

Comparison of Early Stages of Copper Corrosion in Sulfate, Chloride, Humic and Soil Media

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Early stages of copper corrosion behavior in NaCl, Na₂SO₄, humic acid and Tunisian soil have been examined using surface analysis (OM and AFM) as well as polarization curves. For different media, ranking has been established using R_q , E_{corr} , β_a , β_c , I_{corr} , B , R_p and E_b . The results reveal that patina formed at the Cu/Tunisian soil interface is the most protective covering.

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INTRODUCTION

Understanding copper-based alloys corrosion behavior in soil is a great challenge. This is important not only to secure lifetime and reliability of containers used for underground nuclear waste storage, but also to provide valuable inputs concerning the mechanisms of alterations in cultural heritage artifacts.

Numerous studies have been conducted to understand copper-based alloys corrosion in soil environments [1–5]. However, to the best of our knowledge, the contribution of each single soil fraction (humic and inorganic) has not been exhaustively investigated so far. The present work is an attempt to compare the early stages of copper corrosion behavior in the Tunisian soil with those exhibited in chloride, sulfate, and humic electrolytes.

EXPERIMENTAL

Corrosion tests were conducted at room temperature in aerated solutions prepared from analytical grade reagents. Aqueous sulfate and chloride solutions (0.1 mol L⁻¹) were used to simulate burying media. Humic acid (20 g L⁻¹) was also investigated as a corrosive electrolyte. Soil environments were obtained by mixing soil with distilled water until the concentration of 1 kg L⁻¹ was achieved. Soil composition was reported in previous works [6].

In the present investigation pure copper (99.999%) was used. The specimens were dried and hand-polished with emery paper up to the grade of 2500, then degreased with acetone, rubbed with cotton wool soaked in ethanol, dried at room temperature and immersed immediately into different media. After a four-hour immersion, the specimens were analyzed, without further treatments, under transmitting light, using a polarizing Nikon ECLIPSE ME 600 microscope equipped with a digital camera. The atomic force microscopy (AFM) was performed in air with a Nanoscope IIIa Digital Instruments microscope equipped with an optical

deflection system in combination with silicon cantilevers and tips working in tapping mode.

Electrochemical experiments were conducted at room temperature. A classical three-electrode cell was used with a saturated calomel electrode as reference and a platinum wire as a counter electrode. The electrochemical set-up consisted of an autoLab PGSTAT 30 potentiostat (Netherland). The Software GPES was used for voltammetric investigations and the scan rate was fixed at 10 mV s⁻¹. All experiments were replicated minimum three times.

RESULTS AND DISCUSSION

Effect of the electrolyte nature on the electrochemical interface response

After four hours of immersion, the interfaces copper-electrolytes were submitted to linear polarization in the overpotential range of 1 V to 0.1 V. The scan rate was fixed at 10 mV s⁻¹. Such polarization speed is comparable with that used in previous works [6 and references therein]. The polarization curves are given in Fig. 1.

Irrespective of the electrolyte, four sections were evidenced on the polarization curves. The first (I) one, corresponding to the cathodic region, reflects the overpotential domain where the reduction reaction takes place. The second (II) is generally attributed to the plateau of oxygen diffusion. An “apparent Tafel” behavior was detected in the third interval. Mixed charge transfer and mass transport are usually assumed to control the reaction kinetics. Finally, the fourth overpotential interval corresponds to the anodic domain.

Extrapolation of the linear line to the corrosion potential gives a straight line, the slope gives both β_a , β_c , and the intercept gives the corrosion current. We also calculated the linear polarization resistance (R_p) by means of the Stern–Geary relationship:

$$R_p = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \frac{1}{I_{\text{corr}}} = \frac{B}{I_{\text{corr}}} \quad (1)$$

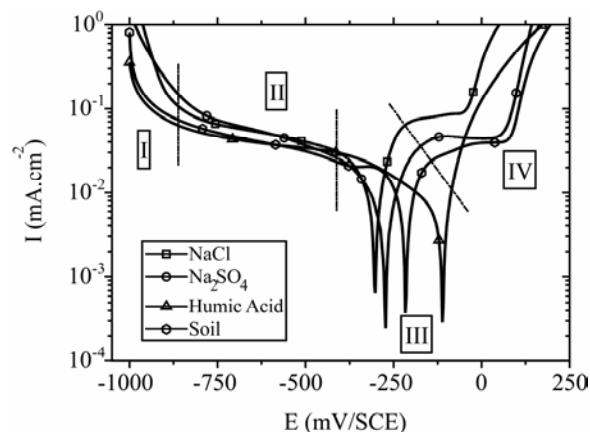


Fig. 1. Polarization curves of copper surfaces obtained after four hour immersion in various electrolytes. The potential was swept from -1V to 0.25V at a scan rate 10 mV s^{-1} .

