Vietnam Journal of Chemistry, International Edition, **55**(6): 787-790, 2017
*DOI: 10.15625/2525-2321.2017-00545*

# Influence of alloying elements on the corrosion of fine art bronze in the strong corrosive environment

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Received 4 July 2017; Accepted for publication 29 December 2017

## Abstract

The influence of Sn, Zn, and Pb on the corrosion of fine art bronze in strong corrosive environment were investigated. The value of loss mass and the potential of the specimens were determined in the artificial sea-water environment. Corrosion of specimens was compared each to other to find the effect of the elements. The corrosion products were determined with the XRD/SEM/EDS analyses. The results shown that, Sn decreases the corrosion rate of the bronze alloy in marine environment while Zn increases it. The corrosion rates and potential curves showed that the corrosion rate of the bronzes reduced with immersion time. Alloy containing 0.7% Pb; 1.6% Zn; 9.7 % Sn; 88% Cu (in %wt.) has the corrosion rate as lowest.

**Keywords.** Corrosion, strong corrosive environments, fine art bronze, Sn, Pb, Zn.

## 1. INTRODUCTION

Copper and copper alloys are found and used very early by humans. Copper have the special properties of the metal such as: good electrical conductivity, good thermal conductivity, iridescence, high plasticity and high strength. Moreover, it has a special property: good corrosion resistance that is why copper and copper alloys were applied in many different fields, especially in the case of working environments in which the details need a good corrosion resistance to increase their life and to reduce the corrosion rate. Copper alloy C83600 (ASTM standard with 85 % Cu, 5 % Sn, 5 % Zn, 5 % Pb in wt.) is widely used in the world, especially in the European countries where casting statues can be placed outside [1-3]. However, Vietnamese climate is a tropical monsoon with a long coastline, so the application of copper alloy C83600 to cast the outside art products should be considered and studied carefully.

When the statues are in direct contact with the marine atmosphere, it will create a favorable environment for corrosion containing a lot of $Cl^-$ with very high humidity. Therewith, alloys will contain the phases that have different electrode voltage in the electrolytic solution, so it will create a pair of battery electrode. Pending the inquiry of the factors affecting the corrosion process such as: the relative dimensions of product, material and the conditions of the working environment (temperature, humidity, degree of salting ...), the last is the one that is impossible to be changed, so the change of materials, mainly the change of their components to create a passive protective film is the most effective way to increase the life of products in the marine atmosphere and this is the aim of this research work.

## 2. EXPERIMENTAL

### 2.1. Preparation of the samples.

The pure metals Cu, Sn, Zn, Pb (pure degree greater than 99.5 %) in proper amount are melted and mixed in a graphite melting pot, placed in the electric furnace which uses silicon carbide bars as heating element. Then, the samples were casted and their composition is determined by atomic emission spectrum method with the measuring apparatus ARL 3460 OES. The composition of the alloys is given in table 1.

The samples were cut to specimens of 20 × 20 × 5 mm, which surface were then polished by the different abrasives papers (granulomere from N◦ 100 to N◦ 1200) to reach an exact geometry.

After polishing, the specimens were washed in two steps:

- Step 1: The mechanical rust was removed by the ultrasonic vibrator LC60H with distilled water for 30s, then acetone solution for 1 min and finally distilled water for 30s again.

- Step 2: Chemical cleaning according to the

ISO-8407-1991standard with the sequences as follows:

+ Soak in HCl 55 % solution for 2 minutes.

+ Soak in $H_2SO_4$ 17 % solution for 2 minutes.

+ Soak in $H_2SO_4$ and $Na_2Cr_2O_7$ solution for 6-10 sec.

After that the specimens are removed from moisture and water which clung to the surface by the placing in the humectant box for 24 hours before weight measuring.

