

Cathodic protection of a ship propeller shaft by impressed current anodes

T. Bellezze, R. Fratesi, G. Roventi

This work studies the application of cathodic protection by potentiostatic polarization method with impressed current anodes for preventing corrosion phenomena on ship propeller shafts made of 17-4PH stainless steel, in seawater. Tests were carried out on a full scale propeller system (more than 3 m long) by using one or two activated titanium wires placed lengthwise in the interspace between the shaft and the stern tube. In order to simulate ship navigation and ship berthed in harbour, flowing (40 L/min) and stagnant seawater were respectively considered. Both technical solutions, consisting in the use of one or two titanium anodes, were able to protect the shaft. The results are compared with the data reported in previous works with different types and geometries of the anode.

Keywords: Localized corrosion - Cathodic protection - Impressed current anodes - Stainless steel - Seawater

INTRODUCTION

The necessity of a high corrosion and high mechanical resistance is fundamental for stainless steels destined to naval industry. They have been studied in the past [1,2] with the purpose of eliminating the localized corrosion phenomena, responsible of the failure of the mechanical parts strongly stressed during their service life. 17-4PH, a precipitation hardened stainless steel, fulfils all the requested characteristics [3-7].

Dangerous crevice and pitting attacks were found in a relatively short time in some propeller shafts as reported in previous works [8,9]. In particular, pitting on the metallic parts subject to mechanical stresses can determine the cracks initiation with the subsequent failure. Considering the examined cases, pitting corrosion was observed in the whole surface of the 17-4PH shaft, while crevice corrosion was found in correspondence of rubber bearings, used for the installation of the shaft concentrically with AISI 304 stern tube [8].

Some authors reported in literature [10] similar corrosion phenomena on AISI 316 propeller shafts. Both this material and 17-4PH stainless steel are suitable for naval industry, but the possibility of localized corrosion has to be considered in any case.

17-4PH stainless steel is particularly prone to stress corrosion cracking, both in those conditions where hydrogen is generated (determining hydrogen embrittlement like most high resistance steel) and in seawater where the shaft failure was taken into consideration [7].

Taking into account the corrosion phenomena found on the propeller shaft, the cathodic protection is unavoidable. In previous works, the efficiency of the cathodic protection was studied in the following experimental conditions:

- 1) working with a reduced version of the full scale propeller system, protected by both impressed currents, using activated titanium anodes, and zinc sacrificial anode [8];
- 2) working with a full scale propeller system protected by sacrificial plain carbon steel anodes [9].

From these investigations, the use of zinc anode can determine an overprotection with a possible production of hydrogen, responsible of the material embrittlement [1,2]. The plain carbon steel anodes are more suitable for protecting the propeller system and for avoiding the hydrogen production [2], however the protection potential cannot be controlled and, in the case of biofilm formation, the potential of the shaft increases giving the risk of corrosion [9]. With regard to this risk, a suitable plot will be showed here for comparing the different efficiency of the old cathodic protection approach with that experimented in this work. In the present experimentation, the cathodic protection of the full scale propeller system was tested by using impressed currents supplied by activated titanium anodes, installed lengthwise in the interspace between the shaft and the stern tube, which was constituted by fiberglass in place of AISI 304. The experimentation was done in stagnant and flowing conditions by collecting seawater from the Ancona harbour.

For a better interpretation of the experimental data and

T. Bellezze, R. Fratesi, G. Roventi

*Dipartimento di Scienze e Ingegneria della Materia,
dell'Ambiente ed Urbanistica,
Università Politecnica delle Marche,
Via Brecce Bianche, 60131 Ancona.*

