THE INFLUENCE OF BENZOTRIAZOLE ON ANODIC BEHAVIOUR OF AgCu50 ALLOY IN THE PRESENCE OF CHLORIDES

Mirjana M. Rajčić-Vujasinović, Vesna J. Grekulović, Zoran M. Stević,
Uroš S. Stamenković
University of Belgrade, Technical faculty in Bor,
**V.J. 12 19210 Bor, Serbia**

ABSTRACT
Chloride ions in concentrations larger than 0.01 mol dm^{-3} significantly intensify anodic processes on AgCu50 alloy. In order to slow down these reactions, it was looked into the possibility of using benzotriazole known as an effective corrosion inhibitor for copper. The influence of benzotriazole in a wide range of concentrations on processes of copper and silver oxides and chlorides formation are described in the paper. It was determined that benzotriazole in concentrations larger than 0.005 mol dm^{-3} lead to nearly complete alloy passivation at all investigated chloride concentrations.
Keywords: AgCu alloy, anodic oxidation, corrosion inhibition

1. INTRODUCTION

Copper and silver as well as AgCu alloys have a wide application range, which can be ascribed to a combination of attractive properties such as good machinability, high thermal and electrical conductivity, and resistance to corrosion [1]. An alloy with 50 mass.% Cu and 50 mass.% Ag is used for solders. The AgCu binary system is a characteristic example of the eutectic type of alloy with mutual restricted solubility of the components in the solid state. The composition of phases in equilibrium at some temperatures can be predicted from a silver–copper phase diagram [2]. Corrosion behaviour of metals and alloys is closely related to their response during anodic polarization in some media. Results of investigations of the electrochemical behavior of copper–silver alloys with low and high silver content in alkaline media were presented in our previous works [3, 4]. Electrochemical reactions that can take place in aqueous solutions are defined by E-pH diagrams for Ag–H$_2$O and Cu–H$_2$O systems [5]. The behavior of pure silver and pure copper in alkaline media has been extensively investigated using different electrochemical techniques and surface analytical methods.

The investigations of pure silver in alkaline media mostly indicate that oxidation of silver over the potential range between hydrogen and oxygen evolution proceeds through the sequence of the following three steps: formation of silver(I) oxide, Ag$_2$O, type I, formation of Ag$_2$O, type II and formation of silver(II) oxide, AgO [11]. The mechanism of copper anodic oxidation in alkaline medium in the potential range between hydrogen and oxygen evolution consists of two steps: formation of copper(I) oxide, Cu2O, and copper(II) oxide, CuO [12]. At the highest potentials, a wide passive area is apparent. All these reactions are preceded by adsorption of hydroxyl ions, whose presence has been proven on both silver and copper electrode surface [13, 14]. Therefore, the first reaction that can occur during anodic polarization of AgCu alloy is adsorption of hydroxyl ions:

$$Ag/Cu + OH^- = Ag/Cu(OH)_{ads} + e^- \qquad (16)$$
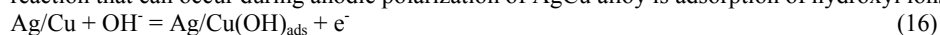
Aside from experiments in pure alkaline solution, corrosion investigations are also widely performed in the presence of chloride ions as an expected corrosion promoting species. Oxidation of silver in solutions containing chlorides leads to formation of silver chloride (AgCl) after adsorption of chloride ions [10-12]. The mechanism of copper anodic oxidation in the presence of chloride ions has been widely investigated [13].

2. EXPERIMENTAL

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was AgCu50 alloy, whose potential was controlled against saturated calomel reference electrode (SCE). Platinum foil served as a counter electrode. The computerized control (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform), fully developed by Technical Faculty in Bor [14], was used to run the electrochemical experiments.

