

THE ACCELERATED CORROSION BEHAVIOUR IN SALINE ENVIRONMENTS OF SOME SAMPLES MADE OF TOMBAC, COPPER AND ALUMINIUM

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Abstract: *The corrosion tests from this paper simulate the exposure conditions in different environments of some samples made from yellow tombac, copper and aluminium. For the tombac samples a salt fog chamber was used, the copper and aluminium samples a 3% NaCl solution was prepared and the exposure time being 144 h at 35 °C temperature. The samples surface morphology before and after the corrosion tests were analyzed by means of the scanning electron microscope (SEM). Also, the crystalline structure of the metallic samples was assayed with the X-ray diffractometer (XRD).*

Keywords: *accelerated corrosion, corrosion rate, tombac, copper, aluminium, structure.*

1. INTRODUCTION

Corrosion is a complex phenomenon which depends on the composition and structure of the metallic material, on the nature and composition of the aggressive environment due to the chemical and electrochemical reactions, and it also depends on the conditions in which the reactions take place [1-3]. The corrosion process study has an important role in the prevention and overcoming of this spontaneous phenomenon.

The corrosion behaviour of various materials depends mostly on the nature of the aggressive environment. The presence of the electrolytes in the aggressive environment influences the corrosion rate. NaCl is also a strongly corrosive electrolyte [4-7].

The goal of this paper was studying the corrosion processes on the three kinds of the metallic samples based on tombac (reddish coloured zinc-copper alloy) [8], copper and aluminium with various geometry shapes. These metallic materials are used for making patrimony items which are subjected to various elements of nature in time [9-12]. The behaviour of the metallic specimens subjected to the accelerated corrosion tests into the saline environment is observed without any inhibitors action. In according to the experiments of corrosion on metallic materials, which work under the action of 3% NaCl solution ranged between 24 and 144 h, the corrosion rate-time relation was analysed and depend on the material nature. The morphology analyses of the metallic surfaces before and after corrosion by means of the electronic microscope. Also, the crystalline structure of the metals was tested.







2. EXPERIMENTAL

It is known the fact that the corrosive destruction is not a constant process, which varies along the duration of exposure, mainly due to the corrosion products build-up onto the metallic surface which can slow down the corrosion, more or less.

The tombac sample was tested into a salt fog chamber in the following conditions: 144 h at 35°C temperature. The copper and aluminium samples were assayed into a 3% saline solution prepared from NaCl, the exposure time being 144 h at 35°C temperature [4-12].

All the specimens were prepared by mechanical polishing with fine grained emery paper (300÷800). The polished substrates were degreased with acetone and ethylic alcohol for a few seconds. Then they are washed with distilled water and dried with warm air.

Table 1. The appearance of the metallic sample before and after corrosion test

	Control sample	Corroded sample
Tombac		
Copper		
Aluminium		

2.1. THE ACCELERATED CORROSION TEST OF TOMBAC SAMPLE IN THE SALT FOG

The corrosion chamber (Fig. 1) is provided with an automated system for the temperature measurement and adjustment for the waste solution or condense exhaustion resulted during the experiment. The chamber is made from plastic material and stainless steel and has a capacity of 0.35 m³. The upper side of the chamber was conceived so that the accumulated drops of solution, which flow to the surface; do not fall down on the specimens.



Fig. 1. The corrosion chamber specifically to salt fog corrosion test

The relative resistance to corrosion of tombac sample can be performed by exposure to a salt fog climate. The preparation of a salt solution consists normally of NaCl containing as a dry compound not more than 0.1% of NaI and not more than 0.2% of total impurities. A 5% solution is prepared by dissolving 5 parts by weight of salt in 95 parts by weight into water that meets the requirements of ASTM D1193-06 Specification for Reagent Water, Type IV is supplied to the chamber at 25±2°C temperature. The solution conductivity is

