

## CORROSION BEHAVIOUR OF TOMBAC USED IN CULT OBJECTS MANUFACTURING

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*Corrosion of metals and metallic alloys is due to their thermodynamic instability in relation to their oxidation form. Corrosion tests performed in this work simulate the exposure conditions in different environments of yellow tombac (brass containing 10-20% Zn). The aim of corrosion test in humid heat is to determine the behaviour of surface samples compared to their durability at high relative humidity conditions. Following the accelerated corrosion test in salt fog chamber, higher rates corrosion for tombac comparative with the corrosion test in continue humid heat are distinguished. Tombac samples show a good corrosion resistance as against aggressive environmental conditions which are tested. Surface morphology of treated samples in both corrosion tests was examined using the scanning electron microscopy. Again, the crystalline structure of metallic samples was analysed using the X-ray diffractometer. Also, the optical properties of tombac were analysed studying the reflectance spectra.*

KEYWORDS: Tombac, Accelerated Corrosion, Structure

### 1. Introduction

Corrosion process represents the partial or total destruction of metallic materials due to chemical and electrochemical reactions occurred through interaction with environmental factors [1-3].

The nature and structure of metallic phase, the chemical composition of the aggressive environment and the conditions for carrying out a certain technological process have a decisive influence on the corrosion form and deterioration capacity of metallic materials [2-4].

The metals and metallic alloys corrosion is due to their thermodynamic instability as a function of their oxidation form [5-7].

### 2. Materials and methods

#### 2.1. Preparation of tombac

The accelerated corrosion tests (in continue humid heat and salt fog chamber), performed in this work, simulate the exposure conditions of tombac in the presence of various corrosion environmental factors [7].

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, made of plastic material and stainless steel, has a capacity of 0.35 m<sup>3</sup>. 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 tested objects.

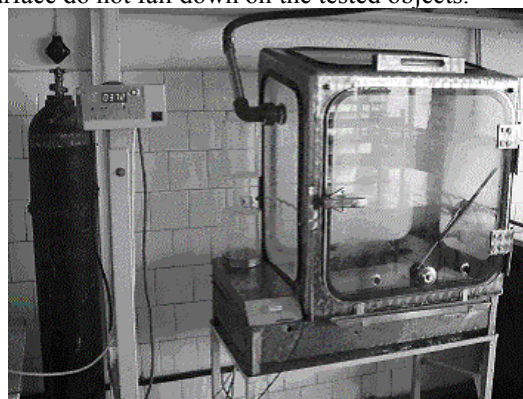


Fig. 1. The corrosion chamber

The aim of corrosion test in continuous humid heat is to determine the corrosion behaviour of samples subjected to high relative humidity conditions. In the corrosion chamber the temperature was kept at 40±2 °C and the relative humidity was

kept at 93±3%. The corrosion test was performed during a 96 h period of time. Initially, the samples were degreased with acetone, weighed using an analytical balance with an accuracy of 0.01 mg. At the end of the test, the samples were subjected to the normal atmospheric conditions for a period return of 1-2 h by quickly transferring of them in another room (maximum 5 min). Then the samples were washed with distilled water and acetone, dried and again weighed using the analytical balance. Finally, the mass loss and the corrosion rate were calculated on the basis of the relationship (1):

$$V_c = S \cdot t \cdot \rho \cdot \Delta m \cdot 10^7 \quad (1)$$

where:  $V_c$  is the corrosion rate [nm/h];

$\Delta m$  is the mass difference between initial and

final weight of the sample [g];

$S$  is the sample area [cm<sup>2</sup>];

$\rho$  is the specific density [g/cm<sup>3</sup>];  $\rho = 8.2$  (tombac);

$t$  is the working time [h].

The specific results are presented in Table 1.

To carry out the accelerated corrosion test in the salt fog chamber, a NaCl solution was prepared. An amount of NaCl was dissolved in distilled water, whose conductivity is less than equal to 20  $\mu\text{S cm}^{-2}$ , at 25±2 °C temperature to obtain a final solution with 50±5 g/l concentration. The relative density of the obtained solution ranged between 1.00255 and 1.0400. The amount of NaCl used contains less than 0001% Cu and 0.001% Ni. Also, the content of NaI must not exceed 0.1% and the total content of impurities must be maximum 0.5%. The pH of saline solution was established so that the collected solution inside the spraying chamber has the pH ranged between 6.5 and 7.2. This pH was measured by means of a pH meter model HI 991001, made by Hanna Instruments provided with a temperature indicator. For this test a similar corrosion chamber to that of corrosion test in humid heat was used. The accelerated corrosion test in the salt fog chamber was performed during a 144 h period of time, at 35 °C temperature. Initially, the samples were degreased with acetone, weighed using an analytical balance with an accuracy of 0.01 mg. Finally, the mass loss and the corrosion rate were calculated on the basis of the relationship (1). The results are presented in Table 2.

