

# Effect of octanoic acid-based inhibitors on the corrosion and electrochemical properties of oxide-ceramic coatings $B_4C-BN-Bi_2O_3-MnO_2$ on unalloyed steel

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## Abstract

The effect of mixed inhibitors based on octanoic acid and compounds of nitrogen in a negative oxidation state on the corrosion properties of an oxide-ceramic coating with  $B_4C-BN-Bi_2O_3-MnO_2$  composition was studied. The coating was synthesized by laser sintering of the powder mixture on the surface of unalloyed low-carbon steel. As a result of laser treatment, an oxide-ceramic layer with antifriction properties and high hardness was formed on the metal surface. The phase composition and surface topography of the composite obtained were studied. It was found that the corrosion resistance of the composite obtained was smaller under conditions of electrochemical corrosion in neutral buffer solution than that on untreated steel. The inhibitor treatment method was applied to increase the corrosion resistance. Octanoic acid, octanoic acid–hexamethylenetetramine, octanoic acid–hydrazine hydrate, and octanoic acid–2,4-dinitrophenylhydrazine formulations were used as the inhibitors. The inhibitors were applied by impregnation followed by heating the samples to 120°C. All the mixed inhibitors studied improved the corrosion resistance of the material against electrochemical corrosion in neutral borate buffer solution.

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## Introduction

Research and development of materials with improved tribotechnical and protective properties constitute a relevant field of materials science. In operation of products, the product surface condition is of great significance, which makes it important to develop various methods of efficient surface modification in order for improvement of the mechanical and anticorrosion properties. Parts and assemblies made of unalloyed steels are most common in mechanical engineering. To meet the current level of specific loads and a wide range of working environments, various methods of surface modification are used, including thermal and thermomechanical surface modification and application of various coatings [1]. Ceramic coatings on the surface of metals significantly improve their physical and mechanical characteristics such as hardness, wear resistance, and heat resistance, and

also reduce the coefficient of sliding friction. However, the presence of such nonmetallic phases on the surface can deteriorate the anti-corrosion properties of iron-based materials [2–5].

During interruptions in the operation of friction units, air moisture can condense on their surfaces, thus creating conditions for electrochemical corrosion. Therefore, to ensure long-term performance of products, it is necessary not only to enhance the hardness and wear resistance of the surface by application of coatings, but also to protect the surface from corrosion. For this reason, it is of importance to study electrochemical corrosion of steels with ceramic coatings based on boron carbide and boron nitride with addition of metal oxides. The addition of metal oxides, especially bismuth and manganese oxides, has been shown [6–9] to significantly improve the tribological properties of the surface, eliminate scouring, and sharply reduce the sliding friction coefficient, even in operation without lubrication. However, the positive effect of improving the hardness and tribological properties may be short-lived due to a significant acceleration of corrosion processes at the points where steel contacts oxide and nitride-carbide ceramics. It was noted in [10, 11] that the presence of carbide and oxide phases in steels could noticeably alter the electrochemical properties, including significant deterioration of the corrosion resistance of materials.

We have found previously [2, 3, 12] that the resistance of such materials to electrochemical corrosion can be enhanced using corrosion inhibitors. In this study, the corrosion-electrochemical properties of samples with an oxide-ceramic coating based on boron carbide, boron nitride, bismuth(III) oxide, and manganese(IV) oxide applied to Steel 10 substrate were examined. A borate buffer solution (BBS) at pH=7.4 under natural aeration conditions was used as the model corrosion medium. Mixed formulations of octanoic acid with hexamethylenetetramine (OA–HM), hydrazine hydrate (OA–HH), and 2,4-dinitrophenylhydrazine (OA–DNPH) were used as inhibitors.

The inhibitory ability of carboxylic acids, used both individually and as mixtures with organic nitrogen compounds, was studied previously [13–17]. The option to use hydrazine and its derivatives as corrosion inhibitors under simulated seawater conditions was examined in [18].

