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THE INFLUENCE OF GELATINE ON THE CORROSION BEHAVIOUR OF COLD WORKED COPPER WIRE IN ALKALINE MEDIA

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Abstract

Copper wire obtained by dip–forming process was cold worked to the deformation degrees of 83, 87, 91, 95 and 99 %. Electrochemical potentiodynamic method was used to investigate corrosion behaviour of these wires in aqueous solutions of Na_2CO_3 (1 mol/dm^3). Open circuit potentials as well as peak potentials are given as a function of deformation degree in Na_2CO_3 without and with addition of gelatine in concentration between 0.1 and 0.5 g/l. It was found that the addition of gelatine does not change the mechanism of the process, but influences on current density. Small concentrations of gelatine (0.1 g/l or less) have positive influence on the corrosion protection of copper in alkaline solution, but the addition of gelatine in concentration 0.5 g/l causes the increasing of its corrosion rate.

Keywords: Corrosion inhibition, gelatine, copper wire, deformation degree

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1. Introduction

Organic inhibitors are extensively used for the protection of metals and alloys in contact with different media [1]. Among them, azoles have been intensively investigated as effective copper corrosion inhibitors. Benzotriazole (BTA) is one of the most important inhibitors for copper and copper alloys. However, a major deficiency of BTA is its toxicity. In line with environmental protection requirements, the use of BTA is nowadays quite limited and toxic inhibitors that are widely used in industrial processes should be replaced with new environmentally friendly inhibitors. Other researchers investigations have shown that imidazole derivatives have good inhibiting properties with respect to the atmospheric and acidic copper corrosion and that they are also environment friendly [2, 3]. It is well known that 2-mercapto-benzothiazole (MBT) inhibits the corrosion of copper and its alloys. This inhibitive property is attributed to the formation an adherent protective film on the metal surface [4 – 6]. Copper and copper alloy resistance to corrosion has been investigated by many researches. Potentiodynamic method is usually used for investigation of corrosion behaviour of metals. Sanchez et al. [7] have investigated the voltammetry polarization of Cu specimens in Na_2CO_3, $NaHCO_3$ and $NaClO_4$ solutions (8-12 pH range). Voltammetry data were complemented with SEM and electron microprobe analysis. The reaction mechanism of the electrooxidation of copper was investigated in alkaline solutions, from pH 12 to 14, by Brisard et al. [8]. Electrochemical experiments provide useful information concerning the chemical species formed from electrochemical as well as chemical reactions involved during the formation and dissolution of copper oxides.

The adsorption of gelatine at the copper electrode in sulphuric acid solution is dependent on electrode potential and, furthermore, is accompanied by coadsorption of anion species [9]. The authors [10] explained the mechanism of the corrosion inhibition of Zn anode in NaOH by gelatine and some inorganic anions. The concentrations needed to establish a certain inhibiting efficiency increase with increase in alkali concentration. The results are interpreted in the light of dissolution – precipitation mechanism. Nelson and Mantoura [11] were found that the non Cu-complexion surfactant, gelatine, has been substituted for natural organic material during assay of estuarine waters. It is shown that the effects of adsorption of natural organic material on the electroreduction and electrooxidation of Cu are diverse and act through the complexion properties of the organic material.

The influence of chloride ions on corrosion behaviour of OFHC (Oxygen Free High Conductivity) copper in a sodium carbonate solution, at pH about 12, as well as the inhibiting effect of gelatine has been investigated by Ivanov et al. [12-14].

During anodic polarisation of copper in alkaline media the following reactions [15] can occur:

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \quad E = 0{,}471 - 0{,}059pH \tag{1}$$

$$Cu + H_2O = CuO + 2H^+ + 2e^- \quad E = 0{,}57 - 0{,}0591pH \tag{2}$$

$$Cu + 2H_2O = HCuO_2^- + 3H^+ + 2e^- \quad E = 1{,}127 - 0{,}0886pH + 0{,}0295\log(HCuO_2^-) \tag{3}$$

This study will present the results achieved by electrochemical investigation of cold worked copper wire. By measuring open circuit potential and using the cyclic voltammetry methods, experiments were carried out in sodium carbonate solutions, without and with the presence of gelatine, at room temperature, at pH 12.

2. Experimental

For the purpose of investigation of corrosion behavior of cold worked OFHC copper to the high deformation degrees in alkaline medium with the addition of gelatine as corrosion inhibitor, it was used an experimental system that consisted of:

– electrochemical cell with three electrodes: working, reference (saturated calomel electrode, SCE) and counter (Pt sheet $A \cong 2$ cm^2);

– hardware (PC, AD/DA converter PCI – 20428 W produced by BURR-BROWN and analogue interface developed on Technical faculty in Bor) and software for excitation and measurement (LABVIEW 6.1 platform and originally developed application software for electrochemical measurements).

