

# Corrosion of Cold Deformed Brass

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**Abstract.** Corrosion behavior and the dezincification process of cold-deformed CuZn-42 brass were tested in an acid sulphate solution at pH-value 2 with additional chloride and copper (II)-ions by use of the linear polarization method. The measured corrosion potential and densities of corrosion currents were observed as characteristics of the dezincification process and the corrosion resistance of tested samples of cold-deformed CuZn-42 brass. The results obtained have shown that pH-value 2 of the tested solutions and increased concentrations of copper (II)-ions result in increased values of densities of corrosion currents of the tested brass samples, as a result of selective zinc dissolution and the individual dissolution of zinc and copper including the process of anodic oxidation. The tested concentrations of chloride ions in certain conditions have an inhibiting effect, whereas in the other conditions they act as distinctive activators of brass corrosion. The lowest values of corrosion currents are present in the brass samples with the highest deformation degree at 80%. The process of dezincification and anode dissolution of cold deformed brass samples were developed in the whole range of tested potentials.

## 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. Dezincification is a well-known (de-alloying) process that designates a loss of brass as an important physical/mechanical characteristic resulting in surface destruction [1-7]. Two basic theories explain the dezincification mechanism of brass as well: One theory assumes a selective zinc dissolution, which is released from alloy, and the porous residue reached with metal copper is lagged, and, the other theory assumes a simultaneous dissolution of zinc and copper where copper redeposition is developed at a suitable degree. Some opposing opinions are still held about copper redeposition as well as the form and character of brass corrosion products that are separated on the sample surface during selective alloy dissolution [8]. Tests carried out in a  $10^{-1}$ M solution of  $\text{Na}_2\text{SO}_4$ , with addition of various concentrations the  $\text{Cu}^{2+}$  and  $\text{Cl}^-$ -ions, showed that the highest corrosion of tested brass was at a concentration of chloride ions of  $5 \cdot 10^{-3}$ N whereas the inhibiting effect presented at higher concentrations of  $\text{Cl}^-$ -ions. Anode polarization potentiometric-dynamic measurements were also carried out in a  $10^{-1}$ M solution of  $\text{Na}_2\text{SO}_4$ , with a varied content of  $\text{Cl}^-$ -ions at pH = 1.5-3.5 [9]. At constant acidity, the polarization curves showed an insignificant influence of  $\text{Cl}^-$ -ions when an added concentration of  $\text{Cl}^-$ -ions is lower than  $1 \cdot 10^{-2}$ N, but, the polarization curves showed the presence of anode inhibition at higher concentrations of  $\text{Cl}^-$ -ions.  $\text{CuCl}$  and  $\text{Cu}_2\text{O}$  films are developed in solutions with a pH-value of 3-3.5, with a presence of chloride ions in concentrations of  $10^{-3}$  to  $10^{-2}$ N and of copper sulphate in concentrations of  $5 \cdot 10^{-2}$ M. An insignificant effect on corrosion was present in the same solution with concentrations of chloride ions lower than  $10^{-3}$ N, explained by the fact that the solid stage is spread in a  $\text{Cu}_2\text{O}$  film in such cases whereas the inhibiting effect presented at higher concentrations of  $\text{Cl}^-$ -ions (1M). This was attributed to the formation of a stable  $\text{CuCl}$  deposit. The mechanism of

Cu (brass) electrodissolution in chloride media has been investigated by many researches [10-12]. It is generally accepted that Cu anodic dissolution is influenced by chloride concentration independently of pH. At chloride concentrations lower than 1M, the mechanism of copper dissolution can be expressed as:



At chloride concentrations >1M, higher cuprous complexes such as  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$  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  $\text{CuCl}_2^-$  from outer Helmholtz plane into the bulk solution [12]. It enables a deposit growth on a deformed base that could have various growths and become more prevalent to the local dissolution.