## Experimental

An oxide-ceramic coating was synthesized on the surface of Steel 10 samples with dimensions of 10×10×1 mm using high-speed laser treatment of a mixture of fine powders with the following composition (wt.%): B<sub>4</sub>C – 60; BN – 14; MnO<sub>2</sub> – 13; Bi<sub>2</sub>O<sub>3</sub> – 13. The powder mixture in the form of a suspension was applied to the steel surface in a uniform layer with a thickness of 50 μm using the suspension application method. A 5% solution of rosin in ethanol was used as a liquid dispersion medium in the preparation of the suspension.

A short-pulse ytterbium fiber laser (commercially available LDesigner F1 short-pulse laser with a maximum power of 50 W, λ=1.065 μm, and τ=40 ns) was used in the experimental laser treatment setup. The powder mixture on the steel surface was treated with laser in one pass in a high-purity argon atmosphere. The pulse energy was set to 1 mJ at

20 kHz, providing an instantaneous power of 25 kW. With a laser beam focal diameter of 30  $\mu\text{m}$ , the resulting instantaneous power density was  $3.5 \cdot 10^{13} \text{ W/m}^2$ . Laser treatment was carried out by scanning the sample surface with a laser beam. The thickness of the resulting oxide-ceramic coating was 5  $\mu\text{m}$ . Detailed methodology and parameters for laser beam scanning and laser treatment are presented in [9].

The structural and phase composition was determined using X-ray diffraction analysis and optical microscopy. The X-ray diffraction study was carried out pointwise using a DRON-3 diffractometer in Co-K $\alpha$  radiation, in the range of Bragg angles of 20–130°, step 0.05°, and pulse acquisition time at one point 5 s. An Olympus GX53 facility for metallographic analysis was used for optical surveying of the sample surface.

The corrosion and electrochemical behavior of the samples was studied by anodic potentiodynamic polarization employing the technique described previously [2,3]. The non-working surface of the samples was insulated with a non-conductive varnish coating. Cathodic training of the samples was carried out for 5 minutes at a potential of  $-700 \text{ mV}$ . The samples were polarized with a potential scan rate of 1 mV/s. A Ipc-Pro L potentiostat and a standard YaSE-2 cell were used. The experiments were performed at an ambient temperature of  $(20 \pm 2)^\circ\text{C}$ . A borate buffer solution with  $\text{pH}=7.4$  (BBS 7.4) was used as the model electrolyte. This electrolyte was selected since borate ions are virtually indifferent to the electrode materials, *i.e.*, neither transfer them to a passive state nor activate them (violation of the passive state). The reference electrode is a saturated silver chloride, relative to which the values of the electrode potentials  $E$  of the polarized samples are presented in millivolts. Current  $I$  was measured in  $\mu\text{A}$  and referred to 1  $\text{cm}^2$  of the electrode surface. Octanoic acid (OA) was applied with a Pasteur pipette over the entire surface of the samples.

