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Mechanism of enhancing corrosion inhibition of carbon steel by nitrilo-tris (methylenephosphonato)zinc in neutral chloride-containing environments: electrochemical and XPS studies

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ABSTRACT

The formation and structure of passive films on steel in a borate buffer environment pH=7.4 containing Chloride ions have been thoroughly investigated. The effect of the inhibitor $Na_4[ZnNTP] \cdot 13H_2O$ with a certain molecular structure have been studied, including the mechanism of its action. The lowest anodic dissolution current is reached at the ZnNTP concentration of about 0.6 g/L. At the initial stage of its formation, the passive film is composed of iron oxides, which may further approach the structure of magnetite. Under conditions of counter-diffusion of ZnNTP and Fe²⁺ ions, the heteropolynuclear complex $Zn_{1/2}Fe_{1/2}(H_2O)_{3\mu}$ -H₄NTP]_n is formed. As for the character of the formed chemical bonds, steel passivation in the presence of ZnNTP differs significantly from both oxide and salt passivation, and thus should be considered as a specific case, called by "coordination passivation".

1. Introduction

The phenomenon of the passivity of metals was first discovered by M. Lomonosow [1], who associated it with the transfer of "air" (or oxygen in more current sense) from the acid into the pores of the metal surface. Later, the passivity was described by Keir [2]. M. Faraday, studying the dissolution of metals and, in particular, their passivity, came to the following conclusion: "My strong impression is that the surface of the iron is oxidized, or that the superficial particles of metal are in such relation to the oxygen of the electrolyte as to be equivalent to oxidation, and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances."[3].

Based on current positions, the passivity is explained by the formation of a chemically resistant layer on a metal surface [4,5]. The concept of the adsorption describes the formation of a chemically resistant layer as a mono- or multilayer adsorption of corrosive medium components on metal surfaces [6–12]. The concept of passive film, which is

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predominant, considers passive layers as relatively thin films possessing a homogeneous structure of a particular phase [13–23]. Interaction of the metal surface with the environment components, especially, corrosion inhibitors, may facilitate the formation of films composed of oxides, hydroxides, salts and others. To reliably describe the passivation, a synthetic approach seems to be the most reasonable, which considers the adsorption of corrosive medium components as the initial stage of the passive film formation [24,25].

Many attempts have been made to investigate the genesis and structure of passive films in various systems [13–21]. The X-ray diffraction analysis of passive films is difficult because of their low thickness of 10^{-10} – 10^{-6} m, which makes various spectroscopies, including Auger, XPS, FTIR, Raman, and others, more applicable for their analysis [15,16,18,19,21] providing direct data on the composition and indirect one on their structure. Nevertheless, many authors try to describe passive films as comprised of several phase layers, most often Fe₃O₄ or γ -Fe₂O₃, which are separated by interfaces [13–18], based on

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the electrochemical data [13,14,17,18] and spectroscopic analysis of the composition.

The passivity is not a static state [24–27], with the corrosion rate being not zero in the passive state. Metal ions unceasingly diffuse through the passive film into the corrosive medium as evidenced by the anodic metal dissolution. To provide the diffusion, a concentration gradient for metal ions through the passive film is required [28,29], which disagrees with the commonly accepted consideration of a phase as a homogeneous part of a system [30].

For the reasons mentioned above, we have to stick to the view considering a passive film as not a thermodynamic phase [24–27]. The phase structure earlier ascribed to surface films in [13–18] should be considered only as a formal description of their elemental composition.

In our opinion, at the initial stage of the formation, a passive film has a structure with a high concentration of defects such as metal vacancies and embedded oxygen atoms, OH^- ions, and hydrated water molecules. With further aging the passive film, fragments of various phases are possibly formed, including those detected by X-ray diffraction methods. But the film remains inhomogeneous as a whole, with its structure being most likely filled with islands of individual phases.

Shortly after the development of industrial technology for the synthesis of organo-polyphosphonic acids [31,32], these compounds showed their anticorrosive activity, in particular nitrilo-tris (methylenephosphonic) acid N(CH₂PO₃)₃H₆, hereinafter called NTP [33,34]. The anticorrosive activity of NTP complexes with metal ions was found to be higher than of free NTP [35]. Among those, the NTP complexes with zinc and cadmium ions were shown to be more effective [35,36]. The structure of NTP complexes with metal ions has been repeatedly investigated and reliably defined, in particular, by single crystal X-ray diffraction analysis [36,37]. It has been shown that Zn- and Cd-NTP complexes which differ in their molecular structure, have also different anticorrosive activity, otherwise all things being equal [36]. Among the Zn- and Cd-NTP complexes, the complex Na₄[ZnNTP]• 13H₂O (hereinafter called ZnNTP) demonstrated the highest inhibition efficiency of steel corrosion [36]. The mechanism of the anticorrosive effect of phosphonates has also been repeatedly studied [18-21,38,39].

The first stage in the formation of a passive film in an inhibited medium is surely mono- or multilayer adsorption of inhibitors on the metal surface, possibly with the formation of surface complexes of inhibitor molecules bound with the metal atoms through the donor-acceptor mechanism [9,19-21].

In the presence of inhibitors, further development of the passive film structure is still debatable. Various studies, including XPS, Auger and FTIR analysis as well as electrochemical impedance spectroscopy studies on passive films formed in the presence of inhibitors, showed inhibitor molecules and their complexes with metal ions in the films [9,18,19,21]. The interaction of metal complexes of organo-phosphonic acids with the iron surface is assumed to initiate the substitution of the central metal atom/ion of the complexes by iron with further evolving as hydroxides [38,39]. Heterometallic complexes of organo-phosphonic acids are also assumed to present in the passive films composition [21,38,39].

The use of Zn-NTP as a corrosion inhibitor was shown to provide the reaction.

$${}^{1/_{2}nFe^{2+}} + n[ZnNTP]^{4-} + 7nH_{2}O = [Fe_{1/2}Zn_{1/2}(H_{2}O)_{3}\mu - H_{4}NTP]_{n} + {}^{1/_{2}nZn}$$

$$(OH)_{2} + 3nOH^{-}$$
(1)

giving the heterometallic complex $[Fe_{1/2}Zn_{1/2}(H_2O)_3\mu$ -H_4NTP]_n hereinafter called $Fe_{1/2}Zn_{1/2}NTP$, and zinc hydroxide. The $Fe_{1/2}Zn_{1/2}$ NTP complex was isolated in crystalline form, and its composition and structure being studied in detail [36]. Nevertheless, the localization of the reaction (1) and its products in the passive films on the steel surface have been unclear so far.

This work studies the development and structure of passive films formed under anodic polarisation of steel at various potentials in a borate buffer acid medium with pH=7.4 in the presence of chloride ions

as depassivating agent, the effect of the corrosion inhibitor ZnNTP and proposes the mechanism of its anticorrosive activity.

2. Material and methods

2.1. Steel samples

Corrosion tests were conducted on steel samples of grade E235 specified by the standard ISO 630–4:2021. The elemental composition of steel is given in Table 1.

The samples were prepared as plates of 15 \times 17 \times 0.5 and 8 \times 10 \times 0.5 mm for the corrosion tests followed by XPS measurements combined with *in situ* heating and depth-profiling with Ar⁺ ion etching, respectively. The sample surface was ground to Ra= 0.6–1 μ m, then degreased with alcohol, etched with a 15% HCl of analytical grade to remove the abrasion deformed layer, and then washed with distilled water.

2.2. Corrosive environments

The choice of the corrosion test medium was restricted by the necessity to keep balance between the required pH range, the desired minimal effect of the buffer solution on the corrosion process, and providing the possibility of reasonable interpretation of spectroscopic data to analyze outermost layers with taking into account the available published data for comparison. The phosphate buffer solution was not chosen because of strong adsorption of phosphate ions on the iron surface and their influence on the corrosion kinetics [40] which makes it difficult to reliably interpret the measured spectra.

