phi_{max})}{1 - \cos \phi_{max}}. \tag{8}$$

In a similar way we are able to derive an equation for R_t. As can be seen from Fig. 3:

$$|\overline{AC}|^2 = |\overline{AB}|^2 + |\overline{BC}|^2 \tag{9}$$

$$R_t' = 2|\overline{AC}| \tag{10}$$

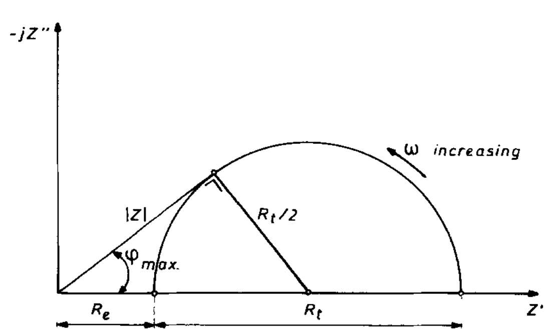

Fig. 2. Schematic representation of the graphical method to determine the charge transfer resistance of corrosion systems with semicircular impedance diagrams.

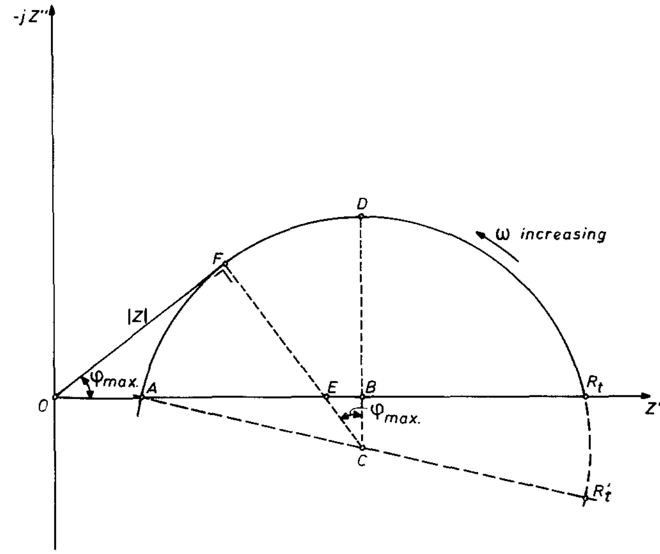

Fig. 3. Schematic representation of the graphical method to determine the charge transfer resistance of corrosion systems with inclined semicircular impedance diagrams.

$$R_t' = 2(|\overline{BC}| + Z''_{max}) \quad (11)$$

$$R_t = 2|\overline{AB}|. \quad (12)$$

Substitution of Equations 10, 11 and 12 in Equation 9 gives:

$$R_t = 2[Z''_{max}(R_t' - Z''_{max})]^{1/2}. \quad (13)$$

Finally, substitution of Equation 8 in Equation 13 gives:

$$R_t = 2\left[\frac{Z''_{max}(Z''_{max} + Z''_{max}\cos\phi_{max} - 2|Z|\sin\phi_{max})}{1 - \cos\phi_{max}}\right]^{1/2}. \quad (14)$$

3. Application to experimental results

Impedance measurements on a conventional dental amalgam (Fluor Alloy, Dentoria) in a

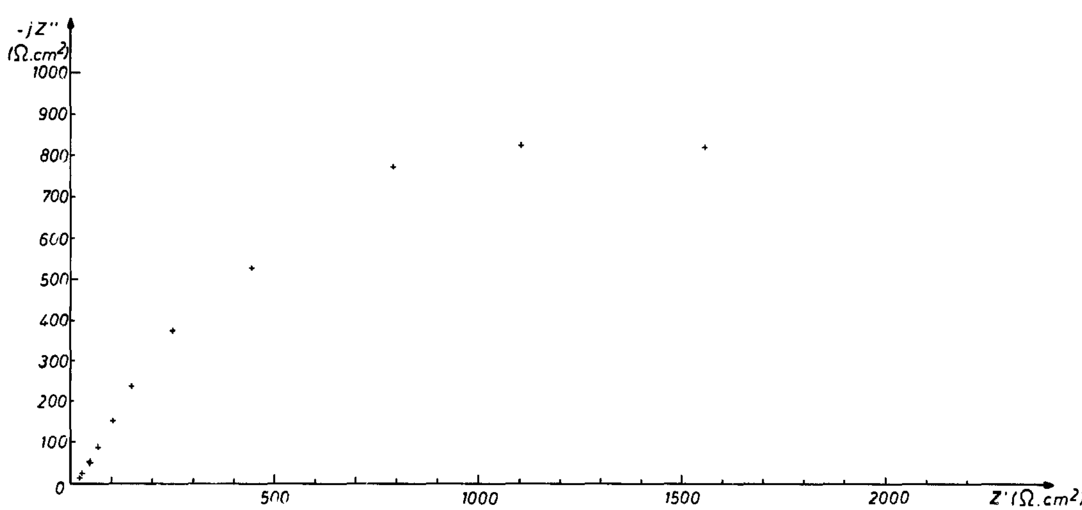

Fig. 4. Complex plane plot of a conventional dental amalgam (Fluor Alloy, Dentoria) in a 0.1 mol dm^{-3} NaCl solution after 24 h at a polarization potential of −250 mV (vs SCE).

0.1 mol dm^{-3} NaCl solution were carried out over a wide range of frequencies. The results are shown in Fig. 4. The high frequency part of the complex plane plot has the shape of an inclined semicircular arc [5]. In order to check the practical importance of our mathematical and graphical approach, the charge transfer resistance (R_t) was determined by means of Equations 1 and 14. The values for the parameters ϕ_{max}, $|Z|$ and Z''_{max} can be calculated using the experimental data

$$\begin{aligned} \phi_{max} &= 58.2° \\ |Z| &= 282.7\,\Omega\,cm^2 \\ Z''_{max} &= 829.4\,\Omega\,cm^2. \end{aligned}$$

After substitution in the formulae for R_t, $R_t = 911.9\,\Omega\,cm^2$ according to Equation 1 and $R_t = 2347.8\,\Omega\,cm^2$ according to Equation 14 is obtained.

Visual inspection of Fig. 4 shows that a good approximation for the value of the charge transfer resistance is obtained by application of the formula derived here.

4. Conclusion

Determination of R_t by graphical analysis as developed by Hladky and co-workers is possible only for very simple systems. If some mathematical and graphical operations are applied, the method can be used for semicircles with their centre lying below the real axis. In addition to $|Z|$ and ϕ_{max}, the maximum imaginary value of the impedance (Z''_{max}) has to be measured before R_t can be calculated.

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