

Initiation of copper dissolution in sodium chloride electrolytes

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Abstract

Initial stages of copper activation in chloride-ion containing neutral aqueous solution were studied. The results point that activation of copper passivity is initiated once the potential exceeds the breakdown value, occurring with well-defined incubation period, similar to that of other passive metals in chloride environments. The effect of applied potential and Cl^- ion concentration on the incubation period is presented. The results indicate that an incubation period for copper activation in chloride containing solutions can be associated with the formation of a two-dimensional CuCl layer on the metal surface. The incubation period is relatively long at negative potentials and it decreases with a positive shift in the potential. At a certain potential, the incubation period is sharply decreased. The time-frame of incubation period is attributed to the formation rate of two-dimensional CuCl layer and its reduction rate. The formation of a stable salt film on the metal surface facilitates localized rapid dissolution of the copper.

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1. Introduction

Copper is known as a metal, which exhibits a passivity state in neutral and alkaline solutions [1]. It was shown by in situ electrochemical scanning tunneling microscopy (STM) that in neutral chloride-free solutions the formation of protective films on copper surface is initiated by OH^- ions adsorption at very negative potentials, close to -1 V (SCE) [2–4]. At more positive potentials the formation of Cu(I) single layer and the Cu(I)/Cu(II) duplex layer was indicated by STM on copper surface [2–6]. Wide region of copper passivity was also detected in acidic solutions at potentials below active copper dissolution [7].

In the presence of chlorides, it is well accepted that copper rapidly dissolves through the formation of soluble complex CuCl_2^- [8–18]. It was demonstrated by polarization studies that copper dissolution through CuCl_2^- occurs at much more positive potentials, compared to potential values where an initiation of oxide films was detected [11]. Hence copper transition from passivity to active dissolution state could occur through

a breakdown process facilitated by chlorides, phenomena well described for many passive metals. Breakdown of copper passivity was clearly demonstrated in studies conducted in neutral solutions with low chloride concentrations. Anodic polarization data obtained by Thomas and Tiller [11] in 0.01 and 0.1 M NaCl revealed copper passivity in a wide potential region, surface activation at potentials above a breakdown potential and a shift of the breakdown potential to more negative values as chloride concentration increased. It was also shown that copper surface activation resulted in a localized corrosion (or pitting) attack.

The present work is focused on the investigation of the mechanism of copper activation and initial stages of copper dissolution in neutral chloride electrolytes. The activation of metal passivity leading to a pit nucleation was widely studied for iron and stainless steels [19–22]. Both iron and stainless steels activation in chloride solutions initiates through chloride ions adsorption and a metastable pit growth, which appears as transient fluctuations of potential or current, depending on the controlled parameters [20–22]. Metastable pit growth occurs at potentials well below the breakdown potential, as well as above this potential during the induction times. Transition from metastable to stable pit growth is associated with a formation of a chloride salt layer over activated sites, which provides a diffusion barrier during metastable pit growth, preventing their repassivation. The conditions for a stable pit growth are established above the pitting

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potential, while below it, a barrier salt film is not formed and metastable pits undergoes repassivation [20–22].

It is reasonable to assume that chloride ions adsorption and formation of a two-dimensional salt layer play an important role in copper passivity breakdown. The adsorption of chloride ions on the copper electrode surface was detected at potentials negative to that of copper active dissolution by several authors [23–28]. Becerra et al. [23] reported in 0.1 M NaCl the formation of chloride adsorbed layer on the copper surface at -0.6 V (SCE). Elsner et al. [24] detected chloride adsorption in 0.3 M NaCl at even more negative potential of about -0.8 V (SCE). It was suggested that based on the degree of metal surface coverage, a relative concentration of Cl^- and OH^- electroadsorbates determines the onset of copper dissolution. They also detected the formation of CuCl deposits on the electrode surface at potentials of copper dissolution [24]. Benedetti et al. [25] suggested that a process, which precedes active dissolution is Cl^- adsorption/desorption equilibrium. Cl^- adsorption on Cu (1 1 1) surface was also detected in diluted HCl solutions by different spectroscopy techniques [26–28]. The effect of Cl^- on surface reconstruction was also conducted by in situ STM [26–28].

This study aims at further understanding of the initial stages of copper activation in chloride ion containing solutions, and the role of the salt layer formation during this process. The effect of chloride-ions concentration and the applied potential on an incubation period of copper activation was studied, as well.