Investigated wires were obtained by drawing initial copper wire [16] produced by dip-forming method [17, 18]. Six samples of wires of different deformation degrees (0, 83, 87, 91, 95 and 99 %) were prepared for electrochemical investigations on the next way: central part of wires was isolated by lacquer, one end with surface area of 1 cm^2 served as working part of electrode, and the other as an electric contact.

Prior each experiment working electrode was degreased, mechanically polished first at abrasive paper 0000, and then by using felt soaked in alumina suspension, α–Al_2O_3 0.05 μm. After polishing had been completed, surface was treated by HNO_3 1:1 water solution, washed by distilled water jet and finally by working solution.

Experiments were carried out in a sodium carbonate solution (C_{Na2CO3} = 1 mol·dm^{-3}). Working solution was prepared from $Na_2CO_3 \cdot 10\ H_2O$ (p. a. purity; Zorka Šabac) and distilled water. Solutions with gelatine (Merck) were prepared from 1 M Na_2CO_3 to which 0.1 – 0.5 g/l gelatine was added.

The methods used were: measuring of the open circuit potential and cyclic voltammetry. The cyclic voltammograms were recorded starting from the open circuit potential established on electrode. Measurements were conducted at a sweep rate of 0.01 V/s under aerated conditions.

3. Results and Discussion

Voltamograms presented in Fig. 1 show the influence of deformation degree on the open circuit potential of copper in 1M Na_2CO_3 water solution at room temperature. Stable value of potential was established on the specimen of wire with 91 % deformation almost immediately after immersing in the solution. For the other specimens, open circuit potential increases very slowly with time (except for the 83 % deformation) indicating formation of some protective layer on the surface of electrodes and stable values of potential were established on electrodes after 120 s from immersion in the solution. The potential of copper in a sodium carbonate solution ranges from – 0.180 to – 0.320 V vs. SCE. Small changes (lower than 140 mV) in positive direction with the increasing of deformation degree can be noticed. On undeformed copper in the same solution after 500 s from immersion, the value of –0.196 V vs. SCE was measured.

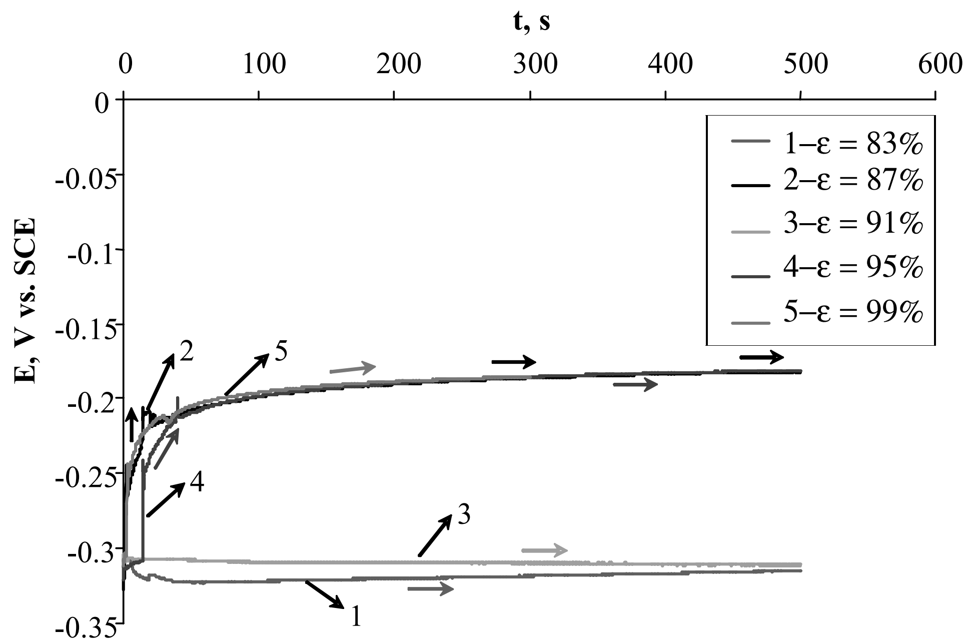

Fig. 1. Open circuit potential of copper in 1M Na_2CO_3 as a function of time

In the next experiments potentiodynamic method was used to investigate electrochemical behaviour of cold worked copper during anodic polarization. Sweep rate in all experiments was 0.01 V/s and sweeping started from the open circuit potential established on electrode after about ten minutes. Voltammograms presented in Fig. 2 show that there is no big difference between peak heights obtained for different electrodes. Small differences can be explained by the deviation of electrode surface areas. First peak on the voltammograms corresponds to formation of copper oxides, first Cu_2O, and then CuO. It is clear that there should be two very close peaks, and they really can be noticed on some voltammograms (on specimens of wires with the deformation degrees of 83 and 95 %), but more often they overlap.

