# Study on the efficiency of benzotriazole and mercaptobenzothiazole as corrosion inhibitors of some high-alloy steels in neutral environment

S.G. Bystrov,<sup>1</sup>\* S.M. Reshetnikov,<sup>1,2</sup> E.M. Borisova,<sup>2</sup> T.A. Pisareva<sup>2</sup> and V.Ya. Bayankin<sup>1</sup>

<sup>1</sup>Udmurt Federal Research Center of the Ural Branch of the Russian Academy of Sciences, 132 Kirova Str., 426000 Izhevsk, Russian Federation <sup>2</sup>Udmurt State University, 1 Universitetskaya Str., 426034 Izhevsk, Russian Federation \*E-mail: <u>bystrov.sg@mail.ru</u>

## Abstract

The efficiency of benzotriazole (BTA) and mercaptobenzothiazole (MBT) as corrosion inhibitors of a number of high-alloy steels in a neutral borate buffer solution has been studied. As shown by the results of potentiodynamic and XPS studies the steels under study (30Kh13, 14Kh17N2, 03Kh18N11) are initially in passive state, which causes rather a low rate of their anodic dissolution. Addition of these inhibitors at concentrations of 0.3, 0.5 and 1.0 mmol/L further reduces the anodic dissolution current of the samples in the passive region. At the same time, BTA is usually more efficient as an inhibitor than MBT. XPS studies have shown that both inhibitors are capable of adsorption on the surface of the samples of the steels studied, including that on partially oxidized surface chromium atoms, as well as on the surface iron atoms that having features of an oxidized state. MBT particles form more efficient surface complexes comprising sulfur. The assumption is made that the sulfur atom of MBT forms surface compounds with partially oxidized chromium and iron atoms that are part of the non-stoichiometric oxides of these elements comprising oxygen atoms. Thus, under the conditions studied, BTA and MBT inhibitors favor an improvement of the passivating (protective) properties of the surface of the high-alloy steels tested.

Received: March 31, 2022. Published: April 22, 2022

doi: <u>10.17675/2305-6894-2022-11-2-13</u>

*Keywords:* high-alloy steels, corrosion inhibitors, chemical composition and structure of surface layers.

# Introduction

Benzotriazole (BTA) and mercaptobenzothiazole (MBT) have long been known as metal corrosion inhibitors [1]. Their effect has been well studied in the inhibition of copper corrosion, which is associated with the formation of insoluble compounds of Cu(II) ions with BTA and MBT particles [2]. Comprehensive information on the effect of azole class inhibitors as of 2008 is given in review [3]. Subsequently, BTA and MBT were intensely studied as corrosion inhibitors of both ferrous [4–8] and non-ferrous metals [1–3, 9].

Attention was also paid to high-alloy chromium and chromium-nickel steels [10-14]. The efficiency of BTA and its formulations with some additives in acid environments, including that at high temperature, was shown. However, there is evidence [10, 14] that the efficiency of, for example, BTA as a corrosion inhibitor of stainless steels is insufficient. This is attributed to the fact that these steels have adsorption or phase passivating layers that efficiently slow down the corrosion of the materials and addition of inhibitors enhances the protective effect only slightly, but does not change it significantly.

In view of this, it should be noted that studies on the corrosion-electrochemical behavior of unalloyed steel after laser treatment in various modes in which oxide passivation layers were formed, it was found that addition of BTA to a neutral borate buffer solution (BBS) with pH=7.4 contributed to a significant reduction in the anodic currents in the passive region [5]. These results comply with the concept of oxygen-free passivation of metals developed by Yu.I. Kuznetsov [15].

Taking the above into account, the goal of this work was formulated: to study the efficiency of BTA and MBT as corrosion inhibitors of some high-alloy easily passivating steels in a neutral buffer solution.

#### Materials and methods of the experiment

Electrodes made of 30Kh13, 14Kh17N2 and 03Kh18N11 steels were studied as samples of high-alloy steels. The composition of the steels fully complied with the effective GOST standards. It is shown in Table 1.