lower or equal to $20 \mu\text{Scm}^{-2}$. Test specimens are placed in an enclosed chamber and exposed to a continuous indirect spray of neutral (pH 6.5 to 7.2) salt water solution, which falls-out onto the specimens at a rate of 1.0 to 2.0 ml/80cm²/hour, in a chamber temperature of 35°C. The pH solution was measured with a pH-meter Consort C860 with 0.2% accuracy and perceived with a temperature indicator. This climate is maintained under constant steady state conditions. The test duration is variable ranged between 24 and 144 h. Salt fog testing is performed by placing samples in a test chamber that has been designed and operated in accordance with conditions of ASTM B117-03. The tombac was measured by means of the electronic balance ESJ 200-4 with 0.0001 accuracy. The tombac has a rectangular geometry (Table 1) shaped with an active area of 1.5 cm².

2.2. THE ACCELERATED CORROSION TEST OF THE COPPER AND ALUMINIUM SAMPLES IN 3% NaCl SOLUTION

Each specimen was treated following the procedure described previously. The initial masses were measured with the same electronic balance. To accomplish the second corrosion test an electrolyte solution is needed. A hypertonic saline, 3% NaCl, solution was prepared at room temperature from double distilled water. Also, the copper and aluminium specimens will subject to accelerate corrosion test ranging 24 and 144 h. Finally, the corrosion rates will be calculated based on the equation (1) taking into account the mass loss during the experiment. The copper and aluminium samples are circular geometry (Table 1) shaped with an active area of 0.785 cm².

2.3. MICROSCOPICAL AND STRUCTURAL CHARACTERIZATION OF METALLIC SAMPLES

The surface morphological features of the metallic specimens were examined by means of scanning electron microscopy (SEM) measurements. The micrographs were registered using Quanta 200 Philips FEI Company device.

The crystallographic characteristics of the samples were analysed through the X-ray diffraction method (XRD) using DRON-3M diffractometer. XRD spectra were recorded at room temperature, X-ray diffractometer using CuK_α radiation in 2θ configuration ranged between 30° and 80°, at 40 kV tension and 30 mA current intensity with a scanning speed of 0.02° min⁻¹ and acquisition time of 0.1 s/step.

3. RESULTS AND DISCUSSIONS

3.1. CORROSION RATE VARIATION AS A FUNCTION OF EXPOSURE TIME

The corrosion rates determination was achieved by means of “mass loss method” [13], in static regime at room temperature and calculated based on equation (1):

$$V_c = \frac{\Delta m}{S \cdot t} \quad (1)$$

where: V_c = the corrosion rate [g/m²h];

$\Delta m = m_1 - m_2$ = the mass loss of the sample before and after the corrosion test [g];

S = the sample area [m²];

t = the working time [h].

Fig. 2 showed the obtained experimental data about the variation of the corrosion rate of each sample into two aggressive environments. If the corrosion rates of all samples are

compared, the tombac indicates the lowest rate into the salt fog. The tombac corrosion rate variation curve (black colour) as a function of time is decreasing and gets very close to the OX axes. It means that the tombac is the corrosion strongest in saline environment in comparison with the copper and aluminium. Therefore, the saline environment (5% NaCl) is less aggressive because the tombac presents a high stability, the corrosion rates being a very low.

Copper has the lower corrosion rate into the 3% NaCl environment (dark grey curve). Then the corrosion rate is constant for few hours and this decrease slowly with time increasing. Therefore, the copper is very stable in time to corrosion in this aggressive environment compared with the aluminium.

The strongly corrosion processes take place on the aluminium surface (light grey curve) in 3% NaCl solution mainly during the first hours of the contact between the aggressive medium and the metal (cca. 48÷65 h). The curve is stabilised between 65÷78 h, then the corrosion rate decreases with increasing time. Therefore, the aluminium has a very low resistant to corrosion as you can see from the appearance (Table 1) and it's very unstable in this medium.