2. Experimental

Electrochemical measurements were conducted in a two-compartment electrochemical cell with copper electrode compartment filled with 0.5 l of the NaCl solution. NaCl concentration was varied from 0.015 to 1.5 M. The solutions were prepared from analytically pure reagents and twice-distilled water. A pencil-type electrode made of 5 mm diameter copper rod (99.995%) mounted in a room temperature-curing-epoxy was used as a working electrode. The electrode was polished (600 grit alumina) and carefully degreased with acetone followed by water rinsing. A Pt wire served as the counter electrode while a saturated calomel reference electrode (SCE) was installed in solution through a Luggin-Haber capillary tip assembly. Potentials reported throughout the paper refer to a saturated calomel reference electrode.

Copper electrodes were pre-conditioned at OCP for 1 h prior to any polarization measurements. In order to reduce pristine air-formed oxide film at the electrode surface, the copper electrode was exposed to -1.5 V for 1 min and to -0.6 V for 10 s. This process was performed in selected experiments. This process was followed by an immediate step of potentiodynamic or potentiostatic polarization.

In situ AFM (Pico IC, MI, contact mode, Au coated SiN cantilevers) was conducted at constant potential. Copper disc coupons ($\varnothing 30$ mm, thickness 2 mm, 99.97%) were used for AFM experiments. Before AFM observation the surface of copper specimen was electro-polished in 80 wt.% H_3PO_4 . AFM cell contained NaCl solution in a volume of 0.65 ml. In order to overcome water evaporation from the cell, leading to increase

in solution concentration, water was added (to a meniscus level of the cell) during the measurement period to the cell, with the use of a microcapillary.

3. Results and discussion

Fig. 1 presents anodic potentiodynamic characteristics of copper measured at a scan rate of 1 mV/s in solutions containing different NaCl concentrations subsequent to 1 h exposure at OCP. The onset of anodic current was measured at -0.3 V in a solution containing 1.5 M NaCl. The anodic current rapidly increased with a positive potential shift, reaching a maximum current density value of ~ 20 mA/cm² at ~ -50 mV. The anodic current density is reduced to a value of 2 mA/cm² as the potential is positively shifted, but then an increase in the current is observed once again. Such type of anodic behavior is associated with copper dissolution through a soluble chloride complex of CuCl_2^- [8–18]. The peak appearance was associated with formation of CuCl film on the electrode surface [8–18].

The onset of anodic current is shifted to more positive potentials and the current peak decreased with a decrease in chloride concentration. The onset of anodic current in a solution containing 0.15 M NaCl was measured at a potential of -0.2 V and the anodic current peak (4.8 mA/cm²) at 0.05 V, while in a solution containing 0.015 M NaCl the anodic current onset was observed at a potential of -0.15 V with a complete disappearance of the anodic peak. Thus, copper corrosion potential in NaCl electrolytes, indicated by the onset of anodic current, is positioned in a range of potentials, between -0.3 and 0 V, where copper may undergo an active dissolution.

Fig. 2 presents the effect of the scan rate on the potentiodynamic characteristics of Cu in 1.5 M NaCl solution following 1 h exposure at OCP. As can be seen, the initial part of the curve, indicating the onset of anodic current and current increase at positive potential shift, remained practically unchanged under all scan rates. Increase in scan rate resulted only in a marked

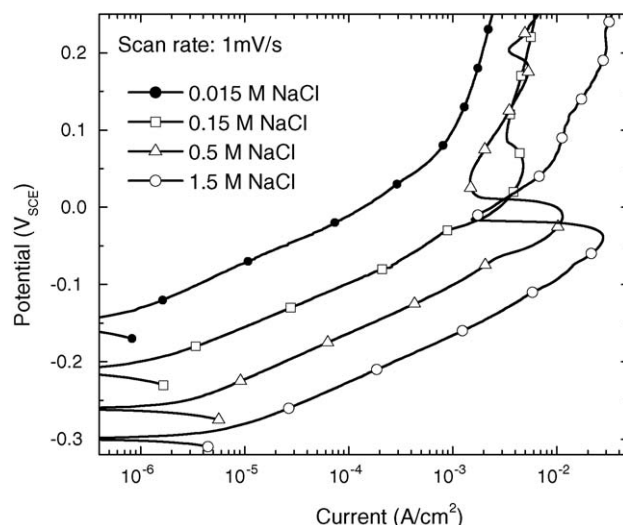


Fig. 1. Effect of NaCl concentration on anodic behavior of copper.

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