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# Electrochemical behaviour of brass in acidic chloride solutions: effect of organic inhibitors

The corrosion behaviour of brass has been studied from an aspect of dezincification mechanism of cold-deformed CuZn-42 brass were tested in acid sulphate solution at pH-value 2 with additional chloride ions and corrosion inhibitors with potentiostatic polarization method. Thiourea (TU), benzotriazole (BTA), ethylene diamine tetraacetic acid (EDTA), hydrazine sulphate (HS) and 2-butin-1,4 diole (DS-3) have been used as effective acid corrosion inhibitors. Increase of a concentration of the Cl ions, exept for value of 5·10<sup>2</sup> moldm<sup>3</sup>, resulted in a significant increase of value for corrosion current densities. In solution without inhibitors, process of dezincification and anode dissolution of CuZn-42 brass was developed in the whole range of tested potentials, and pointed out the unstability of formed on their surface. The results of studies show that only thiourea, in concentration of 10<sup>2</sup> wt.%, inhibit the corrosion of brass in chloride solutions. Inhibitor benzotriazole in concentration of 10 lwt.% inhibit the corrosion of brass with inhibition efficiency more then 94%. The film improved significantly the protecting ability of brass surface to corrosion in chloride solutions. When the films were modified with benzotriazole the quality and corrosion protection of films improved rapidly.

Key words: brass, corrosion, inhibitor, dezincification, polarization

#### INTRODUCTION

Copper and its alloys are widely used in industry because of their excellent electrical and thermal conductivity and are often used in heating and cooling system. Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water systems. Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass [1-3].

Many authors [4-7] investigated various methods in this field and concluded that zinc is dissolved primarily at the first stage of dezincification. The individual attack appers in a short-determined period of time and penetrates into some monolayers on brass surface. Further zinc separation in the same process is a little possible due to a fact that an extra energy is required for this process for zinc atoms diffusion through solid stage to brass surface. As the results, upon certain time expiration, copper also starts to move into solution together with zinc at comparable low rate, including potential change. Copper redeposition is immediately followed by lagged zinc in solution.

Rothenbacher [8] have noticed a rapid dezincification of 70Cu-30Zn brass under static conditions. In undeformed brass samples 70Cu-30Zn and 63Cu-37Zn, corrosion rate is higher than in brass with deformation degree of 50%, until in brass 60Cu-40Zn with deformation degree of 50% corrosion rate is higher than in undeformed brass.

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Brass is widely used in various industrial operations and the study of corrosion of brass and inhibition is subject of practical significance. BTA, thiourea, hydrazine-sulphate, DS-3 and EDTA, have been used as effective acid corrosion inhibitors [9-12]. Many inhibitors have been used to minimize the corrosion of brass in different media [13]. Particularly, heterocyclic organic compounds containing nitrogen, sulphur and/or oxigen atoms are often used to protect metals from corrosion. Benzotriazole (BTA) for example, has been studied and found to have excellent inhibition properties in several corrosive environments [14-18]. This molecule contains nitrogen atoms and has been found useful in preventing copper staining and tarnishing. The effectiveness of BTA has been related to the formation of a Cu [Cu<sup>+</sup>BTA<sup>-</sup>]<sub>n</sub> film and the film formed is considered to be insoluble and polymeric [19].

Presence of Cu<sub>2</sub>O makes easier the starting chemisorption of BTA inhibitor. According to the other authors [20] film Cu(I)-BTA is formed on "empty surface" of copper and brass. General conclusion is that passivation of copper alloys is controlled by copper component regardless to small differences in potentiodynamic characteristics [19], where triazole derivates have an important role for decrease of corrosion rate in various corrosion media. Basically, two mechanisms of inhibition the BTA inhibitor are found in literature [20,21]: adsorption of BTA inhibitor on copper surface and formation of polymeric film where complex ions Cu(I) and (Cu<sup>+</sup>BTA<sup>-</sup>)<sub>n</sub> are included. The addition of BTA to aqueous acidic, neutral and alkaline solution is commonly used and has significantly reduced corrosion [22]. It may be adsorbed only onto the oxide on the surface of copper [23,24], or function on oxide free surfaces [25]. It is a good anodic inhibitor for copper in acidic conditions and in chloride solutions [26]. Walker [27] has shown that the addition of small amounts 1,2,3-BTA inhibit the corrosion of brass in acidic, neutral and alkali solutions at ambient temperature. In BTA inhibitor and its derivates, with increased acidity of solution its inhibition effect decreases and it shows the best results in alcaline and neutral media [11,28,29].