Borate buffer solutions are commonly used as a corrosive medium [13–16,40,41]. Despite the possible adsorption of borate ions on the iron surface [42], the borate buffer solution choice was reasonably chosen as a corrosion test medium to reach compromise between all the mentioned factors and make it possible to most appropriately interpret the data obtained.

Holmes borate buffer solution with pH= 7.4 was prepared as described in [43]. Sodium tetraborate decahydrate of reagent grade and boric acid of reagent grade were used without any additional cleaning.

Chloride ions were added into the prepared solution as sodium chloride of reagent grade without additional cleaning. The following concentration scale of chloride additives (mg/L) was used: 0.0, 1.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0. The selected concentration series of chloride ions in the corrosion test media is well-founded and relevant, as the used concentrations match their typical values in most industrial, domestic and household waters. The analyzed concentration range of Cl⁻ ions allowed us to reveal the main features of their effect on corrosion processes on the steel surface and its passivation.

2.3. Synthesis of Na₄[ZnNTP]•13H₂O

The ZnNTP sample was prepared using the earlier described procedure [36]. In brief, the solution of 0.01 mol twice recrystallized NTP in 50 ml of distilled water were added dropwise into 0.01 mol zinc oxide of analytical grade mixed with 0.04 mol sodium hydroxide of analytical grade under vigorous stirring at 60–90 °C. The resulting clear solution was supplemented with DMSO of reagent grade in amount of 4:1 by vol. and left to crystallize at room temperature. The as-formed large transparent triclinic crystals of the product were isolated, washed with first dry DMSO and then diethyl ether, and air-dried.

Elemental analysis: Calcd for $[ZnN(CH_2PO_3)_3]Na_4.13H_2O:$ P 13.57; Zn 9.55. Found: P 13.65 \pm 0.5; Zn 9.7 \pm 0.2.

Elemental	l composition	of the steel	used for	corrosion	studies.
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Element	С	Cr	V	Ti	Ni	Mn	Si
% mass.	0.2	0.099	0.016	0.012	0	0.22	0

The structure of the synthesized compound has been analysed in detail by single crystal X-ray diffraction analysis [36,37] and deposited at the Cambridge Structural Database, CCDC no. 919565. The crystallographic data are given in Appendix S1 in detail, and a fragment of the molecular structure being shown in Fig. 1*a*. The structure of ZnNTP is a chelate complex with the zinc atom at the centre of the trigonal bipyramid, with the corners of its base occupied by oxygen atoms of three different PO₃ groups of the NTP molecule and the vertices are occupied by the nitrogen atom of this NTP molecule and oxygen atom of the PO₃ group of the neighbour NTP molecule. In the crystal packing, the molecules of the complex are surrounded by a sodium hydrate matrix which includes Na⁺ ions and molecules of water of crystallization.

The inhibitor was added into the corrosive environment in the following concentrations (g/L): 0.025, 0.05, 0.10, 0.20, 0.50, 1.00, 2.00, 3.00, 5.00, 7.00, 10.00, 20.00, 50.00.

2.4. Corrosion behaviour

To study the corrosion behaviour, polarisation techniques were applied with use of an automated potentiostat in a three-electrode conventional electrochemical cell described in detail in Supplementary Materials S2.

Prior to measuring the polarisation curves, the samples were kept at a potential of -0.8 V with respect to the silver-silver chloride electrode (SSCE) (sat.) for 10 min. The polarisation curves were measured in the potential range ϕ from -0.8 V/SSCE to + 1.5 V/SSCE with a potential sweep rate of $2 \bullet 10^{-3}$ V/s under natural aeration of the electrolyte.

2.5. XPS studies

X-ray photoelectron spectra (XPS) were measured from the surface of samples polarised at various anodic potentials in corrosive environments containing and not containing Chloride ions as well as without and with ZnNTP inhibitor.

Passive layers on the samples were formed under anodic polarisation at the chosen anodic potentials in the electrochemical cell for 10 min, since this duration had been previously shown [13] to be enough to form the main part of the passive layer on the steel surface. Then the sample was transferred from the cell to a diethyl ether environment. After that, the ether-wetted sample was quickly put into the working chamber of the spectrometer with its further immediate evacuation down to 10^{-5} – 10^{-6} Pa to prevent the sample surface from the contact with air.

X-ray photoelectron spectra (XPS) with *in situ* heating the samples were measured with an EMS-3 X-ray photoelectron spectrometer [44] (UdmFRC UB RAS) equipped with a magnetic energy analyser and a monochromatic Al-K α radiation source ($h\nu$ = 1486.6 eV). The samples were *in situ* annealed when measuring XPS spectra at 150, 227, and 300 °C, with the most characteristic changes being observed at 227 °C. We suppose the processes taking place at this temperature were.



Fig. 1. A fragment of the molecular structure of the Na_4 [ZnNTP] \bullet 13H₂O complex used in this work as a corrosion inhibitor, which was refined from the single-crystal X-ray diffraction analysis. Hydrogen atoms, sodium ions and crystal water molecules are not shown for clarity.

 $4Fe(OH)_2 \rightarrow Fe_3O_4 + Fe + 4H_2O$

previously described in [45] or.

 $Fe(OH)_2 \rightarrow FeO + H_2O$,

which agrees well with the observed changes in the XPS spectra measured from the outermost surface layer.

X-ray photoelectron spectra (XPS) with depth-profiling of the sample surface were measured with an ES-2401 X-ray photoelectron spectrometer (Experimental Plant of Scientific Instrumentation of RAS) equipped with an electrostatic energy analyser and a monochromatic MgK α radiation source ($h\nu = 1253.6$ eV). The depth-profiling was performed by layer-by-layer etching with 1000 eV Ar⁺ ions.

The electron binding energy $(E_{\rm B})$ scale was calibrated using the C1s line $(E_{\rm B}=284.5~{\rm eV})$. The correction of the background and inelastic scattering was carried out using the Shirley method [46], and the statistical data processing being performed with the *Fityk 0.9.8* [47] software.

3. Results

The applied potentials and current densities of anodic dissolution are given in Supplementary Materials S3 for characteristic points of the measured polarisation curves.

A typical polarisation curve measured for the polarisation of E235 steel samples in a borate buffer solution (pH = 7.4) is shown in Fig. 2.

The following potentials are characteristic for the E235 steel in a pure borate buffer solution (pH = 7.4): an open-circuit potential of -0.68 V/SSCE, a primary passivation potential of -0.21 V/SSCE, and a transpassive potential of 1.17 V/SSCE. The critical anodic current density related to the beginning of the active-to-passive transition is 1.43 A/m². The addition of Chloride ions in amount of 1 mg/L does not significantly change the polarisation curve parameters, but only increases the current of the metal dissolution in the passive region. Starting with 5 mg/L concentration of Cl⁻ ions, the transpassive potential decreases significantly and the passive state range completely disappears at the Cl⁻ ion concentration as higher as 50 mg/L.

In the potential range of 0.0–0.3 V/SSCE in the measured polarization curves, which matches the initial stage of passivation, the increased values of the current density are observed due to apparently the oxidation reaction of Fe^{2+} ions proceeding as follows:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)^+_2 + e^-$$

Based on the published data [48] the standard electrode potential of this reaction is about 0.1 V/SSCE at pH 7.4.



Fig. 2. Anodic polarisation curves measured for the polarisation of the E235 steel samples in a borate buffer solution (pH = 7.4) without and with added Cl⁻ ions. The dependence of the current density of the anodic dissolution of metal, *i*, on the anodic potential applied to the sample, *E*. The curves are marked with numbers related to the concentration of Cl⁻ ions in mg/L. Circled **A**-**H** on the curves show characteristic points for measuring XPS spectra.

