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Electrochemical impedance spectroscopy as a valuable monitoring technique for various forms of corrosion

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Even with many fundamental advantages over other electrochemical techniques, electrochemical impedance spectroscopy remains difficult to use for field corrosion monitoring. In order to bridge the gap between the crude world of field corrosion testing and carefully planned laboratory experiments involving sophisticated instrumentation and expertise, a few simplifications are required. A reduction in the instrumental complexity of this technique can be achieved by firstly optimizing the number of frequencies needed to perform valid measurements. The statistical validation of an RC model from a limited number of data points can be achieved by systematically permutating the three data points which are chosen to extrapolate the centres of semicircular impedance diagrams. Typical results obtained with various systems (Cu–Ni against sea water, carbon steel against inhibited or uninhibited electrolyte) are presented and discussed.

1. Introduction

Electrochemical impedance spectroscopy (EIS) has been very successfully applied to study a multitude of systems [1]. The original work published by Epelboin and co-workers [2] on the system iron–H_2SO_4–propargylic acid has stimulated interest in the use of these techniques for the determination of polarization resistances. While rapid and accurate methods for measuring corrosion rates are of tremendous importance, the difficulties in the interpretation of a.c. impedance data [3] have overshadowed its numerous unique advantages [4]. Serious investigators have even come to the limiting conclusion that the method is only valid for uniform corrosion problems [5].

A method was recently developed which consisted of geometrically finding the centre of an arc formed by three successive data points on a complex impedance diagram [6] which could be successfully applied to study some specific erosion corrosion mechanisms under highly turbulent conditions [7].

This geometric analysis technique was further developed by permutating the limited number of data points thus creating a statistically valid population of arc centres, which are in turn proportional to half R_p's (polarization resistances) according to the Stern Geary approximation. This objective analysis of obtained results revealed subleties not easily accessible otherwise. The systematic analysis of a.c. impedance diagrams obtained with various alloys exposed to different environments has permitted the establishment of a strong correlation between two fundamental characteristics of these diagrams and the propensity of the alloys to suffer from a localized form of corrosion.

Both the relative deviation of permuted R_p's from their respective calculated mean and the depression angle formed between the abscissa and the projected arc centre appear to be intrinsic attributes of the systems investigated, independently of hydrodynamic or passivation film conditions.

2. Experimental details

2.1. *Copper alloys*

Four different alloys were used in this study: a 70–30 Cu–Ni modified with 0.4% Nb, a 70–30 Cu–Ni modified with 2.1% Cr, a more standard 90–10 Cu–Ni and a 90–10 Cu–Ni produced by compacting such an alloy powder prepared by a rapid transformation process [8, 9]. Cylindrical specimens of these alloys were polished to 500 grit then washed with a good degreasing agent, methylene chloride, rinsed with reagent grade acetone before being immersed in an aerated saline (3% NaCl) solution for ten days. This pretreatment procedure is similar to the method proposed by Dobb *et al.* [10]. Macdonald *et al.* [11] have shown that the corrosion potential reaches a stable value after 5 days, indicating a steady state in the film formation. The electrochemical measurements following that initial preparation were made in a two electrode configuration using a set-up described elsewhere [7] (a.c. current peak to peak $< 1\ \mu A\ cm^{-2}$). At least five consecutive measurements were taken at each

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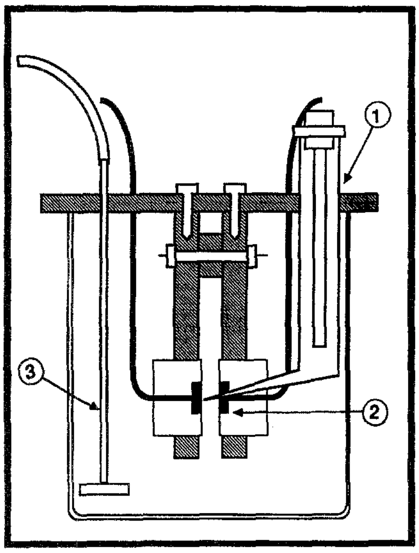

Fig. 1. Schematic representation of the corrosion cell containing (1) a reference calomel electrode; (2) steel specimens; (3) gaz purge.

