ELECTROCHEMICAL BEHAVIOR OF COLD WORKED COPPER WIRE IN PRESENCE OF CHLORIDE IONS

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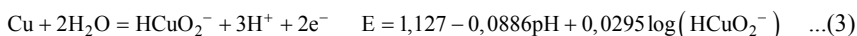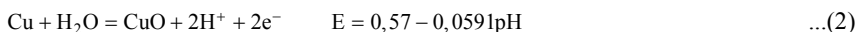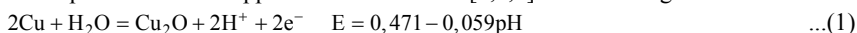**VJ12, P. Box 50, 19210 Bor,**
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ABSTRACT
Copper wire obtained by dip–forming process was cold worked to the deformation degrees of 83 %, 87 %, 91 %, 95 % and 99 %. Electrochemical potentiodynamic method was used to investigate corrosion behavior of these wires in aqueous solutions of Na_2CO_3 (1 mol/dm3). Open circuit potentials as well as peak potentials are given as a function of deformation degree in both Na_2CO_3 without and with presence of chloride ions.
Keywords: copper, cyclic voltammetry, electrochemical behavior, sodium carbonate, chloride ions

1. INTRODUCTION

Potentiodynamic method is usually used for investigation of corrosion behavior of metals. After the Pourbaix atlas [1] next species are stable in investigated aqueous solutions at pH between 11 and 12: Cu, Cu_2O, $HCuO_2^-$, $Cu(OH)_2$, $Cu_2(OH)_2CO_3$ and $Cu_2(OH)_3Cl$ when chloride ions are present in solution.

During anodic polarization of copper in alkaline media [2,3,4] the following reactions can occur:

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \quad E = 0,471 - 0,059pH \qquad ...(1)$$

$$Cu + H_2O = CuO + 2H^+ + 2e^- \quad E = 0,57 - 0,0591pH \qquad ...(2)$$

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

2. EXPERIMENTAL

Investigated wires were obtained by drawing initial copper wire produced by dip-forming method [5,6,7]. 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 abrasion paper 0000 and then by using felt soaked in alumina suspension, Al_2O_3. 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.

Experimental system [8] consisted of:

– electrochemical cell with three electrodes: working, reference (saturated calomel electrode SCE) and counter (Pt sheet A≈2 cm2);

–   hardware (PC, AD~DA converter PCI – 20428 W produced by BURR-BROWN and analog interface developed on TF Bor) and software for excitation and measurement (LABVIEW 6I platform and originally developed application software for electrochemical measurements).

3. RESULTS AND DISCUSSION

Voltamograms presented in figure 1 show the influence of deformation degree on the open circuit potential of copper in 1M Na_2CO_3 water solution at room temperature. Open circuit potential increases with time very slowly indicate formation of some protective layer on the surface of electrodes. Deformation degree has no significant influence on the open circuit potential, but very small change in negative direction with the increasing of deformation degree can be noticed (Fig. 1). On undeformed copper in the same solution after 100 s from immersion, the value of –189 mV vs. SCE was measured.
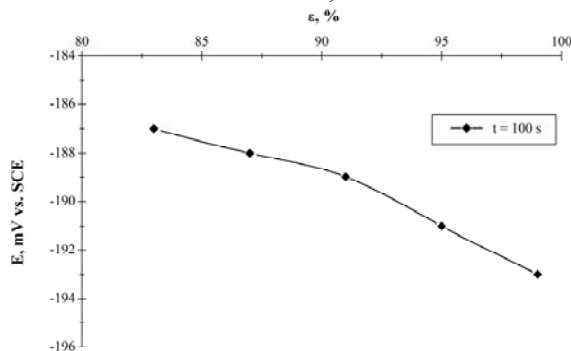

Figure 1. Open circuit potentials of copper after 100 s from immersion of electrode in 1M Na_2CO_3 as a function of deformation degree.

Experiments performed in solution containing chloride ions, beside sodium carbonate, gave similar results concerning the shape of curves showing the dependence of open circuit potential on time (Fig. 2).
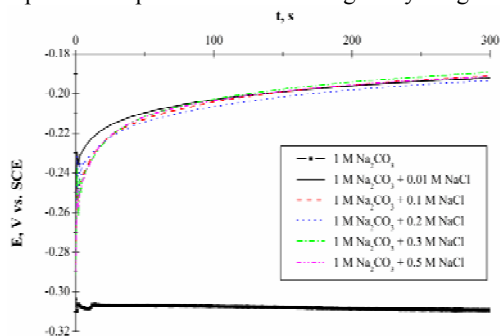Open circuit potential values change very irregularly with the deformation degree (Fig. 3)

Figure 2 .The open circuit potential Cu electrode deformed 91% in the 1M Na_2CO_3 solution without and with presence of chloride ions.
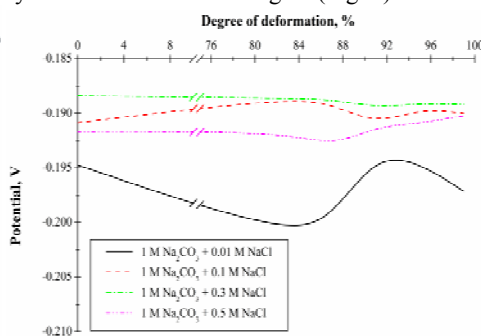
Figure 3.The influence of deformation degree on open circuit potential Cu electrodes in the 1M Na_2CO_3 + xCl$^-$ solution.