Fig. 3 shows typical core-level XPS spectra measured at room temperature from the samples before annealing and the samples annealed *in situ* in the EMS-3 spectrometer sample chamber, and Table S4 providing binding energies and assignments for main peaks of the measured spectra. The samples were polarised in a pure borate buffer at various anodic potentials applied, and literal designations for the spectra in Fig. 3 being the same as circled letters (**A**–**D**) corresponding to characteristic points for measuring XPS spectra in Fig. 2.

The XPS spectra analysis shows that passive films contain OH⁻ ions and iron oxides revealed as peaks at 532.0–533.0 eV and ~530.0 eV, respectively. The contributions observed at binding energies of 709.0–711.0 eV and 711.0–713.0 eV are assigned to Fe²⁺ and Fe³⁺ ions, respectively, and the presence of unoxidized iron is confirmed by the peak at 707.0–707.6 eV. Depending on their formation conditions, the passive films contain also elements present in the corrosive environment, in particular, boron (a feature at 191.5–193.0 eV attributed to H₄BO₄ or B₄O₇²⁻ ions), sodium, and chlorine (a contribution at 199.0–202.0 eV corresponding to Cl⁻ ions), as well as elements contained as constituents in the inhibitor composition, in particular, phosphorus, zinc, and nitrogen.

Point **A** in Fig. 2 and spectrum A in Fig. 3 correspond to active dissolution of the sample surface, and this region being composed of iron oxides and OH^- ions as well as Fe^{2+} ions on the surface of the non-annealed sample (curve **A***a*). But heating the sample up to 227°C (curve **A***b*) results in changes in the Fe2*p* spectrum observed as an

appeared strong contribution attributed to unoxidized iron. Borate and Chloride ions are found in insignificant amount, being apparently adsorbed from impurities contained in the corrosive environment. The respective fragments of the enlarged spectrum are shown in Fig. 3.

At the beginning of the active-to-passive transition which is related to point **B** in Fig. 2 and spectrum **B** in Fig. 3, iron oxides and OH⁻ ions are observed. The surface of the sample measured without heating is composed of oxidized forms of iron attributed to Fe²⁺ and Fe³⁺ ions. The concentration of borate ions increases significantly, while the amount of Cl⁻ ions remains low.

At the complete passivation potential (point C in Fig. 2 and spectrum Ca in Fig. 3), the surface layer is composed of iron oxides and OH⁻ ions. Iron is present not only as Fe²⁺ and Fe³⁺, but also in its unoxidized form. *In situ* annealing at 227 °C (curve Cb) leads to a significant change in the Fe2p spectrum, making it resembling that of magnetite Fe₃O₄ [49]. Borate ions and small amount of Cl⁻ ions are still observed.

In the region of transpassive state (**D** in Fig. 2 and spectrum **D** in Fig. 3), oxygen atoms (iron oxides and OH⁻ ions) are still present in the outermost layer. For the non-annealed sample, the surface layer is composed of both Fe²⁺ ions and unoxidized iron in significant amount as well as borate ions and a small amount of Cl⁻ ions.

The most characteristic fragments of the core-level XPS spectra measured from the samples polarised in a borate buffer with added 50 mg/L Cl⁻ ions are given in Fig. 4. The literal designations for the spectra in Fig. 4 correspond to characteristic points marked with circled



Fig. 3. Typical core-level XPS spectra measured at room temperature (*a*) and under *in situ* annealing of the samples (*b*) from the surface of the samples polarised in a pure borate buffer at different anodic potentials, with the literal designations for the spectra corresponding to the characteristic points marked with circled letters (**A–D**) in Fig. 2.



Fig. 4. Typical core-level XPS spectra measured at room temperature (*a*) and under *in situ* annealing of the samples (*b*) from the surface of the samples polarised in a borate buffer with added 50 mg/L Cl⁻ ions at different anodic potentials, with the literal designations for the spectra corresponding to characteristic points marked with circled letters (F–H) in Fig. 2.



Fig. 5. Depth profiles of the elemental composition of the surface layers for the samples polarised at the Flade potential (complete passivation) in a pure borate buffer (*a*) and with added 50 mg/L Cl⁻ ions (*b*). Concentration of the main elements as depended on Ar⁺ ion etching depth, δ .

letters (F-H) in Fig. 2.

At the beginning of the active-to-passive transition revealed (point **F** and spectrum **F** in Figs. 2 and 4, respectively), iron oxides and much higher amount of OH⁻ ions are observed. The Fe2*p* spectrum contains pronounced contributions from unoxidized iron as well as Fe²⁺ and Fe³⁺ ions. In addition, borate ions are observed in a low amount, while the concentration of Cl⁻ ions is much higher.

For the potentials which are intermediate between active-to-passive transition and transpassive state (point **G** and spectrum **G** in Figs. 2 and 4, respectively), the surface layer is composed of iron oxides and hydroxide ions. The Fe2*p* spectrum (Fig. 4, spectrum **G***a*) contains contributions from unoxidized iron, as well as Fe²⁺ and Fe³⁺ ions. Annealing at 227 °C (Fig. 4, spectrum **G***b*) do not also give magnetite Fe₃O₄, and the contribution from unoxidized iron remaining significant. The amount of borate ions decreases, while the amount of Cl⁻ ions remains significant.

In the transpassive state (point **H** and spectrum **H** in Figs. 2 and 4, respectively), the amount of hydroxide ions OH⁻ reduces. Analysis of the respective Fe2*p* spectra measured at room temperature indicates the presence of both unoxidized iron and Fe²⁺ and Fe³⁺ ions. The concentration of Cl⁻ ions is lower as compared to borate ions.

The main peaks of the XPS spectra measured with depth-profiling as well as the elemental composition of the analysed surface layers are given in Supplementary Materials (Tables S5 and S6, respectively). Fig. 5 demonstrates depth profiles of the elemental composition of the surface layers for the samples polarised at the Flade potential (complete passivation) in a pure borate buffer solution (*a*) and at a potential corresponding to an intermediate state between active-to-passive transition and transpassive state in a borate buffer with added 50 mg/L of Cl⁻ ions (*b*).

The outermost layer of the passive film formed on the sample polarised in a pure borate buffer (Fig. 5a) contains about 20 at% iron which increases up to 60 at% in a depth of 10–15 nm. The oxygen concentration decreases, respectively, from about 60 at% in the outermost layer down to 35 at% in a depth of 10–15 nm.

The passive film formed on the sample polarised in a borate buffer solution containing 50 mg/L Cl⁻ ions (Fig. 5*b*) shows lower iron amount varying from 10 at% in the surface layer to 50 at% in a depth of 10 nm, whereas oxygen concentration is higher and changes from about 70 at% in the surface layer down to 43 at% in a 10-nm depth. The distribution of boron and sodium in the passive film is close to that for passivation in a pure borate buffer, and the concentration of Chloride ions is as low as 0.4–0.6 at%.

Fig. 6 shows the Fe2*p* core-level spectra measured with depthprofiling by etching with Ar^+ ions of the samples polarised at the Flade potential (complete passivation) in a pure borate buffer (Fig. 6*a* corresponding to point **C** in Fig. 2) and at a potential lying between active-to-passive transition and transpassive state (Fig. 6*b* corresponding to point **G** in Fig. 2) in a solution containing 50 mg/L of Cl⁻ ions.