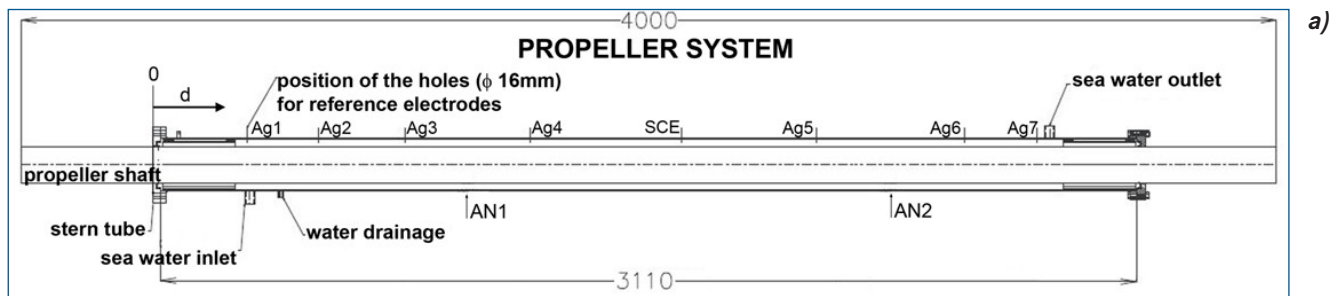


Fig. 1 - (a) Scheme of the propeller system, modified for the installation of the suitable reference electrodes (in the ϕ 16 mm holes: Ag_i = reference Ag/AgCl, $i=1, \dots, 7$; SCE = saturated calomel electrode). The activated Ti anodes are not shown. "0" is the origin for taking the distance "d" (mm) of the reference electrodes. "AN1" and "AN2" indicate the positions of the two sacrificial plain steel anodes present in a previous experimentation [9]. All measure numbers are in mm. (b) Cross section of the propeller system with the relative position of the two Ti anodes with respect to the reference electrodes.

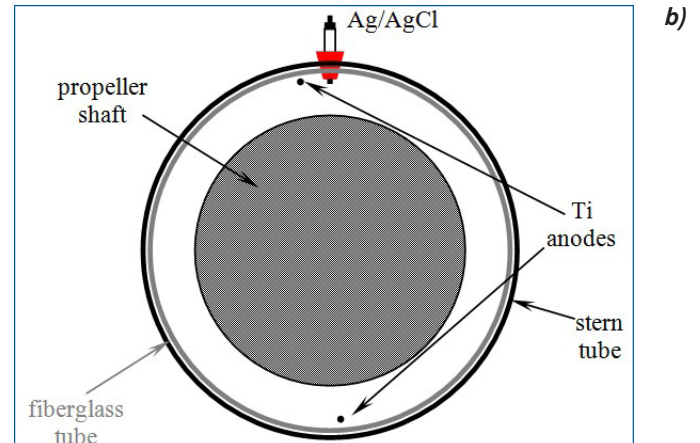


Fig. 1 - (a) Illustrazione schematica del sistema asse (cilindro al centro) e astuccio, con le modifiche per l'inserimento di opportuni elettrodi di riferimento (nella serie di fori da 16 mm: Ag_i = elettrodo di riferimento Ag/AgCl, $i=1, \dots, 7$; SCE = elettrodo di riferimento a calomelano saturo). "0" è l'origine per prendere le distanze "d" (mm) degli elettrodi di riferimento. Gli anodi di Ti attivato non sono mostrati. "AN1" e "AN2" indicano le posizioni dei due anodi sacrificali di acciaio comune presenti in una precedente sperimentazione [9]. Tutte le misure sono in mm. (b) Sezione del sistema di propulsione con la posizione relativa dei due anodi di titanio rispetto agli elettrodi riferimento.

for the optimization of the operating parameters, a computer simulation of the studied system, by means of a finite element analysis, could be a powerful technique, but this approach will be considered in future works.

EXPERIMENTAL PROCEDURE

During this experimentation, a full scale propeller system has been used [9] (Fig. 1a): a 17-4PH shaft (ϕ 115 mm; length, 4 m); an AISI 304 stern tube (ϕ 163 mm; length, 3.11 m). Along the stern tube length, 8 holes were made (Fig. 1a) in order to insert 7 Ag/AgCl/KCl saturated reference electrodes ($E = -0.035 \div -0.045$ V vs. SCE) and a SCE electrode (+0.241 V vs NHE), all suitably built and calibrated in laboratory for continuous monitoring of the potentials at different points of the system.

Before the propeller system assembly, a fiberglass tube ($\phi_{ext} = 150$ mm, $\phi_{int} = 140$ mm) was inserted in the AISI 304 stern tube in order "to substitute" this metallic part with a non-conductive one (Fig. 1b). The reasons for using this stern tube were not only to eliminate corrosion problems in this component, but also for using a new prototype, originally designed with the locations for Ti anodes. They are two activated Ti wires (ϕ 3 mm) firmly installed in the inner walls of the fiberglass tube, along the interspace between it and the propeller shaft (Fig. 1b). During the experimen-

tation, both solutions with one or two anodes were considered.

As current supplier, a potentiostat was used for setting the protection potential [8] at -0.300 V with respect to the SCE visible in Fig. 1a. From BNC I_{out} connector of the potentiostat, even the protection current was monitored.

Despite the use of different reference electrodes, all measured potentials were reported with respect to SCE.