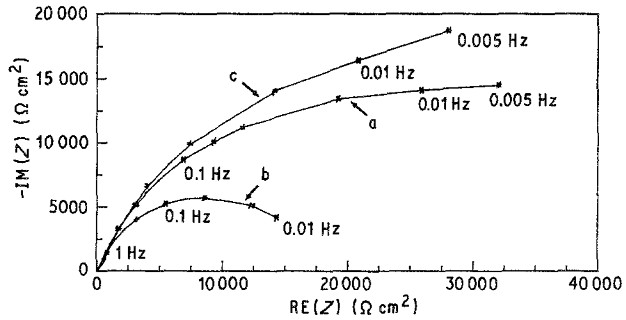

Fig. 2. Impedance diagrams made on a 10-day passivated 70–30 Cu–Ni alloy containing niobium (a) in a quiescent condition; (b) after 8 h of rotation at 5000 rpm; (c) in a quiescent condition 16 h after the rotation period.

frequency to ensure the stability of the system being studied.

2.2. *Carbon steels*

A schematic representation to make similar measurements with 1020 C–steels is shown in Fig. 1. The polished steel specimens were immersed in a two litre beaker cell containing 3% NaCl and/or 1.2% Na-molybdate. The cell was equipped with a nitrogen purge and a SCE reference brought in close electrolytic proximity to the steel specimens by a Luggin capillary. The metallographically mounted specimens separated by 2.5 mm were kept in a stable parallel position with plastic screws. A primer adequate for sea water applications (International Paint Ltd 1-GP-122) was used to mask the specimens perimeter in order to prevent any crevice formation.

2.3. *Impedance data analysis*

A software technique was developed to analyse the a.c. impedance measurements for their deviation from the semicircles of a Nyquist representation. It is well known that an electrical equivalent circuit is required to model an electrochemical interface and access the various parameters that govern its response to a.c. perturbations. Assuming that a simple RC circuit validly represents a metallic surface exposed to electrolytic corrosion, it is possible to obtain the polariztion resistance (R_p) by finding the arc diameter of an impedance plot. The classical Stern Geary approximation can then serve to transform these R_p's into corrosion rates. Because the adherence to this simple model is often limited to only a few data points (frequencies), the interpretation of experimental curves can be complex and at best semi-quantitative. In order to overcome this serious limitation, a three point geometrical extrapolation technique presented elsewhere [6] was further developed which systematically permutes data points to calculate the projected arc centres.

By first discarding the projections that do not fit the RC model and fall in the second and third quadrants of a Nyquist plot, it becomes relatively simple to statistically calculate means and standard deviations for both R_p's and depression angles. These two fundamental parameters of impedance patterns can in turn be related to the system properties.

3. Results

Figures 2 and 3 represent two series of measurements made respectively with a 70–30 Cu–Ni alloyed with 0.4% Nb and a 70–30 alloyed with a 2.1% Cr. Rotating these prepassivated alloys seems to temporarily cause a decrease of their polarization resistance which eventually comes back to initial good values after a few hours of rest. The corrosion resistance of the 70–30 alloyed with Nb seems even to be improved by such a treatment. Table 1 summarizes the results calculated systematically from the large number of projected centres obtained by permuting data points of individual curves presented in Figs 2 and 3. While the results corresponding to the 70–30 Cu–Ni alloyed with Nb correlate well with the visual examination of curves 2a, 2b and 2c, the high standard deviation (S_R) calculated for the mean of centres projected from curve 3a indicates a difficulty in testing that alloy. This behaviour was reproduced for many specimens of the same cast sample.

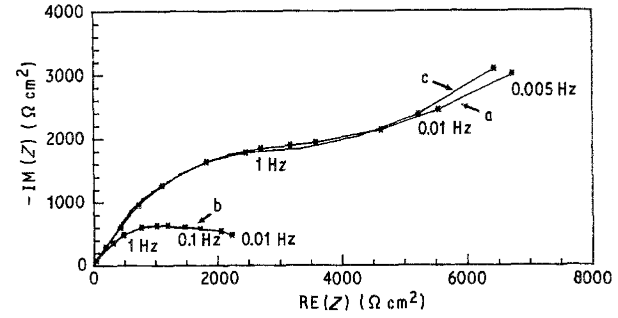

Fig. 3. Impedance diagrams made on a 10-day passivated 70–30 Cu–Ni alloy containing chromium: (a) in a quiescent condition; (b) after 8 h of rotation at 5000 rpm; (c) in a quiescent condition 16 h after the rotation period.