The investigations were performed at 25°C in 0.1 mol dm^{-3} NaOH with and without addition of (0.01-0.2 mol dm^{-3}) NaCl. Second series of experiments was performed in the simultaneous presence of chloride ions and BTA ($5x10^{-5}$ mol dm^{-3} – $1x10^{-2}$ mol dm^{-3}, reagent grade- "Kraemer and Martin GMBH", Duisburg, Germany). Cyclic voltammetry and open circuit potential measurements wre used as experimental methods. Cyclic voltammograms were recorded in a potential range from -1.6 V to +1 V (SCE) with a scan rate of 20 mV/s.

3. RESULTS

Open circuit potential (OCP) measurements in 0.1 mol dm^{-3} NaOH with addition of 0.01 mol dm^{-3} NaCl (Fig. 1) show that the alloy AgCu50 demands longer time than pure metals silver and copper for establishing stady state potential. For pure metals stady state potential was reached in the first few seconds after immersion in electrolyte. The OCP value for the alloy is between the values for silver and copper. Similar relation between the OCPs is found when 0.001 mol dm^{-3} BTA was added in the solution (Fig. 2), but in this solution steady state is established on the alloy for a very short time – in a couple seconds after the electrode immersion.In the presence of BTA the OCPs for pure metals shifted towards more negative values, while the OCP for the alloy remained almost same as previous.
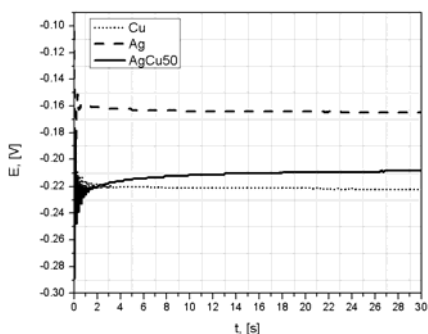

Figure 1. Potential as a function of time for Cu, Ag, AgCu50 in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3} NaCl.
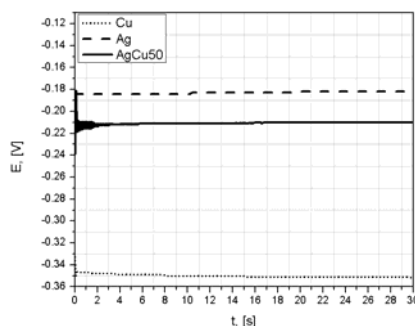
Figure 2. Potential as a function of time for Cu, Ag, AgCu50 in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3} NaCl + 0,001 mol dm^{-3} BTA.

In Fig. 3 cyclic voltammograms for the alloy are compared with those obtained on pure silver and pure copper in presence of chloride ions, but with no addition of BTA, in order to distinguish which current wave corresponds to copper as the alloying element, and which one to silver. On the voltammogram for the alloy seven current waves can be noticed in the anodic part, first of them (marked as A_1) originating from adsorption of OH$^-$ and Cl$^-$ ions, second two (A_2 and A_3) corresponding to oxidation of copper and the last four (A_4, A`, A_5 and A_6)originate from formation of oxides and chlorides of silver. In the cathodic part seven current waves corresponding to the reduction of compounds formed in the anodic period, and one additional anodic current wave corresponding to oxidation of silver appear.

From the E-pH diagram for the Cu–Cl–H$_2$O system presented by Tromans and Sun [5], it can be concluded that in alkaline medium the formation of copper(I) oxide is favoured in comparison to formation of copper(I) chloride. This conclusion was confirmed by Azzarani et al. as well as by Kear et al. [13]. Modestov et al. found that in the presence of chloride in alkaline medium, Cu(I) oxide is formed first, while copper(I) chloride and copper(II) oxide are formed at more positive potentials [15]. Our results are in agreement with these diagrams as well as with the findings of other similar

