STUDY OF CORROSION IN STEEL SCULPTURES BY MEANS OF SOLID STATE VOLTAMMETRY AT PARAFFIN-IMPREGNATED GRAPHITE ELECTRODES

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ABSTRACT: *Solid-state voltammetry is used for studying the composition of corrosion products in a series of sculptures from the Contemporary Sculpture Collection of the Universidad Politècnica de Valencia (Spain). Upon attachment to paraffin-impregnated graphite electrodes, well-defined voltammetric responses were obtained upon immersion in 0.10 M HCl. A hematite with a variable degree of hydration and crystallinity, accompanied by FeO(OH) forms, is identified as the main corrosion product.*

KEYWORDS: solid state voltammetry, corrosion, iron, steel, sculpture, contemporary art

INTRODUCTION

Corrosion of metals in contact with atmospheric environments is a major cause of deterioration of sculptures, panels, and decorative pieces of artistic value. Iden tification of corrosion products, complemented with an environmental analysis, provides useful information as regards to the deterioration mechanism. Corrosion products are usually identified by means of X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), Mössbauer spectroscopy and microscopical examination of the surfaces and cross sections of the corrosion layers by scanning electron microscopy/energy dispersive X-ray detection (SEM/EDX), and several electrochemical techniques involving the determination of polarisation resistance, impedance spectroscopy and electrochemical noise (Morcillo, 2004).

In addition to existing techniques, the voltammetry of microparticles can be used to analyse corrosion products and deterioration processes in metal artefacts. This methodology, developed by Scholz et al. (Scholz et al., 1998; Grygar et al, 2002), provides information on the chemical composition, structure, and granulometry of sparingly soluble solids, and uses very few micrograms, or even nanograms, of the sample.

We herein report the first results obtained by applying this methodology to a series of samples from three Corten steel Contemporary sculptures included in the collection of the Universitàt Politécnica de Valencia (Spain). Samples were taken in December 2006 as part of the annual conservation programme of the collection. The sculptures are exposed to atmospheric corrosion in different locations of the university campus (see Fig. 1), at ca.1 km from the Mediterranean sea. Corrosion of Corten steel has been studied in contact with different wet and dry environments (Jasswicz, 1968; Exel, 1977; Han et al., 2003). β-and γ-FeO(OH) have been identified as corrosion products in contact with $MgCl_2$ solutions (Li et al. (2006), while hematite (α-Fe_2O_3) and α-FeO(OH) were identified in atmospheric environments by Damian and Fako (Damian and Fako, 2000).

Solid-state voltammetry has been applied to the study of iron oxides (Mouhandess et al., 1982, 1984; Mancey et al., 1993; Encinas et al., 1994; Grygar, 1996, 1997). This voltammetry is directly related with that of iron oxide pigments (Doménech et al., 2001; Grygar et al., 2002) and iron-containing ceramic materials (Doménech et al., 2002).

EXPERIMENTAL

Iron(III) oxide (Aldrich), consisting essentially of crystalline hematite, was taken as a reference material.

Samples (ca. 100 mg) from the sculptures: a) “Vuelo” (V1; author José Luis Sánchez, 1996; dimensions: 310 x 175 x 120 cm), b) “Integración” (I1 to I6; author Marcel Martí, 1991; dimensions 400 x 460 x 270 cm), and, c) “Obelisco” (O1 to O5; author Frechilla, 1990; dimensions 540 x 60 x 40 cm) were taken from different areas of the sculptures with the help of a scalpel.

Paraffin-impregnated graphite electrodes (PIGEs) were used in the voltammetry procedure of microparticles experiments. PIGEs consisted of 5 mm diameter cylindrical rods prepared as described by Scholz et al. (1998). The samples (5-10 mg) were powdered in an agate pestle and mortar, and then placed on a glazed porcelain tile forming a spot of finely distributed material. Then the lower end of

Figure 1. “Integración” (Marcel Marti, 1991). Image taken in 1999. Calcareous crusts caused by direct irrigation with tap water can be seen in the basis of the sculpture