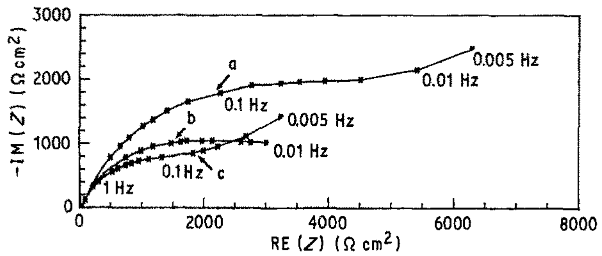

Fig. 4. Impedance diagrams made on a 10-day passivated 90–10 Cu-Ni alloy (a) in a quiescent condition; (b) after 8 h of rotation at 5000 rpm; (c) in a quiescent condition 16 h after the rotation period.

Another interesting characteristic also revealed during the analysis of curves of Figs 2 and 3 is the major difference between the steadily low depression angles observed for the 70–30 with Nb (22°–24°) and the higher angles (33°–37°) calculated for the patterns belonging to the 70–30 with Cr.

Two more series of measurements are presented in Figs 4 and 5. These correspond respectively to impedance plots produced with a prepassivated standard cast 90–10 Cu-Ni and a 90–10 Cu-Ni compacted from rapidly solidified powder. The lower polarization resistances calculated for these alloys is usually explained by their smaller percentage of nickel, an easily passivated element. Table 2 resumes the results of averaging the projected centres corresponding to the curves obtained in Figs 4 and 5. The standard 90–10 Cu-Ni exhibits a behaviour similar to that observed for the previous patterns i.e. a temporary decrease of the polarization resistance during the rotation period followed by a relaxation to higher values after a period of rest. Again the standard deviations and depression angles calculated for the three curves of Fig. 4 seem to be fairly constant characteristics of the system itself.

The measurements made with rapidly transformed 90–10 Cu-Ni specimens show fundamental differences in the passivation mechanism when compared to cast samples measurements. While the a.c. impedance pattern obtained with a prepassivated specimen before applying any rotation (Fig. 5a) fits an RC model reasonably well (S_R = 7%) rotating it seems to affect it more permanently than it does to more standard Cu-Ni alloys, as indicated in the calculated results presented in Table 2.

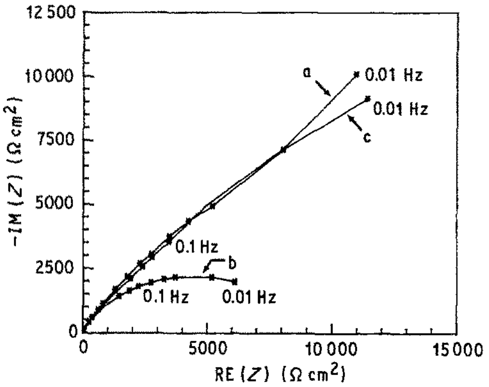

Fig. 5. Impedance diagrams made on a 10-day passivated 90–10 Cu-Ni produced by compacting an RST powder (a) in a quiescent condition; (b) after 8 h of rotation at 8000 rpm; (c) in a quiescent condition 16 h after the rotation period.

Figures 6 and 7 illustrate some typical impedance patterns obtained when freshly polished C-steel specimens were exposed to a deaerated (Fig. 6) or aerated (Fig. 7) environment. The analysis by permutation of data points contained in curves 6a, 6b and 6c (Table 3) confirms the visually obvious fact that these curves are close to being part of perfect circles. In the presence of an inhibited solution (6a) the steel surface has a very high impedance that is drastically decreased by adding salt to the solution. When the same steel is exposed to a deaerated solution (6c) containing only 3% NaCl its surface is even less depassivated. While the absolute R_p values are different in these three experiments it should be noted that both the standard deviation and the depression angles calculated for these curves are nearly constant ($S_R \sim 5\%$ and depression angle $\sim 15°$). The microscopic inspection of samples exposed to these conditions revealed the uniform nature of corrosion attack in all these cases.

