Study of the formation of calcareous deposits on cathodically protected steel in Baltic sea water

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Abstract

Purpose – The purpose of this paper is to investigate whether the sedimentation of calcareous deposits occurs on cathodically protected steel in Baltic sea water.

Design/methodology/approach – Steel electrodes were cathodically polarized in natural Baltic sea water at potential +0.150 V vs Zn electrode in potentiostatic mode. During exposure chronoamperometric measurements were carried out. After the exposure, the electrode's surface was examined by scanning atomic force microscope (AFM) and by scanning electron microscope (SEM). Deposit composition was examined by energy-dispersive X-ray spectroscopy (EDX). Comparative investigation was carried out in 1 percent NaCl solution (comparable to the salinity of Baltic sea water).

Findings – During cathodic polarization in Baltic sea water, non-conducting calcareous deposits developed on steel surface. These deposits significantly lowered the cathodic current demand. Morphology and EDX spectroscopy of the deposit indicated that it was built mainly of aragonite (polymorph of CaCO3). No non-conducting deposits on cathodically protected steel electrodes developed in 1 percent NaCl solution.

Originality/value – Composition of Baltic sea water favours the formation of calcareous deposits on cathodically protected steel. Sedimentation is a beneficial and desired phenomenon from the point of view of cathodic protection system of maritime construction as it facilitates polarization. Evolution of calcareous deposits should be taken into account as one of the environmental factors when designing a cathodic protection system.

Keywords Steels, Cathodic protection, Sea water, Calcareous deposits, Baltic sea water, Atomic force microscopy, Scanning electron microscopy, X-ray spectroscopy

Paper type Research paper

Introduction

Maritime constructions require reliable and effective corrosion protection systems. The protection is provided by contemporary application of cathodic protection and coatings. These two methods are complementary. The better is the quality of the coating, the lower is the cathodic protection current density demand that is required to assure corrosion protection. A well designed cathodic protection system supplements coating protection and provides absolute resistance to the construction.

Cathodic protection of maritime constructions is implemented using sacrificial anodes, impressed current systems or hybrid systems using both of the above (Morgan, 1987). Cathodic protection current flows from the anode through the electrolyte to the construction through defects in the coating system, i.e. holes or pores that are present in the coating. The potential of the construction decreases (cathodic polarization) as a result of the current flow. The metal is fully protected if a sufficiently low potential is reached. Protection potential for steel is in the range from +0.25 to −0.05 V vs Zn electrode (European Standard EN-12473, 2000), which corresponds to the values from −0.80 to −1.10 V vs Ag/AgCl/seawater electrode.

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Each maritime construction requires its own specific concept of cathodic protection system design. Various parameters have to be taken into consideration, such as: local environmental conditions, corrosion aggressiveness (which depends mostly on the resistivity, degree of oxygenation, and the temperature of the sea water), individual cathodic protection current demand (DNV Recommended Practice B401, 2005), interference of stray currents (Darowicki and Zakowski, 2004; Zakowski and Darowicki, 2000, 2003), presence of flora and fauna on the construction surface, and deposits. On cathodically protected constructions, sedimentation of Mg and Ca compounds may occur, usually aragonite and calcite (polymorphs of $CaCO_3$) and brucite $Mg(OH)_2$ (Zamanzade *et al.*, 2007; Neville and Morizot, 2002).

On the steel surface cathodic reaction occurs:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{1}$$

Originated hydroxide ions lead to precipitation of magnesium hydroxide:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \tag{2}$$

Increased concentration of the hydroxide ions has an influence on the concentration of carbonates:

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-} \tag{3}$$

this leads to the sedimentation of $CaCO_3$:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \tag{4}$$

Precipitation of $CaCO_3$ occurs if the pH is above 7.5 (Deslouis *et al.*, 2003).

Thus, the main factor responsible for formation of deposits is alkalization of the environment in the vicinity of cathodically protected steel surface. The presence of the deposits is beneficial from a cathodic protection standpoint, because the surface area to be protected is decreased (the deposits act as a protective coating). The diffusion rate of oxygen to the steel surface is hindered (Chyn Ou and Kuo Wu, 1997) and cathodic protection current demand is lowered.