According to G. Bianchin, the dezincification process was developed with help of a high transfer degree of mass that inhibited a protective film formation of corrosive products, especially the  $\text{Cu}_2\text{O}$ -film [13-15]. The effect of  $\text{Cl}^-$ -ions in solutions on copper oxidation acceleration was in relation to the defect of changed  $\text{Cu}_2\text{O}$ -film structure that had a lower protection degree on it. The stability of  $\text{Cu}_2\text{O}$  is inversely dependent on the concentration of chloride ions. It assumed that the  $\text{Cl}^-$ -ion from solution replaced some  $\text{O}^{2-}$ -ions in the oxide grid, where the primary process of selective brass dissolution (zinc dissolution) was expressed by a sudden increase of the current density, short over corrosion potential. The brass dezincification process in solution with a content of chloride ions was developed by a selective dissolution of a more reactive component (zinc), where surface diffusion of a more stable component (copper) was added.

In this work, the authors have tried to explain the corrosion behavior of samples from cold-deformed CuZn-42 brass in a function of concentration with the chloride and copper(II)-ions, pH-values of solutions, and the deformation degree.

## Experimental Part

The chemical composition (wt.%) of the brass used in the present study was 57.95% Cu, 41.91% Zn, and others-0.14%. Samples were deformed to the following deformation degrees: 20, 40, 60 and 80% and sealed in cold-polymerized acrylate. A non-deformed copper electrode was used as a comparative sample. The samples for the electrochemical measurements had a constant area of  $P = 0.38 \text{ cm}^2$ . Before every polarization measurement, the samples were polished on emery paper (fineness #1000) and alumina rinsed with distilled water and ethyl alcohol. A saturated calomel electrode (SCE) and platinum wire were used as a reference, i.e. counter electrode, separately, in a classic three-electrode electrochemical cell. The all potential values were given regarding the saturated calomel electrode. Tested solutions were:  $10^{-1}\text{M Na}_2\text{SO}_4$ ,  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-2}\text{M CuSO}_4$ ,  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-4}\text{M NaCl}$ ,  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-3}\text{M NaCl}$ ,  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-2}\text{M NaCl}$ ,  $10^{-1}\text{M Na}_2\text{SO}_4 + 1.0\text{M NaCl}$  and preparations of high pure chemicals with distilled water. All experiments have been done with a solution volume of  $50\text{cm}^3$ . The pH-value 2 of solutions was adjusted with a  $10^{-1}\text{M}$  solution of  $\text{H}_2\text{SO}_4$ . The operating temperature was  $20^\circ\text{C}$ , with the use of open atmosphere. Polarization measurements were carried out from a potential of open circuit to a potential of 1000mV (vs.SCE), with the polarization rate of 10mV/s. Corrosion current densities were determined by approximating the right part of anode Tafel's curves to the section with the corrosion potential. The potential region from 0mV (vs.SCE) to 200mV (vs.SCE) was taken for the 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.

## Results and Discussion

**Influence of copper (II)-ions.** Figures 1 and 2 present the dependence of current density from the potential for tested copper and brass samples in an  $10^{-1}\text{M}$  solution of  $\text{Na}_2\text{SO}_4$  with the addition of  $5 \cdot 10^{-2}\text{M}$   $\text{Cu}^{2+}$ -ions at pH-2. Corrosion potentials were established upon 15-20 minute intervals, where the potential for copper electrode was shifted to more negative values, and, for brass electrode to more positive values with time. In the  $10^{-1}\text{M}$  solution of  $\text{Na}_2\text{SO}_4$  with and without the addition of  $\text{Cu}^{2+}$ -ions, the values of corrosion potentials for brass electrodes were approximate and lower than the values for copper electrode where a small pH-value of the solution shifted values of corrosion potential in the more negative region. The concentration increase of  $\text{Cu}^{2+}$ -ions resulted in the movement of corrosion potentials into a less active region, pointing out that the balance realization between  $\text{Cu}^{2+}/\text{Cu}^+$ -ions on a boundary of metal-solution and the values of current densities are also increased [13]. The lowest values of corrosion current densities ( $j_{\text{corr}}$ ) were for brass with a deformation degree of 80%. The dezincification process, present here, is a cause of the increase of the density values of corrosive currents as well as the non-existence of a protective film that mainly consisted of  $\text{Cu}_2\text{O}$  on a sample surface at pH-2. The corrosive morphology of cold-deformed samples has a disadvantage in acid solutions because it has a resistant protective film only to a certain degree, under conditions of local destruction (dissolution) and gives corrosive openings that a little bit later resulted in spreading of one type of corrosion [13].  $\text{Cu}^+$ -ion, present in  $\text{Cu}^+$ -compounds, probably is an intermediate form in a reaction of dissolution followed by a controlled oxidation rate of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ -ions, where more favourable conditions have been provided for brass dezincification [14-17].