The presence of oxygen in the same electrolytes can drastically change the behaviour of the steel. After only a brief exposure to an aerated 3% NaCl solution the unprotected steel surface becomes rusty in this neutral environment. The data obtained with steel specimens in contact with aerated electrolytes had to be normalized in order to present them in one figure. Figure 7 contains data, corresponding to three different experiments, which have been reduced to a common relative scale by dividing them by their respective

Table 1. Results of the analysis of projected centres obtained by permuting impedance data points for two types of 70–30 Cu-Ni alloys prepassivated in 3% NaCl

Type	*Curve*	*Surface velocity* ($m\,s^{-1}$)	R_p ($k\Omega cm^2$)	S_R (%)	*Depression angle (degree)*
+0.4% Nb	2a	0	47	18	24
	2b	3.1	19	6	22
	2c	0	55	14	22
+2.1% Cr	3a	0	31	70	33
	3b	3.1	11	6	37
	3c	0	43	20	37

Table 2. Results of the analysis of projected centres obtained by permuting impedance data points for two types of 90–10 Cu-Ni alloys prepassivated in 3% NaCl

Type	*Curve*	*Surface velocity* ($m\,s^{-1}$)	R_p ($k\Omega cm^2$)	S_R (%)	*Depression angle (degree)*
Standard	4a	0	7.2	24	26
	4b	3.1	2.7	9	31
	4c	0	8.0	20	29
Rapidly transformed	5a	0	6.2	7	22
	5b	3.1	3.6	10	25
	5c	0	2.8	15	25

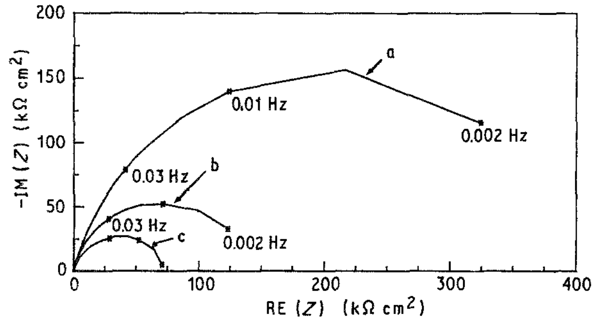

Fig. 6. Impedance diagrams made with 1020 C-steel specimens exposed to a deaerated solution containing (a) 1.2% Na-molybdate; (b) 1.2% Na-molybdate + 3% NaCl; (c) 3% NaCl.

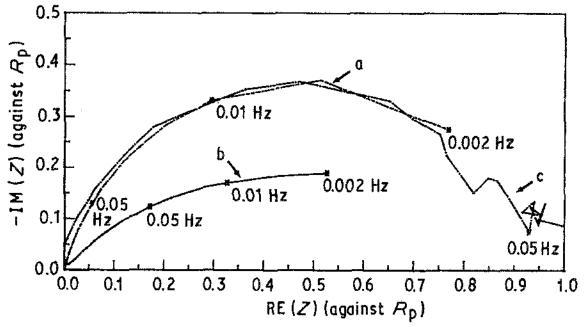

Fig. 7. Impedance diagrams made with 1020 C-steel specimens exposed to an aerated solution containing (1) 1.2% Na-molybdate; (b) 1.2% Na-molybdate + 3% NaCl; (c) 3% NaCl.

calculated R_p's. In the presence of an aerated solution containing 1.2% Na molybdate (Fig. 7a), the steel remains quite passive and corrodes uniformly quite slowly. Both the relative standard deviation (5%) and the depression angle (13°) calculated by permuting data points of curve 7a remain low.

On the other hand, it is impossible to distinguish, with such a representation, curves corresponding to an exposure to either an aerated solution containing 1.2% Na molybdate or one containing 3% NaCl. In the later case corrosion has become very rapid but remains uniform. The calculated results corresponding to these experiments are presented in Table 4 where it can be seen that for an exposure to 3% NaCl the steel is roughly two hundred times less passive than when it is exposed to 1.2% Na molybdate. But it can also be observed that the calculated standard deviation (3%) and depression angle (15°) for a steel surface exposed to 3% NaCl remain small.

By exposing the steel specimens to an aerated solution containing 1.2% Na molybdate and 3% NaCl it is possible to keep the metallic surface partially protected and slow down the corrosion processes thus simulating conditions favourable to the occurrence of localized pitting corrosion. The typical shape of curves when pitting corrosion is dominant is illustrated in Fig. 7b where a generally depressed pattern can be observed. This is translated into a high calculated depression angle (41°) but with a standard eviation still very low (6%) indicating a good agreement to the circular pattern associated with the simple RC model.