## 2.2. Microscopical and structural characterization of tombac

The morphological characteristics of the surface of metallic samples were examined by means of scanning electron microscopy (SEM). The micrographs were recorded by means of Quanta 200 Philips FEI device. The crystallographic

characteristics of specimens were analysed through X-ray diffraction method (XRD), by means of DRON-3M diffractometer. This diffractometer uses the  $\text{CuK}\alpha$  radiation, at 40 kV voltages and 30 mA current intensity. The XRD patterns were recorded at 2 $\theta$  angular range between 30 si 80°, with a scanning speed of 0.02° min<sup>-1</sup> and acquisition time of 0.1 s/step. The behaviour of tombac by interaction with a polychromatic beam was examined by reflectance measurements recorded by means of Perkin Elmer (type Lambda) Spectrophotometer with double beam in the spectral range of 190÷1100 nm.

## 3. Results and discussion

### 3.1. The accelerated corrosion test in continue humid heat

The accelerated corrosion test in continuous humid heat was performed according to the SREN ISO 9227/2007 standard [7].

The change of the visual appearance of sample surfaces 96 h later to maintain in the corrosion chamber in continuous humid heat can be observed. The sample colour is changed due to oxidation process without affecting the corrosion resistance.

To determine the effects produced by the accelerated corrosion in continuous humid heat the corrosion rate,  $V_c$ , was chosen as an indicator. The corrosion rate was calculated based on the measurements between the initial and treated sample weight during a 96 h period of time, according to the relationship (1).

Fig. 2 indicates the mass variation of three tombac samples subjected to the corrosion test in continue humid heat as a function of time. This study exhibits the specimen's behaviour during the accelerated corrosion tests in continuous humid heat.

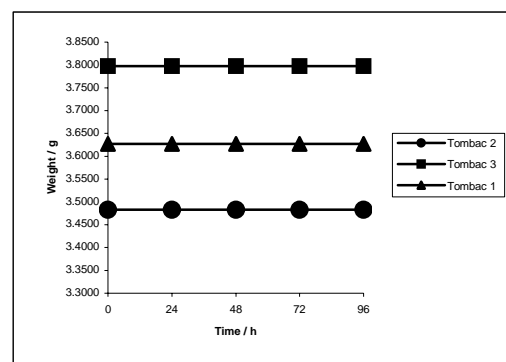


Fig. 2. The behaviour of tombac samples subjected to accelerated corrosion test in continue humid heat

The results indicate the constant maintaining of mass loss over time for each sample. Therefore, the samples present a high corrosion resistance.

**Table 1.** The corrosion rates of tombac samples subjected to the accelerated corrosion test in humid heat

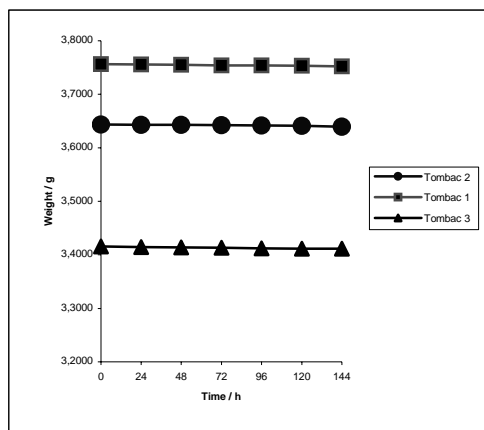
Sample	Corrosion rate (nm/h)
Tombac 1	0.32
Tombac 2	0.39
Tombac 3	0.32

The data presented in Table 1 and the graph of Fig. 2 show that the second sample with  $V_c = 0.39$  nm/h corrodes the fastest because of the higher corrosion rate compared to the other two tombac samples.