*Table 1:* The composition of the alloys

| Sample | The composition of the elements (% wt.) | | | |
|---|---|---|---|---|
| | Pb | Zn | Sn | Cu |
| 1 | 0.61 | 1.01 | 0.99 | 97.39 |
| 2 | 3.28 | 4.25 | 5.08 | 87.39 |
| 3 | 5.33 | 4.69 | 3.93 | 86.05 |
| 4 | 0.96 | 8.22 | 9.92 | 80.90 |
| 5 | 0.77 | 7.26 | 1.13 | 90.84 |
| 6 | 5.23 | 10.50 | 1.65 | 82.62 |
| 7 | 6.06 | 6.15 | 6.33 | 81.46 |
| 8 | 5.41 | 1.56 | 10.10 | 82.93 |
| 9 | 0.72 | 1.60 | 9.68 | 88.00 |

### 2.2. Determine the corrosion rate

After weight measuring, the specimens were placed in the numbered glasses and immersed in the solution simulated the conditions of the Vietnamese coastal atmosphere, which has the composition as follows: NaCl 3.5 % (pH = 6.5, $t^o = 30\pm3$ $^oC$). The soaking cycle is 15 hours wet and 9 hours dry, to simulate sunny and moisture times of the Vietnamese weather. End of the wet – dry cycle, the specimens will be picked out and dried on a rack.

After soaking for pre-planned time, the specimens will be cleansed the corrosion products in two steps as described above, then were dried in the humectant box 24 hours before scaling to determine weigh.

*Calculation of the corrosion rate*: the corrosion rate of metal is expressed by the lost of mass in a unit of time and a unit of area (conventional unit) according to the formula:

$$\rho = \frac{m_0 - m_1}{S.t} = \frac{\Delta m}{S.t} \qquad (1)$$

where: ρ – the corrosion rate ($mg/m^{-2}.year^{-1}$); $m_o$ – specimen weight before soaking (mg); $m_1$ – specimens weight after soaking (mg); S – surface area of the metal ($m^2$); t – time (year).

Because all the specimens were cut and were flat grinded, their surface area is the same:

$$S = 2x20^2 + 4x20x5 = 1200(mm^2) = 0.0012\ (m^2)$$

The corrosion rate of material is calculated as:

$$V_c = \frac{\Delta m}{S.t} = \frac{\Delta m}{0.0012.t}\ (mg.m^{-2}.year^{-1}) \qquad (2)$$

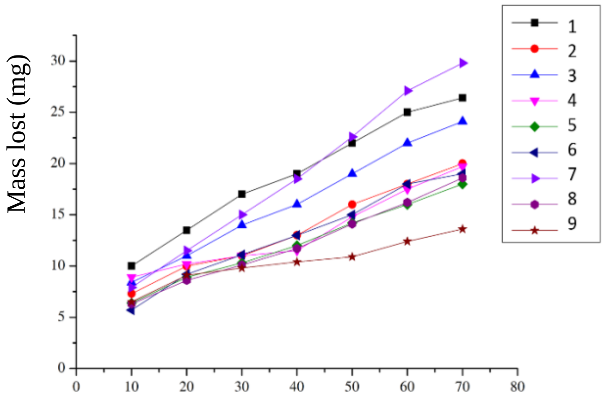
## 3. RESULTS AND DICUSSION

The lost mass of the specimens which were corroded on the saline solution through the timelines is showed in table 2 and Fig. 1. The corrosion rates of alloys is calculated according the formula (2) and are shown in the Fig. 2.

*Table 2:* The mass loss of the specimens in the saline solution (mg)

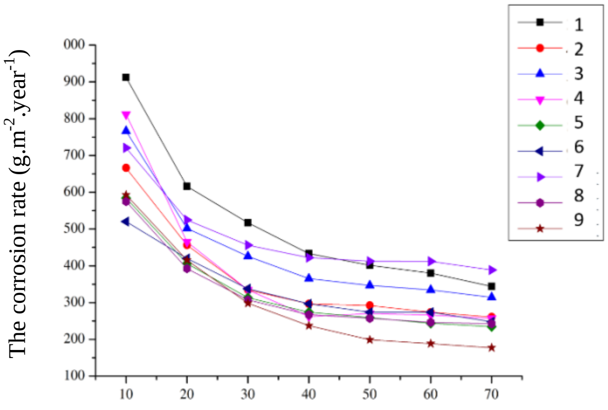
| Time (day) | Sample | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 10 | 10.0 | 7.3 | 8.4 | 8.9 | 6.4 | 5.7 | 7.9 | 6.3 | 6.5 |
| 20 | 13.5 | 10.0 | 11.0 | 10.2 | 8.9 | 9.2 | 11.5 | 8.6 | 9.1 |
| 30 | 17.0 | 11.0 | 14.0 | 11.0 | 10.3 | 11.1 | 15.0 | 10.1 | 9.8 |
| 40 | 19.0 | 13.0 | 16.0 | 11.5 | 12.0 | 13.0 | 18.5 | 11.7 | 10.4 |
| 50 | 22.0 | 16.0 | 19.0 | 14.8 | 14.2 | 15.0 | 22.6 | 14.1 | 10.9 |
| 60 | 25.0 | 18.0 | 22.0 | 17.5 | 16.0 | 18.0 | 27.1 | 16.2 | 12.4 |
| 70 | 26.4 | 20.0 | 24.1 | 19.7 | 18.0 | 19.0 | 29.8 | 18.6 | 13.6 |