First anodic peak potential is about –0.08 V vs. SCE. That value may correspond to the reactions of formation of copper oxides (1) and (2), taking into account that pH of used solutions is about 12. Wide shoulder at about 0.35 V vs. SCE could be attributed to formation of alkali carbonate of copper, $Cu_2(OH)_2CO_3$.

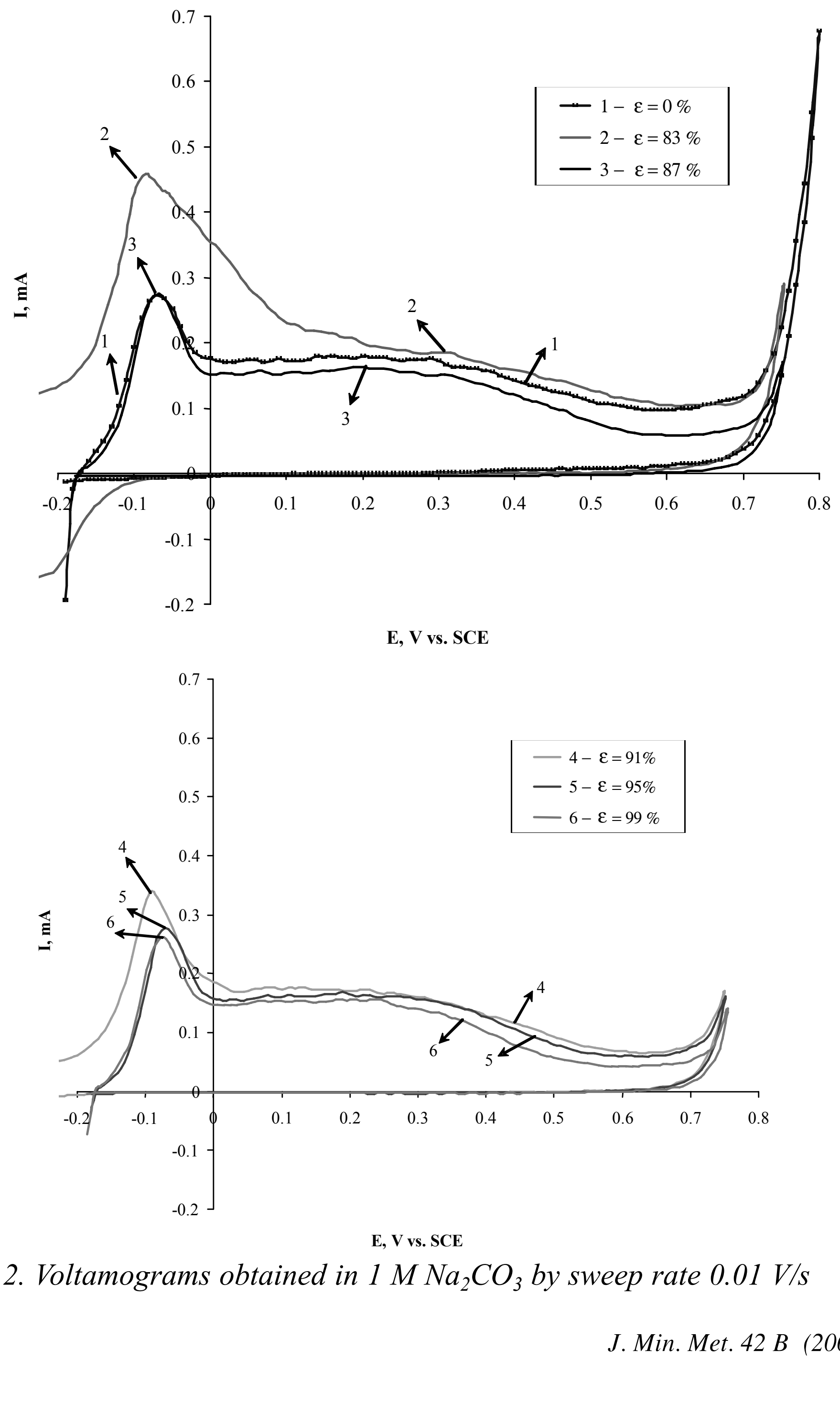

Fig. 2. Voltamograms obtained in 1 M Na_2CO_3 by sweep rate 0.01 V/s

The appearance of copper carbonate was approved with SEM analysis [7]. Sharp rise of current at 0.750 V vs. SCE is referred to oxygen evolution. There is no systematic change of the first peak height with the deformation degree. This could be the consequence of the fact that it consists of two very close peaks and deformation degree can have different influence at every one of them.