The data logger used for potential and current monitoring and the system for collecting the seawater from the harbour mole are described in a previous work [9]. During this experimentation, in the interspace between fiberglass stern tube and 17-4PH propeller shaft, seawater was maintained stagnant or pumped at a flow rate of 40 L/min (0.13 m/sec), corresponding approximately to that of the circulating water in the propeller system during navigation.

For all tests, the potentiostat cell was initially OFF for few minutes in order to record the corrosion potentials along the shaft and the potential of Ag/AgCl reference electrodes with respect to the SCE. The duration of test was limited at the first 24h of protection, during which the distribution is very uneven due to the high current densities required for polarization.

Potentiodynamic cathodic and anodic polarization curves of 17-4PH were recorded in flowing aerated seawater from corrosion potential, using a scan rate of 0.166 mV/s.

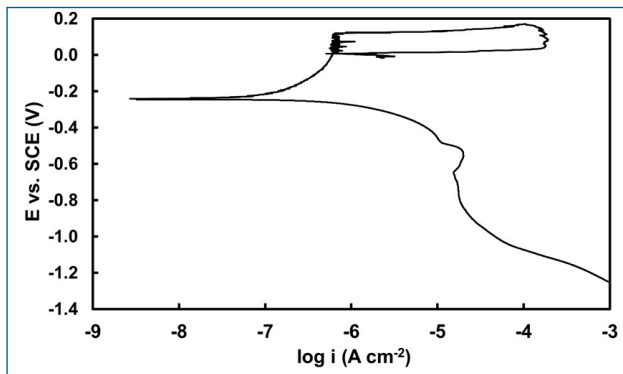


Fig. 2 - Anodic and cathodic polarization curves of as received 17-4PH samples in flowing seawater.

Fig. 2 - Curva di polarizzazione anodica e catodica di campioni tal quali di 17-4PH in acqua di mare in movimento.

RESULTS AND DISCUSSION

Fig. 2 shows the most representative anodic and cathodic curves relative to 17-4PH in flowing seawater.

From previous results [8], the average pitting (E_{pit}) and protection (E_{prot}) potentials were 0,081 and -0,010 vs SCE, respectively. With reference to corrosion potential (E_{corr}), the values changed going from an experimental session to the subsequent one, probably due to biofilm formation on the 17-4PH surface, which was really observed on the shaft and which is responsible of this phenomenon as reported in the literature [11]. E_{corr} increases from the value visible in Fig. 2 (-0.240 V vs SCE) to the values that are showed in the next figures.

Actually, in order to make a comparison and to realize the importance of the impressed current cathodic protection performed by Ti anodes, Fig. 3 shows the potential trends measured in a previous work [9]. In this case, two plain carbon steel anodes were used with the same system showed in Fig. 1a, where the position of the two anodes is indicated by the labels "AN1" and "AN2". Their distance "d" from the "0" origin is showed in Fig. 1a and Fig. 3.

Independently from the time, in Fig. 3 it is visible that the plain steel anodes preserve the propeller shaft from the pitting corrosion, without the risk of hydrogen embrittlement, considering that the hydrogen evolution starts from -0.800 ÷ -0.900 V vs SCE (Fig. 2). Furthermore, the polarization effect was higher in correspondence of the shaft zones closest to the position of the two anodes and measured with the references Ag3, Ag4 and Ag5, Ag6. The possible risks of corrosion are present in correspondence of the references Ag1, Ag2, Ag7 and, after 12h of cathodic protection, also in correspondence of SCE. The propeller shaft potentials measured by these electrodes are in the imperfect passivation region of 17-4PH, where localized corrosion can propagate if it is accidentally initiated.

Fig. 4 shows the results of the test performed using only the Ti anode far from the references (Fig. 1b) and with seawater flowing at 40 L/min. Considering the arrangement of the references and of the Ti anode, in this case the po-

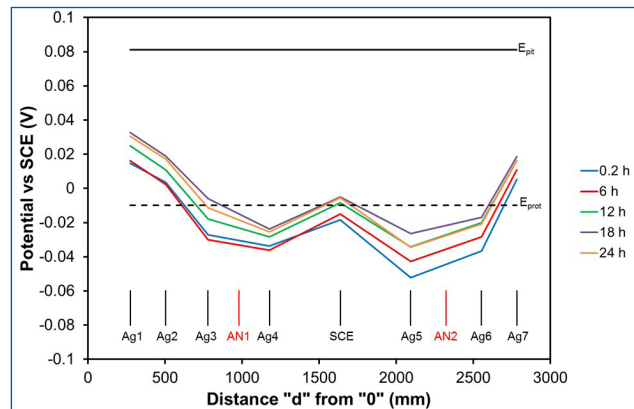


Fig. 3 - Trends of the 17-4PH propeller shaft potentials measured at different time by the reference electrodes shown in Fig. 1a as a function of their positions with respect to the positions of the two plain carbon steel anodes (AN1 and AN2), used in a previous work [9]. Seawater flow at 40 L/min between the shaft and the stern tube interspace.