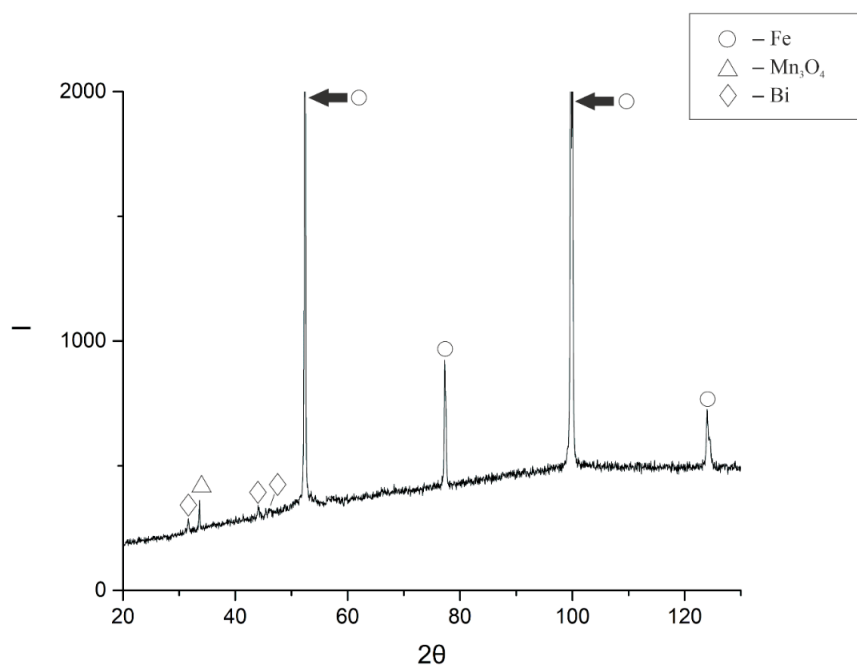
The OA-based inhibitors were prepared by creating binary mixtures with hexamethylenetetramine (OA-HM), hydrazine hydrate (OA-HH), and 2,4-dinitrophenylhydrazine (OA-DNPH). A nitrogen-containing substance weighing 1 g was dissolved in 8 ml of OA with continuous stirring and with heating in a water bath. The mixed inhibitors were applied on the samples over the entire surface using a Pasteur pipette. The samples obtained in this way were heated in an oven to 120°C for 20 minutes. The excess liquid was removed from the samples using a napkin.

## Results and Discussion

### *Results of laser treatment*

Figure 1 presents the results of X-ray diffraction analysis. The X-ray pattern shows that the following phases are present:  $\alpha$ -Fe, manganese oxide ( $\text{Mn}_3\text{O}_4$ ), and metallic bismuth (Bi). The boron carbide and nitride phases were not detected by X-ray diffraction analysis, which is explained by the formation of an amorphous phase of boron carbide with inclusions of boron nitride particles 1–10 nm large [6]. The contacts of three different electrically conductive components with each other and the substrate surface can lead to the formation

of local galvanic elements, which can cause enhanced galvanic corrosion of the surface of coated steel.