The Fe2*p* core-level XPS analysis shows that the passive film formed on the sample polarised in a pure borate buffer medium (Fig. 6*a*, curve 0) does not contain unoxidized iron, with the presence of mainly Fe³⁺ ions being observed. At a depth of 1 nm (curve 1 in Fig. 6*a*), the Fe²⁺ ions predominate. It should be noted that the data on the composition are not considered to be very reliable for 0 and 1 nm of depth, since the average depth of analysis for an XPS measurement is approximately 4–6 nm. At a depth of 5 nm (curve 5 in Fig. 6*a*), a peak assigned to unoxidized iron is observed as well as a broad shoulder attributed to the Fe²⁺ and Fe³⁺ oxidation states. At a depth of 15 nm (curve 15 in Fig. 6*a*), the Fe³⁺ oxidation state is practically absent.

A similar composition was found to be observed in the passive film formed on the sample polarised in a borate buffer medium containing 50 mg/L of Cl^- ions (Fig. 6b).

Fig. 7 gives the O1s core-level XPS spectra with depth-profiling measured from the samples polarised at the Flade potential (complete passivation) in a pure borate buffer solution (Fig. 7*a* matching to point **C** in Fig. 2) and at an intermediate potential between the active-to-passive



Fig. 6. The Fe2 $p_{3/2}$ core-level XPS spectra measured under depth-profiling with Ar⁺ ion etching of the samples polarised at the Flade potential (complete passivation) in a pure borate buffer (*a*) and with added 50 mg/L of Chloride ions (*b*). The spectra are marked with numbers corresponding to the etching depth in nanometres.

transition and the transpassive state (Fig. 7*b* corresponding to point **G** in Fig. 2) in a borate buffer containing 50 mg/L Cl⁻ ions.

Based on the O1s XPS spectra analysis, the composition of the passive films includes OH^- ions and iron oxides, with OH^- ions prevailing over iron oxides in amount.

Fig. 8 shows typical polarisation curves for the E 235 steel samples in a borate buffer solution (pH = 7.4) containing various concentrations of Cl^- ions and ZnNTP inhibitor.

Fig. 8*a* shows that adding the ZnNTP inhibitor in even low amount of 0.05–0.5 g/L into a pure borate buffer solution (pH=7.4) leads to a sharp decrease in the critical corrosion current from 1.43 A/m² down to 0.34 A/m² for the solution containing 0.5 g/L inhibitor. The current density of the anodic dissolution of the metal also decreases in the passive region. In the absence of Cl⁻ ions, the addition of ZnNTP has no noticeable effect on both primary passivation potential and transpassive potential.

Being introduced in a moderate concentration (about 10 mg/L), chloride ions provide a two-stage process of the anodic dissolution of iron depending on the ZnNTP inhibitor amount (Fig. 8*b*). Small amount of the inhibitor leads to decreasing the critical corrosion current from 1.32 A/m^2 (without inhibitor) to 0.49 A/m^2 in the presence of 0.2 g/L



Fig. 7. The O1*s* core-level XPS spectra with depth-profiling measured from the samples polarised at the Flade potential (complete passivation) in a pure borate buffer solution (*a*) and at an intermediate potential between the active-to-passive transition and the transpassive state (*b*) in a borate buffer solution containing 50 mg/L Chloride ions. The spectra are marked with numbers corresponding to the etching depth in nanometres.



Fig. 8. Typical anodic polarisation curves for the E235 steel samples in a borate buffer solution (pH=7.4) containing various concentrations of Cl⁻ ions (*a*-*d*) and ZnNTP inhibitor showing the density of anodic dissolution current, *i*, as depended on the anodic potential, *E*, at the sample. The numbers on the curves show the concentration of the ZnNTP inhibitor in g/L. The circled letters (**J**–**M**) correspond to points for measuring XPS spectra.

ZnNTP and to lower current density of the anodic dissolution of the metal in the passive region. The transpassive potential practically does not change in this range of the inhibitor concentration remaining the value of 0.45-0.38 V/SSCE. A larger amount of ZnNTP (0.5-2.0 g/L) does not significantly decrease the current density of the anodic dissolution of the metal, but leads to increasing the transpassive potential from 0.62 V/SSCE at 0.5 g/L ZnNTP to 1.17 V/SSCE at 2.0 g/L ZnNTP.

With increasing the concentration of chloride ions up to 100 mg/L, the anodic dissolution behaves similarly. But even at the chloride ions concentration of 50 mg/L (Fig. 8*c*), addition of moderate amount of ZnNTP (just a few g/L) results in increasing the transpassive potential accompanied by jumps in the current density of the anodic dissolution of

the metal at potentials between 0.7 V/SSCE and 1.1 V/SSCE. Further increase in the inhibitor concentration up to 10 g/L and higher suppresses this process in this potential range.

At the concentration of chloride ions of 200 mg/L (Fig. 8*d*) and higher, the current density of the anodic dissolution of the metal keeps up decreasing. Nevertheless, higher inhibitor concentrations do not result in growing transpassive potential. With the inhibitor concentration of 20 g/L and higher, the onset potential for passivation decreases significantly, and the current density of the anodic dissolution of the metal increases in the regions of active dissolution and active-to-passive transition.

The most characteristic fragments of the core-level XPS spectra measured from the samples polarised in a borate buffer environment with added 50 mg/L chloride ions and 5 g/L ZnNTP inhibitor at various anodic potentials are given in Fig. 9. The literal designations near the spectra in Fig. 9 correspond to the points for measurements indicated by the circled letters in Fig. 8*c*.

At the beginning of the active-to-passive transition visible as point J in Fig. 8c and spectrum J in Fig. 9, adsorbed [ZnNTP]⁴⁻ inhibitor ions are observed on the sample surface. The presence of [ZnNTP]⁴⁻ ions is confirmed by singlets in the P2p, Zn3s, and N1s spectra, which indicate an equivalent nearest-neighbouring for all atoms in the inhibitor molecules. All the PO₃ groups of the NTP molecules are equally bound with zinc atoms, as evidenced by the only P2p spectrum maximum at a binding energy of ~133 eV. Zinc atoms are surrounded by deprotonated oxygen atoms, as observed by the peak at ~139.0-140.0 eV. Nitrogen atoms are deprotonated, as evidenced by the peak at 397.0-400.0 eV. All the mentioned observations indicate that the passivation of the sample surface starts with the adsorption of the inhibitor as [ZnNTP]^{4–} ions having the structure shown in Fig. 1a and spectroscopic data matching those of the inhibitor initially added into the solution [36]. The O1s and Fe2p core-level XPS spectra are similar to those observed in the absence of the inhibitor, with prevailing OH⁻ ions and iron oxides in the O1s spectra as well as unoxidized areas and various oxides/hydroxides observed in the Fe2p spectra. The borate and chloride ions are also observed at the surface.

At the potential of complete passivation (point K and spectrum K in Figs. 8c and 9, respectively), the spectra measured from the outermost layer of the passive film significantly change for all the elements in the inhibitor composition. The P2p spectrum shifts to higher binding energy with its maximum at 134.2 eV, which indicates the breakdown of some of the bonds between the PO₃ groups of the inhibitor and the metal atom, as well as their protonation. The Zn3s spectrum contains two

contributions with their maxima at 139.6 and 141.0 eV, which may be assigned to Zn atoms in their complexes with NTP and to zinc atoms in Zn(OH)₂, respectively. The N1*s* spectrum also contains two contributions with maxima at 398.2 and 402.3 eV, which are attributed to deprotonated nitrogen atoms in the initial [ZnNTP]^{4–} complex and protonated nitrogen atoms in the product of reaction (1), respectively. A contribution corresponding to the Fe³⁺ ions appears in the Fe2*p* spectrum. The borate ions are also observed, whereas the chloride ions decrease markedly in their amount.

Fig. 10 shows the of the elemental composition depth-profiles extracted from the XPS spectra measured with Ar^+ ion etching of the surface layers of the samples polarised at the Flade potential corresponding to the complete passivation in a borate buffer solution with added 5 g/L ZnNTP (Fig. 10*a* corresponding to point **M** in Fig. 8*a*) and in a borate buffer solution with added 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 10*b* corresponding to point **K** in Fig. 8*c*).

