

# Corrosion Behavior of Cold Worked Copper Wire in Alkaline Media with Presence of Chloride Ions

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**Abstract.** The corrosion behavior of copper was investigated by a constant sweep rate (0.01 V/s) and in different corrosion media (1 M Na<sub>2</sub>CO<sub>3</sub> water solution without and with the presence of chloride ions). Copper wire produced by dip-forming method 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 alkaline solutions. Open circuit potentials as well as peak potentials are given as a function of deformation degree in both the Na<sub>2</sub>CO<sub>3</sub> pure solution and solutions containing chloride ions.

## Introduction

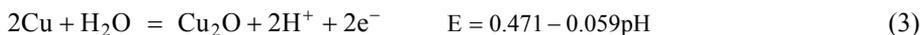
After the Pourbaix atlas [1], next species are stable in investigated aqueous solutions at pH between 11 and 12: Cu, Cu<sub>2</sub>O, HCuO<sub>2</sub><sup>-</sup>, Cu(OH)<sub>2</sub>, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> and Cu<sub>2</sub>(OH)<sub>3</sub>Cl when chloride ions are present in solution.

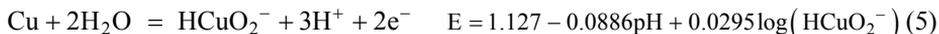
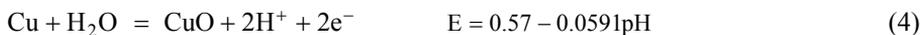
The mechanism of Cu electrodisolution in chloride media has been investigated by many researchers [2, 4-7]. It is generally accepted that Cu anodic dissolution is influenced by chloride concentration independently of pH [6, 7]. At chloride concentrations lower than 1 M, the mechanism of copper dissolution can be expressed as:



At chloride concentrations greater than 1 M, higher cuprous complexes such as CuCl<sub>3</sub><sup>2-</sup> and CuCl<sub>4</sub><sup>3-</sup> are formed [5, 8]. The anodic dissolution of copper is under mixed control by the electrodisolution of copper and the diffusion of soluble CuCl<sub>2</sub><sup>-</sup> [5, 7].

During anodic polarization of copper in alkaline media the following reactions can occur:





Potentiodynamic method is usually used for investigation of corrosion behavior of metals. The object of the present investigation is to study the corrosion behavior of cold worked copper in aqueous solutions of  $\text{Na}_2\text{CO}_3$  without and with the presence of chloride ions by the use of electrochemical potentiodynamic method.

### Experimental

In the present investigation cyclic voltammetry measurements are carried out on cold worked copper wires. Investigated wires were obtained by drawing initial copper wire produced by dip-forming method [8]. Six samples of wires of different deformation degrees (0, 83, 87, 91, 95 and 99 %) were prepared for electrochemical investigations on by the following procedure: central part of wires was isolated by lacquer, one end with surface area of  $1 \text{ cm}^2$  served as working part of electrode, and the other as an electric contact. A three-electrode cell system was used for the electrochemical measurements. The counter electrode was a platinum electrode. All potential values in experiments were given with respect to a saturated calomel electrode (SCE) as a reference.

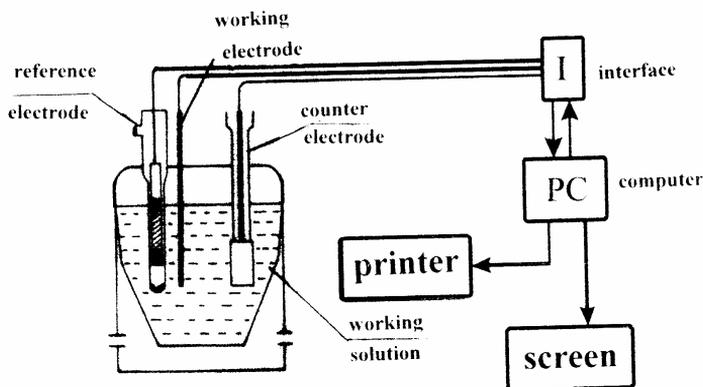


Fig. 1. Schematic view of the system for electrochemical measurements.

Prior to each experiment working electrode was degreased, prepared by abrasion with 0000 emery paper, and polished with alumina ( $\alpha\text{-Al}_2\text{O}_3$ )  $0.05 \mu\text{m}$ . After polishing had been completed, surface was treated by  $\text{HNO}_3$  1:1 water solution, washed by distilled water jet and finally by the working solution.