In 1.05 moldm<sup>-3</sup> solution of hydrochloric acid, at concentration of **thiourea** of 0.05%, inhibition degree is 86.4% for copper. In concentrations of 5·10<sup>-1</sup> mol dm<sup>-3</sup>-1.0moldm<sup>-3</sup> of sodium hydroxide, at concentration of thiourea inhibitor of 0.2%, inhibition degree is 46-76%. As good inhibitor of non-ferrous metals and copper corrosion in acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) thiourea is used with inhibition degree from 65% to 98%, what depends on inhibitor concentration. Investigation interest was focused on establishment the influence of the above mentioned corrosion inhibitors on corrosion behavior of cold-deformed brass samples in acid solution of sodium sulphate with addition of Cu<sup>2+</sup> and chloride ions.

Inhibitor **EDTA** (ethylene diamine tetraacetic acid) has one of the uses in chemical cleaning of nuclear power station generators from copper sediment [30]. Due to a fact that the critical potential for copper dissolution in ammonium solutions in a range of -0.3÷0.2V, the role of EDTA is to maintain potential in the given area to remove copper deposit by amonium and hydrogen peroxide effect from nuclear power plant generator. EDTA is also used as compound in prevention for oxide formation on metal surface [31, 32].

The **hydrazine sulphate** is inhibitor of steel corrosion in solutions of sulphuric and hydrochloric acids, and copper and copper alloys in nitric acid and alkaline solutions. In alkaline solutions, copper is covered by protective membrane; at inhibitor concentrations from 0.01% to 0.25%, protection degree is 73-100%.

Inhibitor **DS-3** is iron and steel corrosion inhibitor in solutions of hydrochloric acid with inhibition degree of 93%. When inhibitor concentration is enough for high degree of inhibition (>80%), adsorption of inhibitor molecule is a dominant process. This type of adsorption prevents anion absorption and also has influence on redeposition process. Under those conditions, brass dissolution is a slow process without any indication of dezincification process.

The aim of this work is to show which of the analyzed corrosion inhibitors shows an inhibition effect and in what concentration. Also, concentrations of chloride ions were determined where the analyzed brass samples show a passive conditions regarding to the corrosion process.

#### EXPERIMENTAL PART

The samples of tested brass that were laboratory produced had the following chemical content (wt.%): Cu-57.95% (99.997% purity), Zn-41.91% (99.85% purity) and others -0.14%. Samples were deformed to the following deformation degrees: 0% and 80% and sealed in cold-polymerized acrylate. A non-deformed copper electrode (99.997% purity) was used as comparative samples. The samples for the electrochemical measurements had a constant area of P = 0.38 cm<sup>2</sup>. Before every polarization measurement, the samples were polished on emery paper (fineness #1000) and alumina rinsed with distilled water and ethyl alcohol. The saturated calomel electrode (SCE) and platinum wire were used as a reference, i.e. counter electrode, separately, in a classical threeelectrode electrochemical cell. The all potential values were given regarding the saturated calomel electrode. Tested solutions were: 10<sup>-1</sup>M Na<sub>2</sub>SO<sub>4</sub>, 10<sup>-1</sup>  $^{1}$ M Na<sub>2</sub>SO<sub>4</sub> + 5·10<sup>-4</sup>M NaCl,  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub> + 5·10<sup>-1</sup>  $^{3}$ M NaCl,  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub> +  $5\cdot10^{-2}$ M NaCl,  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub> + 1.0M NaCl and preparations of high pure chemicals with distilled water. Concentration of the used inhibitors thiourea (TU), benzotriazole (BTA), ethylene diamine tetraacetic acid (EDTA), hydrazine sulphate (HS) and 2-butin-1,4 diole (DS-3) in working solutions were 10<sup>-2</sup>wt.% and 10<sup>-1</sup>wt.%. Polarization measurements were carried out from potential of open circuit to a potential of 1000mV (vs.SCE), with the polarization rate of 10mV/s, by use of the linear polarization method. Corrosion current densities were determined by approximating the right part of anode Tafel's curves to the section with the corrosion potential. The inhibition efficiencies were also calculated from the polarization data by using the equation: %P=(i-i<sub>0</sub>)/ix100, where "i" and "i<sub>0</sub>" are the corrosion currents in the absence and presence of the inhibitor [33]. Potential area from 0mV (vs.SCE) to 200mV (vs.SCE) was taken for calculation area. An AMEL apparatus was used as well as: potentiostat (Model 553), program functional generator (Model 568), interface (Model 560/A/log) and digital x/y – recorder (Model 863).