The sample polarised in a borate buffer solution with added 5 g/L ZnNTP and in the absence of depassivating ions (Fig. 10*a*) demonstrates the increase in the iron concentration from \sim 15 at% in the outermost layer of the passive film to \sim 40 at% at a depth of 20 nm with simultaneous reducing the oxygen concentration from about 60–40 at%. The elements adsorbed from the buffer solution, including boron and sodium, and from the inhibitor, including phosphorous, zinc and nitrogen, are approximately evenly distributed through the passive film thickness.

For the sample polarised in a borate buffer solution containing both 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 10*b*), the iron concentration increases sharper, changing from 10 at% at the surface up to 50 at% at a depth of 5–10 nm, with respective drastic drop of the oxygen fraction from 75 at% on the surface to about 40 at% at a depth of 5–20 nm. The concentration of elements adsorbed on the surface from the buffer solution and inhibitor is somewhat lower than in the absence of depassivating agent. The fraction of the chloride ions is not higher than 0.2 at%.

Fig. 11 shows the Fe2*p* core-level XPS spectra measured with depthprofiling from the samples polarised at the Flade potential (complete passivation) in a borate buffer solution with added 5 g/L ZnNTP (Fig. 11*a* corresponding to point **M** in Fig. 8*a*) and in a borate buffer solution with 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 11*b* corresponding to point **K** in Fig. 8*c*).

The outermost layer of the passive film formed under polarisation in a pure borate buffer solution (Fig. 11*a*, curve 0) contains mainly Fe²⁺ and Fe³⁺ ions with insignificant amount of unoxidized iron. At a depth of 1 nm (Fig. 11*a*, curve 1), the Fe2*p* spectrum is characteristic of Fe²⁺ ions.



Fig. 9. The most characteristic fragments of the core-level XPS spectra measured from the samples polarised in a borate buffer environment with added 50 mg/L chloride ions and 5 g/L ZnNTP as an inhibitor at various anodic potentials. The spectra are designated by letters (J–L) corresponding to the points of measurements indicated by the circled letters in Fig. 8c.



Fig. 10. The depth-profiles of the elemental composition extracted from the XPS data with Ar^+ ion etching of the surface layers of samples polarised at the Flade potential corresponding to the complete passivation in a borate buffer solution with added 5 g/L ZnNTP (Fig. 10*a* corresponding to point **M** in Fig. 8*a*) and in a borate buffer solution with added 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 10*b* corresponding to point **K** in Fig. 8*c*). The concentration of the main elements *c* as depended on the etching depth δ .

For 5-nm- and 15-nm-depths (Fig. 11*a*, curves 5 and 15), the maximum of the Fe2*p* spectrum is attributed to unoxidized iron, with the characteristic shoulder corresponding to iron oxides. The passive film formed on the sample polarised in a borate buffer solution with 50 mg/L chloride ions and 5 g/L ZnNTP has a similar composition and structure (Fig. 11*b*).

Fig. 12 shows the P2*p* core-level XPS spectra measured with depthprofiling from the outermost layer of the samples polarised for 10 min at the Flade potential in a borate buffer solution with 5 g/L ZnNTP which corresponds to point **M** in Fig. 8*a*.

The P2*p* core-level XPS spectrum measured from the outermost layer of the passive film (Fig. 12, curve 0) contains the only contribution at 132.5–133.5 eV which is identical to the measured from a pure crystalline ZnNTP having the structure shown in Fig. 1*a*. The P2*p* spectrum measured from 1-nm-depth (Fig. 12, curve 1) is broader due to intermediate states of phosphorus in reaction (1). For a depth of 5 nm (Fig. 12, curve 5), the spectrum demonstrating two pronounced contributions is shifted towards higher binding energies as compared to that measured from the outermost layer of the passive film. The spectrum measured from a depth of 15 nm (Fig. 12, curve 15) contains two contributions at 133.6 and 135.2 eV, which is identical to that measured from individual heterometallic complex $Zn_{1/2}Fe_{1/2}NTP$.

4. Discussion

Fig. 5*a* demonstrates that the passive film formed on a steel surface in a pure borate buffer at the complete passivation potential (point **C** in Fig. 2, spectrum **C** in Fig. 3) contains oxygen and iron, and the O/Fe molar ratio decreases gradually from \sim 3 (which is close to that in Fe (OH)₃) in its outermost layer) to 0.53 in a depth of 10–15 nm. An oxygen-free layer was failed to be observed even for long-term ion etching of the sample surface. The passive layer composition does not reveal any abrupt changes which have been previously calculated for a multilayer multiphase passive film [13]. The layer underlying the passive film, which is characterized by the O/Fe ratio less than 1, may apparently be described as iron suboxide FeO_{1-x}, and the passive film being a mixture of iron oxides and hydroxides of various compositions and structures, with the O/Fe ratio being as higher as 1. The O/Fe ratio equal to 1.0, characteristic of the lower iron oxide FeO, is reached at a depth of 5 nm which may be considered as a thickness of the oxide layer of the passive film (Figs. 5 and 13*a*).

The analysis of the core-level XPS spectra measured with depthprofiling (Fig. 7*a*) from the passive film formed in a pure borate buffer solution shows that at a depth of down to 5 nm, the fraction of oxygen involved in ionic bonds prevails over its fraction in iron oxides. According to the Fe2*p* core-level XPS spectrum containing several spectral contributions (spectrum *Ca* in Fig. 3), any specific phase containing iron cannot be distinguished in the passive film composition. *In situ* annealing at 227 °C which resembles the process of natural aging results in changes in the Fe2*p* spectrum making it characteristic of magnetite Fe₃O₄ (spectrum *Cb* in Fig. 3). Thus, the passive film at the initial stage of its formation is not a phase but a disordered mixture of Fe²⁺ and Fe³⁺ oxides and hydroxides. The magnetite phase is apparently formed under further aging of the passive film.

Fig. 5*a* presents the distribution of the elements (Fig. 5*a*) adsorbed from buffer solution, in particular, B and Na in the oxide layer of the passive film with O/Fe ratio less than 1.0 observed at a depth of 5 nm and in the underlying iron suboxide layer with O/Fe ratio as higher as 1.0. The observed difference in the elemental distribution is most likely explained by differences in the process of adsorbing impurities from buffer solution into the surface layer. For the oxide layer of the film, impurities are adsorbed from buffer solution simultaneously with the formation of a passive layer under counter-diffusion of oxygen ions O^{2–} and hydroxide OH[–], on the one hand, and Fe²⁺ ions, on the other hand (Fig. 13*a*). As for the underlying suboxide layer, the adsorption of impurities occurs owing to their diffusion from outer layers of the film into the substrate depth.

The addition of chloride depassivating ions into a corrosive environment changes significantly the parameters of the passive film, including its thickness, composition and structure.