In Fig. 2, we present E_{corr} (a), β_a (b), β_c (c), I_{corr} (d), B (e), and R_p (f) evolutions for various environments.

After four hours of immersion in the humic medium, copper corrosion potential was the most anodic as it tended towards -0.111 V/SCE . Cathodic values for E_{corr} were measured for the material when submitted into inorganic media: -301 mV/SCE and -272 mV/SCE , chloride and sulfate, respectively. The intermediate value of E_{corr} , about -0.216 V/SCE , was delivered by copper when buried in the Tunisian soil, (Fig. 1a).

The apparent anodic Tafel slope was found to be close to 0.06 V^{-1} for the humic electrolyte (Fig. 2b). This value is equal to that generally observed for a pure material freshly immersed in aerated aqueous chloride electrolytes [7]. In spite of the existence of some patina layer at the surface, the rate of the copper anodic dissolution in humic medium, close to the corrosion potential, was under the influence of both charge transfer and mass transport.

For other media, β_a ranged from 0.08 V^{-1} to 0.11 V^{-1} . These values were higher than those reported in literature [7]. It is assumed that for filmed surfaces the measured anodic Tafel slope changes to values corresponding to an activated step determining electron transfer rate. That is, where the transfer coefficient α_A is approximately equal to 0.5 (rather than zero for a freshly polished copper surface), it produces a β_a value of 0.11 V^{-1} . Hence, the kinetics of the charge transfer decreased to a level where mass transport no longer influenced the electrodisolution rate. This phenomenon is medium-dependent, as follows: $\beta_a(\text{NaCl}) < \beta_a(\text{Na}_2\text{SO}_4) < \beta_a(\text{Soil})$.

We measured an apparent cathodic slope of -0.264 V^{-1} for copper immersed in aqueous chloride medium for four hours (Fig. 2c). This is consistent with the earlier published Tafel slopes for oxygen reduction [7]. For other environments, the following ranking was established: $\beta_c(\text{Na}_2\text{SO}_4) < \beta_c(\text{soil}) < \beta_c(\text{Humic acid})$.

The proportionality constant B was 26.4 mV for the chloride electrolyte. For the same medium, a review of the respective literature showed that B is ranging from 5 mV to 31 mV [7]. The soil gave the most important constant value of 65 mV (Fig. 2d). The deviation in this value is probably not only due to experimental characteristics but also to varying states of the surface condition [7].

For the corrosion current, the humic acid electrolyte exhibited the lowest value of $0.92 \mu\text{A}\cdot\text{cm}^{-2}$, whereas inorganic electrolytes delivered the highest ones (Fig. 2e). The corrosion current for the Tunisian soil environment was quite similar to that measured for the humic medium. The linear polarization resistance was also medium-dependent as evidenced in Fig. 2f, where: $R_p(\text{NaCl}) < R_p(\text{Na}_2\text{SO}_4) < R_p(\text{Humic Acid}) < R_p(\text{soil})$.

It was also observed that copper anodic behavior (domain IV detected in Fig. 1) is strongly affected by environments. In fact, for chloride, sulfate and soil media a passive-like reaction occurred whereas for the humic electrolyte the current increased with the raise of the applied potential, indicating surface alteration.

In order to evaluate the effectiveness of the patina layer as a means of the material surface protection, the breakdown potential (E_b) was plotted vs. the media (Fig. 3).

It was shown that E_b varied when the electrolyte changed. Indeed, patina formed at the copper-Tunisian soil interface exhibited the most pronounced protecting effect.

Effect of the electrolyte nature on copper surface

After four hours of immersion in various electrolytes the material surfaces were examined by optic microscopy (Fig. 4).

