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Professional paper

ELECTROCHEMICAL INFLUENCE OF AMINO ACIDS ON THE CORROSION OF BIOALLOYS

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ABSTRACT

Shape memory alloys are of great commercial importance from biomedical applications to smart materials. The electrochemical behavior of Cu-Al-Zn alloy in phosphate buffer without and in the presence of amino acid was investigated. Electrochemical researches were performed in a traditional three-electrode system by means of the Tafel extrapolation method. The results showed that the presence of amino acid leads to a decrease in the corrosion rate and the density (values) of the corrosion current, which indicates that the tested inhibitor is efficient.

Keywords: shape Memory alloys, corrosion, amino acid

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1. INTRODUCTION

Shape memory alloys (SMA) are materials that have the ability to return to a former shape when subjected to an appropriate thermomechanical procedure. Pseudoelastic and shape memory effects are some of the behaviors presented by these alloys [1].

The key transformation responsible for the behavior of shape-memory alloys is the martensitic transformation. Martensitic transformation is a reversible crystallographic reorientation process between two stable phases. The transformation takes place when the Gibbs energy of martensite becomes lower than the Gibbs energy of austenite at a temperature below the critical temperature t_0, which represents the temperature of thermodynamic equilibrium at which the Gibbs energies of both phases are equal [2,3].

The chemical composition of the alloy, the heat treatment procedure, the cooling rate, the grain size and the number of transformation cycles are the main factors that influence the transformation temperature of shape-memory alloys [3].

The transformation of austenite into martensite is associated with the release of heat (exothermic phase transformation). The reverse transformation of martensite into austenite is associated with supplying energy for the reaction (endothermic phase transformation).

NiTi alloys possess good properties of shape memory effect, pseudoelasticity and biocompatibility. However, these alloys are significantly more expensive than copper-based shape memory alloys. Right after NiTi, the second commercially applied shape-memory alloy is the Cu-Al-Zn alloy, which is cheaper and simpler to manufacture, and has better electrical and thermal conductivity. The disadvantage compared to the NiTi alloy is that the Cu-Al-Zn alloy has worse shape memory properties.

However, shape memory Cu-Al-Zn alloys show a significant shape memory effect in a certain range of chemical composition.

Metal biomaterials have by far been used in biomedicine for the longest time. Numerous biomaterials and medical devices are commonly used today as prosthetic devices in dental, orthopedic, cardiovascular, ophthalmological and reconstructive surgery. They are also successfully used in interventions, such as angioplasty (stents) and hemodialysis (membranes), for surgical sutures or bioadhesives, but also as devices for the controlled release of drugs. E.g. they are used for fixing and replacing hard tissue (artificial hip, artificial knee, plates for fixing broken bones, various applications in dentistry, etc.) and for making surgical instruments.

The reactions of living organisms to biomaterials are different; under certain circumstances, some material is well accepted by the organism, while, under other circumstances, the same material is not accepted by the organism [4,5]. Corrosion is defined as the destructive and unintentional degradation of a material caused by its environment. Today, corrosion is one of the important causes of the global material and energy crisis and is the cause of significant losses in the economy of every country [6]. The harmful effects of corrosion can cause numerous negative consequences, such as to lead to a decrease in the utility value of materials, more expensive maintenance and shortened durability of structures, production stoppages, accidents, etc.

Corrosion control of metal is of technical, economical, environmental and aesthetical importance. The use of inhibitor is the best way to prevent metal and alloys from corrosion [7].

A corrosion inhibitor is a substance applied to an environment that significantly reduces the corrosion rate of materials (especially metals) exposed to that environment.

Organic compounds, predominantly, those with O, N, S, P and/or π electrons in their molecular structure have received considerable attention as a metals corrosion inhibitor. It is believed that organic compounds get adsorb onto a metal surface through their active center (heteroatom or π-bond) and form a protective layer that prevents the corrosive agents in the aggressive environment from gaining access to the metal surface.

Compared to the inorganic metal corrosion inhibitors, the organic inhibitors are less toxic to both human and the environment making discontinuation not to be the best option [8,9].

Cysteine has the ability to control the corrosion of various metals. Generally, cysteine is a very interesting amino acid that contains amino group, carboxyl group, and thiol group. It can coordinate with metals through the nitrogen atom, oxygen atom of the carboxyl group, and Sulphur atom of thiol group [10].

Compounds that contain polar functional groups that allow them to be efficiently adsorbed have found application in corrosion inhibition because of their effectiveness. Amino acids are also included in such compounds [11].

Amino acids are considered green inhibitors, and they are characterized by non-toxicity, biodegradability, cheap production and a high degree of purity of the produced compound, and solubility in aqueous media [12].

