Inhibition of copper local depassivation in alkaline media with oxygen-containing anions

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Abstract

Using complex physical and chemical methods, a comparative estimation of the capability of benzotriazole (BTAH) to act as an inhibitor of copper local activation (LA) was carried out in alkaline–nitrate and alkaline–sulphate solutions in a temperature range of 20–60°C. It was shown that in both systems studied, BTAH hinders copper LA according to an adsorption–polymerization mechanism. Furthermore, the effect is the stronger, the higher the temperature of the working solution is.

Key words: copper, pitting corrosion, elevated temperature, benzotriazole.

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Introduction

It is known that in heat exchange and water supply systems, copper that has a high general corrosion resistance, undergoes various types of dangerous local destruction. Taking into account that equipment in systems of this type often work on the closed cycle principle, among the protection methods it is expedient to analyze the capability of water-soluble inhibitors to affect the media corrosiveness. In the present work, we chose benzotriazole well studied in the practice of metal protection against general corrosion in acidic and neutral media. At the same time, the use of BTAH as a metal local activation inhibitor in alkaline solutions is rarely covered in the literature. In view of this, the aim of this study was to find out the possibility of BTAH application as a copper LA inhibitor in alkaline media containing nitrate and sulfate ions under various temperatures.

Experimental

The experiments were carried out in a glass three electrode electrolytic cell ($V = 0.250 \text{ dm}^3$) with non-separated cathodic and anodic spaces. A copper plate (M1, 99.9 wt% Cu) mounted in epoxy resin and having a working surface of $S = 7.85 \times 10^{-5} \text{ m}^2$ played the role of the electrode. A silver chloride electrode (E = 0.200 V (NHE)) was used as the reference electrode, which was connected to the working electrode through a salt bridge

filled by a working solution and having a Haber–Luggin capillary at the end. A platinum counter electrode was used.

Two systems were chosen as the background electrolytes: $I - 1 \times 10^{-2}$ M NaOH + 1×10^{-2} M NaNO₃ and II - 1×10^{-2} M NaOH + 1×10^{-2} M Na₂SO₄ (pH 12). According to literature data [1, 2] confirmed by our own experimental data [3], copper undergoes local activation in the background electrolytes. The BTAH concentrations in the system were varied from 1×10^{-7} to 1×10^{-2} M. All electrolytes were prepared from analytical grade chemicals using distilled water. The studies were carried out in the temperatures range from 20 to 60°C. In the experiments at elevated temperatures, the electrolytic cell was placed in an LW-4 water bath (the temperature in the latter was maintained to within $\pm 1^{\circ}$ C) [4]. The working cell temperature was monitored with a mercury thermometer.

The following physicochemical methods were used to obtain systematic and valid experimental data: inversion voltammetry (IVA), cyclic voltammetry (CVA), chronoamperometry, and microscopy methods. The studies were carried out using a P-5827M potentiostat and a potential scan rate of 0.2 V/min according to the standard technique described in [5]. Monitoring of the copper surface before and after the experiment was performed using the microscopes: MBS-2 (×7 magnification) and MIM-7 (×500 magnification). Additional studies were carried out using a JEOL 6380LV scanning electron microscope equipped with an EDS INCA 250 energy-dispersive unit to estimate the qualitative and quantitative composition of the products on the copper surface.

Prior to each experiment, the surface of the electrode was polished with abrasive papers with gradually decreasing grain size, degreased with alcohol, rinsed with distilled water, and dried with filter paper. After being dipped in the electrolyte, the electrode underwent cathodic pre-polarization (E = -1.000 V; $\tau = 10$ min) to rebuild the natural oxide films and reproduce the initial copper surface, and then the electrode was studied by the potentiodynamic method (recording of IVA or CVA curves in the potential range from -1.000 to +0.800 V). The electrode potential was always recalculated *versus* normal hydrogen electrode (NHE).

Results and discussion

The results obtained (Tables 1, 2) show that BTAH addition in background electrolytes (Figures 1, 2), results in gradual copper LA supression. On achieving $C_{\text{BTAH}} = 2 \times 10^{-5}$ M (system I) and $C_{\text{BTAH}} = 8 \times 10^{-4}$ M (system II), the metal acquires the stable passive state, which is retained at higher BTAH concentrations. In this state, independence of current density on potential is observed on the anodic part of the voltamogramm in a wide potential range (Figures 3, 4), while the chronoamperograms obtained at this region have a typical dropping shape. The latter confirms the conclusion made above.