Sample	Composition of samples in the initial state, mass.%,	Heat treatment of samples				
Steel 30Kh13	Fe – base; Cr – 12.93; C – 0.32; Mn – 0.65; Si – 0.62; Ni – 0.16	Annealing in a vacuum of $10^{-4}$ Pa at a temperature of 900°C for 60 minutes with cooling to ambient temperature in the vacuum furnace				
Steel 14Kh17N2	Fe – base; Cr – 17.13; Ni – 2.04; C – 0.14; Mn – 0.30; Si – 0.28	Annealing in a vacuum of $10^{-4}$ Pa at a temperature of 770°C for 60 minutes with cooling to ambient temperature in the vacuum furnace				
Steel 03Kh18N11	Fe – base; Cr – 17.76; Ni – 10.08; C – 0.03; Mn – 1.43; Si – 0.40	Annealing in a vacuum of $10^{-4}$ Pa at a temperature of 870°C for 120 minutes, with cooling to ambient temperature in the vacuum furnace				

Table 1. Composition and modes of heat treatment of the steels studied.

The samples had the form of plates with dimensions of  $10 \times 10 \times 3$  mm made using electric spark cutting from a bar in as-delivered state. After cutting, the steels were heat treated (see the modes in Table 1). Further, samples were mechanically treated, namely,

ground with abrasives and polished with GOI paste to a roughness of  $R_a = 0.02$  microns (grade 13 roughness), followed by cleaning in an ultrasonic bath in organic solvents.

The samples were examined by plotting anodic potentiodynamic curves in a neutral medium, *i.e.*, borate buffer solution with pH=7.4. An Eco-Lab 2A-100 potentiostat was used. The solutions were prepared with distilled water. Natural aeration of solutions was used; the temperature was  $20\pm2^{\circ}$ C. A standard YaSE-2 electrochemical cell was used. A saturated silver chloride reference electrode was used and the electrode potentials (*E*, mV) below in the text and in the figures are given with respect to it. The potential scanning rate used to record the potentiodynamic curves was 2 mV/s. The current density *i* ( $\mu$ A/cm<sup>2</sup>) was calculated with respect to the visible (geometric) surface of the electrodes.

X-Ray photoelectron spectroscopy (XPS) was used to determine the surface composition of samples both before and after electrochemical tests. The studies were performed on an ES-2401 spectrometer using Mg  $K\alpha$  radiation (E=1253.6 eV). To remove residual surface contamination, the surface of each sample was etched with argon ions for 30 seconds in the spectrometer chamber (the estimated etching rate was 1 nm/min). The spectra were processed with the licensed CasaXPS software using reference data from [16, 17]. The relative error in calculating the concentration of atoms from XPS data was 3% of the measured value.

## **Results and Discussion**

Figures 1–3 show some of the polarization curves obtained. The concentration of BTA and MBT in the background solution was 0 (background), 0.3, 0.5, or 1.0 mmol/L. The change in the concentration of inhibitors had an effect on both the rate of conditionally active (prepassivation) dissolution of samples and the rate of their dissolution at potentials in the passive region. It appeared most interesting to estimate the effect of inhibitors specifically at potentials in the passive region. Figures 1–3 show the anodic potentiodynamic curves at the maximum concentration used, *i.e.*, 1 mmol/L.



**Figure 1.** Anodic potentiodynamic curves of the studied 30Kh13 steel samples: 1 - in the initial % buffer solution without an inhibitor; 2 - with added 1 mmol/L of BTA inhibitor; 3 - with added 1 mmol/L of MBT inhibitor.



**Figure 2.** Anodic potentiodynamic curves of the studied steel samples 14Kh17H2: 1 – in the initial borate buffer solution without an inhibitor; 2 – with added 1 mmol/L of BTA inhibitor; 3 – with added 1 mmol/L of MBT inhibitor.



**Figure 3.** Anodic potentiodynamic curves of the studied steel samples 03Kh18N11: 1 – in the initial borate buffer solution without an inhibitor; 2 – with added 1 mmol/L of BTA inhibitor; 3 – with added 1 mmol/L of MBT inhibitor.

Analysis of the above figures shows that all the studied samples are characterized by rather low anodic currents, which is typical of these steels that inherently have passivation layers. To characterize the efficiency of the inhibitors, the anodic current density at a potential of E = 500 mV was chosen. This potential approximately corresponds to the middle of the region of stable passive state of the samples under these conditions.

A complete summary of the data characterizing the effect of the inhibitors on the anodic current density is given in Table 2.