Experimental system shown in Fig. 1, consisted of:

- electrochemical cell with three electrodes: working, reference (saturated calomel electrode SCE) and a counter (Pt sheet  $A \approx 2 \text{ cm}^2$ );
- hardware (PC, AD/DA converter PCI – 20428 W produced by BURR-BROWN and analog interface developed at TF Bor) and software for excitation and measurement (LABVIEW 6I platform and originally developed application software for electrochemical measurements).

## Results and discussion

Voltamograms presented in Fig. 2 show the influence of deformation degree on the open circuit potential of copper in 1 M  $\text{Na}_2\text{CO}_3$  water solution at room temperature. Open circuit potential increases with time very slowly, indicating formation of some protective layer on the surface of electrodes. Deformation degree has no significant influence on the open circuit potential, which is explained by a fact that all specimens of wires were cold worked to the high deformation degrees. But smaller changes (lower than 100mV) in positive direction with the increasing of deformation degree can be noticed (Fig. 2). On undeformed copper in the same solution after 300 s from immersion, the value of  $-196$  mV vs. SCE was measured.

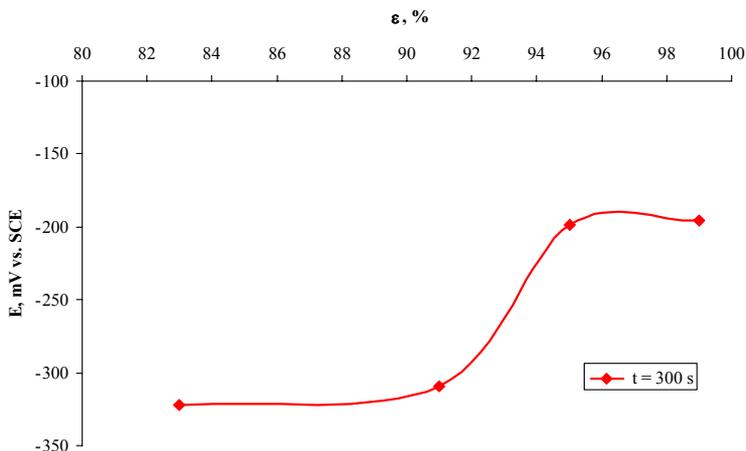


Fig. 2. Open circuit potential of copper after 300 s from immersion of electrode in 1M  $\text{Na}_2\text{CO}_3$  as a function of deformation degree.

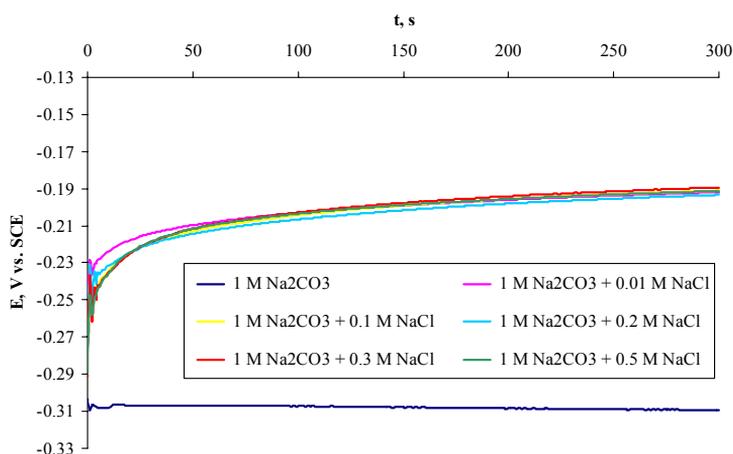


Fig. 3. Open circuit potentials obtained on wire with the deformation degree of 91% in solutions with and without presence of chloride ions.

Experiments performed in a 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. 3). Values of open circuit potential are just a few millivolts lower

than those obtained in 1 M  $\text{Na}_2\text{CO}_3$ , but they change very irregularly with the deformation degree. In diluted solutions of sodium carbonate with presence of various concentrations of chloride ions, open circuit potential vary from about  $-320$  to about  $-180$  mV vs. SCE in the