The aim of this work was to investigate if deposits evolve on cathodically protected steel surface in natural Baltic sea water. The results were utilized in the design of the cathodic protection system for a Baltic offshore construction (Zakowski, 2011). Deposit formation in sea water is well known, but in the scientific literature there is a lack of publications on this phenomenon in the Baltic sea.

Experimental

Evaluation of the sedimentation process on cathodically protected steel surfaces in natural Baltic sea water was carried out based on chronoamperometric measurements and surveying of the specimen surface using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

The investigated electrodes were made of construction steel S235JR and were mounted in resin. The surface area of the electrodes was 19.6 mm^2. Before exposure, the specimens were ground with abrasive paper (200-2,000 grit), polished with an alumina suspension, cleaned with distilled water and degreased.

Cathodic polarization was done in potentiostatic mode, i.e. the potential of the investigated specimen was kept at fixed value during the entire experiment. A Gamry Instruments potentiostat was used. The exposure was carried out at potential $E_{Zn} = 0.150\,V$ (E_{Zn} – potential vs zinc reference electrode). Such a potential is the typical potential value of cathodically protected steel using zinc or aluminium sacrificial anodes. The auxiliary electrode was made of platinised titanium and a Zn/saturated $ZnSO_4$ electrode was used as the reference electrode. The experiment was carried out in natural Baltic sea water at room temperature. The cell volume was 10 dm^3. Such a high electrolyte volume compared to the specimen surface ensured that the electrolyte composition during entire duration of the experiment was virtually unchanged. The experiment lasted for 25 days. The sea water in the cell was not stirred. Measurement data were collected with digital data logger. The cathodic protection current flowing through the specimen and voltage between specimen and auxiliary electrode were registered. The measurement accuracy was 1 pA and 1 μV, respectively. Instantaneous values of current and voltage were used to calculate instantaneous resistance of the investigated circuit. As a result, the time dependency of the resistance was determined. A comparative test was carried out in 1 per cent NaCl solution, because it is comparable with the salinity of Baltic sea water. Baltic sea salinity (approximately 1 per cent) is lower than other seas (approximately 3.5 per cent).

After the exposure, the specimen surface was investigated using scanning microscope AFM and SEM.

AFM senses changes in interatomic interactions between the specimen and a sharp tip as it moves over the specimen surface. The interatomic forces change the tip and cantilever bend and the degree of bending is proportional to the surface topography. AFM is often used in corrosion science, for instance to investigate organic protective coatings (Szocinski *et al.*, 2010; Darowicki *et al.*, 2010, 2011) or oxide films on metals and alloys (Arutunow *et al.*, 2011). The measurements were performed with the NTEGRA AURA AFM produced by NT-MDT. The measurements were carried out in contact mode with a 1 Hz scanning frequency. The maximum scan area was 8,100 μm^2 (90 μm × 90 μm). The resolution of the measurement was 0.35 μm. Local direct current measurements were performed for 10 V bias voltage applied between the tip and the specimen. The AFM tip was made of silicon nitrate plated with a 20 nm thick layer of platinum that made the tip conductive. The radius of the tip curvature was between 15 and 20 nm.

Specimens were investigated also with the SEM microscope. Structural investigations were performed with a Hitachi S-3400N scanning electron microscope. In order to obtain the best surface characterization, secondary electron imagining mode was chosen. Energy dispersive X-ray spectroscopy was utilized in order to investigate elemental composition of the samples. A Thermo Scientific EDS X-ray detector was used. SEM combined with EDX microanalysis is commonly used in corrosion and material science. The ~10 mm working distance ensures the best sensitivity of the EDS X-ray detector, yet the image depth is still very good. Accelerating voltage was set to 20 kV in order to assure sufficient X-ray yield. The magnification was set to be 1,000.

Results

Experimental chronoamperometry data obtained during specimen polarization at potential $E_{Zn} = 0.150\,V$ in natural Baltic sea water is shown in Figure 1(a), and in 1 per cent NaCl solution in Figure 1(b).

The surfaces of the specimens were scanned in three AFM modes: 2D surface imagining, height profile and d.c. profile. A 2D image of the specimen surface before the exposure is shown in Figure 2(a). The specimen surface profile after 4 h of polarization in Baltic sea water is shown in Figure 2(b), and after 25 days – in Figure 2(c).