Experiments performed in solutions containing gelatine, beside sodium carbonate, gave similar results concerning the shape of curves showing the dependence of open circuit potential on time (Fig. 3). Values of open circuit potential are about 130 to 160 mV lower than those obtained in 1 M Na_2CO_3. In diluted solutions of sodium carbonate with addition of various concentrations of gelatine (0.1 – 0.5 g/l), open circuit potential vary from about –0.151 to about –0.178 V vs. SCE respectively in the same experiment (for wire with the deformation degree of 91 %). Average values of potential are less negative then those obtained in more concentrated solution.

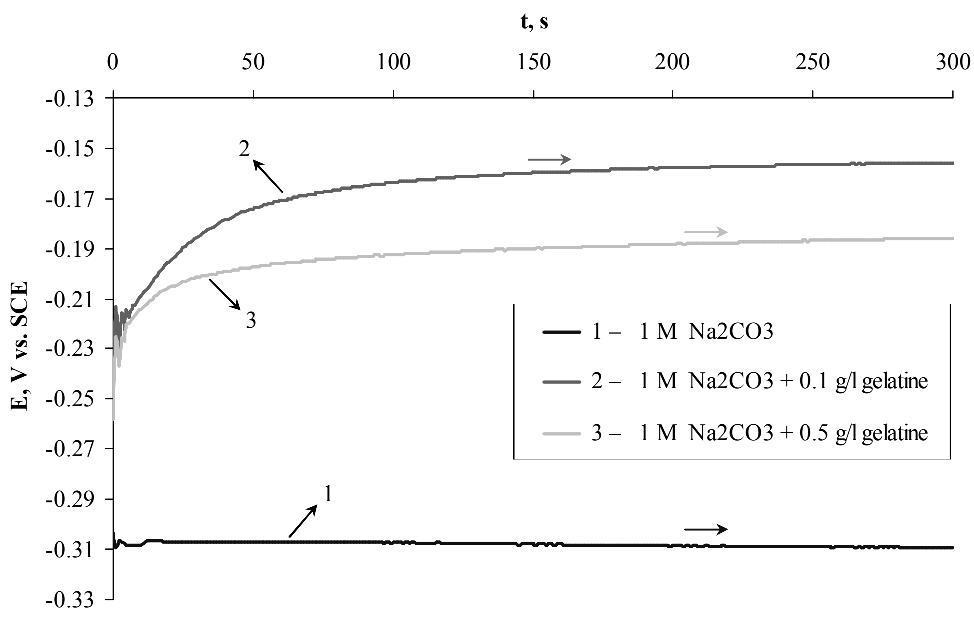

Fig. 3. Open circuit potentials obtained on wire with the deformation degree of 91 % in solutions without and with addition of gelatine

Complete image about the influence of gelatine as inhibitor on electrochemical behaviour of cold worked copper in a sodium carbonate solution can be obtained from potentiodynamic voltammograms recorded for copper wire in solutions with and without of gelatine (Fig. 4). It can be seen that the current peak is the highest in inhibitor free solution; in the first place it decreases with the addition of inhibitor in concentration of 0.1 g/l and next it increases again when the concentration of gelatine is 0.5 g/l. It can be noticed that presence of gelatine in solution had positive influence from the corrosion point of view only in small concentrations (0.1 g/l or less).

Namely, current is lower in presence of gelatine in the whole active region, i.e. from the rest potential till about 0.5 V vs. SCE. The shape of voltammograms is equal as at the voltammogram obtained in 1M Na_2CO_3 meaning that there is one sharp peak, but with some shoulders on it and one wide shoulder on more positive potential. Only the potential of the first peak is a little bit shifted to the right and the shoulder is better defined in presence of gelatine. At cathodic part of voltammograms no current peak is noticed.