In another series of experiments crevice corrosion conditions were simulated by neglecting to apply the protecting layers of primer on the edge of the steel specimens. A typical pattern of impedance measurements obtained in these cases is illustrated in curve 7c where it can be seen that both ends of the impedance spectrum are affected. While the high frequency data points cross over to negative resistance values, the low frequency measurements become erratic and unreliable. The calculations made by permuting data points of curve 7c translate these discontinuities into a large relative standard deviation (35%) accompanied by an also large depression angle (30°).

4. Conclusion

Whether the corrosiveness of a system is known or only suspected, the monitoring techniques available are all useful tools for determining corrosiveness, defining the corrosion mechanism, establishing corrosion rates, tracking a corrosion control program and optimizing chemical treatment expenditures. An effective corrosion-monitoring program should make use of numerous monitoring techniques in order to reduce downtime and lost production, optimize chemical treatment expenses of control programs, and reduce capital expenditures by extending the life of existing production equipment [12]. The results of two surveys of users of corrosion monitoring equipment showed up a serious desire to be able to monitor the occurrence and location of pitting or other localized corrosion problems [13].

The results presented in this paper indicate that the symptoms of non-adherence to a perfect RC model by electrochemical impedance data are very rich in infor-

Table 3. Results of the analysis of projected centres obtained by permuting impedance data points for a 1020 carbon steel exposed to deaerated electrolytes

Solution	E_{corr} (*mV vs SCE*)	R_p ($k\Omega cm^2$)	S_R (*%*)	*Depression angle (degree)*
3% NaCl	−740	140	7	16
1.2% Na molybdate	−420	840	4	15
3% NaCl + 1.2% Na molybdate	−740	260	3	13

Table 4. Results of the analysis of projected centres obtained by permuting data points for a 1020 carbon steel exposed to aerated electrolytes

Solution	E_{corr} (*mV vs SCE*)	R_p ($k\Omega cm^2$)	S_R (*%*)	*Depression angle (degree)*
3% NaCl (uniform)	−680	4	3	15
3% NaCl (crevice)	−730	12	35	30
1.2% Na molybdate	−100	640	5	13
3% NaCl + 1.2% Na molybdate	−550	8	6	41

mation concerning the types of corrosion processes occurring on a metallic surface. The analytical method developed to reveal these fundamental characteristics of impedance patterns is not only sound in terms of scientific calculations but it would be easily implemented by a pocket programmable calculator.

The permutation of impedance data points used to project the centre of an arc in Nyquist plots permits an operator to qualitatively distinguish between:

- general and intergranular erosion corrosion
- uniform and pitting corrosion
- crevice and any other type of corrosion attack

The quantification of these localized processes would still require a serious standardization effort before the technique could produce meaningful numbers related to pitting rates or pitting depths, but before that can be attempted the most important aspect of corrosion monitoring has to be addressed, i.e. the positioning and sizing of probes in the system being monitored.

References

[1] R. L. Zeller III and R. F. Savinell, *Corros. Sci.* **26** (1986) 591.

[2] I. Epelboin, M. Keddam and H. Takenouti, *J. Appl. Electrochem.* **2** (1972) 71.

[3] W. J. Lorenz and F. Mansfeld, *Corros. Sci.* **21** (1981) 647.

[4] C. F. Britton and B. C. Tofield, *Mat. Performance* **27** (1988) 41.

[5] D. C. Silverman and J. E. Carrico, *Corrosion* **44** (1988) 280.

[6] P. R. Roberge and R. Beaudoin, *J. Appl. Electrochem.* **18** (1988) 38.

[7] *Idem, ibid.* **18** (1988) 601.

[8] S. H. Lo, W. M. Gibbon, R. S. Hollingshead and S. Corbin, 'Materials and Design', Scientific and Technical Press Ltd, Surrey, G.B. VIII (1987) p. 1.

[9] S. H. Lo, W. M. Gibbon and R. S. Hollingshead, *J. Mater. Sci. Lett.* **6** (1987) 441.

[10] D. E. Dobb, J. P. Storvick and G. K. Pagenkopf, *Corros. Sci.* **26** (1986) 525.

[11] D. D. Macdonald, B. C. Syrett and S. S. Wing, *Corrosion* **34** (1978) 289.

[12] C. K. Walker and G. C. Maddux, *Mat. Performance* **28** (1989) 64.

[13] C. F. Britton and B. C. Tofield, *U.K. Corrosion 85*, Harrogate, G.B. (1985).