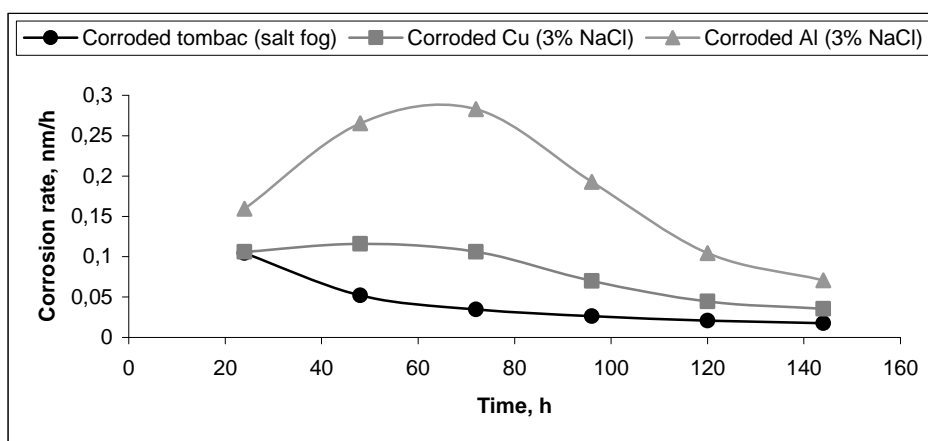


Fig. 2. The variation of corrosion rate as function of exposure time for all samples into salt fog and 3% NaCl environment

3.2. STRUCTURAL CHARACTERIZATION OF THE METALLIC SAMPLES

By treatment in salt fog corrosion environment the tombac sample presents an XRD pattern with the specific lines. Fig. 3a points the most intensive diffraction line of tombac is (111) [9,14]. The corrosion exposure to salt fog test highlights the diffraction lines of oxide compounds formed during the experiment (Fig. 3b). Therefore, the crystalline network is rearranged; the internal stresses are reduced by testing the sample in salt fog conditions. Also, the intensity peaks of tombac decrease during the test. The oxides operated like a protective layer against the aggressive environmental factor. This fact is confirmed by the appearance (Table 1), the corrosion rate (Fig. 2) and then by the microscopical analyses (Fig. 6b).