Sulfate medium was confirmed to be the most damaging, as a thick corrosion layer was detected at most of the specimens surfaces. For the humic electrolyte, the pseudoprotection behavior could be due to the medium organic matter adsorption.

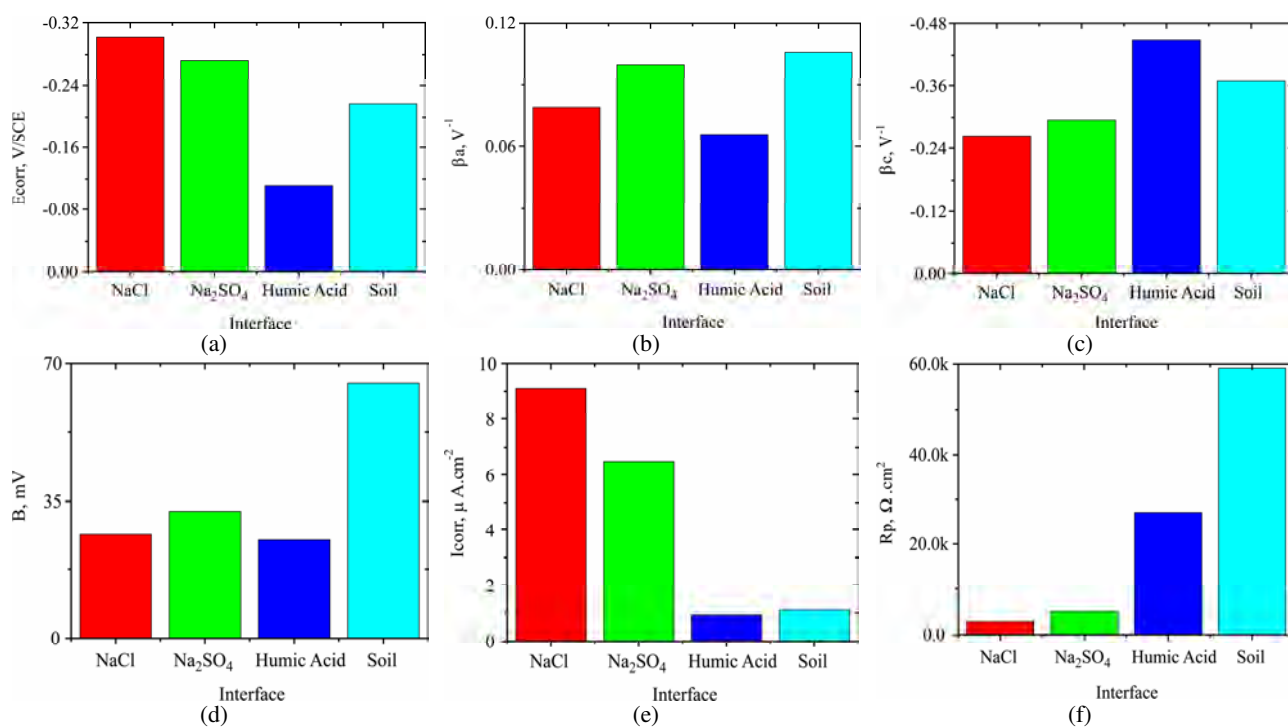


Fig. 2. Evolution of electrochemical parameters E_{corr} (a), β_a (b), β_c (c), B (d), I_{corr} (e) and R_p (f) for copper immersed in various environments.

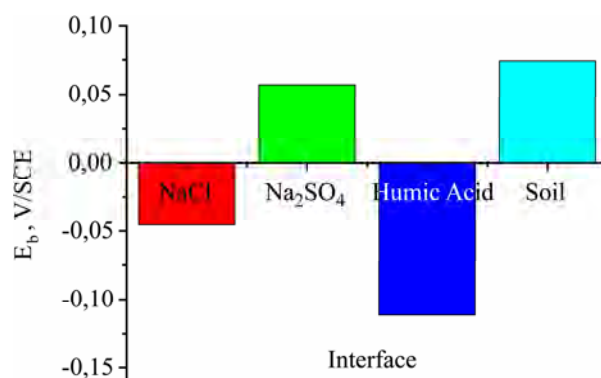


Fig. 3. Breakdown potential evolution for various environments.