Fig. 3 - Andamenti dei potenziali dell'asse in 17-4PH misurati a tempi differenti dagli elettrodi di riferimento mostrati in Fig. 1a, in funzione delle loro posizioni rispetto alle posizioni dei due anodi di acciaio comune (AN1 and AN2), usati in un lavoro precedente [9]. L'acqua di mare scorreva a 40 L/min nell'interspazio tra l'asse e l'astuccio.

tential trends did not show a "geometrical dependence" in terms of the distance d (Fig. 1a), as that relative to Fig. 3, therefore the average potential trend along the shaft and the relative standard deviation are reported as a function of test time. This indicates a not homogeneous potential distribution along the shaft, although the values range within ± 0.029 V. On the other hand, the low protection currents monitored and the consequent ohmic drops caused by current circulating in the titanium anode [12], are not sufficient to give potential changes along the shaft higher than the standard deviation.

Initially, with the potentiostat cell switched OFF, the corrosion potential of the 17-4PH propeller shaft was around 0.000 V vs SCE (E_{corr} in the inset of Fig. 4), that is above E_{prot} (-0.010 V). Switching ON the potentiostat cell, the shaft potentials went to the perfect passivity range (below E_{prot}), assuming values around -0.300 V as expected. At these values, there are not risks of corrosion.

The comparison of these results with respect to that of Fig. 3 shows the importance of using impressed currents cathodic protection for eliminating the risks of localized corrosion.

An average value of 25 mA was found for protection current (Fig. 4). Considering that the protected metallic part was only the propeller shaft (ϕ 115 mm, length 3.11 m, Fig. 1a), its surface is 1.12 m² and the protection current density is 22.3 mA/m². This value is not comparable with that (9.1 mA/m²) obtained in a previous experimentation [8], although the cathodic protection system was the same. In-

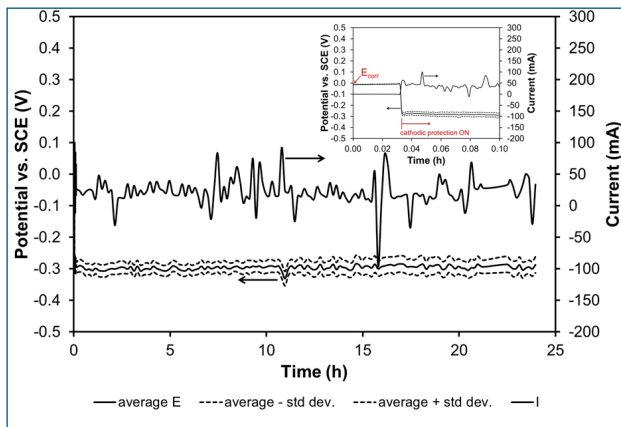


Fig. 4 - Trend of the average potential (left y-axis) of the propeller shaft obtained with the values measured with the references showed in Fig. 1a. Trend of protection current I (right y-axis). The cathodic protection was performed with seawater flowing at 40 L/min and by using only the Ti anode far from reference electrodes (Fig. 1b). The inset shows a magnification of the initial monitoring period where the switching OFF-ON event and the initial corrosion potential of the shaft are visible.

Fig. 4 - Andamento del potenziale medio (asse y di sinistra) dell'asse di propulsione ottenuto con i valori misurati con i riferimenti mostrati in Fig. 1a. Andamento della corrente di protezione I (asse y di destra). La protezione catodica è stata effettuata in acqua di mare che fluiva a 40 L/min ed utilizzando il solo anodo di Ti lontano dagli elettrodi di riferimento (Fig. 1b). L'insero mostra un ingrandimento della fase iniziale del monitoraggio dove sono visibili l'evento OFF-ON ed il potenziale iniziale di corrosione dell'asse.