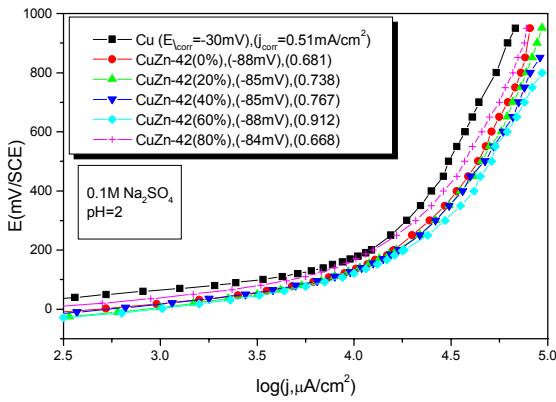


Fig. 1. Polarization curves for tested samples in  $10^{-1}\text{M}$   $\text{Na}_2\text{SO}_4$ , at pH-2

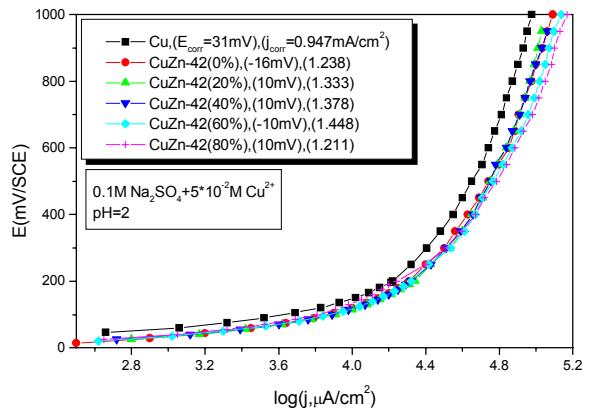


Fig. 2. Polarization curves for tested samples in  $10^{-1}\text{M}$   $\text{Na}_2\text{SO}_4 + 5 \cdot 10^{-2}\text{M}$   $\text{Cu}^{2+}$ , at pH-2

**Influence of chloride ions.** The polarization curves in Figures 3 and 4 are shown for copper and brass with various deformation degrees in a  $10^{-1}\text{M}$   $\text{Na}_2\text{SO}_4$  solution with the addition of chloride ions in a concentration of  $5 \cdot 10^{-4}\text{M}$  and  $5 \cdot 10^{-3}\text{M}$  at pH-2. Immediately upon the setting of corrosion potential, all tested samples are moved into an active state where they are in the whole range of tested potential. The comparison of the polarization curves of brass with those of copper show that the reactions which take place during the anodic polarization of brass is similar. As a result of this comparison we can conveniently claim that brass is in a passive state due to the  $\text{ZnO}$  layer present on its surface before the experiment which protect the surface during the first anodic polarization. The anode polarization curves have a similar form unless the values for  $j_{\text{corr}}$  are also increased with an increased brass deformation degree up to 60%, whereas values of the corrosion current densities are the lowest for a deformation degree of 80%. Only copper electrode has lower values for  $j_{\text{corr}}$  of brass with a deformation degree of 80%.