For the sample polarised in a borate buffer solution with 50 mg/L chloride ions at the potential of complete passivation (point **G** in Fig. 2), the passive film with the O/Fe ratio equal to 1.0 is not thicker than \sim 3 nm. Thus, the passive oxide film is thinner than that formed in the absence of chloride ions. Whereas the outermost layer of the passive film contains oxygen as mainly involved in the formation of OH⁻ ions, the layer lying as deeper as 1 nm is mainly composed of oxides (Fig. 7b), which can be explained by a high-rate transfer of iron ions in the form of



Fig. 11. Core-level Fe2*p* XPS spectra measured with depth-profiling from the samples polarised at the Flade potential (complete passivation) in a borate buffer solution with added 5 g/L ZnNTP (Fig. 11*a* corresponds to point **M** in Fig. 8*a*) and in a borate buffer solution with 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 11*b* corresponding to point **K** in Fig. 8*c*). The spectra are marked with numbers corresponding to the etching depth in nanometres.

readily soluble complexes [Fe(OH)_xCl] into the corrosive environment, facilitated by depassivating chloride ions (Fig. 13b). Unoxidized iron observed in the passive film in addition to Fe^{2+} and Fe^{3+} oxides and hydroxides, confirmed by the XPS spectra analysis (Fig. 4, spectrum G), indicates a porous structure of the passive film formed in the presence of chloride ions (Fig. 13b). Heat treatment of the passive film does not give the Fe₃O₄ magnetite, and the structure composed of mixed oxides and unoxidized iron in a significant amount is retained. The underlying suboxide layer contains more sodium (Fig. 5b) as compared to the sample polarised in a pure borate buffer solution, which may indicate its higher permeability and adsorption capacity due to greater porosity and concentration of cationic vacancies and agree well with lower iron fraction in this region. Compared to other constituents of the corrosive environment, the chloride ions concentration is quite low (0.4–0.6 at%) because of probably high solubility of the [Fe(OH)_xCl] complexes followed by their transfer into the corrosive medium under passive film dissolution (Fig. 13b).

The film formed at the potential of complete passivation in a borate buffer environment containing 5 mg/L ZnNTP differs in the composition and structure. In addition to the Fe²⁺ and Fe³⁺ oxides and hydroxides, the film contains heterometallic polynuclear complexes of iron and zinc Fe_{1/2}Zn_{1/2}NTP, as well as hydroxide zinc (Fig. 9, spectrum K). The molar O/Fe ratio gradually decreases in the film from about 4 in the outermost



Fig. 12. P2*p* core-level XPS spectra measured with depth-profiling from the outermost layer of the samples polarised for 10 min at the Flade potential in a borate buffer solution with 5 g/L ZnNTP corresponding to point **M** in Fig. 8*a*. The spectra are marked with numbers corresponding to the etching depth in nanometres. The spectra for ZnNTP and heterometallic complex $Zn_{1/2}Fe_{1/2}NTP$ are taken from [36].

passive layer to 1 at a depth of 20 nm. The thickness of the oxide layer of the passive film (Fig. 10*a*) reaches 20 nm. Higher values of thickness and density of the passive film together with its lower penetrability for the metal ion diffusion earlier observed in [35,36,38], are confirmed by lower values of the critical current density of corrosion and current density of anodic dissolution of the metal in the passive region (Fig. 8).

The mechanism of the passive film formation in the presence of ZnNTP inhibitor could be understood from the analysis of the XPS spectra. The uniform distribution of the inhibitor elements, in particular, P, Zn, and N, in the oxide layer of the passive film (Fig. 10a) indicates this layer is doped with these elements as it grows. The film composition changes in-depth (Fig. 12) as follows. The outermost layer contains the inhibitor as initial ions [ZnNTP]^{4–}. But layers lying as deeper as 15 nm contain the inhibitor as heterometallic complexes $Fe_{1/2}Zn_{1/2}NTP$ and Zn (OH)₂, which are the products of reaction (1). In fact, various explanations may be proposed to explain this observation. The first one supposes primary formation of deeper layers of the film, in which reaction (1) has been already finished, whereas outer layers are formed later and reaction (1) has not been completed in them. But this explanation does not take into account that preparations needed to perform XPS measurements take enough time to completely finish reaction (1) even in the outermost layer of the passive film. More probable explanation is that reaction (1) proceeds in a passive film under counter-diffusion of ions of the initial complex $[ZnNTP]^{4-}$ and Fe^{2+} ions (Fig. 13c). Under these conditions, the degree of conversion of the initial complex into the reaction products changes through the film thickness following the law of mass action owing to increasing concentration of the Fe²⁺ ions as closer as the metal surface.

The thickness of the oxide layer of the passive film formed at the Flade potential in the presence of 50 mg/L chloride ions and 5 g/L ZnNTP (Fig. 10b) is estimated to be 4–5 nm. This allows us to make conclusion that depassivating ions added in the same amount facilitates

c) Buffer solution + CI^{-} -ions + ZnNTP



Fig. 13. Schematic of the formation and structure of a passive film in a pure buffer solution (a), buffer solution containing Chloride ions (b), and buffer solution containing Chloride ions and ZnNTP inhibitor (c).

worse dissolution of the oxide film formed in the presence of the ZnNTP inhibitor as compared to the film formed in the absence of ZnNTP.

The iron fraction in the oxide layer of the passive film formed on the sample polarised in a borate buffer solution with the added 50 mg/L chloride ions and 5 g/L ZnNTP drops sharper as compared to that formed in the absence of chloride ions (Fig. 10). This indicates that ZnNTP inhibitor impedes the diffusion transfer of iron ions from the deeper layer of the passive film to its outermost layer, in which iron ions interact with chloride ions and transfer as soluble complexes [Fe $(OH)_xCl$ into the solution. The impeded diffusion of Fe2 + ions in the presence of the inhibitor seems to be due to heterometallic complexes $Fe_{1/2}Zn_{1/2}NTP$ and $Zn(OH)_2$ formed in the passive layer.

Chloride ions make a destructive effect on the passive film, resulting in its instability at a chloride concentration of 50 mg/L and moderate ZnNTP concentration of several g/L. This effect initiate pitting, i.e. local breakdowns of the passivity, observed in Fig. 8c as jumps in the anodic current density of metal dissolution in the potential range of 0.7–1.1 V/ SSCE. Nevertheless, doping the passive film with ZnNTP makes it thicker and denser, increasing its resistance to chloride ions and, thus, decreasing the rate of its dissolution.

The nature of the effect which ZnNTP inhibitor additives make on the corrosion behaviour of steel E235 in the presence of chloride ions may be observed in the dependences of the critical corrosion current density i_c , A/m², and transpassive potential E_{tp} , V/SSCE, on the concentration of ZnNTP inhibitor C_{inh} , g/L (Fig. 14).

With increasing its concentration in the corrosive environment, the ZnNTP inhibitor works in two stages. At low concentrations, the addition of ZnNTP lowers the critical corrosion current density i_c , facilitating the onset of the passive film formation, but does not affect the transpassive potential E_{tp} and not increase the resistance of the passive film to



Fig. 14. Dependences of the critical corrosion current density i_c , A/m², and the transpassive potential E_{tp} , V/SSCE, on the concentration of ZnNTP inhibitor $C_{\rm inh}$, g/L for different concentrations of depassivating Cl⁻ ions.

the dissolution. The minimum i_c value is reached at C_{inh} of ~0.6 g/L, and this value not depending on the concentration of the depassivating Cl⁻ions (Fig. 14).

At the second stage, larger inhibitor amounts lead to increasing transpassive potential. The higher the concentration of chloride ions in a corrosive environment, the higher the concentration of the inhibitor

needed to increase E_{tp} .

The two-stage character of the corrosion inhibition by ZnNTP is apparently explained by decreasing the critical corrosion current density i_c and the passive film permeability for Fe²⁺ ions, respectively, immediately with the first appeared particles of the $Fe_{1/2}Zn_{1/2}NTP$ heterometallic complexes in the oxide layer of the passive film. The Fe^{2+} ions are bound in these complexes through coordination bonds which are stronger than ionic ones in iron oxides. The binding of the Fe^{2+} ions in the $Fe_{1/2}Zn_{1/2}NTP$ complex prevents their diffusion to the passive film surface, where the reaction of Fe^{2+} ions with depassivating Cl^- ions proceeds. To increase the transpassive potential $E_{\rm tp}$ and, thus, the resistance of the passive film to its dissolution with increasing the anodic potential, more substantial changes in the oxide film structure are required. Apparently, higher values of $E_{\rm tp}$ are achievable provided the fraction of the Fe_{1/2}Zn_{1/2}NTP complexes reaches the known threshold value or in the case of their formation as continuous polymer chains (Fig. 13c). The structural form characteristic of the $Fe_{1/2}Zn_{1/2}NTP$ heterometallic complex in deeper layers of the passive films on steel needs further comprehensive analysis.