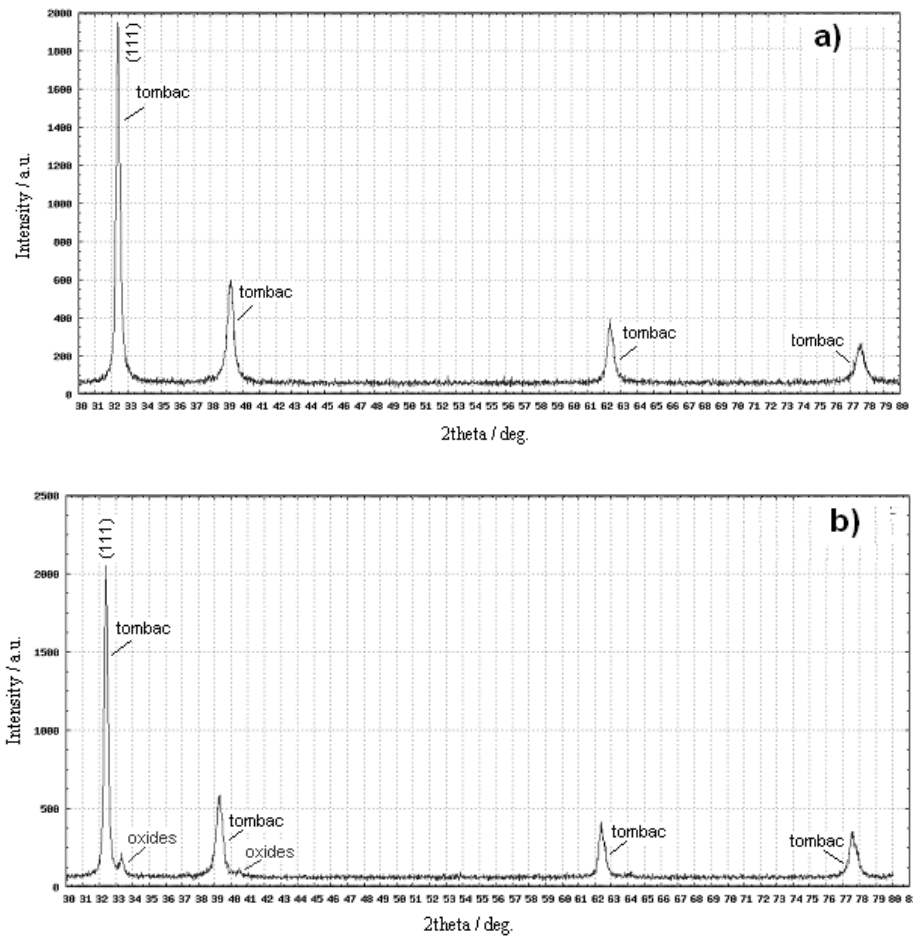


Fig. 3. The XRD pattern of the a) control and b) corroded tombac sample in the salt fog

Fig. 4a shows a much higher background radiation for the corroded copper (red colour) than the other one of the control sample (black colour). The intensity is higher approximately 60 u.a. for the corroded specimen into 3% NaCl solution. A presence of numerous point defects can be seen onto the surface in comparison with the control sample. The crystallographic defects can be the vacancies, interstitials or replaced atoms of the crystal lattice. The XRD patterns give the peaks of the copper crystallographic planes: 50.1; 74.5 and 90 as $2\theta^\circ$. In other words, the copper samples are crystalline materials but they are not perfect, the regular pattern of atomic arrangement is interrupted by crystallographic defects.

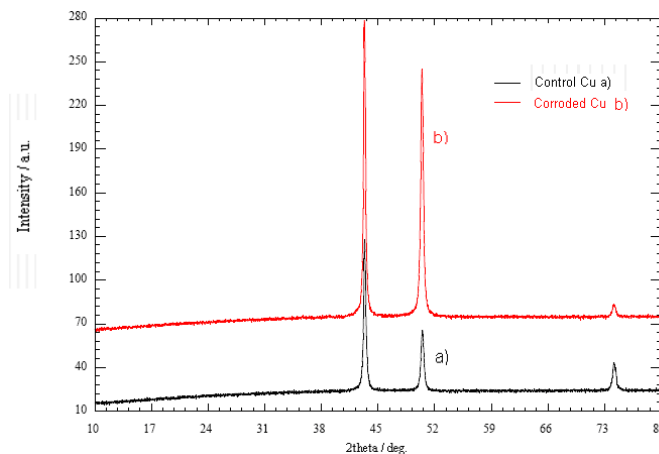


Fig. 4. XRD patterns of the control and corroded copper samples into 3% NaCl solution

XRD patterns from Fig. 5 show that the corroded aluminium has a much higher background radiation than of the control aluminium sample. Figs. 4 and 5 prove that the intensity radiation of the aluminium is 140 u.a. which means that it contains a double amount of point defects on the surface in comparison with copper. The peaks are in a good agreement with the aluminium crystallographic planes: 38.54; 44.74 and 78.20 as $2\theta^\circ$.

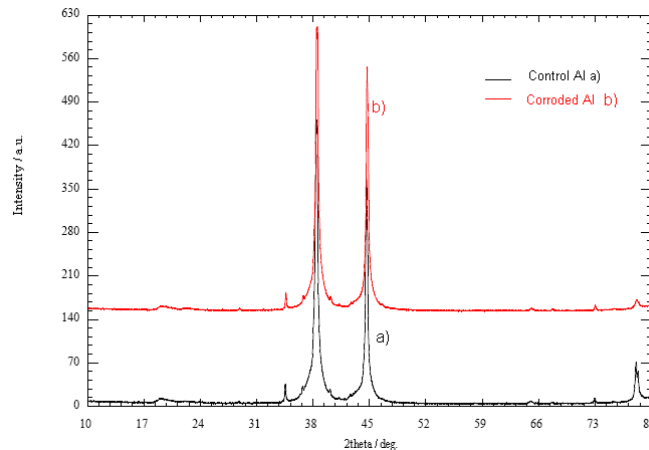


Fig. 5. XRD patterns of the control and corroded aluminium samples into 3% NaCl solution