Steel grade	Background solution (without inhibitor) $i_a$ , $\mu A/cm^2$	MBT inhibitor concentration, mmol/L					BTA inhibitor concentration, mmol/L						
		0.3		0.5		1.0		0.3		0.5		1.0	
		ia	γ	<i>i</i> a	γ	<i>i</i> a	γ	<i>i</i> a	γ	<i>i</i> a	γ	<i>i</i> a	γ
30Kh13	48	28	1.7	18	2.7	8	6.0	30	1.6	26	1.8	20	2.4
14Kh17N2	56	38	1.5	29	1.9	18	3.1	51	1.1	40	1.4	30	1.9
03Kh18N11	58	28	2.1	19	3.1	16	3.6	50	1.2	44	1.3	40	1.5

**Table 2.** Anodic dissolution current density of steel samples ( $i_a$ ,  $\mu A/cm^2$ ) and the inhibition factor ( $\gamma$ ) at a potential of E = 500 mV in the presence of BTA and MBT inhibitors at various concentrations (mmol/L).

To characterize the efficiency of the inhibitors, the anodic current densities  $i_a$ ,  $\mu A/cm^2$  in the background BBS solution, *i.e.* without an inhibitor, and at the inhibitor concentrations noted above are shown in Table 2. The inhibition factor of the corrosion process ( $\gamma$ ) under the effect of the inhibitors was also calculated:

$$\gamma = i_{a \text{ background}} / i_{a \text{ inhibitor}},$$

where:  $i_{a background}$  is the current density in the background solution and in the solution with added inhibitor;  $i_{a inhibitor}$  is the current density in the solution with an inhibitor.

This factor shows how the anodic current decreased in the presence of a given inhibitor concentration.

It should be noted at once that from all the data obtained, it follows that the MBT is a more efficient inhibitor than BTA.

According to the XPS data, the relative concentrations of elements on the surface of the studied samples were calculated (Table 3) both before the action of inhibitors, *i.e.* on the samples in the initial state, and after the action of the inhibitors.

Steel	Inhibitor, 1.0 mmol/L	<b>Relative concentrations of elements, %</b>									
		С	0	Fe	Cr	Ni	Ν	S			
30Kh13	BTA	32.0	49.3	15.3	1.9	_	1.5	_			
	MBT	53.3	34.3	7.2	1.5	_	1.6	2.2			
14Kh17N2	BTA	49.7	39.3	7.5	1.1	traces	2.4	—			
	MBT	34.1	49.0	11.3	2.5	traces	1.3	1.9			
03Kh18N11	BTA	38.5	46.5	11.7	2.3	traces	1.0	—			
	MBT	33.9	47.2	12.8	3.0	traces	1.3	1.9			

Table 3. Relative concentrations of elements in the studied samples.

It can be seen from the above data that if MBT is used as a corrosion inhibitor, the amount of chromium on the surface increases compared to the samples treated with BTA. Moreover, this trend goes in line with an increase in the corrosion current inhibition coefficient (Table 2). This is apparently due to the formation of compounds that prevent corrosion. Moreover, the more chromium a steel contains, the more such compounds are formed.



**Figure 4.** XPS spectra of the Fe  $2p_{3/2}$  line of steel 03Kh18N11. 1 – initial steel; 2 – initial steel with added BTA; 3 – initial steel with added MBT.

The amount of nitrogen on the surface of the studied samples is approximately the same. This may indicate that the presence of sulfur atoms in the MBT molecule plays a significant role in reducing the corrosion rate due to the adsorption of the inhibitor.

The fine structure of XPS spectra of the samples under study is shown in Figures 4–6. The XPS spectra of steel 03Kh18H11 were selected as examples illustrating the changes occurring in the chemical structure of the surface of the samples under study upon exposure

to corrosion inhibitors. The largest increase in the corrosion current inhibition coefficient was observed on this steel, according to Table 2. The concentration of the corrosion inhibitors was 1.0 mmol/L.

Figure 4 shows the XPS spectra of the Fe  $2p_{3/2}$  line of steel 03Kh18N11 both in the initial state and after treatment with corrosion inhibitors.



**Figure 5.** XPS spectra of the Cr  $2p_{3/2}$  line on steel 03Kh18N11. 1 – initial steel; 2 – initial steel with added inhibitor BTA; 3 – initial steel with added inhibitor MBT.