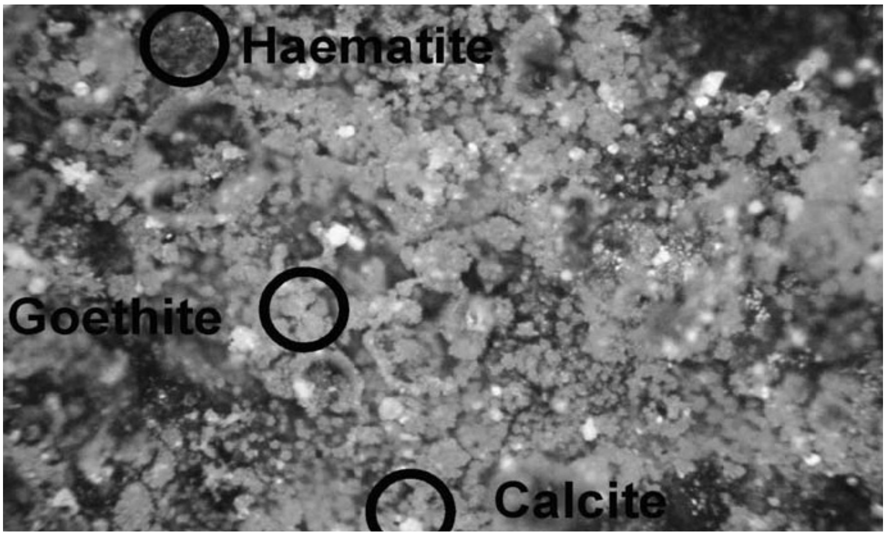

Figure 2. Microphotograph of the corrosion products formed in the sculpture “Integración”

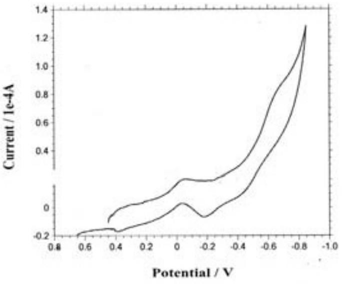

Figure 3. CV of a O1-modified PIGE immersed into 0.10 M HCl. Potential scan rate 50 mV/s

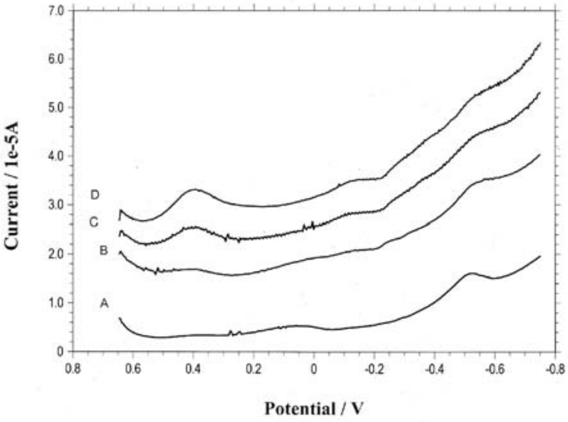

Figure 4. SQWVs of sample O1 in contact with 0.10 M HCl. Potential scan initiated at +650 mV in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency, A: 2, B: 5, C: 15, and D: 25 Hz

the graphite electrode was gently rubbed over that spot of sample and finally cleaned with tissue paper.

All electrochemical experiments were performed at 298 K after the immersion of the modified electrodes in deaerated solutions using the CH I420 equipment. A conventional three-electrode arrangement was used with a PIGE working electrode, a Pt-wire auxiliary electrode and an AgCl (3 M NaCl)/Ag reference electrode. Cyclic and square wave voltammetries (CV and SQWV, respectively) were used as detection modes.

RESULTS AND DISCUSSION

Prior experiments by means of optical microscopy (see Figure 2) and x-ray diffraction evidenced the major content in hematite as well as goethite as the main corrosion products on the steel surface. Interestingly, significant amounts of calcite were identified in the diffractograms, which is formed as a consequence of the deposition of calcium carbonate precipitated from the tap water used to irrigate the grass gardens.

A typical CV of samples is shown in Fig. 3, corresponding to sample O1. In the initial cathodic scan voltammogram, a reduction peak appears ca. -50 mV, followed by a prominent reduction wave initiated at ca. -350 mV, and overlapped with the solvent discharge occurring at -700 mV. In the subsequent anodic scan, no well-defined anodic counterparts were observed for the above electrochemical processes, so that an unique weak oxidation peak at -170 mV was recorded.

SQWV provides a more structured voltammetric profile. As shown in Fig. 4 for sample O1, cathodic peaks at ca. +380, +60, -150, -400 and -500 mV are recorded on initiating the potential scan at +650 mV in the negative direction. The peaks at +380, -150 and -400 mV are enhanced at the expense of the peaks at +50 and -500 mV when the square wave frequency is increased.