Electrolyte	Pit depth, µm	Surface	$E_{\rm LA}, { m V}$	$\Delta E_{\rm LA}, { m V}$	<i>Z</i> , %	
1×10 ⁻² M NaOH + 1×10 ⁻² M NaNO ₃	2		0.500	0.610		
1×10^{-2} M NaOH + 1×10^{-2} M Na ₂ SO ₄	3		0.390	0.470	_	
1×10^{-2} M NaOH + 1×10^{-2} M NaNO ₃ + 1×10^{-5} M BTAH	.2		0.520	0.650	75	
1×10^{-2} M NaOH + 1×10^{-2} M Na ₂ SO ₄ + 5×10^{-4} M BTAH	< 3		0.440	0.540	70	
1×10^{-2} M NaOH + 1×10^{-2} M NaNO ₃ + 2×10^{-5} M BTAH					100	
$1 \times 10^{-2} \text{ M NaOH} + 1 \times 10^{-2} \text{ M Na}_2 \text{SO}_4 + 8 \times 10^{-4} \text{ M BTAH}$	_		_	_	100	

Table 1. Effect of BTAH concentration on copper LA in 1×10^{-2} M NaOH + 1×10^{-2} M NaNO₃ (Na₂SO₄) + *x*M BTAH at 20°C.

A quantitative estimation of BTAH efficiency as a copper LA inhibitor was made by two independent methods using data about the LA induction period (τ_{ind}). Taking into account that under the conditions of interest, $1/\tau_{ind}$ is a criterion of LA rate, the protection coefficient (*Z*) was calculated according to classical Equation (1) [3].

$$Z = \frac{\left(\frac{1}{\tau_{\text{ind}}}\right)_0 - \left(\frac{1}{\tau_{\text{ind}}}\right)_{\text{inh}}}{\left(\frac{1}{\tau_{\text{ind}}}\right)_0} \times 100\%, \qquad (1)$$

where $\left(\frac{1}{\tau_{ind}}\right)_0$ and $\left(\frac{1}{\tau_{inh}}\right)_{inh}$ are LA rate of copper in the background electrolyte and in the presence of the inhibitor, respectively.

Table 2. The nature and quantitative ratio of elements present in the copper surface film after chronoamperometric studies at E_{LA} in the solutions at 20°C.

Electrolyte	$E_{\rm LA}, { m V}$	Element	Weight %	Atomic %	Surface
1×10 ⁻² M NaOH + 1×10 ⁻² M NaNO ₃	0.500	0	11.65	32.91	1 ASA
		Cu	88.35	67.09	20kU X35 500mm
1×10^{-2} M NaOH + 1×10^{-2} M Na ₂ SO ₄		0	52.83	72.90	
	0.390	S	9.45	9.80	1 miles
		Cu	37.73	17.29	251 P. C. THE IS IN 1284 DR 28-51
1×10^{-2} M NaOH + 1×10^{-2} M NaNO ₃ + 2×10^{-5} M BTAH		С	2.79	11.76	
	0.520	Ν	0.80	2.88	
		Ο	3.54	11.22	20KU X1.000 10mm
1×10^{-2} M NaOH + 1×10^{-2} M Na ₂ SO ₄ + 8×10^{-4} M BTAH		С	15.73	46.33	
	0.430	Ν	2.40	6.06	
		0	1.21	2.69	
		Cu	80.66	44.92	20kU X1.300 10xm 0242 10 42 SEL



Figure 1. (a) A CVA curve of copper in 1×10^{-2} M NaOH + 1×10^{-2} M NaNO₃ solution at 20°C, where A1/C1 indicate Cu/Cu₂O, A2/C2 indicate Cu₂O/CuO, Cu(OH)₂; (b) a chronoamperogram at $E_{LA} = 0.500$ V.



Figure 2. (a) A CVA curve of copper in 1×10^{-2} M NaOH + 1×10^{-2} M Na₂SO₄ solution at 20°C, where A1/C1 indicate Cu/Cu₂O, A2/C2 indicate Cu₂O/CuO, Cu(OH)₂; (b) a chronoamperogram at $E_{LA} = 0.390$ V.



Figure 3. (a) A voltammogram of Cu in 1×10^{-2} M NaOH + 1×10^{-2} M NaNO₃ + 2×10^{-5} M BTAH at 20°C, (b) a chronoamperogram recorded in the LA region in the background solution (at E = 0.520 V).



Figure 4. (a) A voltammogram of Cu in 1×10^{-2} M NaOH + 1×10^{-2} M Na₂SO₄ + 8×10^{-4} M BTAH at 20°C, (b) a chronoamperogram recorded in the LA region in the background solution (at E = 0.440 V).

According to experimental data (Table 2), the Z value raises upon BTAH concentration increase in both systems studied and reaches 100% at boundary inhibitor concentrations ($C_{\text{BTAH}} = 2 \times 10^{-5}$ M (system I) and $C_{\text{BTAH}} = 8 \times 10^{-4}$ M (system II), respectively).