The  $E_b$  ranges for metals at various oxidation states are indicated in Figures 4 and 5 as segments of a certain length next to the symbols of the elements.

It can be seen that the positions of the iron spectral lines and their relative intensity change insignificantly after exposure to inhibitors. Therefore, it may be assumed that the inhibitors are bound to iron through physical interaction. The formation of an electrostatic bond is possible, since nitrogen in azoles can be partially protonated [3].

Figure 5 shows the XPS spectra of the Cr  $2p_{3/2}$  line on steel 03Kh18N11 both initial state and after treatment with corrosion inhibitors.

For chromium compounds in oxidized state, a certain range of  $E_b$  values is reported in the literature for each oxidation state of the element [16, 17]. For Cr<sup>3+</sup> 2p<sub>3/2</sub>,  $E_b$ =575.9– 576.8 eV; for Cr<sup>6+</sup> 2p<sub>3/2</sub>,  $E_b$ =578.1–579.7 eV. The  $E_b$  ranges for chromium compounds in various oxidation states can partially overlap. This may be due to the complex structure of oxide films with variable and non-stoichiometric composition formed on the surface of such steels. The formation of oxides with variable composition where formally fractional oxidation states of metals are realized is noteworthy [17–20].

The chromium spectrum of the initial steel (Figure 5.1) contain lines of pure chromium  $(E_b = 574.7 \text{ eV}, 16 \text{ rel. \%})$ , chromium in  $Cr^{3+}$  oxidation state  $(E_b = 576.4 \text{ eV}, 67 \text{ rel. \%})$ , and chromium  $Cr^{6+}$  oxidation state  $(E_b = 578.2 \text{ eV}, 17 \text{ rel. \%})$ .

There is no line of pure chromium in the chromium spectrum of the steel under study after BTA treatment (Figure 5.2). It contains lines of chromium in  $Cr^{3+}$  oxidation state ( $E_b$ =576.3 eV, 75 rel. %) and the chromium line in the oxidation state  $Cr^{6+}$  ( $E_b$ =578.2 eV, 25 rel. %). That is, the position of these lines coincides with the chromium lines in the original steel, but their relative intensity is different.

The chromium spectrum of the steel under study after MBT treatment (Figure 5.3) also contains a chromium line in  $Cr^{3+}$  oxidation state ( $E_b$ =575.7 eV, 43 rel. %). However, it also contains a new intense line with  $E_b$ =577.1 eV, 57 rel. %, that is not present in the spectra discussed above. It can be seen that the binding energy of this line does not fall either in the range of binding energies characteristic of chromium in oxidation state +3, nor in the range for chromium +6. Apparently, as already noted, in this case, complex chromium compounds with the inhibitor are formed, in which formally fractional metal states oxidation are realized. It can be assumed that these compounds have high adsorption activity for sulfur atoms of MBT molecules. This contributes to a more efficient hindrance of the anodic process.

Figure 6 shows the XPS spectra of the S2p line both of the original MBT inhibitor and after treatment of the steels studied with this inhibitor.

The S2p line of the original MBT inhibitor (Figure 6.1) has a binding energy of  $E_b = 163.5$  eV. This line is symmetrical, which indicates that there is one type of bond of sulfur atoms in the initial inhibitor. On application to a metal, the spectra of the sulfur line have a distinct shoulder in the region of  $E_b = 168.4$  eV (Figure 6.2–4). This peak is most pronounced in the inhibitor applied to steel 03Kh18H11 (Figure 6.2). According to reference data [16], this binding energy is characteristic of sulfur in compounds where sulfur forms a bond with a metal through an oxygen atom. In our case, formation of sulfur compounds with chromium through oxygen bridges is most likely. Apparently, such compounds allow the inhibitor to be firmly fixed on a steel surface, which provides more efficient inhibition of the anodic dissolution of the sample. Moreover, the more chromium the steel surface contains, the more efficient MBT behaves as an inhibitor.



**Figure 6.** XPS spectra of the S2p line. 1 – original MBT; 2 – steel 03Kh18H11 with added MBT inhibitor; 3 – steel 14Kh17H2 with added MBT inhibitor; 4 – steel 30Kh13 with added MBT inhibitor.