### 3.2. The accelerated corrosion test in salt fog chamber

The change of the appearance of metallic surfaces 144 h later to maintain them in salt fog chamber to test the corrosion can be observed.

Fig. 3 indicates the mass variation of tombac subjected to the corrosion test in salt fog chamber as a function of time. Like in the case of corrosion in humid heat, the tombac specimens are very resistant to corrosion in the salt fog. This fact means that the mass variation of the samples is constant during the corrosion process.



**Fig. 3.** The behaviour of tombac samples subjected to accelerated corrosion test in salt fog chamber

The data presented in Table 2 and the graph of Fig. 3 show that the first sample corrodes the fastest because of the higher corrosion rate compared to the other two tombac samples.

Therefore all results indicate that the specimens subjected to the salt fog test have higher corrosion rates compared with those recorded during the humid heat test. This increase of the corrosion rates is explained by the increase of aggressive conditions of the environment inside the salt fog chamber.

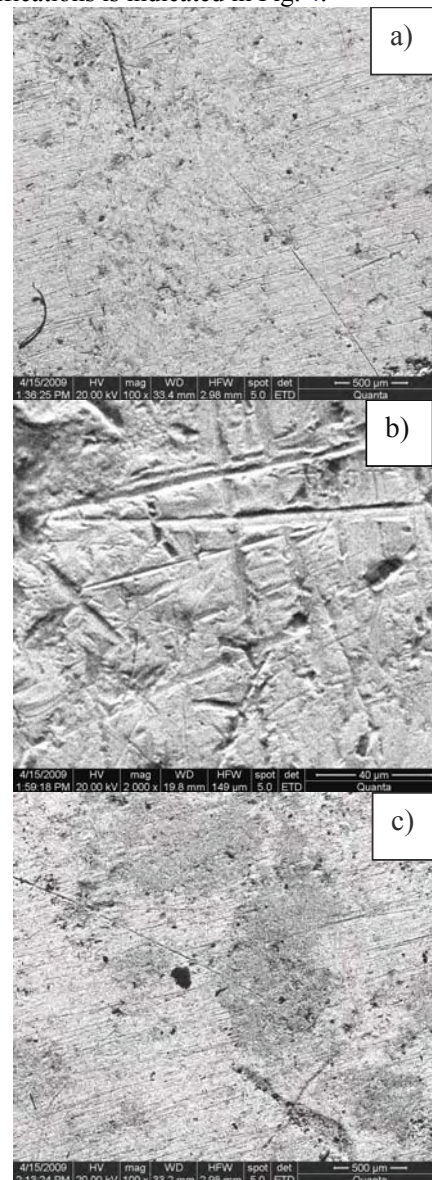
**Table 2.** The corrosion rates of tombac samples subjected to the accelerated corrosion test in salt fog chamber

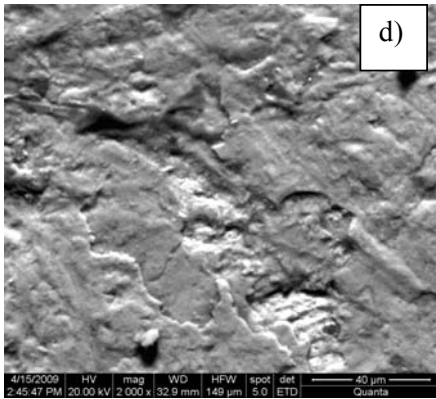
Sample	Corrosion rate (nm/h)
Tombac 1	4.70
Tombac 2	4.66
Tombac 3	4.13

According to the obtained results, the metallic samples present high corrosion resistance by the formation of an oxide layer meant to protect than against the aggressive conditions of the environment.

### 3.3. Morphological study of tombac

The surfaces morphology of tombac 1 subjected to both tests in humid heat and salt fog at different magnifications is indicated in Fig. 4.