The presence of heteroaromatics in the structure of amino acids (they contain at least one carboxylic acid and an amino group, usually attached to the same carbon) increases their ability to be used as corrosion inhibitors. Previous tests have shown that the effectiveness of inhibition primarily depends on the molecular structure of the amino acid being tested, the size of the molecule and the type of interaction with the metal surface [13,14]. The highest efficiency of inhibition in the presence of cysteine was attributed to the fact that the amino acid containing S can be adsorbed as a bidentate ligand, whereby coordination takes place both through the amino group (or carboxyl) and through the –SH group [15].

2. EXPERIMENTAL

The aim of this study is focused on the effect of cysteine concentration (2 mM, 4 mM, 8 mM) on the corrosion behavior of Cu-18,05Zn-5,35Al bioalloys in phosphate buffer, pH = 7.

This tested bioalloy was prepared using solution annealing at a temperature of 850 ^{0}C for 10 min., then quenched into water at 15 ^{0}C.

Phosphate buffer was prepared by dissolving 3.405 g of potassium dihydrogen phosphate (KH_2PO_4) in distilled water in a 500 mL olumetric flask and 4.450 g disodium hydrogen phosphate (Na_2HPO_4) in distilled water in a volumetric flask.

A 0.5 mol/L cysteine solution was prepared by dissolving 1.5145 g of cysteine in distilled water in a 25 mL volumetric flask.

The sample was prepared for electrochemical research after polishing with grinding paper, degreasing in ethanol, and washing with distilled water. The work surface of the tested bioalloy was 25 cm^2.

Electrochemical research was performed in a traditional three-electrode system by means of the Tafel extrapolation method. Tafel extrapolation is a mathematical technique used to estimate either the corrosion current (I_{corr}) or the corrosion potential (E_{corr}) in an electrochemical cell, and by extension, the corrosion rate [16]. The three-electrode system consists of a working electrode, counter electrode, and reference Ag/AgCl electrode.

Potentiostat/galvanostat Vertex one, Ivium Technologies is being used for electrochemical testing of corrosion rate.

3. RESULTS AND DISCUSSION

The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were obtained by employing the Tafel extrapolation method. The Tafel extrapolation line is based on the polarization curve obtained when the overpotential is between -0,300 V do 0,05 V. The scan rate was 20 mV /s.

The efficiency of the inhibitor, Ei (%), was calculated based on following equation:

$$\mathrm{Ei} = \frac{\pi - \pi'}{\pi} \qquad (1)$$

where: π - corrosion rate in solution without corrosion inhibitor (mm year^{-1}), π'-corrosion rate in solution with corrosion inhibitor (mm year^{-1}).

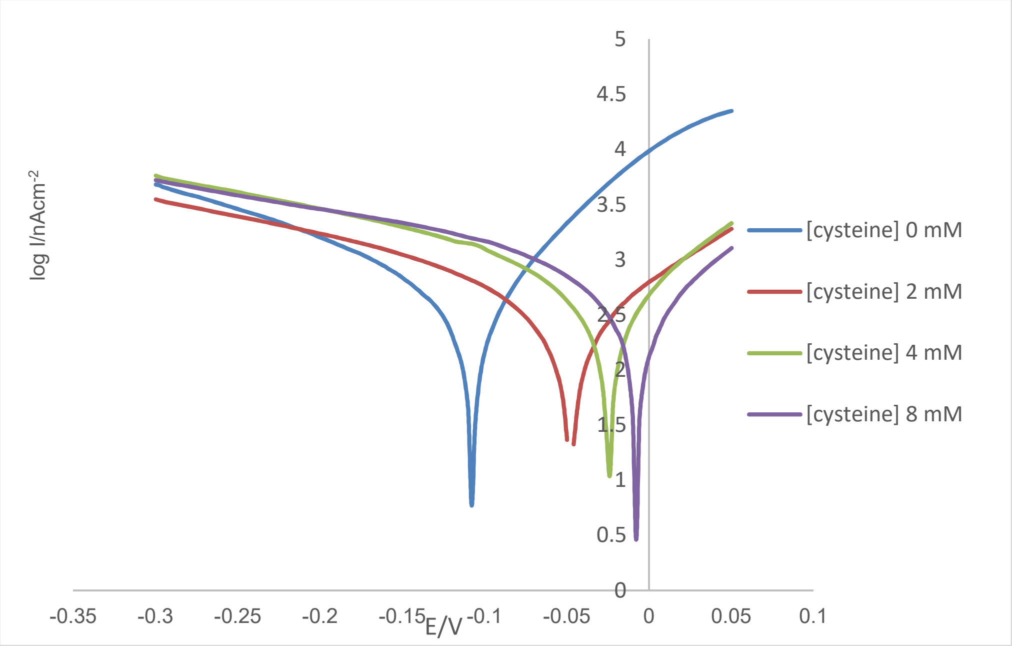

Figure 1. Tafel extrapolation graph of the effect of cysteine concentration on the corrosion behavior of Cu-18.05Zn-5.35Al bioalloy