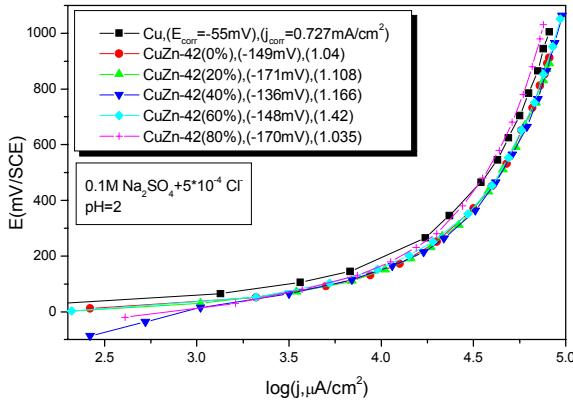


Fig. 3. Polarization curves for tested samples in  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-4}\text{M Cl}^-$ , at pH-2

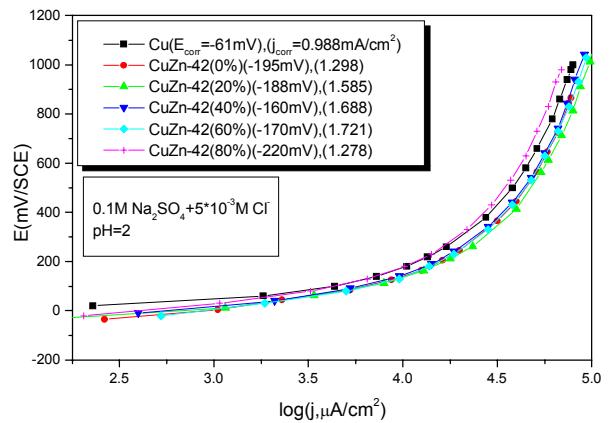


Fig. 4. Polarization curves for tested samples in  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-3}\text{M Cl}^-$ , at pH-2

Densities of corrosion currents are higher than solutions with a concentration of chloride ions of  $5 \cdot 10^{-3}\text{M}$ . It could be noted here that the values for  $j_{corr}$  with a  $10^{-1}\text{M}$  solution of  $\text{Na}_2\text{SO}_4$  and an addition of chloride ions in a concentration of  $5 \cdot 10^{-3}\text{M}$  are higher than values for  $j_{corr}$  with a solution concentration of  $\text{Cl}^-$ -ions of  $5 \cdot 10^{-4}\text{M}$  and  $5 \cdot 10^{-2}\text{M}$ , even higher than some values with a solution concentration of chloride ions of  $10^{-1}\text{M}$ . Figures 5 and 6 give anode polarization curves for tested brass samples in a  $10^{-1}\text{M}$  solution of  $\text{Na}_2\text{SO}_4$  with an addition of chloride ions in a concentration of  $5 \cdot 10^{-2}\text{M}$  and  $1.0\text{M}$ .

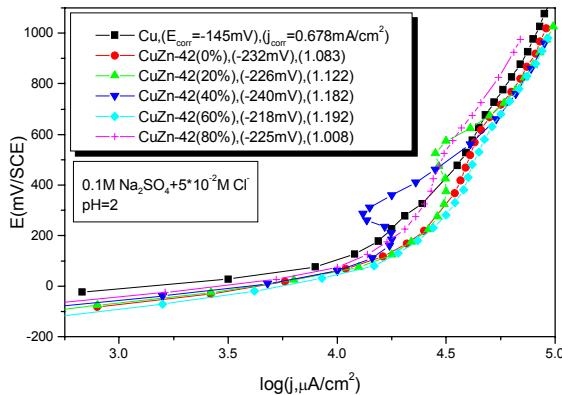


Fig. 5. Polarization curves for tested samples in  $10^{-1}\text{M Na}_2\text{SO}_4 + 5 \cdot 10^{-2}\text{M Cl}^-$ , at pH-2