## EXPERIMENTAL RESULTS AND DISCUSSION

Effect of Various Concentrations of Chloride Ions on Corrosion Behaviour CuZn-42 Brass

Figures (1 and 2) presents the polarization curves of CuZn-42 brass with two deformation degrees: 0% and 80%, in 10<sup>-1</sup>moldm<sup>-3</sup> solution of Na<sub>2</sub>SO<sub>4</sub>, with addition of various concentrations of chloride ions. By increased concentration of chloride ions, the values of current densities are also increased. The outstanding current tips appear at concentrations of chloride ions higher than 10<sup>-1</sup>moldm<sup>-3</sup>.

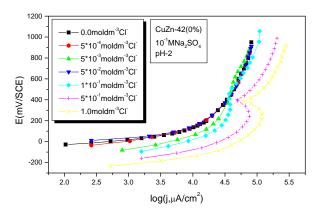


Figure 1 - Polarization curves of CuZn-42(0%) brass in solution of sodium sulphate with addition of various concentrations of chloride ions

The mechanism of Cu (brass) electrodissolution in chloride media has been investigated by many researches [6-14]. It is generally accepted that Cu anodic dissolution is influenced by chloride concentration indipendently of pH. At chloride concentrations lower than 1M, the mechanism of copper dissolution can be expressed as:

$$Cu + Cl \leftrightarrow CuCl + e^{-}$$
 (1)

$$CuCl + Cl \rightarrow CuCl_2$$
 (2)

At chloride concentrations >1M, higher cuprous complexes such as CuCl<sub>3</sub><sup>2-</sup> and CuCl<sub>4</sub><sup>3-</sup> are formed. In the apparent Tafel region, the anodic dissolution of copper is under mixed control by the electrodissolution of copper and the diffusion of soluble CuCl<sub>2</sub><sup>-</sup> from outher Helmholtz plane into the bulk solution [34].

Table (1) gives values of corrosion potentials and corrosion current densities obtained by extrapolation of Tafel's lines for brass CuZn-42(0%) and brass CuZn-42(80%) in 10<sup>-1</sup>M solution of Na<sub>2</sub>SO<sub>4</sub> with addition of various concentrations of chloride ions.

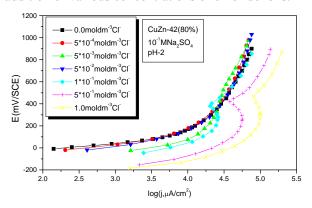


Figure 2 - Polarization curves of CuZn-42(80%) brass in solution of sodium sulphate with addition of various concentrations of chloride ions

Table 1 - Values of corrosion parameters for various concentrations of chloride ions for CuZn-42(0%) (A) brass and CuZn-42(80%) (B) brass.

C <sub>Cl</sub>	0.0	M	5.10	) <sup>-4</sup> M	5.	10 <sup>-3</sup> M	5.10	) <sup>-2</sup> M
Sample	A	В	A	В	A	В	A	В
E <sub>corr</sub> (mV)	-88	-84	-149	-170	-195	-220	-232	-225
j <sub>corr</sub> (mA/cm <sup>2</sup> )	0.681	0.668	1.04	1.035	1.298	1.278	1.083	1.008

C <sub>Cl</sub>	1·10 <sup>-1</sup> M		5.10	) <sup>-1</sup> M	1.0M	
Sample	A	В	A	В	A	В
E <sub>corr</sub> (mV)	-244	-246	-310	-304	-335	-333
j <sub>corr</sub> (mA/cm <sup>2</sup> )	1.485	1.475	1.553	1.488	3.158	3.005

According to Moreau's study [35] to investigate the behavior of copper (brass) in acidic media, there are three distinct steps during the anodic polarization. The first step is  $CuCl + Cl^- = CuCl_{ads} + e^-$  followed by a physical conversion second step  $CuCl + Cl^- \rightarrow CuCl_2^-$  and third rate determining step  $Cu + 2Cl^- = CuCl_2^- + e^-$ . This mechanism proposed for acidic media is also valid for NaCl medium.