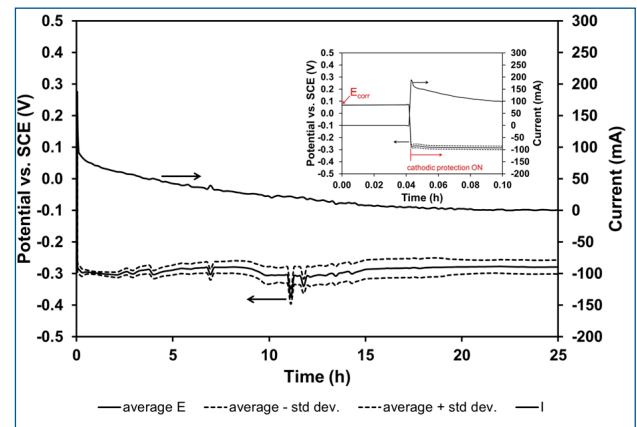


Fig. 5 - Trend of the average potential (left y-axis) of the propeller shaft obtained with the values measured with the references showed in Fig. 1a. Trend of protection current I (right y-axis). The cathodic protection was performed with stagnant seawater and by using only the Ti anode far from reference electrodes (Fig. 1b). The inset shows a magnification of the initial monitoring period where the switching OFF-ON event and the initial corrosion potential of the shaft are visible.

Fig. 5 - Andamento del potenziale medio (asse y di sinistra) dell'asse di propulsione ottenuto con i valori misurati con i riferimenti mostrati in Fig. 1a. Andamento della corrente di protezione I (asse y di destra). La protezione catodica è stata effettuata in acqua di mare stagnante ed utilizzando il solo anodo di Ti lontano dagli elettrodi di riferimento (Fig. 1b). L'insero mostra un ingrandimento della fase iniziale del monitoraggio dove sono visibili l'evento OFF-ON ed il potenziale iniziale di corrosione dell'asse.

deed, in the previous experimentation, three fundamental differences are present with respect to the present one: 1) the water flow rate was about four times lower than that of this case; 2) the shaft and the stern tube were both protected while in this case only the shaft was protected, considering the fiberglass stern tube; 3) the high current density necessary in this work to protect the shaft at -0.300 V is due to the higher initial E_{corr} of 17-4PH (inset of Fig. 4) with respect to that of the previous case, corresponding to E_{corr} of as received 17-4PH sample (see Fig. 2).

As Fig. 4, Fig. 5 shows the average potential trend, its standard deviation and the protection current measured for the propeller shaft in a test with stagnant seawater and using the same Ti anode. Even in this case, the cathodic protection is fundamental considering in particular the initial corrosion potential of the shaft (0.067 V vs SCE, inset of Fig. 5). This value is very close to the pitting potential of 17-4PH stainless steel and the risk of corrosion is real. After switching ON cathodic protection, the potential values reached again the expected value of -0.300 V (the maximum standard deviation was 0.030 V), which guaranteed again the absence of pitting corrosion. During this period, these potential values are maintained by potentiostatic

control with a decrease of the protection current (Fig. 5) determined by a progressive consumption of the oxygen present in seawater.

The cathodic protection was effective even using both Ti anodes and both with flowing and stagnant seawater. For the sake of brevity, they are not reported here.

In conclusion, only one Ti anode could be sufficient to avoid localized corrosion of 17-4PH propeller shaft. Nevertheless, in this case there is the risk of high negative polarization of the shaft surface in front to the Ti anode, in order to reach the potential of -0.300 V in the opposite position (Fig. 1b), as in this work was done. If these potentials are sufficiently negative the hydrogen develops in front to the anode, with the risk the hydrogen embrittlement of 17-4PH shaft. This possibility can be evaluated only with another experimentation, measuring the potentials distribution in radial positions, by installing other Ag/AgCl electrodes, and/or by modelling this cathodic protection system.

CONCLUSIONS

In this work, the efficiency of an impressed currents cathodic protection system, performed by using activated Ti wires on a propeller shaft of a ship in seawater, was tested. The results were compared in particular with those obtained in a previous work, where the cathodic protection with two plain carbon steel anodes was performed.

Using these sacrificial anodes, the risk of corrosion was found, while using the present approach, Ti anodes were able to protect the propeller shaft, setting potentiostatically its potential to -0.300 V vs. SCE. To obtain these results only one activated Ti wire anode could be used, by installing it lengthwise in the interspace of the propeller system, in correspondence of the inner walls of a fiberglass stern tube.

However, in a future work, there is the necessity to evaluate the possibility of hydrogen evolution in the shaft surface in front to Ti anode, if the impressed cathodic protection system is managed potentiostatically, setting the protection potential with respect to a reference electrode, installed diametrically opposite from Ti anode.