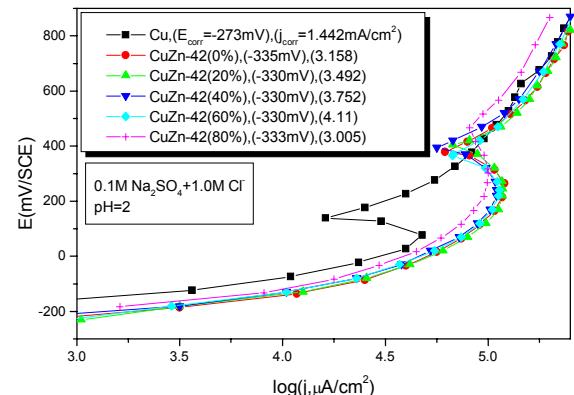


Fig. 6. Polarization curves for tested samples in  $10^{-1}\text{M Na}_2\text{SO}_4 + 1.0\text{M Cl}^-$ , at pH-2

The values of corrosion current densities were moved into a more positive area at small pH-values of solution and an increase of brass deformation degree up to 60%, where values for  $j_{corr}$  are the highest. The most negative values for  $j_{corr}$  are in brass with a deformation degree of 80%. According to Moreau's study [18] to investigate the behavior of copper (brass) in acidic media, there are three distinct steps during the anodic polarization. The first step is  $\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_{ads} + e^-$  followed by a physical conversion second step  $\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^-$  and third rate determining step  $\text{Cu} + 2\text{Cl}^- \rightarrow \text{CuCl}_2^- + e^-$ . This mechanism proposed for acidic media is also valid for  $\text{NaCl}$  medium. If the corrosion potential of the metal in a medium is close to the potential at which the copper oxides are formed, the corrosion products formed are the copper oxides. Since the medium contains chloride, there is insoluble  $\text{CuCl}$  on the surface and  $\text{CuCl}_2^-$  in solutions. This hypothesis is supported by the electrolysis data carried out at a potential range between -0.6 and +1.0V for various periods. The  $\text{Cu(I)}$ -chloro-complex that will be formed ( $\text{CuCl}_2^-$  or  $\text{CuCl}_3^{2-}$ ) depends on the concentration of chloride ions. In concentration values of chloride ions of  $5 \cdot 10^{-2}\text{M}$ , a drop of value

for  $j_{corr}$  was noticed regarding to the solutions with an addition of chloride ions in a concentration of  $5 \cdot 10^{-3} M$ , explained by an inhibitory effect of higher concentrations of chloride ions (See Figure 7).

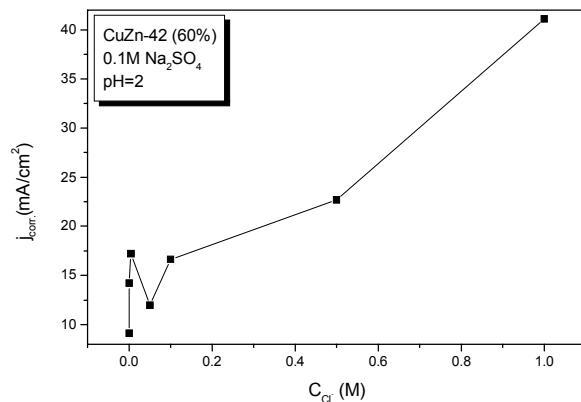


Fig. 7. Dependence of  $j_{corr}$  on concentration of  $Cl^-$ -ions for CuZn-42 (60%), at pH-2