3.3. MORPHOLOGICAL ASPECTS OF THE METALLIC SAMPLES

The surface morphology of tombac at different magnifications is indicated in Fig. 6a clean and shiny surface of the control tombac can be observed in Fig. 6a. This specific structure presents a few small scratches like material defects [9]. By taking out the sample from the salt fog chamber some corrosion marks appear due to the pitting phenomenon. Also, the cavities formation on the surface by loss of a small amount of substrate can be observed due to the corrosion effect of depth. Shade of grey differences of the samples can be observed between the control and the corroded tombac. The salt fog climate is aggressive but not enough that the corrosion rate decreases with increasing the exposure time due to the chemical composition of copper-zinc alloy. The growing of a protective oxide layer onto the corroded tombac surface having a dark colour can be shown (Fig. 6b). This aspect is due to the oxidation phenomenon without being influenced the corrosion resistance (Fig. 2).

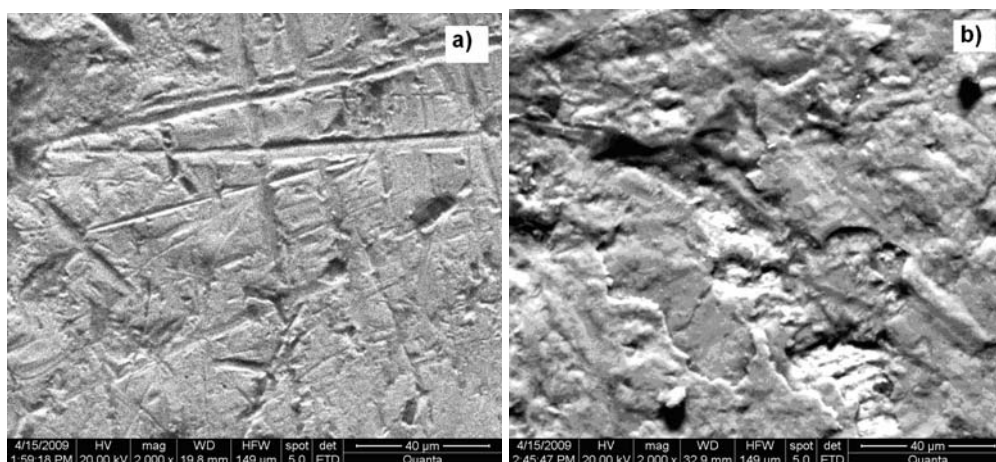


Fig. 6. SEM micrographs of a) control and b) corroded tombac during the salt fog experiment

The copper is more resistant to 3% NaCl solution than aluminium (Fig. 2). The point defects can be observed in Fig. 7a and confirmed by the XRD results (Fig. 4a). The corrosion

products can be seen growing onto the copper surface (Fig. 7b) having low dimensions and a heterogeneous aspect.