**Fig. 4.** SEM micrographs at different magnifications of tombac 1 subjected to humid heat (a,b) and salt fog (c,d) tests

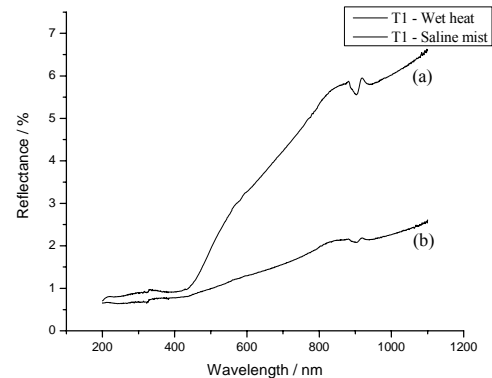
SEM images of tombac 1 subjected to humid heat test emphasize the specific structure of tombac with a clean and shiny surface, which presents a few small scratches like material defects (Fig. 4a and b). A colour difference of the samples can be observed (Fig. 4c and d). By taking out the samples from 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. The scratches existing on the sample surface subjected to humid heat test amplify the pitting process. Both environmental factors are more aggressive, the corrosion rate increases and the pinches are developed. On the other hand, the growing of an oxide layer on tombac surface subjected to salt fog having a dark colour can be shown.

### 3.4 Characterization of optical properties of tombac

Optical properties of reflectance of metallic samples are determined through interaction between a polychromatic beam and material surface. The incident radiation has the wavelength ranged between 190 nm and 1100 nm. The tombac 1 surface subjected to humid heat indicates higher values of reflectance than those of tombac 1 subjected to salt fog. For a certain value of wavelength, for example  $\lambda = 880$  nm, the subjected sample to humid heat presents a reflectance of  $R = 5.86\%$  and the subjected sample to salt fog presents a low value of reflectance of  $R = 2.16\%$ . Therefore, tombac subjected to more aggressive corrosion conditions (salt fog) exhibits more opaque and darker (low reflectance capacity) due to the oxide compounds formed on the material surface.

The curve from Fig. 5, corresponding to tombac 1 subjected to humid heat, indicates the formation of an inverse pick more evident than in case of tombac 1

subjected to salt fog. It means that a minimum value of reflectance ( $R \approx 6\%$ ) appears at a maximum value of absorbance.



**Fig. 5.** UV-VIS-IR spectra of tombac 1 subjected to humid heat (a) and salt fog (b)

The reflectance plot follows almost exponentially the increase of the reflectance values with the increase of wavelength at the beginning in the visible region. The variation of reflectance decreases at higher wavelengths. By means of relationship (2) the reflexive index ( $n$ ) can be calculated.

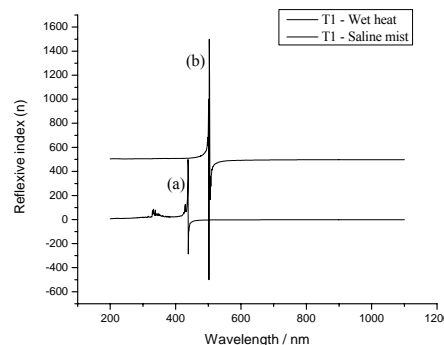
The reflexive index characterizes the type of dispersion specific to treated sample to a certain corrosion environment [8]:

$$R = \frac{(n-1)^2}{(n+1)^2} \Rightarrow n = \frac{1+R}{1-R} \quad (2)$$

where:  $R$  is the reflectance [%];  $R < 1$ ;

$n$  is the reflexive index.

The variation of optical constants (reflexive index) depending on wavelength for tombac 1 subjected to both corrosion tests are shown in Fig. 6. Both curves corresponding to two tests indicate a quick increasing to positive followed by a rapid decreasing to negative values when passing through zero value of reflexive index.



**Fig. 6.** The plot of reflexive index depending on wavelength for tombac 1 subjected to humid heat (a) and salt fog (b)

The first curve (Fig. 6a) shows a jump at  $\lambda \approx 440$  nm and the second curve (Fig. 6b) at  $\lambda \approx 500$  nm in visible range. The formation of an inverse pick is more evidently than it from the case of tombac 1 subjected to salt fog. At the beginning, the first plot of reflexive index (Fig. 6a) follows almost exponential to decrease with increasing the wavelength (330–400) nm. The second plot (Fig. 6b) indicates a simple increasing of curve due to the inorganic compounds formed on the surface.

### 3.5. Structural characterization of tombac

By treatment in salt fog corrosion medium the tombac 1 presents a XRD pattern which is in agreement with that of tombac subjected to humid heat, except for some picks with low intensity. The specific lines of tombac are shown in Fig. 7. The most intensive diffraction line of tombac is (111) [9, 10].