The AFM height profile of the specimen surface before the exposure is shown in Figure 3(a), after 4 h exposure – in Figure 3(b), and after 25 days exposure – in Figure 3(c).

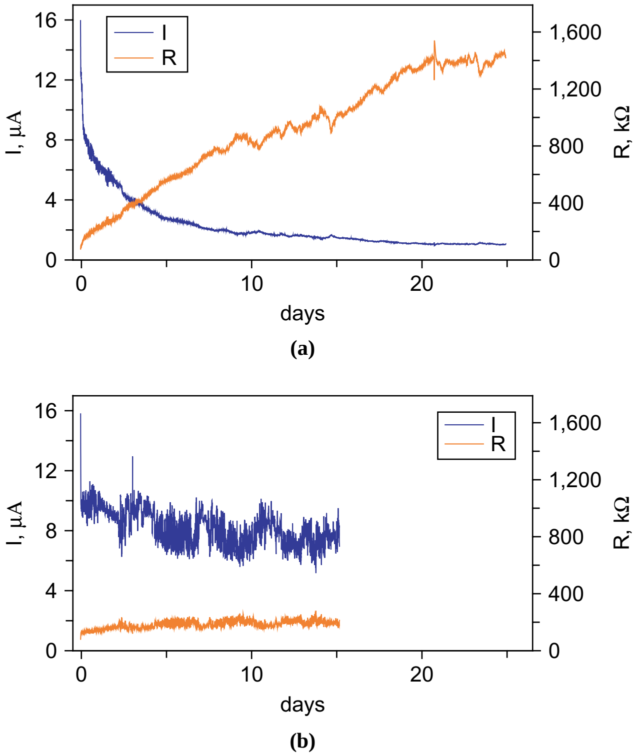
The AFM current profiles present local direct current intensity that is conducted through the specimen as a result of the applied voltage between the AFM tip and the specimen. The current profile for the specimen surface before the exposure is shown in Figure 4(a), and after 25 days exposure in Figure 4(b).

The SEM image of the specimen surface after 25 days exposure is shown in Figure 5(a), and EDX spectra of the cauliflower-shaped deposit in Figure 5(b).

Discussion

Chronoamperometry data obtained during cathodic polarization in Baltic sea water indicate that the cathodic protection current demand decays over time: the current required to polarize the specimen over 25 days decayed from 16 to 1 μA (Figure 1(a)). The resistance of the investigated circuit increased to a value of about 1.4 MΩ and proved that non-conductive deposits evolve on the steel surface. Note that

Figure 1 Cathodic protection current "I" and circuit resistance "R" against time during specimen polarization at potential $E_{Zn} = 0.150\,V$



(a)

(b)

Notes: (a) In Baltic sea water; (b) in 1 per cent NaCl solution

the calculated resistance is not the resistance of the deposits. However, it indicates that the barrier properties of the deposit coating are enhanced over time. During specimen polarization in 1 per cent NaCl, current demand varied between 6 and 9 μA (Figure 1(b)). Cathodic protection current demand did not decrease over the exposure time. The resistance of the investigated layer was virtually unchanged and did not exceed 200 kΩ. Thus, there were no non-conductive deposits on the specimen surface.

The AFM image of the specimen surface before the exposure in Figure 2(a) shows only impurities contours and scratches introduced during polishing process. The next images show gradual evolution of the deposits. After just 4 h of cathodic polarization in Baltic sea water, the steel surface was covered with deposits, no scratches were visible, and small aggregates of the deposit had evolved (Figure 2(b)). After a 3.5 week exposure, the deposit was cauliflower-shaped (Figure 3(c)), which is typical for aragonite $CaCO_3$ (Morizot *et al.*, 2002; Wang, 2008).

The height difference on the AFM surface profile before the exposure did not exceed 70 nm (Figure 3(a)). The profile after 4 h exposure in Figure 3(b) showed that there were features about 700 nm high on the scanned surface. In Figure 3(c) (height profile after 25 days exposure), the image was unfocused. The reason was that there were significant variations in the AFM microscope cantilever deflection that were associated with significant height variations on the scanned surface. The extremes of deposit layer were 1.8 μm in several places.