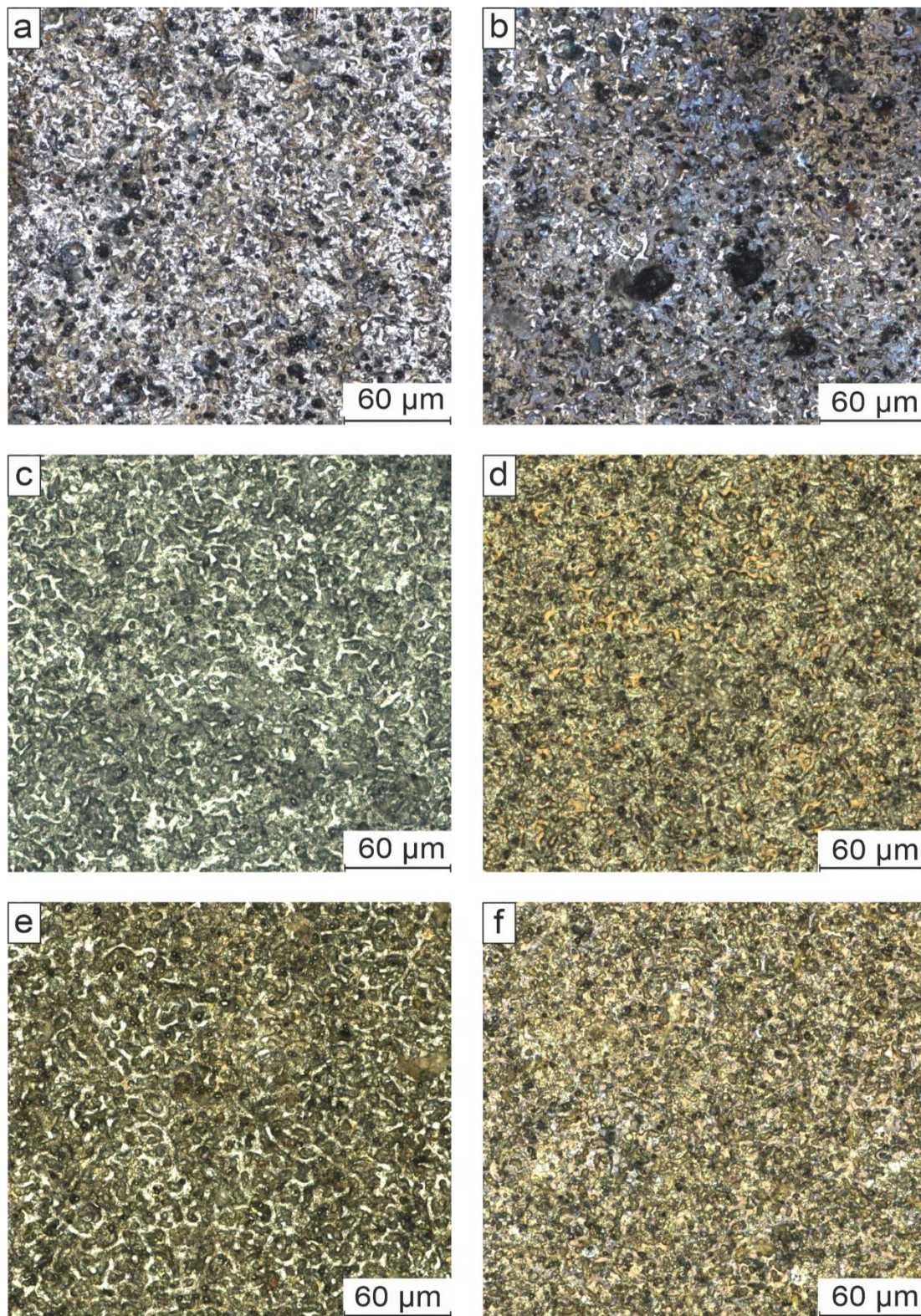


**Figure 1.** Results of X-ray diffraction analysis of the  $B_4C$ – $BN$ – $Bi_2O_3$ – $MnO_2$  coating. The symbols in the upper part of the figure correspond to the composition of the phases in the spectrum.

### *Corrosion and electrochemical behavior*

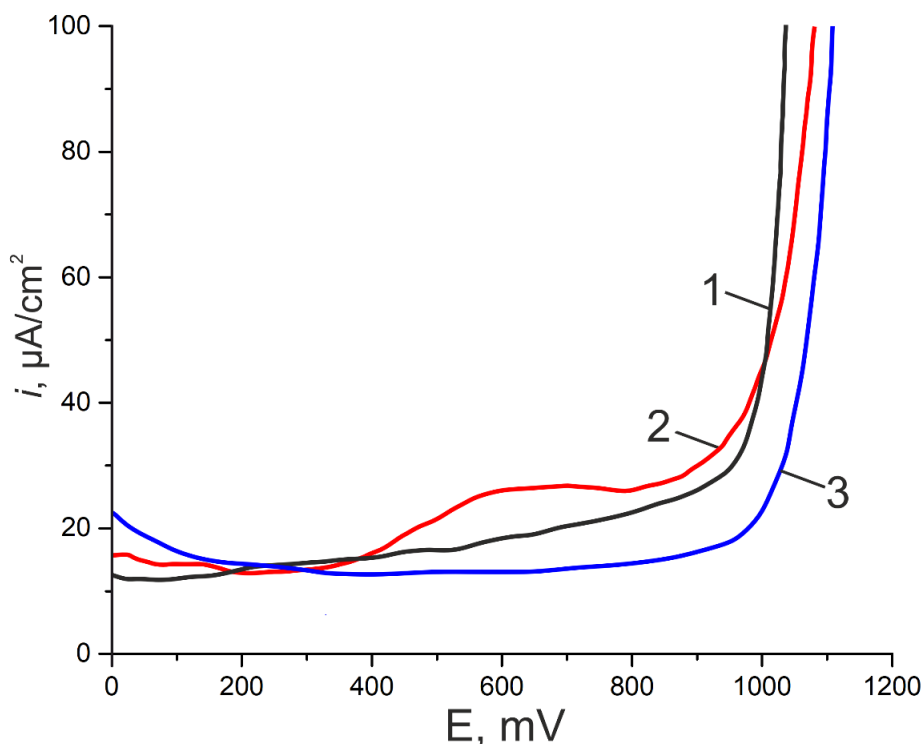
Oxide, carbide, silicide, and boride inclusions are known [10] to manifest electrocatalytic activity and resistance to electrochemical corrosion. However, contact of such particles with a metallic phase, for example, with unalloyed steel, can cause electrochemical corrosion [11].