Following the previous literature on the electrochemistry of iron oxides and hydroxy-oxides (Grygar, 1996; Doménech et al., 2001; Grygar et al., 2002), the electrochemical reduction of iron oxide-based materials can be described in terms of reductive dissolution processes resulting in the formation of Fe^{2+} ions in solution, which further reduced to iron metal at potentials ca. -750 mV. The overall reduction process can be represented as follows for hematite:

$$1/2\ Fe_2O_3\ (solid) \xrightarrow[-3/2H_2O]{3H^+,\ e^-} Fe^{2+}\ (aq) \xrightarrow{2e^-} Fe\ (solid)\ (1)$$

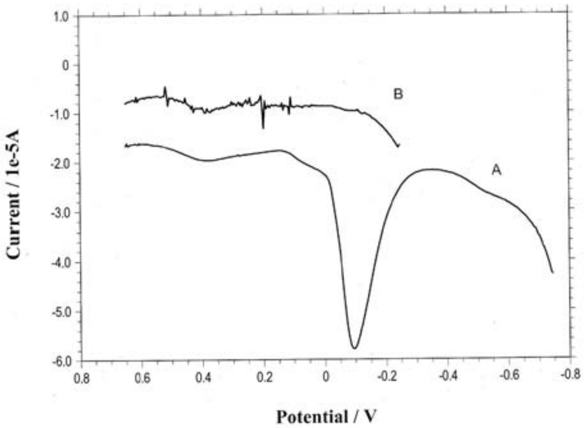

Figure 5. SQWVs of PIGEs modified with sample O1 immersed into 0.10 M HCl. Potential scan initiated at: A: -750 mV; B: -250 mV, in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

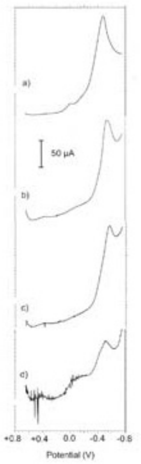

Figure 6. SQWVs of: a) hematite, and samples: b) V1, c) I2, d) O2, immersed into 0.10 M HCl. Potential scan initiated at +650 mV in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

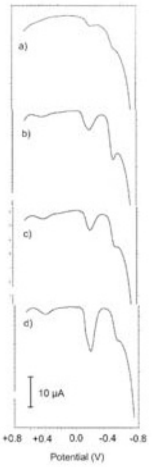

Figure 7. SQWVs of: a) hematite, and samples: b) V1, c) I2, d) O2, immersed into 0.10 M HCl. Potential scan initiated at -750 mV in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

In principle, the advance of the electrochemical reaction is determined by the pH and the presence of other chemisorbing ions and/or complexant species. The kinetics of the electrochemical process can be described on the basis of the models described by Grygar (1996, 1997). Accordingly, the rate of reductive dissolution is driven by the detachment via the ion diffusion or the complexation reaction of metal centres from the reduced metal sites on the surface of solid particles. The position and shape of the voltammetric peaks depend on the average particle size and the homogeneity of the particle size distribution, so that the wider peaks correspond to less consolidated and probably more heterogeneous iron oxide materials.

On scanning the potential in the positive direction, the voltammetric profile is seen to be highly dependent on the initial potential. As seen in Fig. 5, peaks at -480, -90, +50, and +440 mV are recorded if the potential is initiated at -750 mV. In contrast, the prominent peak at -90 mV disappears entirely if the potential is initiated at -250 mV. These features indicate that this last process can be attributed to the oxidative dissolution of iron metal previously deposited, yielding Fe^{2+} ions in solution.

A comparison of the SQWVs for hematite and samples is shown in Fig. 4. Here, the voltammetric curves for: a) hematite, and samples, b) V1, c) I2, d) O2, are depicted. Voltammograms of samples from each sculpture were similar to those represented in Fig. 6, although some minor differences appear, depending on the location of the corroded region in the sculpture.

The most relevant feature was recorded for samples I1 to I6, for which the quotient between the peak currents of processes at -480 and -540 mV ($I = i_p(-480\ \text{mV})/i_p(-540\ \text{mV})$) varied significantly from the portion of the sculpture in the E direction ($I = 0.79$) to the remaining faces (I ranging between 0.59 and 0.62). This difference can be attributed to the influence of the marine atmospheric influence so that the hydration degree of the iron oxide was larger in the area of the sculpture exposed to sea winds.

As shown in Fig. 4-A, only one prominent peak at -480 mV, preceded by a weak peak at -10 mV, is recorded in the case of hematite. Samples V1 and I2 exhibit a similar profile with a peak at +380 mV and overlapping peaks at -480 and -540 mV. These last two peaks are attributable to the reductive dissolution of hematite and hydrated hematite, whereas the peak at +380 mV must correspond to highly hydrated iron oxide forms. In the case of sample O2 however, the abovementioned peaks are accompanied by overlapping peaks at +130 and -200 mV. In agreement with prior data on iron oxide materials (Doménech et al., 2001), such peaks can be attributed to FeO(OH) forms.