REFERENCES

- [1] R.E. Groover, T.J. Lennox, M.H. Peterson, Fourth Annual Offshore Technology Conference, May 1-3, 1972, Houston (Texas), Paper N. OTC 1580.
- [2] B.G. Allen, R. H. Heidersbach, S. F. Mealy, 12th Annual Offshore Technology Conference, May 5-8, 1980, Houston (Texas), Paper N. OTC 3856.
- [3] M. Karaminezhad, S. Sharafi, K. Dalil, J. Mater. Sci., 2006, 41, 3329-3333.
- [4] R. L. Liu, M.F. Yan, D.L. Wu, J. Mater. Processing Technol., 2010, 210, 784-790.
- [5] M. Esfandiari, H. Dong, Surf. Coat. Technol., 2007, 202, 466-478.
- [6] I. Costa, C.V. Franco, C.T. Kuniyoshi, J.L. Rossi, Corrosion, 2006, 62, 357-365.
- [7] C. Fahir Arisoy, Gokhan Başman, M. Kelami Şeşen, Eng. Failure Analysis, 2003, 10, 711-717.
- [8] T. Bellezze, G. Roventi, R. Fratesi, Corrosion Engineering, Science and Technology, Vol. 48(5) (2013) pp. 340-345.
- [9] T. Bellezze, R. Fratesi, G. Roventi, la metallurgia italiana, 105 (6) (2013) pp. 31-36.
- [10] D.R. Lenard, J.G. Moores, Corrosion, 1993, 49, 769-775.
- [11] M.V. Biezema, Microbial Corrosion, European Federation of Corrosion Publications N. 29, IOM Communications Ltd., London (2000), 36-46.
- [12] B. Bazzoni, S. Lorenzi, P. Marcassoli, T. Pastore, Corrosion Vol. 67 (2) (2011) pp. 026001-1 - 026001-10.

Protezione catodica di un asse portaelica di una nave tramite anodi a corrente impressa

Parole chiave: Corrosione localizzata - Protezione catodica - Anodi a corrente impressa - Acciaio inossidabile - Acqua di mare

Considerando i fenomeni di corrosione localizzata osservati sull'asse portaelica in 17-4PH di una nave e alcune criticità riscontrate in precedenti test di protezione catodica, eseguiti mediante anodi sacrificali in acciaio dolce, in questo lavoro è stata analizzata l'efficacia della protezione catodica a correnti impresses.

La sperimentazione è stata effettuata su un sistema di propulsione di dimensioni reali (Fig.1a), in cui sono stati installati degli elettrodi di riferimento Ag/AgCl e un SCE e due fili di titanio attivato (Fig. 1b), funzionanti da anodi, in direzione longitudinale, nell'intercapedine tra asse e astuccio in vetroresina. L'alimentazione del sistema di protezione catodica è stata effettuata con un potenziostato, che manteneva l'asse a -0,300 V vs. SCE. Per simulare le condizioni che si hanno in fase di fermo e di navigazione della nave, i test sono stati eseguiti sia con acqua di mare stagnante che in movimento nell'intercapedine, con la portata di 40 L/min.

Dai dati elettrochimici dell'acciaio 17-4PH (Fig. 2) e dal confronto con i risultati ottenuti in precedenti sperimentazioni, in cui sono stati utilizzati gli anodi di acciaio dolce, si è visto che esistono in questo caso dei rischi di corrosione (Fig. 3), mentre con il sistema a correnti impresses l'asse può essere efficacemente protetto anche da un solo anodo di Ti attivato, dei due originariamente installati, sia in condizioni di acqua in movimento (Fig. 4) che stagnante (Fig. 5). Per questa soluzione, con acqua in movimento a 40 L/min, è risultata necessaria una densità di corrente di protezione di 22,3 mA/m² (Fig. 4) mentre con acqua stagnante essa si portava a 0 mA/m² (Fig. 5), dopo circa 24 h di prova, per il consumo dell'ossigeno in essa presente.

Correnti di protezione più elevate sono state talvolta necessarie per portare E_{corr} dell'asse al potenziale di protezione di -0,300 V perché, tra una sessione di prova e l'altra, esso aumentava (cfr. E_{corr} in Fig. 2 con E_{corr} nelle figure 4 e 5) probabilmente per la formazione di biofilm sulla sua superficie, come poi è stato realmente osservato.