Based on presented polarization curves and data from Table (1), it could be concluded that an inhibition effect on CuZn-42 brass corrosion has chloride concentration of 5·10<sup>-2</sup>moldm<sup>-3</sup>, where values of corrosion current densities are lower than concentration of 5·10<sup>-3</sup>moldm<sup>-3</sup> (for brass CuZn-42(0%)), that is concentrations of 5·10<sup>-3</sup>moldm<sup>-3</sup> and 5·10<sup>-4</sup>moldm<sup>-3</sup> (for brass CuZn-42(80%)). The highest values of corrosion current densities are for concentrations of chloride ions of 5·10<sup>-1</sup>moldm<sup>-3</sup> and 1.0moldm<sup>-3</sup>, what is explained by exceptional agressivity of increased concentrations of chloride ions. Flow of anode polarization curves shows that anode brass dissolution starts with an initial zinc dissolution, then also zinc and copper, depending on potential.

The initial dissolution takes place as Zn<sup>2+</sup> in an aqueous media containing the chloride. As it starts as CuCl<sub>2</sub>, the dissolution is presented by the axchange of copper and zinc. This prevention continues up to CuCl formation potential. CuCl film does not prevent the formation of Cu(II) oxides. The copper oxides initially formed can dissociate by the effect of zinc atoms upon the surface.

Primary process of selective brass dissolution is distinctive in sudden increase of values of current densities immediately upon starting process of polarization and those observations are in accordance with discussions of the other authors [36,37]. The obtained values for corrosion potentials, for chloride ions concentrations:  $5\cdot10^{-2}$ moldm<sup>-3</sup>,  $1\cdot10^{-1}$ moldm<sup>-3</sup> and 1.0 moldm<sup>-3</sup>, are completely identical with presented results in work [38]. According to the literature data [39, 40], the inhibition effect of chloride ions was noticed for concentration of chloride ions of  $8\cdot10^{-3}$ moldm<sup>-3</sup>.

Dezincification process is developed by the help of high degree of mass transfer which inhibits protective film formation of corrosive products, specially  $\text{Cu}_2\text{O-film}$  [41]. Less values of corrosion current densities in tested samples with deformation degree of 80% and at higher concentrations of chloride ions, are explained by easier process of substitution  $\text{O}^2$ -ions with chloride ions in crystal lattice. Also, protective film is formed faster in deformed samples of 80% on its surface what causes lower values for  $j_{\text{corr}}$ .

Effect of corrosion inhibitor in solutions of  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub>, with addition of  $5 \cdot 10^{-1}$ M and 1.0M Cl ions

The most distinctive corrosion process, according to the present results, is at chloride ions concentration from 1.0moldm<sup>-3</sup>. This part of work will give an explanation of inhibition process of brass corrosion CuZn-42, with deformation degrees of 0 and 80%, in 1.0moldm<sup>-3</sup> solution of Cl<sup>-1</sup> ions.

Figures (3 and 4) present dependence of corrosion behavior of analyzed samples of deformed brass with deformation degrees of 0% and 80%, in solution of 1.0moldm<sup>-3</sup> Cl<sup>-1</sup> ions with and without presence of corrosion inhibitors: BTA, thiourea, hydrazine sulphate, DS-3 and EDTA, in concentration of 10<sup>-2</sup>wt.%.

In analyzed solutions, with concentrations of chloride ions of  $1.0 \text{moldm}^{-3}$ , at inhibitor concentrations of  $10^{-2} \text{wt.\%}$ , values of corrosion current densities increase in a range for CuZn-42(0%) brass: TU (1.55mA/cm²) < without inhibitors (3.158mA/cm²) < BTA(3.53mA/cm²) < EDTA(3.41mA/cm²) < HS (3.575mA/cm²) < DS-3(3.872mA/cm²) and for CuZn-42(80%) brass: TU(1.51mA/cm²) < without inhibitors (3.005mA/cm²) < BTA(3.61mA/cm²) < EDTA (3.70 mA/cm²) < HS(3.74mA/cm²) < DS-3 (3.8mA/cm²).