Table 1. The corrosion parameters determined by Tafel extrapolations method

Inhibitor	$c_{inh.}$ (mM)	$E_{corr.}$ (V)	I (A)	I (A/cm^2)	R_p (Ω)	$β_a$ (V/dec)	$β_k$ (V/dec)	$v_{corr.}$ (mm/yr.)
-	0	-0.1034	$4.65×10^{-7}$	$4.65×10^{-6}$	$5.09×10^4$	0.078	0.182	0.05405
Cysteine	2	-0.0209	$3.75×10^{-7}$	$3.75×10^{-6}$	$8.15×10^4$	0.095	0.272	0.04364
Cysteine	4	-0.0048	$5.96×10^{-7}$	$5.96×10^{-6}$	$4.15×10^4$	0.070	0.298	0.06928
Cysteine	8	0.0290	$7.07×10^{-7}$	$7.07×10^{-6}$	$3.06×10^4$	0.058	0.374	0.08221

Based on the values of corrosion parameters determined by Tafel extrapolation (Table 1) it was confirmed that cysteine can be applied in order to reduce the corrosion rate. In the investigated concentration range of the cysteine in phosphate buffer, the lowest rate of corrosion is at the concentration of inhibitor (cysteine) of 2 mmol/L and which amounts to 0.04364 mm/year and its effectiveness amounts to 19.10%. Thus, amino acid adsorption inhibits anodic and cathodic processes by inhibiting active sites.

By further increasing of the concentration of cysteine, the inhibitory effect decrease, because the corrosion rate is greater than the rate of corrosion of the examined bioalloy without the presence of the inhibitor. In other words, at a concentration of 4 mmol/L and 8 mmol/L inhibitor functions as an activator because the corrosion rate is higher than the rate of corrosion without an inhibitor. The cathodic reaction is more inhibited than the anodic reaction; the amino acid-adsorbed layers serve as a cathodic barrier, inhibiting the transport of O_2 or NO^{3-} to the metal's cathodic sites. In addition, this barrier layer delays the metal's decomposition. Therefore, corrosion rates decrease proportionately with the number of adsorbed inhibitor molecules that obstruct the electrochemically active sites. Author Zee et al. investigated the influence of select amino acids on the corrosion of Cu under naturally aerated and deaerated conditions using a phosphate-free buffer. Amino acids increased the corrosion of Cu under both aeration conditions at pH 7.4. Cu release was also significantly (up to 18-fold) increased in the presence of amino acids, investigated at pH 7.4 and 37 °C for 24 h under naturally aerated conditions [17]. Badawy et al. also observed that cysteine] displayed outstanding protective efficiency on Cu–Ni alloys in neutral chloride solutions. The experimental results have shown that a simple amino acid like glycine can be used as efficient corrosion inhibitor for the Cu–Ni alloys in neutral chloride solutions. An inhibition efficiency of about 85% could be achieved at very low concentrations of the amino acid (0.1 mM). For low Ni content alloy (Cu–5Ni), 2.0 mM cysteine shows a remarkable high (~96%) corrosion inhibition efficiency [18]. Multiple functional groups have often resulted in variations in the electron density of a molecule, which may alter its adsorption behavior. These compounds most likely adsorption through C[double bond, length as m-dash] O, –OH, –NH_2, or –S– groups, regarded as active adsorption centers. When a new chemical (corrosion inhibitor) is introduced into the metal–electrolyte interface, its electrical double layer undergoes composition and structural modifications. Consequently, the inhibitor adsorption could be monitored by measuring the double layer capacitance before and after the addition of the corrosion inhibitor.

Interestingly the presence of functional groups containing both N and S in a compound has been shown to often result in enhanced inhibition effectiveness. This has been attributed to an adsorption mechanism involving both the N and S atoms of the molecule and has been highlighted in studies using mercaptotriazole derivatives and S-containing amino acids (methionine, cysteine, cystine, N-acetylcysteine) as non-toxic inhibitors for iron in acidic solutions [19-20].

4. CONCLUSION

As the obtained results have shown, the presence of cysteine in concentration 2 mmol/L leads to a decrease in the corrosion rate and the density (values) of the corrosion current, as well as to an increase in polarization resistance values, which indicates that the corrosion inhibitor is efficient in appropriate concentration.

Conflicts of Interest

The authors declare no conflict of interest.

5. REFERENCE

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