5. Conclusions

The protective properties of the ZnNTP inhibitor taken in an individually defined structural form were analysed on steel E235 samples in a borate buffer environment (pH = 7.4) with depassivating Cl⁻ ions added in different concentration.

For moderate concentrations of the chloride ions, the inhibitor was found to effectively reduce the current density of the anodic dissolution of the metal. The critical current density of the anodic dissolution reaches its minimum at the inhibitor concentration of about 0.6 g/L, with this value not depending on the concentration of the chloride ions. At higher concentrations of the chloride ions, increasing the transpassive potential requires a larger amount of inhibitor than needed to reduce the current density of the anodic dissolution of the metal.

The composition and structure of passive films formed on E 235 steel samples under their polarisation at different anodic potentials in a borate buffer environment without and with chloride ions as depassivating agents were characterized by XPS spectroscopy with *in situ* heat treatment of the sample and depth-profiling.

At the initial stage of the formation, a passive film is not a phase layer, but a disordered mixture of iron oxides/hydroxides. Magnetite is apparently formed only under following aging of the passive film.

The passive film may be nominally divided into an oxide layer with the O/F ratio more than 1 and an underlying layer with the O/Fe ratio less than 1, which is iron suboxide or a solid solution of oxygen atoms in the α -Fe crystalline phase. The depth related to the O/Fe ratio equal to 1 can be conventionally taken as the boundary of the oxide layer of the passive film. Such a division of the passive film in layers should be noted to be just nominal and the composition actually changes smoothly.

The addition of ZnNTP as an inhibitor into a corrosive medium has been shown to change the passive film composition and structure. The outermost layer of the passive film contains [ZnNTP]^{4–} ions of the inhibitor in the initial form, which are then converted to heteropolynuclear complex $Fe_{1/2}Zn_{1/2}NTP$ and hydroxide $Zn(OH)_2$ in deeper layers. This difference may be explained by taking into account that reaction (1) proceeds in the conditions of counter-diffusion of initial inhibitor ions and Fe^{2+} ions in the passive film, and the degree of conversion of the initial complex into reaction products changes through the film thickness following the law of mass action.

The Fe_{1/2}Zn_{1/2}NTP heteropolynuclear complexes contained in the passive film provide reducing penetration of iron ions through the passive film and its lower solubility, with a contribution being also not excluded from the formed zinc hydroxide to these effects. Thus, initially, with addition of ZnNTP inhibitor at low concentration, the current density of the anodic dissolution of the metal decreases, while higher concentration of the inhibitor facilitates increasing transpassive

potential in the presence of chloride ions.

The electronic configuration of the Fe–O coordination bond in the $Fe_{1/2}Zn_{1/2}NTP$ heteropolynuclear complex differs essentially from other Fe–O bonds, which makes it stronger as compared to that in iron oxides and hydroxides and certainly in the iron ionic bond in salt films responsible for passivation. As a result, the steel passivation in the presence of the ZnNTP inhibitor differs from conventional oxide and salt passivation in both the nature of the formed chemical bonds and the degree of the corrosion protection, and these differences being significant and interplayed.

We believe that in full agreement with Faraday's assumption [3], in these heteropolynuclear complexes, ". the superficial particles of metal are in such relation to the oxygen. as to be equivalent to oxidation, and that having thus their affinity for oxygen satisfied, and not being dissolved.". This phenomenon and similar are proposed to be considered as a special kind of metal passivity and name it like "coordination passivation".

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CRediT authorship contribution statement

Irina S. Kazantseva: Investigation, Formal analysis, Resources, Writing – original draft, review & editing. Feodor F. Chausov: Conceptualization, Methodology, Project administration, Supervision, Investigation, Validation, Formal analysis, Resources, Writing – original draft, review & editing. Natalya V. Lomova: Investigation, Formal analysis. Vasiliy L. Vorob'yov: Investigation, Formal analysis. Alyona N. Maratkanova: Validation, Formal analysis, Writing – original draft, review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2022.104022.

References

- M. Lomonosow, Dissertatio de actione menstruorum chymicorum in genere, Novi Comment. Acad. Sci. Imp. Petrop. 1 (1750) 245–266.
- [2] J. Keir, Experiments and observations on the dissolution of metals in acids, and their precipitations; with an account of a new compound acid menstruum, useful in some technical operations of parting, Met., Philos. Trans. R. Soc. Lond. 80 (1790) 359–384, https://doi.org/10.1098/rstl.1790.0024.
- [3] M. Faraday, Experimental Researches in Electricity, Vol. 2, Dover Pub., New York, 1965.
- [4] U.R. Evans, The Corrosion and Oxidation of Metals, Edward Arnold Ltd, London, 1960.

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- [5] N.D. Tomashov, G.P. Chernova, Passivity and Protection of Metals Against Corrosion, Springer, Boston, MA, 1967.
- [6] G. Saha, N. Kurmaih, The mechanism of corrosion inhibition by phosphate-based cooling system corrosion inhibitors, Corros. Sci. 42 (1986) 233–235, https://doi. org/10.5006/1.3586001.
- [7] E. Kálmán, B. Várhegyi, I. Bakó, I. Felhősi, F.H. Kármán, A. Shaban, Corrosion inhibition by 1-Hydroxyethane-1,1-diphosphonic acid: an electrochemical impedance spectroscopy, Study, J. Electrochem. Soc. 141 (1994) 3357–3360, https://doi.org/10.1149/1.2059339.
- [8] J.G. Van Alsten, Self-assembled monolayers on engineering metals: structure, derivatization, and utility, Langmuir 15 (1999) 7605–7614, https://doi.org/ 10.1021/la981694g.
- [9] I. Felhősi, Zs Keresztes, F.H. Kármán, M. Mohai, I. Bertóti, E. Kálmán, Effects of bivalent cations on corrosion inhibition of steel by 1-hydroxyethane-1,1-diphosphonic acid, J. Electrochem. Soc. 146 (1999) 961–969, https://doi.org/10.1149/ 1.1391706.
- [10] I. Felhosi, J. Telegdi, G. Palinkas, E. Kalman, Kinetics of self-assembled layer formation on iron, Electrochim. Acta 47 (2002) 2335–2340, https://doi.org/ 10.1016/S0013-4686(02)00084-1.
- [11] S. Marcinko, A.Y. Fadeev, Hydrolytic stability of organic monolayers supported on TiO₂ and ZrO₂, Langmuir 20 (2004) 2270–2273, https://doi.org/10.1021/ la0349141.
- [12] G.-Y. Li, H. Ma, Y. Jiao, S. Chen, An impedance investigation of corrosion protection of copper by self-assembled monolayers of alkanethiols in aqueous solution, J. Serb. Chem. Soc. 69 (2004) 791–805, https://doi.org/10.2298/ JSC0410791L.
- [13] M. Nagayama, M. Cohen, The anodic oxidation of iron in a neutral solution: i. The nature and composition of the passive Film, J. Electrochem. Soc. 109 (1962) 781–790, https://doi.org/10.1149/1.2425555.
- [14] M. Nagayama, M. Cohen, The anodic oxidation of iron in a neutral solution: II. Effect of Ferrous Ion and pH on the Behavior of Passive Iron, J. Electrochem. Soc. 110 (1963) 670–680, https://doi.org/10.1149/1.2425849.
- [15] M. Seo, M. Sato, J.B. Lumsden, R.W. Staehle, Auger analysis of the anodic oxide film on iron in neutral solution, Corros. Sci. 17 (1977) 209–217, https://doi.org/ 10.1016/0010-938X(77)90046-4.
- [16] M. Cohen, D. Mitchell, K. Hashimoto, The composition of anodically formed iron oxide films, J. Electrochem. Soc. 126 (1979) 442–444, https://doi.org/10.1149/ 1.2128899.
- [17] J.L. Delplancke, Anodic oxidation of iron and cathodic reduction of the anodic film: a review, Surf. Technol. 20 (1983) 71–81, https://doi.org/10.1016/0376-4583(83) 90078-X.
- [18] A. Shaban, E. Kalman, I. Biczo, Inhibition mechanism of carbon steel in neutral solution by N-phosphono-methyl-glycine, Corros. Sci. 35 (1993) 1463–1470, https://doi.org/10.1016/0010-938X(93)90372-N.
- [19] Y. Gonzalez, M.C. Lafont, N. Pebere, F. Moran, A synergistic effect between zinc salt and phosphonic acid for corrosion inhibition of a carbon steel, J. Appl. Electrochem. 26 (1996) 1259–1265, https://doi.org/10.1007/BF00249928.
- [20] A.P. Morizot, A. Neville, Insights into electrodeposition of an inhibitor film and its inhibitive effects on calcium carbonate deposition, J. Colloid Interface Sci. 245 (2002) 40–49, https://doi.org/10.1006/jcis.2001.7963.
- [21] M. Prabakaran, K. Vadivu, S. Ramesh, V. Periasamy, Corrosion protection of mild steel by a new phosphonate inhibitor system in aqueous solution, Egypt. J. Pet. 23 (2014) 367–377, https://doi.org/10.1016/j.ejpe.2014.09.004.
- [22] T.R. Beck, Formation of salt films during passivation of iron, J. Electrochem. Soc. 129 (1982) 2412–2418, https://doi.org/10.1149/1.2123558.
- [23] J. Benzakour, A. Derja, Electrochemical passivation of iron in phosphate medium, Electrochim. Acta 38 (1993) 2547–2550, https://doi.org/10.1016/0013-4686(93) 80151-0.
- [24] A. Yu Popov, The main aspects of the modern theory of the passive state of metals, Russ. Chem. Rev. 74 (2005) 397–412, https://doi.org/10.1070/ BC2005v074n05ABEH000883
- [25] V.I. Alekseev, M.M. Perkas, V.S. Yusupov, G. Yu Lazarenko, The mechanism of metal corrosion passivation, Russ. J. Phys. Chem. A 87 (2013) 1380–1385, https:// doi.org/10.1134/S0036024413080049.