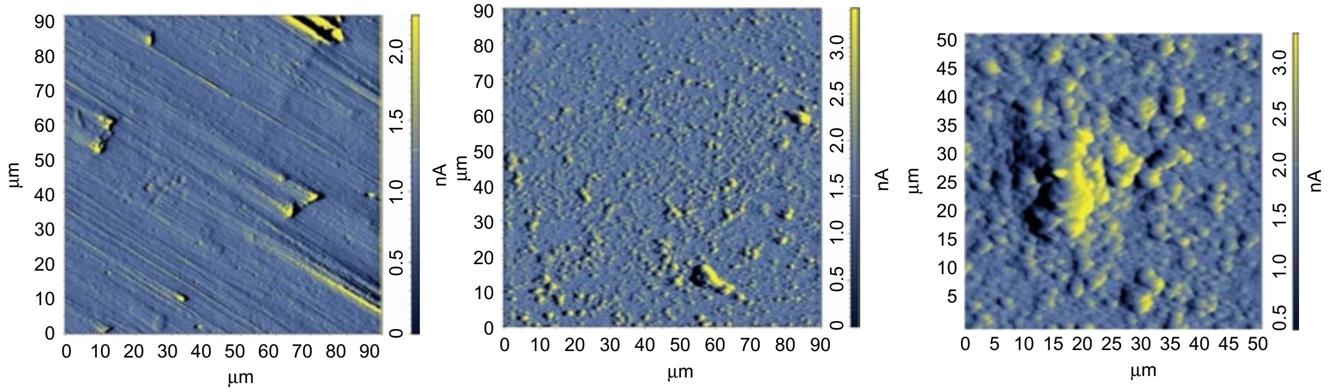
In the AFM d.c. profile for the specimen surface before the exposure (Figure 4(a)), the current reached up to 100 pA. The profile after exposure (Figure 4(b)) indicates that a uniform insulating deposit coating had evolved, because current on the scanned surface did not exceed 6 pA. Thus, the deposit layer had barrier properties.

Scanning electron microscope imagining indicated that the deposits were cauliflower-shaped (Figure 5(a)). Their size was in agreement with the results obtained from the AFM technique (Figure 2(c)). It can be seen that the deposits were charged by the SEM electron beam. This phenomenon occurs when the tested sample is an insulator and the charge introduced by the beam is not removed. As a result, the image of the insulating species is very bright. Furthermore, the elemental composition of the deposit was obtained by EDX. Carbon, calcium and oxygen were identified (Figure 5(b)), which indicate the presence of $CaCO_3$.

Conclusions

The results of chronoamperometric measurements and the atomic force microscopy survey proved that on cathodically polarized steel in Baltic sea water, non-conducting deposits evolved. Studies of the morphology of the deposit, using AFM

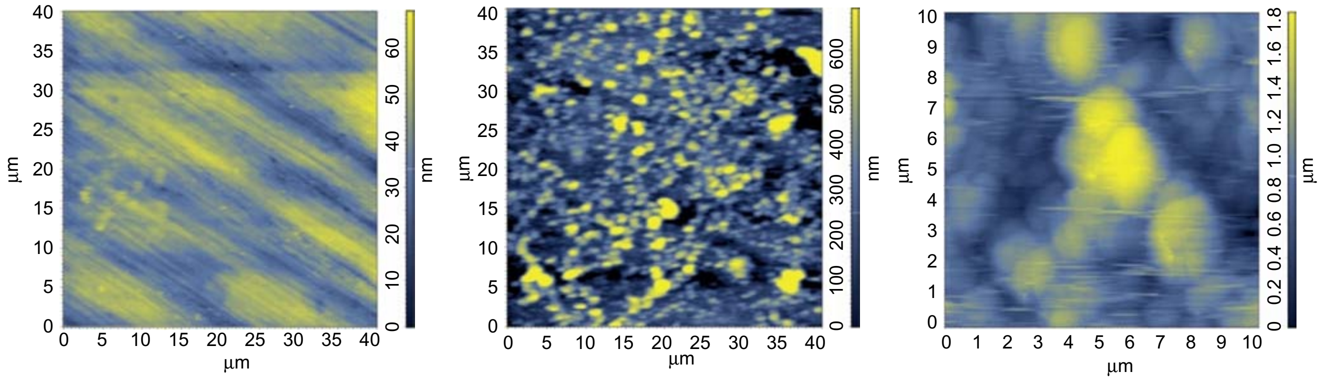
Figure 2 AFM 2D surface profile of the specimen