In futuro, prendendo in considerazione la soluzione che prevede l'utilizzo di un solo anodo di titanio, sarà necessario verificare se sulla superficie dell'asse affacciata ad esso si raggiungono valori di potenziale tali da dare sviluppo di idrogeno, con il relativo rischio di infragilimento dell'acciaio 17-4H. Per assicurarsi che questo fenomeno non avvenga, occorrerà effettuare una nuova sperimentazione con altri elettrodi di riferimento Ag/AgCl, installati radialmente nell'astuccio e/o modellizzando il sistema di protezione catodica proposto.



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Effect of temperature on pulsed current chromium electrodeposition from Cr(III) aqueous solutions

R. Giovanardi, A. Bozza

Chromium electrodeposition is widely used industrially to obtain protective coatings with high corrosion resistance combined with other important properties such as high hardness and wear resistance (hard chromium plating) or high surface finishing (decorative chromium plating).

In recent years, much attention was given to finding alternative electroplating methods that could achieve similar coatings without the use of hexavalent chromium, given the known toxicity of its compounds. Ideally the deposition of metallic chromium from trivalent chromium aqueous solutions represent the easier strategy to obtain such coatings without the use of hazardous solutions; unfortunately a lot of complications concerning the chemistry of trivalent chromium in aqueous solution make this way very difficult to pursue. In this work some deposition strategies have been developed, obtaining, on carbon steel substrate, metallic chromium coatings with good properties (high adhesion to the substrate, micro-hardness, surface finishing) starting from aqueous solutions of Cr (III) and formic acid. The developed strategies are based on the use of pulsed current (and optimization of its process parameters, such as duty cycle, period and magnitude of current applied) and low temperatures.

Keywords: Electrodeposition - Chromium - Corrosion - Pulsed current -

INTRODUCTION

The deposition of chromium from Cr(III) aqueous solution ideally would provide the easiest way to obtain chromium coatings without using dangerous (for operator and environment) solutions, but there are several chemical complications which made this way not easily available; the main complication can be summarized in the following three point, exhaustively explained in a previous work [1]:

- i) Cr^{3+} ions form, in aqueous solution, an esa-aquo ion complex (formula $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$) which hinder, by the kinetic point of view, the process of electroreduction of chromium [2, 3];
- ii) the reduction reaction from Cr^{3+} to Cr^0 is characterized by a standard reduction potential more negative than the reduction potential of hydrogen in water, which means that the minimum polarization required to activate the reduction process of trivalent chromium will produce a considerable hydrogen evolution [4, 5] at the expense of faradic efficiency for the desired reaction.
- iii) hydrogen evolution and the contemporary formation of

OH^- ions occur at the cathode and cause a significant pH increase near the electrode surface; at pH values higher than 4.5 the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ hydrolyzes, establishing a series of reactions that have, as final products, high molecular weight polymers (phenomenon known as olation) [2, 3], which can precipitate near the cathode surface limiting the availability of Cr^{3+} and hindering the desired reduction reaction.

Limiting parts of the phenomena described is possible using appropriate complex agents for Cr^{3+} such as oxalic acid, malonic acid, urea, glycine. These organic compounds form with Cr^{3+} complexes thermodynamically more stable than its esa-aquo ion; so the organic ligands may sequester a considerable amount of chromium ions from its esa-aquo complex, making them available for the reduction reaction at the cathode. According to literature, the more suitable ligand for this purpose is the formic acid (or better formate ions) [6-8], so in this work formic acid will be used as a specific complexing agent for Cr(III).

A second chemical species able to greatly affect chromium deposition from both Cr(VI) and Cr(III) solution is the sulphate ion. This ion acts directly in the reaction mechanism leading to the gradual reduction of hexavalent chromium [9, 10], and its influence on the reduction process of formic-Cr(III) complexes has been already evaluated in a previous work [1].

The aim of this work is to continue the investigation of

Roberto Giovanardi, Andrea Bozza
 University of Modena e Reggio Emilia,
 Department of Engineering "Enzo Ferrari",
 Via Vignolese 905, 41125 Modena, ITALY

chromium galvanic deposition from Cr(III) aqueous solution in order to develop new strategies to improve the process quality varying the electrical parameters. The main studies concern the use of pulsed current, working therefore with a current density which varies periodically in time, trying to optimize the process variables (current density, period and duty cycle) in order to improve the performance of the coatings obtained.

In addition a study concerning the plating temperature was performed: the deposition temperature was decreased to values lower than those typical of the galvanic depositions, trying to modify in this way the kinetics of the various chemical reactions involved (complexation, plating) in order to prevent the phenomena previously described, which complicate the process of reduction of trivalent chromium in aqueous solution.