On scanning the potential from -750 mV in the positive direction, significant differences appear between hematite and the different samples. Thus as shown in Fig. 7a, hematite displays only weak peaks at -540 and -150 mV. A similar response was obtained for samples I1 to I5, as illustrated in Fig. 7b, but an additional peak at +410 mV appears. In contrast, sample V1 and samples O3 to O6 exhibit two overlapping peaks at -150 and -200 mV (see Figs. 7c,d). The appearance of such peaks can be attributed to the oxidative dissolution of any Fe(II) species in the corrosion layer.

These features can be rationalised on the basis of models for steel corrosion. Following classical corrosion models, when steel surfaces are exposed to humid environments, certain surface points experience an anodic behaviour which can be represented as:

$$\text{Fe (solid)} \rightarrow Fe^{2+}\text{ (aq)} + 2e^- \quad (2)$$

Lepidocrocite (γ-FeO(OH)) is produced under the action of oxygen which can subsequently form and consume magnetite (Skerry et al., 1988):

$$4Fe^{2+}\text{ (aq)} + O_2 + 6H_2O \rightarrow 4FeO(OH)\text{ (solid)} + 8H^+\text{ (aq)} \quad (3)$$

$$Fe^{2+}\text{(aq)} + 8FeO(OH)\text{ (solid)} + 2e^- \rightarrow 3Fe_3O_4\text{ (solid)} + 4H_2O \quad (4)$$

Recent data reported by Morcillo (2004) for a wide variety of environments indicate that lepidocrocite and goethite (α-FeO(OH)) appear in lamellar and acicular structures of corrosion layers whereas magnetite is absent. This is consistent with the results of Misawa et al. (1974) who proposed a mechanism based on the redissolution of lepicocrocite and the subsequent precipitation of a hydrated oxide-hydroxyde, further converted into goethite via solid-state transformation:

$$\gamma\text{-FeO(OH) (solid)} = FeO_x(OH)_{3-2x}\text{ (solid)} \rightarrow \alpha\text{-FeO(OH) (solid)} \quad (5)$$

In the presence of high chloride concentrations however, it has been reported (North and Pearson, 1977; Stahl et al., 2003) that FeOCl and akaganeite ($Fe_{0.833}(OH)_{1.667}Cl_{0.167}$) are formed to eventually form hematite. Similarly, Walker (2001) reported that iron sulphides become unstable on recently excavated artefacts.

In the studied samples however, hematite appears as the main corrosion product. This situation parallels that described by Damian and Fako (2000) for the corrosion of Corten steel in atmospheres of various degrees of pollution in Romania.

FINAL CONSIDERATIONS

Solid-state voltammetry of samples from corrosion layers in steel sculptures in the collection of the Universidad Politècnica de Valencia provides well-defined responses. The main component of corroded layers is hematite with a variable degree of hydration, accompanied by FeO(OH) (goethite and possibly lepidocrocite).

Identification of corrosion products via solid-state voltammetry provides a rapid and efficient method for analysing the composition of corroded layers in iron and steel sculptures, and may be used in future research to monitor the degree of alteration and the conservative/restorative strategies used in the study of such pieces.

ACKNOWLEDGMENTS

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BIBLIOGRAPHY

Damian, L., Fako, R. (2000): "Weathering structural steels corrosion in atmospheres of various degrees of pollution in Romania", *Materials and Corrosion* **51**, 547-578.

Doménech, A.; Doménech, M.T.; Gimeno, J.V.; Bosch, F.; Saurí, M.C.; Sánchez, S. (2001): "Electrochemistry of iron oxide pigments (earths) from pictorial microsamples attached to graphite/polyester composite electrodes", *Analyst* **126** 1764-1772.

Doménech, A., Sánchez, S., Doménech, M.T., Gimeno, J.V., Bosch, F., Yusá, D.J., Saurí, M.C. (2002): "Electrochemical determination of the Fe(III)/Fe(II) ratio in archaeological ceramic materials using carbon paste and composite electrodes", *Electroanalysis* **14** 685-696.

Dunwald, J., Otto, A. (1989): "An investigation of phase transitions in rust layers using raman spectroscopy", *Corrosion Science* **29** 1167-1176.

Encinas-Bachiller, P., Tascón-García, M.L., Vázquez-Barbado, M.D., Sánchez-Batanero, P. (1994): "Electroanalytical study of copper and iron compounds in the solid state: application to copper ferrite characterization", *Journal of Electroanalytical Chemistry* **367** 99-108.