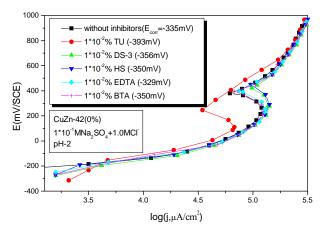


Figure 3 - Polarization curves of CuZn-42(0%) brass in  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub>+1.0M CI solution, without and with inhibitors at  $10^{-2}$ wt.%

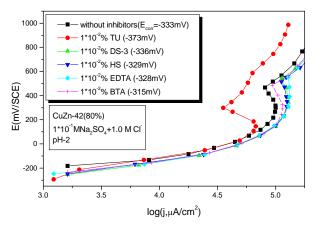


Figure 4 - Polarization curves of CuZn-42(80%) brass in 10<sup>-1</sup>M Na<sub>2</sub>SO<sub>4</sub>+1.0M CI solution, without and with inhibitors at 10<sup>-2</sup>wt.%

On anode polarization curves, the presence of anode peaks could be noticed, what presents an active dissolution of tested samples and formation of Cu(I)– chloro-complex, formed by primary reaction: Cu +  $2Cl \leftrightarrow CuCl_2^- + e^-$ . Which Cu(I)-chloro-complex will be formed (CuCl<sub>2</sub> or CuCl<sub>3</sub><sup>2</sup>-) depends on concentration of chloride ions. A distinct dissolution of Cu(I)chloro-complex in solutions with increased concentration of Cl<sup>-</sup> ions makes conditions for development the selective dissolution process of brass (dezincification) as well as a loss of already formed copper – chloride film on its surface. According to the balance diagram for content of Cu-CuCl, at various pHvalues of NaCl solution, it was found out that the majority participation of more dissoluble copper compounds (Cu<sup>+</sup>, CuCl<sub>2</sub><sup>-</sup>, CuCl<sub>3</sub><sup>2-</sup>) are present at higher pH-values regarding to participation of less dissoluble (CuCl, Cu<sub>2</sub>O). Based on the obtained results, brass dezincification process is developed, in solutions with content of chloride ions, by selective dissolution of more reactive component (zinc) where surface diffusion of more stable component (copper) is added to. Thiourea is the best corrosion inhibitor in analyzed solution. The other inhibitors act as corrosion activators regarding to solution without corrosion inhibitor. Absence of BTA inhibitor effect is explained by its low concentration, due to a fact that the lowest inhibitor concentration for copper protection is in aqueous solutions 0.05% [11]. In approximately neutral 3% solution of NaCl, inhibitor BTA has no inhibition effect [42].

Effect of thiourea produces transfer of anode polarization curves into more negative values of corrosion current densities, and also results into transfer of anode current peak towards lower values of potential and current densities (Figures 3 and 4). Corrosion potentials are established after 8-10 minutes and the most negative values are in solution with addition of thiourea of the all analyzed inhibitors. The change in j<sub>corr</sub> in the presence of inhibitor indicates the interference of inhibitor in the mechanism of corrosion of brass and copper as the rate-determining step.

Figures (5 and 6) give polarization curves for brass CuZn-42 with deformation degrees of 0% and 80%, in 10<sup>-1</sup>moldm<sup>-3</sup> solution of Na<sub>2</sub>SO<sub>4</sub>, with concentration of chloride ions of 1.0moldm<sup>-3</sup> and inhibitor concentration of 10<sup>-1</sup>wt.%. BTA and thiourea (Table 2) are the best corrosion inhibitors in analyzed samples. Other inhibitors act as corrosion activators regarding to solution without corrosion inhibitor.

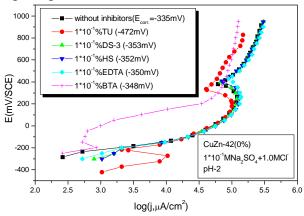


Figure 5 - Polarization curves of CuZn-42(0%) brass in  $10^{-1}$ M Na<sub>2</sub>SO<sub>4</sub>+1.0M Cl solution, without and with inhibitors at  $10^{-1}$ wt.%

Effect of BTA and thiourea produces transfer of anode polarization curves into more negative values of corrosion current densities, and also results into transfer of anode current peak towards lower values of potential and current densities. As noticed earlier [41], Cu-BTA film formation on the surface may be controlling factor, which depends on the availability of Cu<sup>+</sup> ions near the surface and BTA in the diffusion layer.