Figure 2 displays optical microscopic images of the surface of the oxide-ceramic composite. The relief of the composite before treatment with an inhibitor and corrosion tests (Figure 2a) is a gray-silver surface with numerous pores with sizes of about  $1\ \mu\text{m}$ . In Figure 2 the pores are visible as round dots with a size of about  $1\ \mu\text{m}$ . After anodic polarization, pits with a size of up to  $30\ \mu\text{m}$  formed on the surface of the composite not treated with an inhibitor (Figure 2b), and the surface became darker. When the composite is treated with inhibitors based on octanoic acid, the surface after anodic polarization acquires a yellowish-golden color. It can be seen that on the surface of samples treated with inhibitors, anodic polarization does not result in the formation of pits.



**Figure 2.** Optical microscopic images (magnification x500) of the surface of samples with B<sub>4</sub>C-BN-Bi<sub>2</sub>O<sub>3</sub>-MnO<sub>2</sub> oxide-ceramic coating: samples without inhibitor treatment before (a) and after (b) anodic polarization; samples treated with the OA-HH inhibitor before (c) and after (d) anodic polarization; samples treated with the OA-DNPH inhibitor before (e) and after (f) anodic polarization.

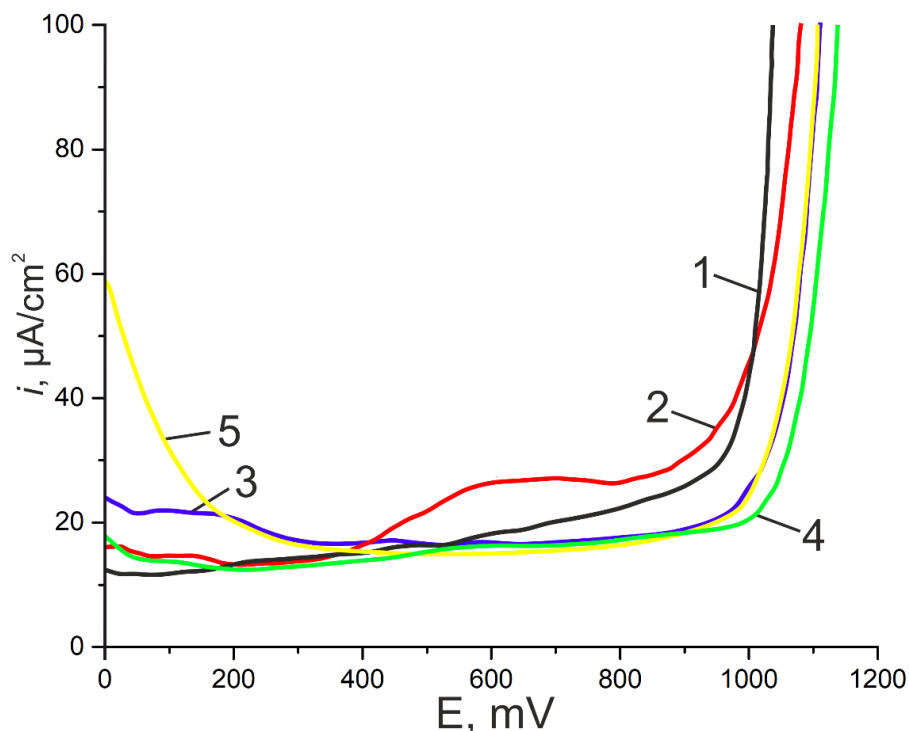
Figure 3 displays the anodic potentiodynamic curves of samples made of steel 10, steel 10 with the oxide-ceramic coating, and steel 10 with the oxide-ceramic coating after treatment with octanoic acid. The anodic polarization curve of steel 10 samples has the shape typical of a material that is easily passivated in a borate buffer solution at pH=7.4. If an oxide-ceramic coating is applied, the transpassivation potential virtually does not change (see Table 1), but for a coated sample, the anodic dissolution current increases at potentials within +400 to +700 mV. Pre-treatment of the oxide-ceramic coating with octanoic acid leads to a decrease in the anodic current in the passive region and to an increase in the transpassivation potential.