researches. For example, Zaky [16] investigated two CuAg alloys (Ag 80 mass.% + Cu 20 mass.% and Ag 20 mass.% + Cu 80 mass.%) using the cyclic voltammetry method in carbonate solution and concluded that an increase in Cl⁻ ion concentration in solution resulted in the formation of $CuCl_2 \cdot H_2O$, $CuCl_2 \cdot 3[Cu(OH)_2]$ and AgCl on the surface.
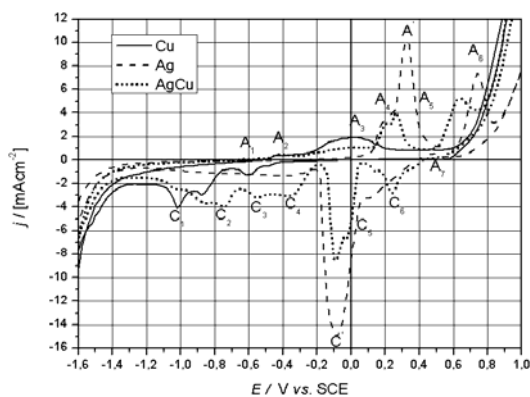
Figure 3. Cyclic voltammograms of Cu, Ag, AgCu50 in 0.1 mol dm⁻³ NaOH with addition of 0.01 mol dm⁻³ NaCl; v = 20 mV s⁻¹.

The influence of chloride ion concentration was investigated in range 0.01 to 0.1 mol dm⁻³. Obtained voltammograms presented in Fig. 4 clearly illustrate the activation effect of these species at all reactions taking place in investigated alkaline solution. Also, increase of Cl⁻ ion concentration leads to the increase of current densities in the whole flow of voltammetric curves and to the shifting of anodic current peaks to more positive potentials while cathodic peaks shift to more negative ones.
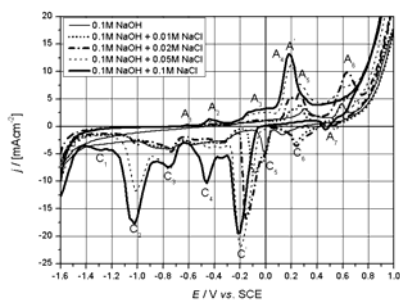

Figure 4. Cyclic voltammograms of alloy AgCu50 in 0.1 mol dm⁻³ NaOH with and without addition of (0.01-0.2 mol dm⁻³) NaCl v = 20 mV s⁻¹.
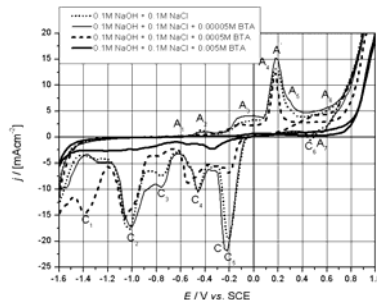
Figure 5. Cyclic voltammograms of AgCu50 in 0.1 mol dm⁻³ NaOH +0.1 mol dm⁻³ NaCl with and without addition of BTA in different concentrations; v= 20 mV s⁻¹.

In our previous work it was shown that without the presence of chlorides, BTA had no effect on development of new reactions [25]. However, it was effective in regard to intensify of anodic current peaks, which decrease with increase of BTA concentration. Figure 5 presents the effect of BTA on the electrochemical behavior of AgCu50 alloy in presence of chloride ions. The effect is investigated using five different BTA concentrations, but only three selected voltammograms are presented because of clarity.

At the lowest examined concentration of 0.00005 mol dm⁻³, BTA acts as an corrosion activator, which is in accordance with the rule that solution should always contain sufficient amount of inhibitor. With further increase of benzotriazole concentration, the inhibition is achived by filming of Ag-Cu alloy surface with the CuBTA and AgBTA complexes. Inhibition effect increasis with the increasing of

BTA concentration. Oxides and chlorides of both metals present in the alloy are being formed simultaneously with formation of CuBTA and AgBTA complexes until the whole surface is covered by these complexes.

