



Evaluation of the corrosion protection of steel by anodic processing in metasilicate solution using the scanning vibrating electrode technique



J. Izquierdo^{a,b}, B.M. Fernández-Pérez^a, L. Martín-Ruiz^a, V. Mena^c, R. Rodríguez-Raposo^a, J.J. Santana^c, R.M. Souto^{a,b,*}

^a Department of Chemistry, University of La Laguna, P.O. Box 456, E-38200 La Laguna, Tenerife, Canary Islands, Spain

^b Institute of Material Science and Nanotechnology, University of La Laguna, P.O. Box 456, E-38200 La Laguna, Tenerife, Canary Islands, Spain

^c Department of Process Engineering, University of Las Palmas de Gran Canaria, E-35017 Las Palmas de Gran Canaria, Canary Islands, Spain

ARTICLE INFO

Article history:

Received 2 March 2015

Received in revised form 18 July 2015

Accepted 19 July 2015

Available online 26 July 2015

Keywords:

corrosion protection

steel

metasilicate ions

surface modification

anodic treatment

scanning vibrating electrode technique

ABSTRACT

Anodic processing in metasilicate solution was investigated for the improvement of the corrosion resistance of various steels, namely F111 low alloy carbon and 304 stainless steels, as well as on galvanized steel cut edges. The efficiency of the prior electrochemical treatment for each material was tested during their exposure to naturally-aerated aqueous chloride solutions of different aggressiveness. Analysis was performed using the scanning vibrating electrode technique (SVET) in order to detect local ionic current distributions over the samples under study associated to the corrosion reactions. The onset of corrosion processes was greatly inhibited after anodic processing with metasilicate on both the low alloy carbon steel and the galvanized steel cut edge. Conversely, SVET analysis of unbiased 304 steel samples tested in 0.1 M chloride-containing solution did not show differences between pristine and metasilicate-treated surfaces. Differences in the electrochemical reactivity between treated and non-treated 304 steel surfaces were only observed after partial removal of the corresponding passive layers under operator-controlled polarization.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Due to its low toxicity, sodium silicates are used as corrosion inhibitor for iron-based materials in water supply networks [1]. Stable thin layers are rapidly formed onto the metal surfaces, that are favoured by the alkalization provoked by the silicate anions [2,3]. Rather than involving chemical reactions, inhibition is regarded to proceed through neutralization of charged particles, namely iron cations and silicate anions [4,5]. They may coagulate and adsorb on the metal surface, provided that corrosion products are first formed and precipitate. The observed electrochemical behaviour is typical of a two-interface system, where most of the formed iron cations remain as iron oxides and iron silicates, originating a polymerized silica layer through Fe-O-Si bonds [6,7]. This results not only in the inhibition of the anodic dissolution process, but also in the hindrance of the cathodic half-reaction involving oxygen reduction (i.e., mixed inhibitive behaviour), because the corrosion reaction

preferentially occurs with hydrogen evolution even upon exposure to well-aerated electrolytes [7,8].

Since corrosion must first occur for the silica layer to precipitate and be bound to the oxide layer, prior surface modification of the material involving silicate species have been attempted more recently. In this way, enhanced resistance against both metastable and stable pitting in chloride-containing aqueous environment was found following prior anodic treatment of stainless steel in metasilicate solution [9]. This strategy overcame the limitation stemmed from the needed continuous interaction between the material and silicate salt solutions for the inhibitive properties to be exploited, thus eventually allowing this protection to continue in operation even in the absence of the inhibitor. Other surfaces which have proven to be protected by sodium silicate are zinc metal and galvanized layers, the latter used for the sacrificial anodic protection of iron-based structures. Thus, high inhibitive efficiency accompanied with the presence of silica, possibly as zinc silicates, was reported by Aramaki following an optimized treatment of zinc in sodium silicate solution [10]. This report contradicted the existing opinion that the treatment of zinc with sodium metasilicate did not provide further protective effects beyond the passivation due to the alkalization effect [3]. Multi-analytical technique analysis has indeed shown the formation of a thin outer layer of polymerized

* Corresponding author. University of La Laguna, Department of Chemistry, P.O. Box 456, 38200 La Laguna (Tenerife), Spain. Tel.: +34922318067; fax: +34922318005.

E-mail address: rsouto@ull.es (R.M. Souto).

Table 1
Composition of the steels employed in this work.

| | F111 steel | 304 stainless steel |
|----|------------|---------------------|
| Cr | 0.015 | 18.2 |
| Ni | 0.005 | 8.02 |
| Mn | 0.208 | 1.91 |
| Si | 0.042 | 0.333 |
| Mo | 0.005 | 0.315 |
| Cu | 0.023 | 0.304 |
| V | | 0.091 |
| N | | 0.057 |
| C | 0.042 | ≤0.052 |
| Nb | | 0.037 |
| P | | 0.032 |
| S | | ≤0.01 |
| Ti | 0.005 | 0.008 |
| Al | 0.041 | |
| Co | 0.005 | |
| Fe | balance | balance |

silica attached to an inner layer containing zinc silicate over the galvanized steel [11–13]. The final layer structure of the protecting surface film varied with the actual treatment procedure performed, that involved electrochemical treatment and surface polarization for optimization purposes [11].