(a) (b) (c)

Notes: (a) Before exposure; (b) after 4 h exposure; (c) after 25 days exposure in Baltic water; the nA is a default unit of the AFM microscope imaging software

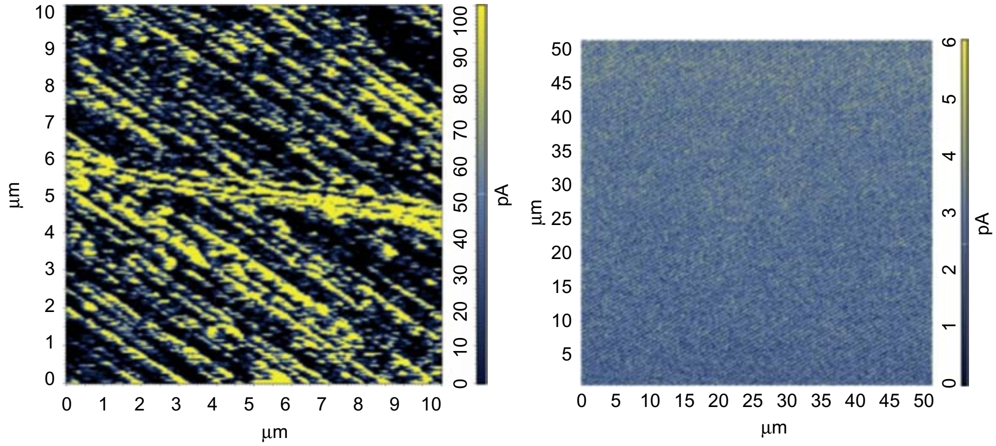
Figure 3 AFM height image of the specimen surface



(a) (b) (c)

Notes: (a) Before exposure; (b) after 4 h exposure; (c) after 25 days exposure in Baltic sea water

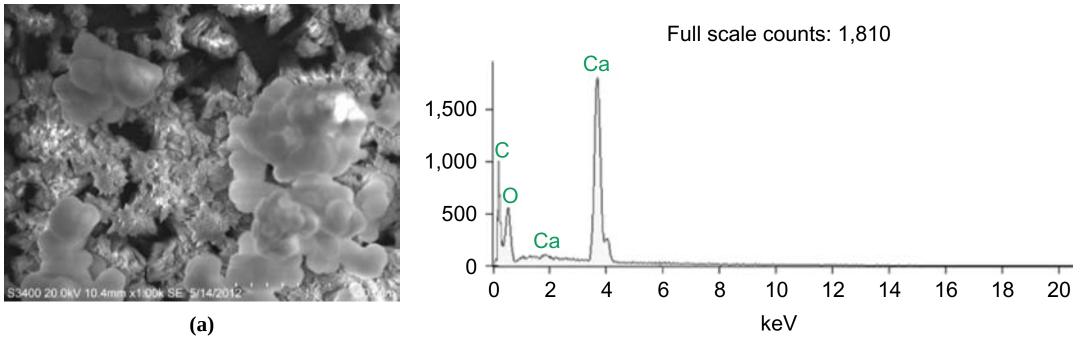
Figure 4 AFM current profile of the specimen surface



(a) (b)

Notes: (a) Before exposure; (b) after exposure in Baltic sea water

Figure 5 (a) SEM image of specimen surface after 25 days exposure; (b) EDX spectra of deposit



(a) (b)

and SEM, indicated that it is mainly built of aragonite (polymorph of $CaCO_3$). This was confirmed by EDX analysis of the deposit composition.

When the calcareous deposits develop, the cathodic protection current demand is reduced significantly. Thus, sedimentation is a beneficial and desired phenomenon from the point of view of cathodic protection systems on maritime constructions as it facilitates polarization. Evolution of calcareous deposits should be taken into account as one of the environmental factors when designing a cathodic protection system.

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