MATERIAL AND METHODS

All the deposition tests were performed using an electrochemical thermostated cell whose geometry has been already explained in previous work [1]. The working electrode (cathode) was a carbon steel disk (C40), a platinum coil was used as counter electrode and an saturated silver chloride electrode (SSCE) as reference electrode.

All the galvanic depositions were performed using a solution whose composition was optimized in previous work⁽¹⁾ (CrCl_3 200 gdm^{-3} , H_2SO_4 0.37 gdm^{-3} , HCOOH 30 gdm^{-3}) [1].

In the present work pulsed current (PC) deposition techniques have been exploited, controlling the deposition current. A square wave mode was chosen, in which the current magnitude was shifted between two constant levels. The main electrical parameters varied during PC depositions were: *time-on* (t_{on}), time period in which the higher current density (cathodic) was applied, *time-off* (t_{off}), time period in which a lower (or zero) current density was applied, *period* (τ), sum of t_{on} and t_{off} , *duty-cycle* (DC%), ratio between t_{on} and τ , expressed as percentage, *current density during time-on* (j_{on}) and *current density during time-off* (j_{off}).

In order to allow a homogeneous comparison of the deposition results, all the pulsed current configurations, developed combining different electrical features, were characterized by a number of cycles that guarantees the same amount of total charge (Q) provided during the deposition process.

The temperature during electrodeposition was controlled by a JULABO F32 thermostat; different tests were carried out at the following temperatures: 23 ± 1 , 20 ± 1 , 16 ± 1 , 12 ± 1 and 10 ± 1 °C.

The most significant chromium coating obtained were characterized evaluating: i) structure and morphology of the coating, by optical and SEM micrographs obtained from surface and cross section of the samples; ii) faradic efficiency ($\eta\%$), calculated as ratio between the experimental and theoretical weight uptake after electrodeposition [11], iii) $\text{HV}_{0.2}$ ⁽²⁾ micro-hardness, by indentation of the cross sec-

tion of coatings with a WOLPERT 401 MVD Micro-hardness Tester, iv) thickness, evaluated as average thickness from optical and/or SEM micrographs of the cross section, v) apparent density, calculated as ratio of the coating weight and the coating volume, vi) roughness, by a Sama Tools 6200 series digital profilometer (Rz and Rz data, obtained as average of at least five measurements for each sample).

RESULTS AND DISCUSSION

The aim of the first set of experiments performed was to optimize the pulsed current parameters.

The period (τ) was changed from 20 ms to 2 s, using constant values of current density during time-on and time-off intervals (-0.6 Acm^{-2} and 0 Acm^{-2} respectively) and considering three different duty cycle (25%, 50%, 75%) for each τ tested.

All the tests performed with the shortest τ led to a total absence of chromium in the coatings: only a thin copper layer was obtained (confirmed by XPS analysis) probably deriving from the low percentage of Cu impurities present in the commercial reagent used for preparing the deposition solution (CrCl_3). These results show that too short periods, characterized by extremely fast pulses (milliseconds) fail to ensure the necessary conditions for chromium reduction, whose kinetic is probably very slow. Interesting results were obtained raising τ up to 2 s, but only applying high duty cycle; in particular the sample obtained with a 75% DC showed high faradic efficiency⁽³⁾ (22.0%), very high micro-hardness (1700 HV) and good surface finishing ($R_a = 7 \pm 1 \mu\text{m}$). All the samples coated in this way, however, show a poor substrate adhesion, mainly related to the growth of iron corrosion products at the steel/chrome interface during the deposition process. This phenomena was ascribed to a corrosion process that occur on the carbon steel substrate during the time-off intervals, due to the chemical composition of the deposition solution (extremely acidic and not able to passivate the steel). To avoid such corrosion phenomena, the current level during time-off interval was shifted toward slightly cathodic values, in order to ensure cathodic protection of the steel without activating the reduction reaction of chromium.

The introduction of a cathodic current level (-0.2 A cm^{-2}) during time-off has resulted in some interesting improvements in terms of adhesion, in particular the best results were obtained with a duty-cycle of 50% (setting lower DC% the efficiency falls down, while at higher DC% problems of substrate adhesion are still observed, because with time-

1) The solution was prepared at room temperature and stored at 4 °C until use. No pH correction was applied (the pH of freshly prepared solution is approximately 0.7)

2) When the thickness of the sample allow it, otherwise a reduced load was applied.

3) When compared with the average efficiency of chromium electrodeposition from Cr(VI) solution (about 18%)