Table (2) gives values of corrosion current densities and inhibition degree for analyzed brass samples in solutions with concentration of chloride ions of 1.0moldm<sup>-3</sup> and inhibitors BTA and thiourea in concentrations of 10<sup>-1</sup>wt.%.

In sulphuric acid solution, in presence of BTA, in concentration of 10<sup>-2</sup>M, corrosion rate of copper is 0.012mg/cm<sup>2</sup>/h, at temperature of 30<sup>0</sup>C [43]. Temperature increase at 60<sup>0</sup>C, results into mass sample loss of 0.0398mg/cm<sup>2</sup>/h. In concentration of BTA inhibitor of 10<sup>-6</sup>M, in the same solution, inhibition degree is 41%, until for BTA concentration of 2.5·10<sup>-3</sup>M, inhibition degree is 60%. For concentration of BTA inhibitor of 10<sup>-2</sup>M, inhibition degree is 76%.

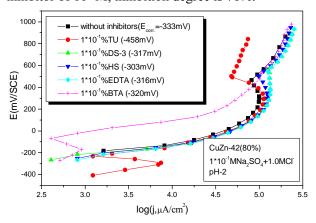


Figure 6 - Polarization curves of CuZn-42(80%) brass in 10<sup>-1</sup>M Na<sub>2</sub>SO<sub>4</sub>+1.0M Cl solution, without and with inhibitors at 10<sup>-1</sup>wt.%

Table 2 - Values of corrosion current densities and inhibition degree for analyzed samples in solutions with concentration of chloride ions 1.0moldm<sup>-3</sup> and BTA inhibitor and thiourea in concentrations of 10<sup>-1</sup>wt.%

$10^{-1}$ M Na <sub>2</sub> SO <sub>4</sub> + 1.0M Cl <sup>-</sup> + $10^{-1}$ wt.% BTA					
Sample		CuZn-42 (0%)	CuZn-42 (80%)		
ьн э	$j_{corr}(mA/cm^2)$	0.14	0.125		
pH-2	P (%)	95.57	95.84		
10 <sup>-1</sup> M Na <sub>2</sub> SO <sub>4</sub> + 1.0M Cl + 10 <sup>-1</sup> wt.% TU					
S	ample	CuZn-42 (0%)	CuZn-42 (80%)		
pH-2	$j_{corr}(mA/cm^2)$	1.78	1.77		
	P (%)	43.64	41.10		

In analyzed solutions, with chloride ions concentration of 1.0moldm<sup>-3</sup>, in inhibitor concentrations of 10<sup>-1</sup>wt.%, values of corrosion current densities increase in a range; for CuZn-42(0%) brass: BTA(0.14 mA/cm<sup>2</sup>) < TU(1.78) < without inhibitor(3.158) <

EDTA (3.45)< HS(3.487 )< DS-3(3.66) and for CuZn -42 (80%) brass: BTA(0.125mA/cm<sup>2</sup>) < TU (1.77) < without inhibitor(3.005) < EDTA(3.38) < HS(3.57) <DS-3(3.62). Besides this, an effect on general kinetics of individual dissolution process of copper and zinc, besides present components (SO<sub>4</sub><sup>2</sup>, Cl), has also inhibitor concentration in analyzed media. When inhibitor concentration is low or inhibitor is ineffective, and inhibition degree is lower than 80%, relation of individual dissolution rates and dezincification degree is negligible. Also, when inhibition degree is higher than 80%, dissolution rate of alloy components has relative influence with a tendency of simultaneously dissolution. In presented results of investigation the effect of various corrosion inhibitors on corrosion behavior of analyzed samples, we have established that BTA (10<sup>-1</sup>wt.%) appears as an effective corrosion inhibitor in solution of chloride-ions, and the other inhibitors are partly effective, until in same solutions, an inhibition effect is shown only by thiourea in concentration of 10<sup>-2</sup>wt.%, but with low inhibition degree (Figures 7 and 8).