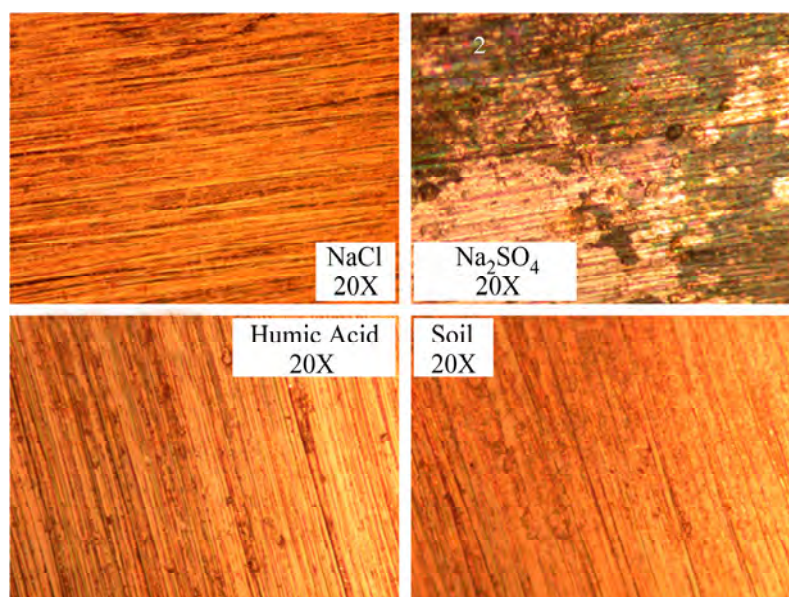


Fig. 4. Comparison of copper surface morphology after four hour immersion in various environments.