4. CONCLUSION

Chloride ions have activation effect on all processes taking place on AgCu50 alloy during anodic polarization in sodium hydroxide solution. On cyclic voltammograms of AgCu50 alloy in the presence of chloride ions it was registered one additional current peak, which doesn't appear on voltammograms without Cl^- ions, and it was ascribed to the formation of silver chloride (AgCl). Due to intensification of anodic processes, current peaks appear with higher current density values. BTA has no effect on development of new reactions but it has an inhibition effect, which increases whit the increase of BTA concentration. The exception appears at the lowest examined concentration of 0.00005 mol dm^{-3}, when BTA acts as a corrosion activator.

5. ACKNOWLEDGEMENT

6. REFERENCES

[1] Nestorović S.D., Marković I.I., Marković D.D., Influence of thermomechanical treatment on the properties of sintered Cu-4at%Au alloy, 16th International Research/Expert Conference Trends in the Development of Machinery and Associated Technology" TMT 2012, Dubai, UAE, 2012.

[2] Dies K., Kupfer und Kupferlegierungen in der Technic, Springer-Verlag Berlin, New York, 1967.

[3] Rajčić-Vujasinović M., Nestorović S., Rangelov I., Grekulović V., Simov S., Corrosion behavior of sintered CuAg4at.% alloy, 7th International Scientific Conference on Production Engineering, Egypt, Cairo, RIM 2009.

[4] Rajčić-Vujasinović M., Grekulović V., Stević Z., Potentiostatic investigation of AgCu alloy in alkaline medium in presence of chloride ions, 15th International Research/Expert Conference"Trends in the Development of Machinery and Associated Technology" TMT 2011, Prague, Czech Republic, 2011, 969-972.

[5] Tromans D, Sun R., Anodic polarization behavior of copper in aqueous chloride/benzotriazole solutions, J. Electrochem. Soc. 138 (1991) 3235-3244.

[6] Jović B.M., Jović V.D., Stafford G.R., Cyclic voltammetry on Ag(111) and Ag(100) faces in sodium hydroxide solutions, Electrochem. Commun. 1(1999) 247-251.

[7] Strehblow H.H., Maurice V., Marcus P., Initial and later stages of anodic oxide formation on Cu, chemical astects, structure and electronic properties, Electrochim. Acta 46(2001) 3755-3766.

[8] Hepel M., Tomkiewicz M., Study of the Initial Stages of Anodic Oxidation of Polycrystalline Silver in KOH Solutions, J. Electrochem. Soc., 131 (1984) 1288-1294.

[9] Kunze J., Maurice V., Klein L.H., Strehblow H.H., Marcus P., In situSTM study of the effect of chlorides on the initial stages of anodic oxidation of Cu(111) in alkaline solutions, Electrochim. Acta 48 (2003) 1157-1167.

[10] Ha H., Payer J., The Effect of Silver Chloride Formation on the Kinetics of Silver Dissolution in Chloride Solution, Electrochim. Acta 56 (2010) 2781-2791.

[11] Jin X.,. Lu J, Lui P., Tong H., The electrochemical formation and reduction of a thick AgCl deposition layer on a silver substrate, J. Electroanal. Chem. 542 (2003) 85-96.

[12] Rajčić-Vujasinović M., Grekulović V., Stević Z., Vuković N., Potentiostatic oxidation of AgCu50 alloy in alkaline solution in the presence of chlorides, Corrosion Science 70 (2013) 221–228

[13] Kear G., Barker B.D., Walsh F.C., Electrochemical corrosion of unalloyed copper in chloride media—a critical review Corros. Sci. 46 (2004) 109-135.

[14] Rajčić-Vujasinović M., Stevic Z., Antić D., A new system for electrochemical investigations based on PC and LabView package, 11th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2007, Hammamet, Tunisia, 2007.

[15] Modestov A.D., Zhou G.D., Ge H.H., Loo B.H., A study by voltammetry and the photocurrent response method of copper electrode behavior in acidic and alkaline solutions containing chloride ions, J. Electroanal.Chem. 380 (1995) 63-68.

[16] Zaky A.M., Role of Cl$^-$ in breakdown of Cu-Ag alloys passivity in aqueous carbonate solutions, Electrochim. Acta 51 (2006) 2057-2062.