Nitrogen in the original BTA has an N1s line's binding energy of 398.2 eV (Figure 7.1). On applying BTA onto steel 03Kh18H11, the binding energy of this nitrogen line increases slightly (to 399.4 eV, Figure 7.3). This implies that the interaction of some nitrogen atoms in the BTA molecule with steel components has an adsorption nature, especially, as noted above, with chromium atoms in various oxidation states.

The binding energy of nitrogen the (N1s line) in the initial MBT is 400.0 eV (Figure 7.2), which can be attributed to the presence of electronegative sulfur atoms in the MBT molecule. On applying MBT onto steel 03Kh18H11, the binding energy of this nitrogen line decreases to a value of 399.2 eV (Figure 7.4). Since in this case, the binding energy of the nitrogen line coincides almost completely with that in the BTA spectrum on steel (Figure 7.3), it may be assumed that the nature of the interaction of nitrogen atoms with steel components is almost the same in both inhibitors.



**Figure 7.** XPS spectra of the N1s line. 1 – original BTA; 2 – original MBT; 3– steel 03Kh18H11 with added BTA inhibitor; 4 – steel 03Kh18H11 with added MBT inhibitor.

#### Conclusions

The efficiency of BTA and MBT as corrosion inhibitors of a number of high-alloy, easily passivating steels in a neutral buffer solution has been studied. It follows from the data obtained that the use of inhibitors can significantly (several-fold) reduce the current density of anodic dissolution, and the MBT inhibitor acts more efficiently than BTA.

It has been found that the use of MBT as a corrosion inhibitor increases the amount of chromium on the surface in comparison with to BTA-treated samples. This trend goes in line with the higher anodic current inhibition factors of sample dissolution provided by MBT compared to BTA.

The assumption was made that the increase in the amount of chromium on the surface of samples being studied is associated with the formation of surface compounds that prevent the anodic process. Moreover, the more chromium the steel contains, the larger amount of such compounds is formed. It has been found that contact of BTA with steel surfaces results in its physical adsorption via BTA nitrogen atoms with formation of protective layers of the inhibitor that are weakly bound to the surface.

It has been shown that in the case of MBT, complex chromium compounds with the inhibitor are formed, in which formally fractional metal oxidation states are realized. These compounds allow the inhibitor to be firmly bound on the steel surface and reduce the solubility of metal chromates, which provides a more efficient reduction in the anodic dissolution current.

The studies were carried out using the equipment of the Center Collective Use "Center for Physical and Physicochemical Methods of Analysis, Study of the Properties and Characteristics of Surfaces, Nanostructures, Materials and Products" of the Udmurt Federal Research Center of the Ural Branch of the Russian Academy of Sciences.

## References

- 1. A.I. Altsybeeva and S.Z. Levin, *Inhibitors of metal corrosion*, Khimiya, Leningrad, 1968, p. 262 (in Russian).
- 2. E.S. Ivanov, *Inhibitors of metal corrosion in acid media*, Metallurgiya, Moskva, 1986, p. 175 (in Russian).
- 3. Yu.I. Kuznetsov and L.P. Kazansky, Physicochemical aspects of metal protection by azoles as corrosion inhibitors, *Russ. Chem. Rev.*, 2008, **77**, no. 3, 219–232. doi: 10.1070/RC2008v077n03ABEH003753
- 4. S.M. Reshetnikov, I.N. Shabanova, E.A. Naimushina, N.S. Terebova and A.V. Kholzakov, A study of benzotriazole and mercaptobenzothiazole as inhibiting additives to mineral oil, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 3, 924–931. doi: 10.17675/2305-6894-2021-10-3-6
- E.V. Kharanzhevskiy, S.M. Reshetnikov, A.V. Efimov, F.Z. Gil'mutdinov and M.D. Krivilev, Application of some inhibitors for improving the corrosion resistance of ceramic coatings deposited on non-alloy steel by short-pulse laser treatment, *Int. J. Corros. Scale Inhib.*, 2020, 9, no. 1, 44–55. doi: <u>10.17675/2305-6894-2020-9-1-3</u>
- Ya.G. Avdeev, M.V. Tyurina and Yu.I. Kuznetsov, Protection of low-carbon steel in phosphoric acid solutions by mixtures of a substituted triazole with sulfur-containing compounds, *Int. J. Corros. Scale Inhib.*, 2014, 3, no. 4, 246–253. doi: <u>10.17675/2305-6894-2014-3-4-246-253</u>
- Ya.G. Avdeev, I.G. Gorichev and A.Yu. Luchkin, Effect of IFKhAN-92 inhibitor on scale removal during sulfuric acid pickling of steel, *Int. J. Corros. Scale Inhib.*, 2012, 1, no. 1, 26–37. doi: 10.17675/2305-6894-2012-1-1-026-037
- Ya.G. Avdeev and A.Yu. Luchkin, Effect of IFKhAN-92 inhibitor on electrode reactions and corrosion of mild steels in hydrochloric and sulfuric acid solutions, *Int. J. Corros. Scale Inhib.*, 2013, 2, no. 1, 53–66. doi: <u>10.17675/2305-6894-2013-2-1-053-066</u>