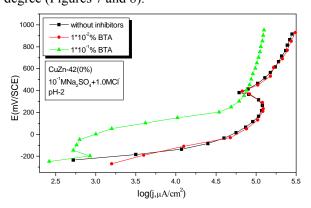


Figure 7 - Polarization curves of the CuZn-42(0%) brass in a  $10^{-1}$  moldm<sup>-3</sup>  $Na_2SO_4+1.0$  moldm<sup>-3</sup> solution, without and with inhibitor BTA in concentrations of  $1\cdot10^{-2}$  wt.% and  $1\cdot10^{-1}$  wt.%

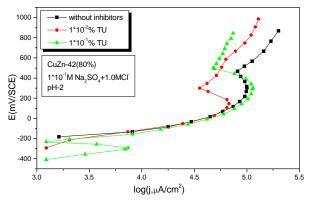


Figure 8 - Polarization curves of the CuZn-42(80%) brass in a  $10^{-1}$  moldm<sup>-3</sup>Na<sub>2</sub>SO<sub>4</sub>+1.0moldm<sup>-3</sup>Cl solution, without and with inhibitor TU in concentrations of  $1 \cdot 10^{-2}$  wt.% and  $1 \cdot 10^{-1}$  wt.%

Increase of corrosion inhibitor at 10<sup>-1</sup>wt.% results into a significant increase of inhibition degree of BTA inhibitor and it is more than 95%.

#### **CONCLUSIONS**

- 1. In solution of 10<sup>-1</sup>moldm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>, with addition of 1.0moldm<sup>-3</sup> Cl<sup>-1</sup> ions, only thiourea shows inhibition effect in concentration of 10<sup>-2</sup>wt.%. Inhibition degree is in a rangew from 35%-44%, in solution with 1.0moldm<sup>-3</sup> Cl<sup>-1</sup> ions.
- Inhibition effect on corrosion process of brass CuZn-42 is shown by concentration of chloride ions of 5·10<sup>-2</sup>moldm<sup>-3</sup>.
- Increase of inhibitor concentration at 10<sup>-1</sup>% results into a significant increase of inhibition degree of BTA inhibitor and it is the most efficient inhibitor of brass corrosion in the observed conditions.
- 4. Deformation degree has no important effect on inhibition degree change, but it has effect on values of corrosion current densities. Brass with deformation degree of 80% has the lowest values of corrosion current densities, for inhibitors concentration of 10<sup>-1</sup>wt.%.
- In very acid solutions (pH-2), in presence of increased concentrations of chloride ions, thiourea could be used in lower concentrations as corrosion inhibitor besides relatively low inhibition degree.

#### REFERENCES

- [1] Dinnappa,R.K., Mayanna,S.M., Corrosion Science 27 (1987) 349
- [2] Sayed,S.M., Ashour,E.A., Ateya,B.G., Corrosion Science 36 (1994) 221
- [3] Nagiub, A., Mansfeld, F., Corrosion Science 43 (2001) 2147
- [4] Kabasakaloglu, M., Kiyak, T., Sendil, O., Asan, A., Applied Surface Sience 193 (2002) 167
- [5] El-Mahdy, G.A., Journal of Applied Electrochemistry 3 (2005) 347
- [6] El-Mahdy, G.A., Corrosion Science 47 (2005) 1370
- [7] S.M.Milic,M.M.Antonijevic, Zastita materijala 49(2008)33
- [8] Rothenbacher, P., Corrosion Science 10 (1970) 391
- [9] Nagiub, A., Mansfeld, F., Corrosion Science 43 (2001) 2147
- [10] Shukla, J., Pitre, K.S., Corrosion Rev. 20 (2000) 217
- [11] Mladenovic, S., Corrosion and Materials Protection 318 (1985), Belgrade
- [12] S.A.A.El-Maksoud, Zastita materijala 49 (2008) 3

- [13] M.A.Elmorsi, A.M.Hassanein, Corrosion Science 41 (1999) 2337
- [14] Zhang, D.Q., Gao, L.X., Zhou, G.D., Applied Surface Science 225 (2004) 287
- [15] N.Bellakhal, M.Dachraoui, Mater.Chem.Phys. 85 (2004) 366
- [16] D.Tromans, J.C.Silva, Corrosion 53 (1997) 16
- [17] Youda, R., Nishihara, H., Aramaki, K., Corrosion Science 28 (1) (1988) 87
- [18] M.M.Antonijevic, M.Radovanovic, M.Petrovic, Z.Lju bomirovic, Zastita materijala 49(2008)31
- [19] Babic, R., Metikos-Hukovic, M., Lonchar, M., Electrochim. Acta. 44 (1999) 2413
- [20] Papanayotov, D., Deligianni, H., Alkire, R.C., J. Electrochem. Soc. 145 (1998) 3016
- [21] Polo, J.L., Pinilla, P., Cano, E., Bastidas, J.M., Corrosion 59,5 (2003) 414
- [22] R. Walker, Corrosion 31 (1975) 97
- [23] F.Mansfeld, T.Smith, Corrosion 29 (1973) 105
- [24] D.Modestov, G.D.Zhou, H.H.Ge, J.Electroanal. Chem. 375 (1994) 293
- [25] D.Thomas, R.H.Sun, J.Electrochem.Soc. 138 (1991) 3235
- [26] Y.Ling, Y.Guan, K.N.Ham, Corrosion 51 (1995) 267
- [27] R. Walker, Corrosion 56 (2000) 1211
- [28] Stupnisek-Lisac, E., Loncharic-Bozic, A., Cafuk, I., Corrosion 54 (1998) 713
- [29] M.M.Antonijevic, V.Gardic, S.M.Milic, S.C.Alagic, A