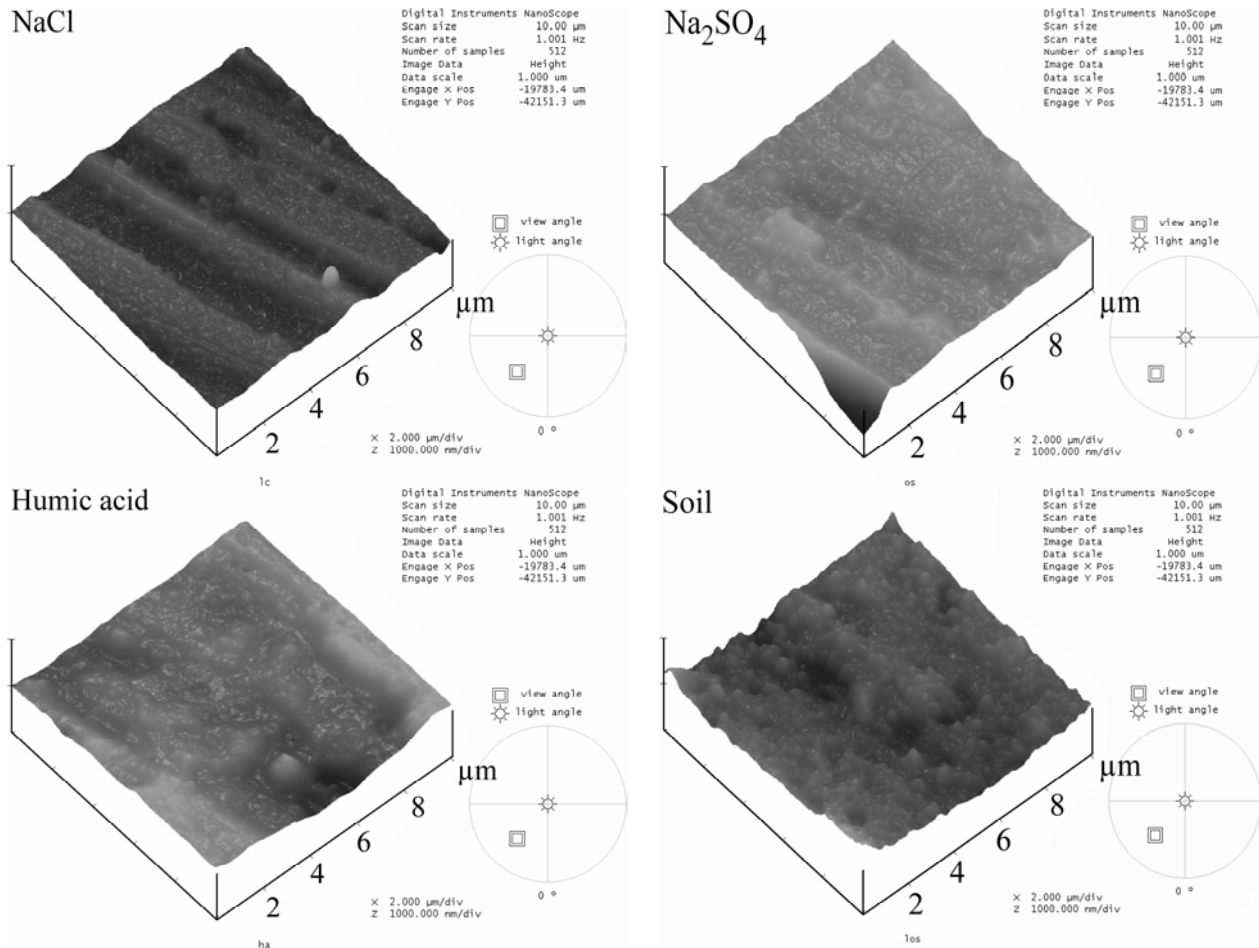


Fig. 5. AFM analysis of copper surface immersed for four hours in various environments.

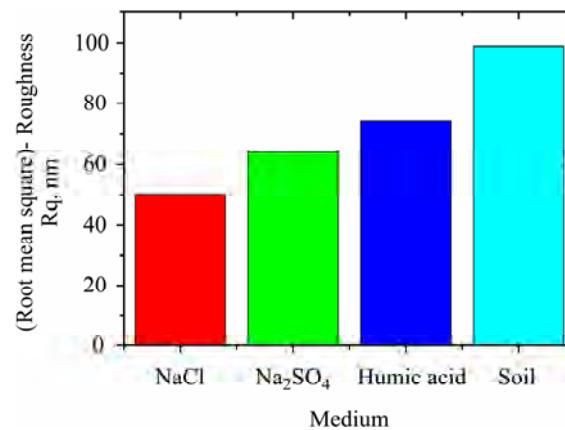


Fig. 6. (Root mean square) – Roughness evolution for copper surface.

Material surfaces were also analyzed using the AFM (Fig. 5).

Drastic changes in the material surface topography were detected when the environments varied. In fact, in the presence of the soil electrolyte, a heavily deteriorated metal surface was observed, whereas pits density decreased for inorganic media (sulfate and chloride).

The smoothness/roughness of metal surfaces, after four hours of immersion in various electrolytes, was quantitatively analyzed by measuring the (root mean) – roughness ($RMS = R_q$). Fig. 6 shows R_q

trend of the investigated copper surfaces vs the environment nature.

The Tunisian soil electrolyte was found to reduce copper smoothness as the surface material roughness obeyed the ranking: NaCl < Na₂SO₄ < humic acid < soil.

CONCLUSIONS

The main aim of the present research was to study early stages of copper corrosion in various environments such as: sulfate, chloride, humic acid, and the Tunisian soil. After four hours of immersion,

the soil electrolyte was found to increase the copper surface roughness. The apparent Tafel slope indicated that an activated step determining the electron transfer rate is controlling the electrodisolution reaction. The linear polarization resistance and the breakdown potential were also medium-dependent. However, the patina layer formed at the interface Cu/soil exhibited the most pronounced preservation effect, as R_p and E_b for the soil medium were the most important.

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Реферат

Исследованы начальные стадии коррозии меди в NaCl, Na₂SO₄, в гуминовой кислоте и почве Туниса, используя анализ поверхности (оптическая и атомно-силовая микроскопия), а так же поляризационные измерения. Для различных сред было установлено ранжирование, используя R_q , $E_{согг}$, β_a , β_c , $I_{согг}$, B , R_p и E_b . Результаты показывают, что патина, образующаяся на границе раздела медь/почва Туниса, является покрытием с высокими защитными свойствами.