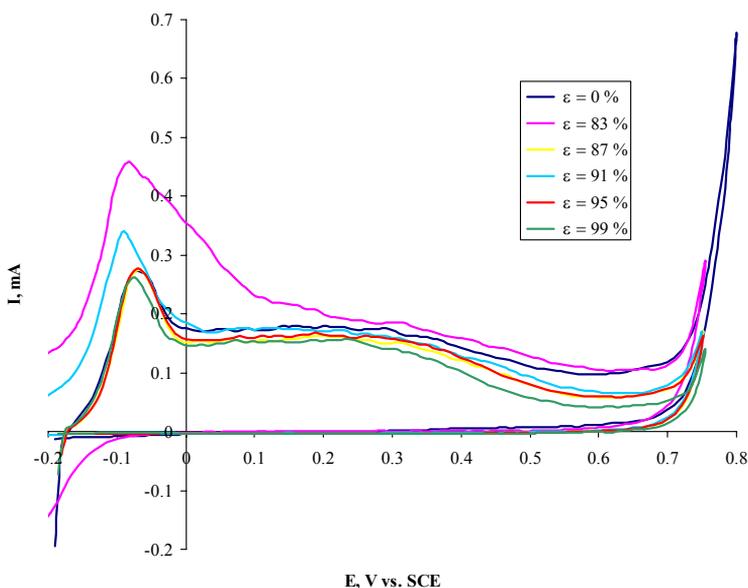


Fig. 4. Voltammograms obtained in 1 M  $\text{Na}_2\text{CO}_3$  by sweep rate 0.01 V/s.

same experiment, which is explained by low conductivity of the solution. Average values of potential are less negative than those obtained in more concentrated solution.

In the next experiments potentiodynamic method was used to investigate electrochemical behavior 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. 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 the formation of copper oxides, first  $\text{Cu}_2\text{O}$ , and then  $\text{CuO}$ . 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.

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 the formation of alkali carbonate of copper,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . Sharp rise of current is referred to active gaseous oxygen evolution and all voltammograms were recorded to that potential.

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  $0.01 - 1 \text{ mol/dm}^3$  NaCl in solution had a relatively small, but a positive influence from the corrosion point of view. The shape of voltammograms is the same as the voltammogram obtained in 1M  $\text{Na}_2\text{CO}_3$  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 slightly shifted on the right and the shoulder is better defined. It could be

concluded that the presence of chloride ions in concentrations of  $1 \text{ mol/dm}^3$  or less does not influence the mechanism of the reactions occurring on the electrode surface. Smaller peak heights may be explained by the assumption that adsorbed chloride anions are the result of the decrease of active surface area and to the lower currents on the same geometric area. At cathodic part of voltammograms no current peak is noticed with 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.

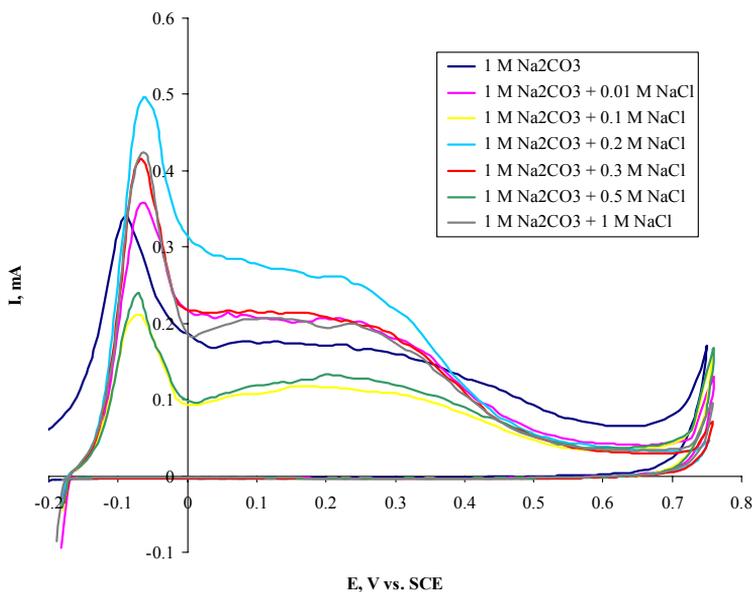


Fig. 5. Potentiodynamic voltammograms obtained on copper wire with the deformation degree of 91 % in different solutions by sweep rate  $0.01 \text{ V/s}$ .

## Conclusion

Corrosion behavior of cold deformed copper wire is characterized by its open circuit (corrosion) potential and by its behavior during anodic polarization. It was experimentally found that deformation degree between 83 % and 99 % had a relatively small influence on the open circuit potential as well as on the behavior of copper during anodic polarization in  $1 \text{ M Na}_2\text{CO}_3$ . The reaction mechanism consists of at least three steps. The first step is the formation of  $\text{Cu(I)O}$ , the second is formation of  $\text{Cu(II)O}$ , 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. The addition of chloride in concentration  $1 \text{ M}$  or less does not change the mechanism of process, but the lowering of current intensity with small concentration of chloride ions may have a positive influence to the corrosion resistance of copper in such solutions.

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