With independence of the metal-inhibitor system under consideration, both the inhibitor interaction and the eventual corrosion processes are initiated at micrometer or submicrometer scales, through the development of microcells associated to their dynamic electrochemical processes. Precise monitoring of these processes in this spatial range is mandatory to elucidate their mechanisms, as well as to improve the protective efficiencies of the inhibitors. In this context, the scanning vibrating electrode technique (SVET) is particularly helpful, because it images the ionic fluxes arising from metallic surfaces undergoing electrochemical degradation and its eventual hindrance as result of the implementation of corrosion protection methodologies [14,15]. Accurate characterization of galvanic corrosion processes [16–18], including those occurring at the cut edges of galvanized steel substrates [19–21], have been possible using this technique. In addition, SVET has proven to be particularly effective for the rapid screening of inhibitor efficiency for the corrosion protection of materials of technological interest [22–26]. Yet, the SVET has been scarcely employed for the characterization of the protective layers formed on metallic materials containing Si for chemical bonding. In fact, applications have been constrained to the characterization of a few pre-treatments with organic-silane molecules [27], and $\text{SiO}_x/\text{ZrO}_x$ sol-gel coatings [28], the latter eventually further doped with encapsulated corrosion inhibitors to promote self-healing behaviour [28–30].

The present work reports on the enhanced corrosion protection operated on low alloy carbon steel, galvanized steel, and 304 stainless steel by anodic processing in sodium metasilicate solution. The effect of the surface modification on the corrosion behaviour of the three materials was spatially-resolved using SVET during their exposure to chloride-containing aqueous solution. The range of protection gained by the materials was determined in terms of the minimum aggressive conditions required by each system to experience corrosion.

2. Experimental section

Three different steel samples were considered in this work, namely, low alloy carbon steel (grade F111), galvanized low alloy carbon steel and 304 grade austenitic stainless steel. The compositions of the steels were determined by Spark Emission Spectrometry and are given in Table 1. The galvanized low alloy carbon steel consisted of 400 μm steel substrate, 5 μm chromate

conversion layer, and 20 μm of Aluzinc coating (composition 45% Al + 55% Zn). F111 and 304 steels were supplied as 1 mm thick sheets, and they were cut into metal strips of ca. 2 mm \times 1 mm section. Two strips of the same steel were embedded vertically in an insulating resin (Epofix kit, Struers, Ballerup, Denmark), with an approximate separation of 5 mm between them. In this way, both pristine and metasilicate-treated surfaces could be monitored in a single experiment. The metal strips were allowed to protrude at the rear of the mount to facilitate electrical connection to ensure either galvanic coupling or the application of a polarization. On the other hand, the galvanized steel sheet was cut into 4 mm width strips and mounted vertically in the Epofix resin to expose a cut edge of ca. 4 mm \times 450 μm rectangular section. In this case, only one galvanized carbon steel strip was embedded per mould, because the length of the sample was enough to allow only a half of the surface to be treated in metasilicate solution, whereas the rest of the surface remained untreated. The electrode surface area was ground using a sequence of SiC papers up to 4000 grit, and finished with 0.3 μm particle size alumina aqueous slurries prior to electrochemical processing following a procedure adapted from ref. [9]. After each polishing step, the samples were cleaned using ultrapure deionized water.

Anodic processing of the various steel samples was performed in 1.0 M sodium metasilicate (Na_2SiO_3) solution. For the sake of comparison, only half of the total metal exposed in the mounts was immersed in the treatment solution. This was accomplished by exposing either half of the length of the galvanized steel cut edge, or only one of the strips for the mounts containing the stainless and the carbon steels. The three-electrode electrochemical arrangement was completed using an Ag/AgCl/3 M KCl reference electrode, and a platinum ring as counter electrode. Potentiostatic control was accomplished using an EG&G Princeton Applied Research potentiostat model 283A (Oak Ridge, TN, USA). The processing potential for 304 stainless steel and carbon steel samples was set at -0.36 V vs. Ag/AgCl/3 M KCl following the indications given in ref. [9]. But in the case of the galvanized steel cut edge, a more negative potential was applied, namely -0.65 V vs. Ag/AgCl/3 M KCl, to avoid eventual precipitation of zinc salts on the surface. The duration of the electrochemical treatment was 40 minutes in all cases. Upon completion of the treatment, the mounts were removed from the solution and thoroughly rinsed with ultrapure deionized water.

SVET measurements were performed using a setup manufactured by Applicable Electronics Inc. (Forestdale, MA, USA) and controlled by dedicated software. The sensing probes were 10 μm Pt/Ir (80%/20%) wires insulated with paralene C[®] and arced at the tip to expose the metal. These wires were platinized in order to produce a spherical platinum black deposit of 10–20 μm diameter. A video camera connected to an optical microscope was included in the setup both to establish the probe to sample distance, and to follow the movement of the vibrating electrode over the sample during operation. Additionally, the video camera was employed to obtain optical images of the samples in situ, as to establish a correspondence between the images and the measured ionic current data. The mounts with the metallic samples embedded in resin were surrounded laterally by sellotape, thus creating a small container for the electrolyte solution, and the electrolyte covered the specimen under investigation by a ca. 4 mm liquid column. The electrochemical cell for SVET operation was completed with the inclusion of the corresponding microelectrodes, namely the spherical platinized probe and a Pt wire as reference electrode. A reference measurement with the microelectrode away from the active area was subtracted from the values measured during the scan. The measurements were made with the probe vibrating in a plane perpendicular to the sample at amplitude of 10 μm . The mean distance between the microelectrode and the sample surface was 60 μm . Some selected experiments were performed on biased 304 stainless

Download English Version:

<https://daneshyari.com/en/article/183651>

Download Persian Version:

<https://daneshyari.com/article/183651>

[Daneshyari.com](https://daneshyari.com)