Anode polarization curves show that the lowest values for corrosive current densities are in Cu-electrodes; and, from brass samples, that brass with a deformation degree of 80% has the lowest values for  $j_{corr}$ . Brass with a deformation of 60% has the highest values for  $j_{corr}$ . Regarding the Cu-electrode, the anode peaks of brass electrodes are moved to more positive potential values. Flow of anode polarization curves pointed out that anode dissolution of brass in solutions with chloride ions started with an initial primary dissolution of zinc, and then zinc and copper, depending on potential region, but not in a stoichiometric relationship. The primary process of selective brass dissolution was expressed by a sudden increase of current density immediately upon the corrosion potential, at the beginning of anode polarization. By chemical analysis of the analyzed solution, presence of some  $Zn^{2+}$  and  $Cu^{2+}/Cu^+$ -ions was found to point out that, under the afore mentioned experimental condition, the dezincification process of brass could be developed with the following process of its anode dissolution. Various electrode potentials of zinc, that is copper, have considerable influence on the degree, intensity, and rate of the primary anode dissolution. Zinc passage into a solution in the form of  $Zn^{2+}$ -ion and the formation of complex and undissolved salts contributes to the irreversible nature of development in the dezincification process under the above mentioned conditions. Metallic copper drops back, partly as a porous metallic mass on an electrode surface of CuZn-42 brass, whereas the other part of Cu-ions diffuses on a brass sample surface, where it is separated again in a form of copper and various Cu-compounds by further kinetics control of total alloy dissolution. According to the balance diagram for content of Cu-CuCl<sup>-</sup>, at various pH-values of NaCl solution, it was found that the major participation of more dissolvable copper compounds ( $Cu^+$ ,  $CuCl_2^-$ ,  $CuCl_3^{2-}$ ) are present at higher pH-values relevant to the participation of less dissolvable copper compounds ( $CuCl$ ,  $Cu_2O$ ) [14-18]. Based on the obtained results, the brass dezincification process is developed, in solutions with a content of chloride ions, by the selective dissolution of a more reactive component (zinc) where surface diffusion of more a stable component (copper) has been added to. The dezincification process was developed by help of a high degree of mass transfer that inhibited the protective film formation of corrosive products, especially  $Cu_2O$ -film. Lesser values of corrosion current densities, in tested samples with a deformation degree of 80% and at higher concentrations of chloride ions, are explained by an easier process of substitution  $O^{2-}$ -ions with chloride ions in crystal lattice. Also, a protective film is formed faster in deformed samples of 80% on its surface that causes lower values for  $j_{corr}$ .

## Conclusion

Based on the presented testing results of corrosion behavior of CuZn-42 brass, with various deformation degrees, the following conclusions could be made:

1. The initial dissolution takes place as  $Zn^{2+}$  in an aqueous media containing the chloride. As it starts as  $CuCl_2^-$ , 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.
2. Increase of  $Cu^{2+}$ -ion concentration results in an increased value for  $j_{corr}$ .
3. Inhibiting effect of chloride ions was noticed for concentrations of ions of  $5 \cdot 10^{-2} M$  and  $10^{-1} M$  in an  $10^{-1} M$  solution of  $Na_2SO_4$ .
4. Increase of a concentration of the  $Cl^-$ -ions, except for values of  $5 \cdot 10^{-2} M$  and  $10^{-1} M$ , resulted in a significant increase of value for  $j_{corr}$ .
5. The process of dezincification and anode dissolution of CuZn-42 brass was developed in the whole range of tested potentials, and pointed out the instability of formed films on their surface.
6. The complex form of anode curves pointed out the phase reactions of selective a dissolution process of CuZn-42 brass.
7. Surface film formation of corrosion products was developed through some phases of and distinctive presence of copper layers and spot corrosion present on surface of corroded electrode. In conclusion  $ZnO$  provides the passivity of brass. Under the conditions that this  $ZnO$  layer is ruptured, both copper and zinc atoms pass into the solution. The corrosion mainly continues by the passage of zinc ions into the solution. Even in the passivation region in the polarization curve, the dissolution of zinc continues.
8. Brass with a deformation degree of 80% has the lowest values for corrosion current densities.

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