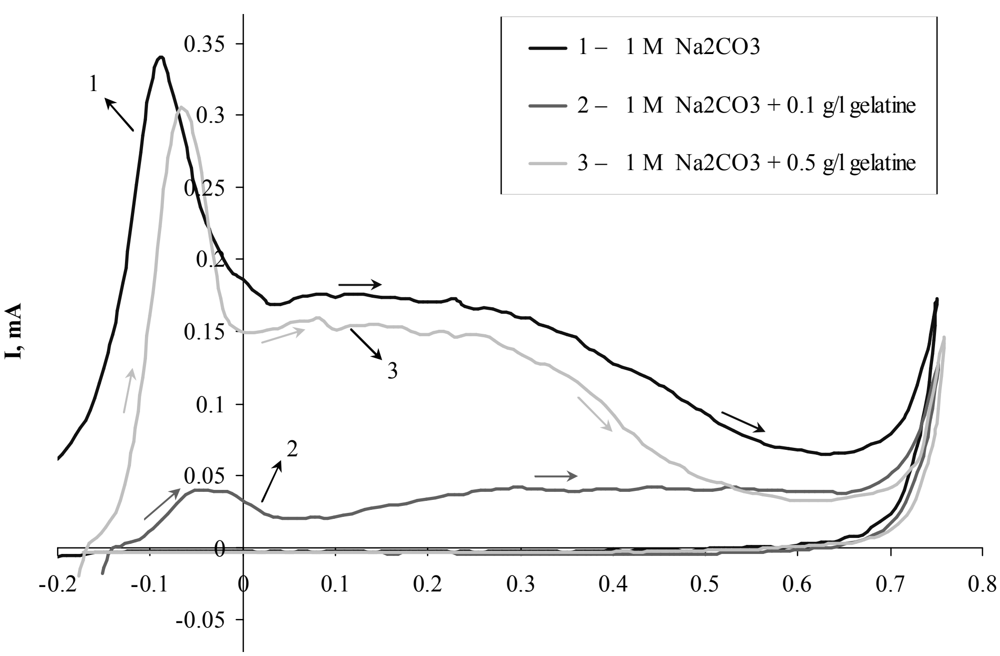

Fig. 4. Potentiodynamic voltammograms obtained on copper wire with the deformation degree of 91 % in different solutions by sweep rate 0.01 V/s

It could be concluded that the presence of gelatine in concentration 0.1 – 0.5 g/l does not influence on mechanism of the reactions occurring on the electrode surface. Smaller peak heights are explained by presume that adsorption of gelatine resulted with the decreasing of active surface area and with more positive open circuit potential, so smaller over voltage at the same anodic potential. Taking into account that anodic current corresponds to the corrosion rate of metals, it can be concluded that small concentrations of gelatine (0.1 g/l or less) in sodium carbonate solution may have positive influence on the corrosion protection of copper. The addition of gelatine in concentration 0.5 g/l causes the increasing of copper corrosion rate in alkaline solution (1M Na_2CO_3).

4. Conclusion

Corrosion behaviour of cold deformed copper wire is characterized by its open circuit (corrosion) potential (ranges from -0.180 to -0.320 V vs. SCE) and by its behaviour during anodic polarisation. It was experimentally found that deformation degree between 83 and 99 % had no big influence on the open circuit potential as well as on the behaviour of copper during anodic polarisation in 1 M Na_2CO_3. Voltammograms show that there is no big difference between peak heights obtained for different electrodes. Small differences can be explained by the deviation of electrode surface areas.

The reaction mechanism consists of at least three steps. The first of them is formation of Cu_2O, the second is formation of CuO, and the third can be attributed to the formation of alkali carbonate of copper. Potentials of the first two peaks are very close, so in most voltammograms they overlap forming one sharp peak on potential about -0.08 V vs. SCE. There are no regular changes of peak heights on voltammograms with deformation degree. That could be the consequence of the different influence of deformation degree on the rate of reaction steps in the mechanism of formation of copper oxides. Approximately the same current density of about 0.18 mA cm^{-2} corresponds to the wide shoulder on potential about 0.35 V vs. SCE for all specimens.

Gelatine was used as copper corrosion inhibitor in 1 M Na_2CO_3 water solution. After immersion in electrolyte, open circuit potential quickly raised in all tested solutions. The shape of voltammograms is equal in different solutions (without and with gelatine). Addition of gelatine does not change the mechanism of process, but influences on current density. Small concentrations of gelatine (0.1 g/l or less) have positive influence on the corrosion protection of copper in alkaline solution, but the addition of gelatine in concentration 0.5 g/l causes the increasing of its corrosion rate.

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