Sweep rate in all experiments was 0.01 V/s. Voltammograms presented in figure 4 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.
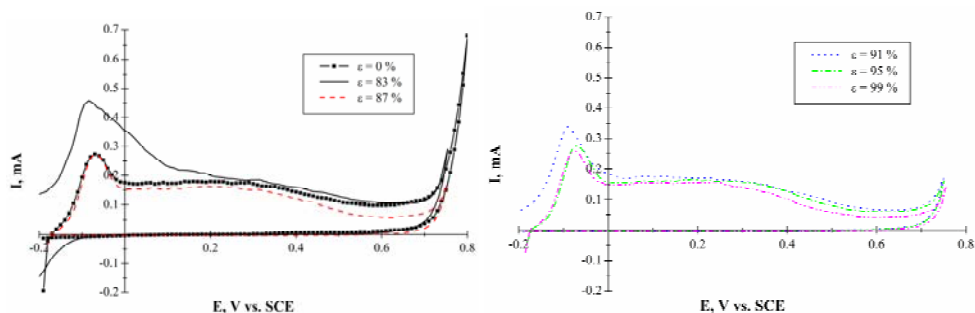

Figure 4. Voltammograms obtained in 1 M Na_2CO_3 by sweep rate 0.01 V/s.

Potential of the first anodic peak is about −0.08 V vs. SCE. That value may correspond to the reactions of formation of copper oxides 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, $Cu_2(OH)_2CO_3$. The current peak on potential of about 0.35V vs. SCE correspond to approximately the same current densities for every specimen (about 0.18 mA/cm^2). Sharp rise of current on about 0.750V vs. SCE is referred to active gaseous oxygen evolution and all voltammograms were recorded to that potential.
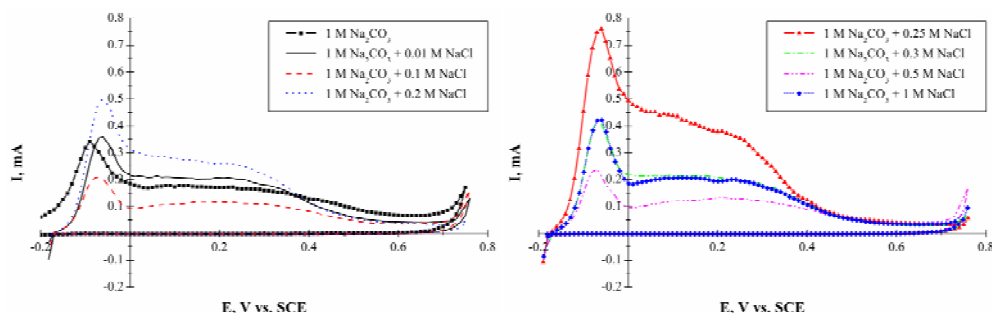

Figure 5. Potentiodynamic voltammograms obtained on copper wire with the deformation degree of 91 % in different solutions by sweep rate 0.01 V/s.

Potentiodynamic voltammograms obtained for copper wire with the deformation degree of 91 % in solutions with and without chloride ions are presented in Fig. 5. It can be seen that addition of 0.01 – 1 mol/dm^3 NaCl in solution had no big, but positive influence from the corrosion point of view. The shape of voltammograms is equal as at the voltammograms obtained in 1M Na_2CO_3 meaning that there is one sharp, but with some shoulders on it, peak and one wide shoulder on more positive potential. Only the potential of the first peak is a little bit shifted on the right and the shoulder is better defined. It could be concluded that the presence of chloride ions in concentration 1 mol/dm^3 or less does not influence on mechanism of the reactions occurring on the electrode surface. Smaller peak heights are explained by presume that adsorbed chloride anions resulted with the decreasing of active surface area and to the lower currents on the same geometric area. At cathodic part of voltammograms no current peak is noticed on both investigated solutions. Taking into account that anodic current corresponds to the corrosion rate of metals, it can be concluded that small concentrations of chloride ions in carbonate solutions may have positive influence on the corrosion protection of copper.

4. CONCLUSIONS

Corrosion behavior of cold deformed copper wire is characterized by its open circuit (corrosion) potential (measured values of potentials are between −0.180 and −0.320V vs. saturated calomel electrode (SCE)) and by its behavior during anodic polarization. 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 behavior of copper during anodic polarization in 1 M Na_2CO_3. Voltammorgrams show that there are no big differences between peaks obtained for various electrodes. Small differences can be explained by electrode surface differences.

The reaction mechanism consists of at least three steps. The first of them is formation of Cu(I)O, the second is formation of Cu(II)O, 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 of about −0.08V vs. SCE. There is no regular change of current density of the highest peak on voltammograms with deformation degree. The addition of chloride in concentration 1 M or less does not change the mechanism of process, but influences on current intensity by lowering it that means the positive influence to corrosion resistance of copper in such solutions.

5. ACKNOWLEDGEMENT

6. REFERENCES

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