**Figure 3.** Anodic potentiodynamic polarization curves: 1 – steel 10; 2 – steel 10 with the  $B_4C-BN-Bi_2O_3-MnO_2$  oxide-ceramic coating; 3–steel 10 the  $B_4C-BN-Bi_2O_3-MnO_2$  oxide-ceramic coating and OA as the inhibitor.

Our previous study showed that the combination of octanoic acid with nitrogen compounds with negative oxidation state exhibits anti-corrosion properties against electrochemical corrosion in neutral environments [12]. Figure 4 displays the anodic curves obtained by polarization of coated samples after treatment with mixed inhibitors.

In addition to the reduction of the anodic dissolution currents, the efficiency of inhibitors can be estimated by the increase in the transpassivation potential. Table 1 shows the transpassivation potentials, along with the anodic currents at a potential in the passive state ( $E= +600$  mV).



**Figure 4.** Anodic potentiodynamic polarization curves: 1 – steel 10; 2 – steel 10 with the  $B_4C$ –BN– $Bi_2O_3$ – $MnO_2$  oxide-ceramic coating without inhibitor treatment; 3 – steel 10 with the  $B_4C$ –BN– $Bi_2O_3$ – $MnO_2$  oxide-ceramic coating treated with the OA–HM inhibitor; 4 – steel 10 with the  $B_4C$ –BN– $Bi_2O_3$ – $MnO_2$  oxide-ceramic coating treated with the OA–HH inhibitor; 5 – steel 10 with the  $B_4C$ –BN– $Bi_2O_3$ – $MnO_2$  oxide-ceramic coating treated with the OA–DNPH inhibitor.

**Table 1.** Current in the passive state region and the transpassivation potential of samples coated with  $B_4C$ –BN– $Bi_2O_3$ – $MnO_2$ .

Sample	Current in the passive state region (+ 600 mV), $\mu A$	Transpassivation potential, mV
Steel 10 without a coating	19	1003
Without treatment with inhibitors	26	999
Treatment with OA	15	1053
Treatment with OA–HM	15	1051
Treatment with OA–HH	16	1083
Treatment with OA–DNPH	15	1052

It can be seen that all the mixed inhibitors studied enhance the anti-corrosion properties of the samples.

## Conclusions

1. It has been shown that  $B_4C-BN-Bi_2O_3-MnO_2$  oxide-ceramic coatings that feature good adhesion to the substrate, high hardness, and improved tribological properties can be applied on the surface of unalloyed steel.
2. The corrosion-electrochemical properties of samples with the resulting coatings have been studied in a neutral borate buffer solution at  $pH=7.4$ . The increase in anodic dissolution currents compared with that of steel 10 sample recorded in potentiodynamic mode is explained by the acceleration of the anodic process due to dissolution of the substrate material.
3. The effect of preliminary treatment of coated samples by inhibitors on their corrosion-electrochemical properties has been studied. It has been found that pre-treatment of samples with OA, OA-HM, OA-HH, OA-DNPH inhibitors followed by heat treatment significantly reduces the anodic dissolution rate and increases the transpassivation potential, thereby enhancing their resistance to electrochemical corrosion under these conditions.

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