Exel, N. 1977. "Corrosion resistance of Corten steel", *Zelezarski Zbornik* **11** 37-40.

Grygar, T. (1996): "The electrochemical dissolution of iron(III) and chromium(III) oxides and ferrites under conditions of abrasive atripping voltammetry", *Journal of Electroanalytical Chemistry* **405** 117-125.

Grygar, T. (1997): "Dissolution of pure and substituted goethites controlled by the surface reaction under conditions of abrasive atripping voltammetry", *Journal of Solid State Electrochemistry* **1** 77-82.

Grygar, T.; Bezdicka, P.; Hradil, D.; Doménech, A.; Marken, F.; Pikna, L.; Cepriá, G. (2002): "Voltammetric analysis of iron pigments", *Analyst* **127** 1100-1107.

Grygar, T., Hradilová, J., Hradil, D., Bezdiéka, P., Bakardjieva, S. (2003): "Analysis of earthy pigments in grounds of Baroque paintings", *Analytical and Bioanalytical Chemistry* **375**, 1154-1160.

Han, W., Wang, J., Wang, Z., Yu, G., Li, H. (2003): "Atmospheric corrosion of five low alloy steels", *Fushi Kexue Yu Fanghu Jishu* **15** 315-319.

Jasswicz, L. (1968): "Field and laboratory investigation on resistance of steel products to atmospheric corrosion", *Prace Instit.ute Hutnic* **10** 226-236.

Li, Q., Wang, Z., Han, W., Han, E. (2006): "Corrosion behaviour of weathering steel in a wet/dry environment containing $MgCl_2$", *Zhongguo Fushi Yu Fanghu Xuebao* **26** 136-140.

Mancey, D.S., Shoesmith, D.W., Lipkowski, J., McBride, A.C., Noel, J. (1993): "An electrochemical investigation of the dissolution of magnetite in acidic electrolytes", *Journal of the Electrochemical Society* **140** 637-642.

Misawa, T., Asami, K., Hashimoto, K., Shimodaria, S. (1974): "The mechanism of atmospheric rusting and the protective amorphous rust on low alloy steel", *Corrosion Science* **14** 279-289.

Mouhandess, M.T., Chassagneux, F., Vittori, O. (1982): "Electrochemical behaviour of α-iron oxide using carbon paste electrodes: influence of particle size", *Journal of Electroanalytical Chemistry* **131** 367-371.

Mouhandess, M.T., Chassagneux, F., Vittori, O., Accary, A., Reeves, R.M. (1984): "Some theoretical aspects of electrodissolution of iron oxide (α-Fe_2O_3) in carbon paste electrodes with acidic binders", *Journal of Electroanalytical Chemistry* **181** 93-105.

Morcillo, M. (2004): "Atmospheric corrosion in Ibero-America, in Brillas", E., Cabot, P.-L. Eds. *Trends in electrochemistry and corrosion at the beginning of the 21st century*, Universitat de Barcelona, Barcelona 633-658.

North, N.A., Pearson, C. (1977): "Thermal decomposition of iron oxide chloride (FeOCl) and marine cast iron corrosion products", *Studies in Conservation* **72** 146-157.

Skerry, B.S., Johnson, J.B., Wood, G.C. (1988): "Corrosion in smoke hydrocarbon and sulphur dioxide polluted atmospheres-I: General behaviour of iron", *Corrosion Science* **287** 657-695.

Stahl, K., Nielsen, K., Jiang, J., Lebech, B., Hanson, J.C., Norby, P., van Lanschot, J. (2003): "On the akaganeite crystal structure, phase transformation and possible role in post-excavational corrosion of iron artefacts", *Corrosion Science* **45** 2563-2575.

Walker, R. (2001): "Instability of iron sulfides on recently excavated artefacts", *Studies in Conservation* **46** 141-152.

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Versión española

TÍTULO: *Estudio de la corrosión en las esculturas de acero por medio de la voltamperometría de estado sólido con electrodos de grafito impregnados de parafina*

RESUMEN: La voltamperometría de estado sólido se ha utilizado para estudiar la composición de los productos de corrosión en una serie de esculturas de la Colección de Escultura Contemporánea de la Universitat Politècnica de València (España). Utilizando electrodos de grafito impregnados de parafina, se obtuvieron respuestas voltamperométricas utilizando como electrolito una disolución 0.10 M HCl. La hematita con grado variable de hidratación y de cristalinidad se identifica como el producto principal de corrosión, acompañado por las especies hidratadas FeO (OH).

PALABRAS CLAVES: *voltamperometría de estado sólido, corrosión, hierro, acero, escultura, arte contemporáneo*