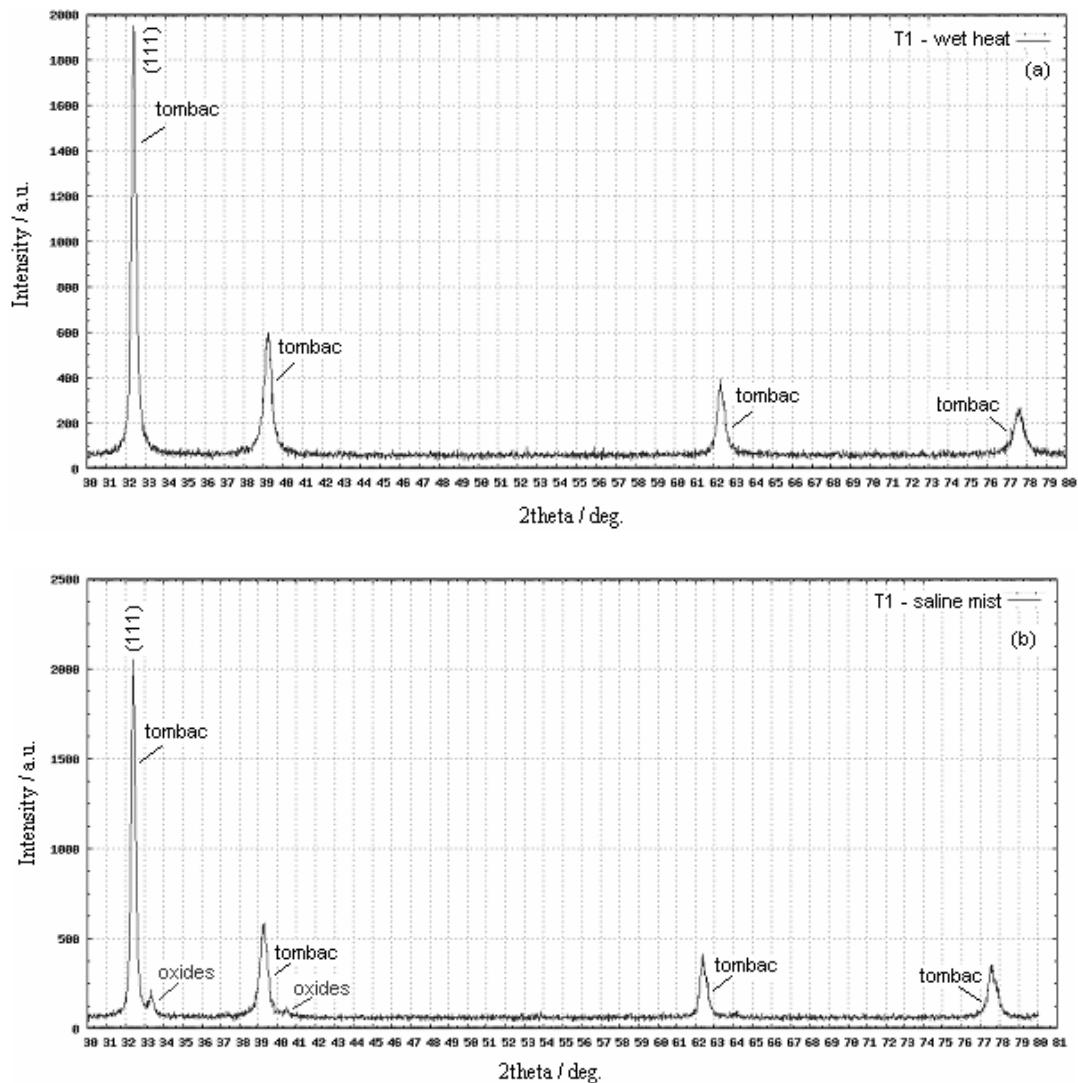


Fig. 7. XRD patterns of tombac 1 subjected to humid heat (a) and salt fog (b)

Furthermore, well noticeable are diffraction lines of oxide compounds formed during corrosion tests (Fig. 7a and b).

Therefore, the crystalline network is rearranged; the internal stresses are reduced by testing the sample in salt fog conditions. Also, the intensity picks of tombac decrease.

## 4. Conclusions

Based on experimental results regarding the corrosion of metallic samples, subjected to accelerated corrosion tests in continuous humid heat and salt fog chamber the corrosion rates and the mass variation of samples depending on the time of corrosion were calculated.