- .T.Stamenkovic,B.N.Grgur,Zastita materijala 50 (2009)19
- [30] Hur, D.H., Choi, M.S., Lee, E.H., Nuclear Engineering and design 224 (2003) 207
- [31] Tamura, H., Ito, N., Takasaki, S., Furuichi, R., Corros, Eng. 49 (2000) 22
- [32] Tamura, H., Ito, N., Kitano, M., Takasaki, S., Corrosion Science 43 (2001) 1675
- [33] Nandeesh, L.S., Sheshadri, B.S., Corrosion Science 28 (1988) 19
- [34] A.L.Bacarella, J.C.Griess, J.Electrochem.Soc. 120 (1973) 459
- [35] A.Moreau, Electrochim. Acta 26 (1981) 1609
- [36] Kear, G., Barker, B.D., Walsh, F.C., Corrosion Science 46 (2004) 109
- [37] El-Sherif, R.M., Ismail, K.M., Badawy, W.A., Electrochimica Acta 49 (2004) 5139
- [38] Sieradzki, K., Kim, J.S., J. Electrochem Soc. 134 (1987) 1635
- [39] El-Rehim, S.S.A., Assaf, F.H., El Sayed, A., Mat. Trans., JIM Vol. 36, No6 (1995) 770
- [40] Buselmen, J.P., Vazquez, M., De Sanchez, S.R., Electrochimica Acta 47 (2002) 1857
- [41] De Sanchez, S.R., Schiffrin, D.J., Corrosion Science 28 (1988) 141
- [42] Altura, D., Nobe, K., Corrosion 28 (1972) 345
- [43] Mayanna, S.M., Setty, T.H.V., Corrosion Science 15 (1975) 627

## **IZVOD**

# ELEKTROHEMIJSKO PONAŠANJE MESINGA U KISELOM RASTVORU HLORIDA: EFEKAT ORGANSKIH INHIBITORA

Koroziono ponašanje mesinga je studirano sa aspekta mehanizma raspada hladno deformisanih CuZn-42 mesinga i testirani su u rastvoru sumporne kiseline, pH 2 sa dodatkom hloridnih jona i inhibitora korozije, polarizacionom metodom. Tiourea (TU), benzotriazol (BTA), etilen diamin tetraacetatna kiselina (EDTA), hidrazin sulfat (HS) i 2-butin-1,4 diol (DS-3) se koriste kao efikasni kiseli inhibitori korozije. Povećanje koncentracije Cl jona, osim za vrednost od 5 · 10<sup>-2</sup> moldm<sup>-3</sup>, rezultiralo je značajnim povećanjima vrednosti gustina struje korozije. U rešenju bez inhibitora, proces dezintegracije i anodnog raspada CuZn-42 mesinga je razvijen u celom opsegu ispitivanih potencijala i istakao nestabilnost čestica formiranih na njihovoj površini. Rezultati ispitivanja pokazuju da samo tiourea, u koncentraciji od 10,2% tež., sprečava koroziju mesinga u rastvoru hlorida. Inhibitor benzotriazol u koncentraciji od 10,1% tež., sprečava koroziju mesinga sa inhibicionim efektom od 94%. Naneti film znatno poboljšava zaštitne sposobnosti mesingane površine na koroziju u rastvoru hlorida. Kada su naneti filmovi modifikovani sa benzotriazolom kvalitet i zaštita od korozije je veoma brzo poboljšana.

Ključne reči: mesing, korozija, inhibitori, raspadanje, polarizacija

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