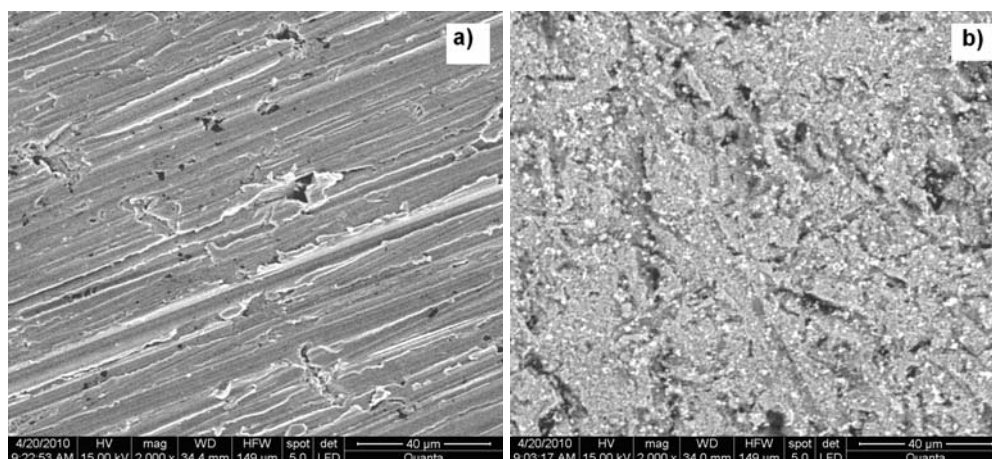


Fig. 7. SEM micrographs of a) control and b) corroded copper into 3% NaCl solution

The aluminium is not resistant to the 3% NaCl environment due to the higher corrosion rate (Fig. 2). Fig. 8b indicates a homogeneous surface of corroded aluminium coated with corrosion products. 3% NaCl environment is sufficiently corrosive to cause intergranular corrosion maybe due to the more point defects of the surface. In such media, is recommended that the aluminium sample must be coated with the micro- or nano-particles to enhance resistance to intergranular corrosion.

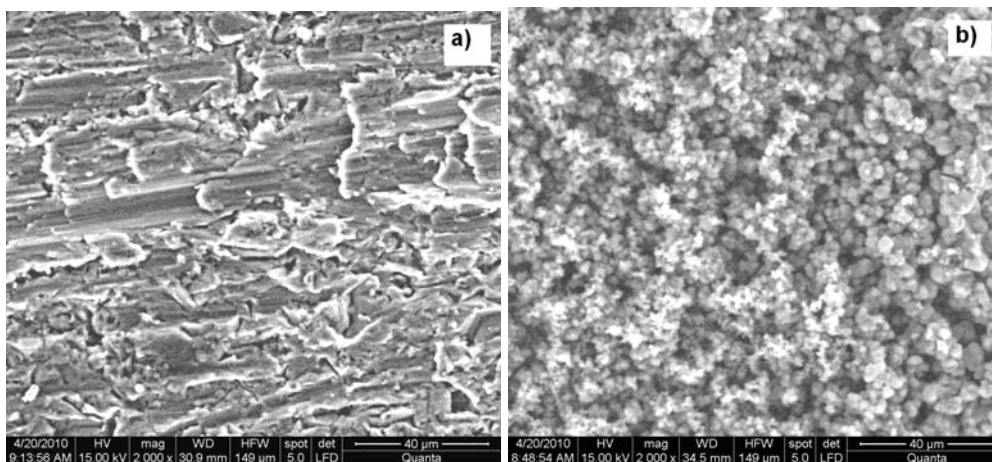


Fig. 8. SEM micrographs of a) control and b) corroded aluminium sample into 3% NaCl solution

4. CONCLUSIONS

- ✓ The corrosion process depends on the nature of the material for all the samples.
- ✓ The variation corrosion curves are plotted by means of the “loss mass method” as a function of the exposure time of the metallic materials (tombac, cooper and aluminium) into the salt fog and 3% NaCl solution tests.
- ✓ In the case of the tombac sample (zinc-copper alloy) a thick layer of corrosion products is deposited with a black colour in salt fog test. This fact is due to the strongly corrosion process at the beginning of the exposure. Then, this layer has a protective effect and the corrosion rate decreases slowly with increasing the exposure time.

- ✓ For the individual chemical element such as copper the resistance to accelerated corrosion into the 3% NaCl is higher than the other one of the aluminium. A flattening tendency of the corrosion curve appears to 75 h, then the corrosion rate decreases with increasing time.
- ✓ Aluminium is very low resistant to the corrosive environment in static regime. The strongly corrosion processes onto the aluminium surface take place.

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