- I.A. Arkhipushkin, Yu.E. Pronin, S.S. Vesely and L.P. Kazansky, Electrochemical and XPS study of 2-mercaptobenzothiazole nanolayers on zinc and copper surface, *Int. J. Corros. Scale Inhib.*, 2014, 3, no. 2, 78–88. doi: <u>10.17675/2305-6894-2014-3-2-078-088</u>
- G.O. Tatarchenko, N.F. Tyupalo and V.S. Kuzub, Inhibitive effect of benzimidazole and benzotriazole on corrosion of 12Kh18N10T steel in sulfuric acid, *Zashch. Met.*, 1992, 28, no 5, 842–845 (in Russian).
- 11. Ya.G. Avdeev, D.S. Kuznetsov, M.V. Tyurina, A.Yu. Luchkin and M.A. Chekulaev, Protection of chromium-nickel steel in hydrochloric acid solution by a substituted triazole, *Int. J. Corros. Scale Inhib.*, 2015, **4**, no. 1, 1–14. doi: <u>10.17675/2305-6894-2015-4-1-001-014</u>
- Ya.G. Avdeev, D.S. Kuznetsov, M.V. Tyurina and M.A. Chekulaev, Protection of nickel-chromium steel in sulfuric acid solution by a substituted triazole, *Int. J. Corros. Scale Inhib.*, 2015, 4, no. 2, 146–161. doi: <u>10.17675/2305-6894-2015-4-1-146-161</u>
- Ya.G. Avdeev, L.V. Frolova, D.S. Kuznetsov, M.V. Tyurina and M.A. Chekulaev, Protection of stainless steel in sulfuric acid solution containing hydrogen sulfide by inhibitors, *Int. J. Corros. Scale Inhib.*, 2016, 5, no. 2, 147–158. doi: <u>10.17675/2305-6894-2016-5-2-4</u>
- 14. D.S. Robinson, Corrosion inhibitors, Metallurgiya, Moskva, 1983, p. 272 (in Russian).
- 15. Yu.I. Kuznetsov, Physicochemical aspects of metal corrosion inhibition in aqueous solutions, *Russ. Chem. Rev.*, 2004, **73**, no. 1, 75–87. doi: 10.1070/RC2004v073n01ABEH000864
- 16. C.D. Wagner, W.M. Riggs, L.E. Davis and J.F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin–Elmer Corporation, Physical Electronics, 1979, p. 192.
- 17. NIST X-ray Photoelectron Spectroscopy Database, URL, accessed 26.12.2021.
- E.V. Kharanzhevskiy, M.D. Krivilyov, S.M. Reshetnikov, E.E. Sadiokov and F.Z. Gil'mutdinov, Corrosion-electrochemical behavior of nanostructured chromium oxide layers obtained by laser irradiation of unalloyed steel by short pulses, Prot. Met. Phys. Chem. Surf., 2014, 50, 777–783. doi: <u>10.1134/S2070205114060070</u>
- 19. A.G. Akimov, Regularities of the formation of protective oxide layers in systems metal (alloy) environment, *Zashch. Met.*, 1986, **22**, no. 6, 879–886 (in Russian).
- 20. V.L. Volkov, G.S. Zakharova and M.V. Kuznetsov, Polyvanadiumchromium acid, *Zh. Neorg. Khim.*, 1994, **39**, no. 6, 877–882 (in Russian).

**\* \* \***