- [26] D.D. Macdonald, Passivity the key to our metals-based civilization, Pure Appl. Chem. 71 (1999) 951–978, https://doi.org/10.1351/pac199971060951.
- [27] D.D. Macdonald, Some personal adventures in passivity a review of the point defect model for film growth, Russ. J. Electrochem 48 (2012) 235–258, https://doi. org/10.1134/S1023193512030068.
- [28] A. Fick, Ueber diffusion, Ann. der Phys. 94 (1855) 59–86, https://doi.org/ 10.1002/andp.18551700105.
- [29] A. Fick, On liquid diffusion, Philos. Mag. 10 (1855) 30–39, https://doi.org/ 10.1080/14786445508641925.
- [30] J.B. Clarke, J.W. Hastie, L.H.E. Kihlborg, R. Metselaar, M.M. Thackeray, Definitions of terms relating to phase translation of the solid state, J. Pure Appl. Chem. 66 (1994) 577–594, https://doi.org/10.1351/pac199466030577.
- [31] K. Moedritzer, R.R. Irani, The direct synthesis of α-aminomethylphosphonic acids. mannich-type reactions with orthophosphorous acid, J. Org. Chem. 31 (1966) 1603–1607, https://doi.org/10.1021/jo01343a067.
- [32] R.R. Irani, K. Moedritzer, Processes for preparing organophosphonic acids, US Patent 3288846.
- [33] R.S. Benner, L.A. Green, Treating water to retard corrosion, US Patent 3901651.
- [34] D.A. Carter, F.G. Vogt, Silicate-based corrosion inhibitor, US Patent 3960576.
- [35] Yu.I. Kuznetsov, Organic Inhibitors of Corrosion of Metals, Springer, New York, 1996.
- [36] F.F. Chausov, I.S. Kazantseva, S.M. Reshetnikov, N.V. Lomova, A.N. Maratkanova, N.V. Somov, Zinc and cadmium nitrilotris(methylenephosphonate)s: a comparative study of different coordination structures for corrosion inhibition of steels in neutral aqueous media, ChemistrySelect 5 (2020) 13711–13719, https://doi.org/ 10.1002/slct.202003255.
- [37] N.V. Somov, F.F. Chausov, Structure of tetrasodium nitrilotrimethylenetriphosphonatozincate tridecahydrate Na₄[N(CH₂PO₃)₃Zn] · 13H₂O, an inhibitor of scaling and corrosion, Crystallogr. Rep. 59 (2014) 66–70, https://doi.org/10.1134/S1063774513050118.
- [38] I. Yu Kuznetsov, Current state of the theory of metal corrosion inhibition, Prot. Met. 38 (2002) 103–111, https://doi.org/10.1023/A:1014904830050.
- [39] Yu.I. Kuznetsov, Physicochemical aspects of metal corrosion inhibition in aqueous solutions, Russ. Chem. Rev. 73 (2004) 75–87, https://doi.org/10.1070/ RC2004v073n01ABEH000864.
- [40] J. Benzakour, A. Daerja, Electrochemical passivation of iron in phosphate medium, Electro Acta 38 (1993) 2547–2550, https://doi.org/10.1016/0013-4686(93) 80151-0.
- [41] J.L. Delplanke, Anodic oxidation of iron and cathodic reduction of the anodic film: a review, Surf. Technol. 20 (1983) 71–81, https://doi.org/10.1016/0376-4583(83) 90078-X.
- [42] Emilse M.A. Martini, Iduvirges L. Muller, Passivation of iron in solution containing borate using rotating ring-disk mesuarments, J. Braz. Chem. Soc. 10 (6) (1999) 505–511, https://doi 10.1590/S0103-50531999000600013.
- [43] W. Holmes, Silver staining of nerve axons in paraffin sections, Anat. Rec. 86 (1943) 157–187, https://doi.org/10.1002/ar.1090860205.
- [44] V.A. Trapeznikov, I.N. Shabanova, A.V. Kholzakov, A.G. Ponomaryov, Studies of transition metal melts by X-ray electron magnetic spectrometer, J. Electron Spectrosc. Relat. Phenom. 137 140 (2004) 383–385, https://doi.org/10.1016/j. elspec.2004.02.115.
- [45] B. Beverskog, I. Puigdomènech, Revised pourbaix diagrams for iron at 25–300 °C, Corros. Sci. 38 (1996) 2121–2135, https://doi.org/10.1016/S0010-938X(96) 00067-4.
- [46] D.A. Shirley, High-resolution X-ray photoemission spectrum of the valence bands of gold, Phys. Rev. B 5 (1972) 4709–4714, https://doi.org/10.1103/ PhysRevB.5.4709.
- [47] M. Wojdyr, Fityk: a general-purpose peak fitting program, J. Appl. Crystallogr 43 (2010) 1126–1128, https://doi.org/10.1107/S0021889810030499.
- [48] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Corrosion Engineers, Houston, 1974.
- [49] N.S. McIntyre, D.G. Zetaruk, X-ray photoelectron spectroscopic studies of iron oxides, Anal. Chem. 49 (1977) 1521–1529, https://doi.org/10.1021/ ac50019a016.