In addition to electrochemical studies, for control purposes, the composition of the products on the copper electrode surface after the experiments was studied by SEM combined with an EDS INCA 250 energy-dispersive unit (Table 2). Analysis of the results obtained permits us to conclude that addition of BTAH to an alkaline nitrate electrolyte results in nitrogen appearance on the oxidized copper surface, in contrast to the copper surface in the background electrolyte. The N content increases with an increase in the BTAH concentration. It indirectly confirms that protective copper benzotriazolate compounds are present on the electrode surface.

In the alkaline sulphate solution, the presence of BTAH results in a decrease in the amount of sulphur on the copper surface, whereas C and N simultaneously appear on the surface. In this case, the atomic and weight percentage of C and N increases in parallel with a decrease in the S element content with an increase in the BTAH concentration. The observation of C and N elements, which are parts of the BTAH molecule, on the metal surface and the strong dependence of their quantity on the inhibitor concentration possibly indicate the existence of copper benzotriazolate protective compounds on the metal surface.

At an elevated temperature, the BTAH efficiency in both systems studied increases and at 60°C the smallest inhibitor concentration is required for LA supression (Table 3).

t, °C	20	40	50	60
1×10^{-2} M NaOH + 1×10^{-2} M NaNO ₃ + x M BTAH	2×10 ⁻⁵	5×10 ⁻⁶	4×10 ⁻⁶	8×10 ⁻⁷
1×10^{-2} M NaOH + 1×10^{-2} M Na ₂ SO ₄ + xM BTAH	8×10^{-4}	2×10 ⁻⁶	2×10 ⁻⁶	5×10 ⁻⁷

Table 3. Dependence of the BTAH concentration boundary on temperature in 1×10^{-2} M NaOH + 1×10^{-2} M NaNO₃ (Na₂SO₄) + *x*M BTAH solution

It is known [7] that the protective action of BTAH is due to its high adsorption ability and formation of a dense (in alkaline media), poorly soluble, stable copper benzotriazolate film on the metal surface. On the one hand, this film [Cu(I)–BTA] is a physical barrier screening the metal surface from the corrosive ions present in solution, and on the other hand, it binds copper atoms, preventing anodic dissolution and decreasing the electrical conductivity of the surface layer [7]. The following reactions [7–10] describe the interaction of BTAH and copper surface in alkaline media:

$$Cu + BTA^{-} \rightarrow Cu : BTA^{-}_{ads}$$
 (2)

$$Cu + BTA^{-} \rightarrow Cu(I) - BTA + e^{-}$$
(3)

Reaction (2) corresponds to the BTA^- adsorption on the copper surface. Reaction (3) is related to the chemical formation of the [Cu(I)–BTA] complex, which subsequently forms mono- and poly-layer structures, depending on the experiment conditions.

Thus, experiments demonstrate that BTAH can be used as an efficient copper LA inhibitor in alkaline–nitrate and alkaline–sulphate solutions at 20°C. However, while small BTAH concentrations just slow down copper LA due to the formation of a protective complex with a low polymerization degree from the metal and benzotriazole [11], copper is not subject to local destruction at $C_{\text{BTAH}} \ge 2 \times 10^{-5}$ M in alkaline–nitrate solutions and at $C_{\text{BTAH}} \ge 8 \times 10^{-4}$ M in alkaline–sulphate solutions owing to the formation of a dense protective film that is impenetrable for corrosive ions.

The inhibitor efficiency increase with a temperature raise is probably due to an increase in the polymerization degree of the protective complex [11]. Simultaneously, the share of oxide–hydroxide products on the metal surface increases with a temperature raise. It also promotes the stabilization of the copper triazolate protective film due to the presence of chemical Cu–N bonds as well as hydrogen bonds between the oxygen in the copper oxide and hydrogen in the benzene ring (C–H) of the benzotriazole molecule [9].

Conclusion

- 1. Using a combination of electrochemical and physicochemical methods, comparative data on the regularities of copper local activation in alkaline–nitrate and alkaline–sulphate solutions in the presence of benzotriazole $(1 \times 10^{-7} \le C_{BTAH} \le 1 \times 10^{-2} \text{ M})$ at temperatures of 20–60°C have been obtained.
- 2. It has been shown that BTAH is an effective inhibitor of copper LA in both investigated systems.
- 3. At 20°C, full copper protection against LA is achieved at $C_{\text{BTAH}} = 2 \times 10^{-5}$ M in alkaline– nitrate electrolytes and at $C_{\text{BTAH}} = 8 \times 10^{-4}$ M in alkaline–sulphate electrolytes.
- 4. At the same time, the inhibitor is more effective in these solutions at 60°C: the metal local destruction process stops at concentrations by two orders lower than at 20°C, namely, $C_{\text{BTAH}} = 8 \times 10^{-7}$ M in the alkaline–nitrate electrolyte and at $C_{\text{BTAH}} = 5 \times 10^{-7}$ M in the alkaline–sulphate electrolyte.

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