From Fig 2 can see that the corrosion rate of the alloys in saline solution reduces quickly in the first 20 days. After 30 days the corrosion rate is relativity stable and keeps almost unchanged until 70 days. The fact that the corrosion rate decreases over time is explained by the corrosion mechanism of the fine art bronze. In the beginning, the outer layer of the alloy was corroded because it is in direct contact with the ionized solution. The electrode voltage of the Sn, Zn, Pb rich regions is more negative than Cu, so they should be corroded. Some corrosion products will create an insoluble layer in the specimen's surface, but some others are soluble in the ionization solution, making the holes or groves on the specimen surface. The holes, the groves both will allow the ionization solution penetrate into the layers inside. However, the corrosion rate of the inside layers will be slower than the outer layers, because the deeper it is, the more difficult the solution can circulate and the concentration gradient of the elements will not be high. At the same time, on the surface a durable protective oxide film will be created. This film prevents the penetration of the ionized solution inward, so the corrosion will drop slightly over time as show in Fig. 2.



Time (day)

*Figure 1:* The loss mass of the specimens



Time (day)

*Figure 2:* The corrosion rate of the specimens

The scan electron microscopy (SEM) images of the corrosion product layer of specimen 9 after 70 days (Figs. 3&4) were shown its structure is tight and uniform. The phases presented at the corrosion product layer were characterized by the X-ray diffraction method and is shown in Fig 5. Table 3 shows that the corrosion products are mainly oxides and chloride salts of both Cu and Sn. There is no Pb in the layer of the corrosion product because its corrosion products dissolved in the ionization solution.

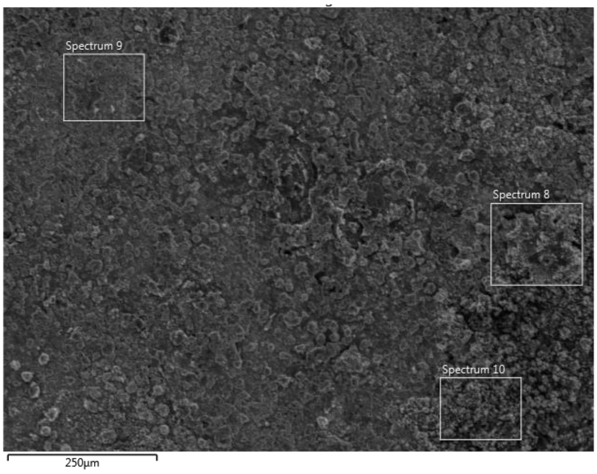


*Figure 3:* SEM image of the specimen 9 surface after 70 soaking days

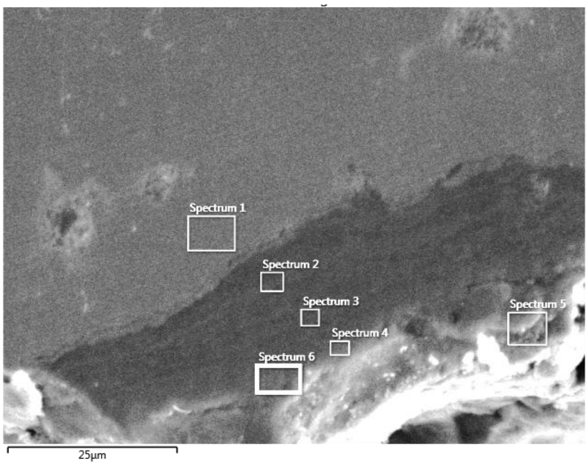


*Figure 4:* SEM image of the specimen 9 cross section after 70 soaking days

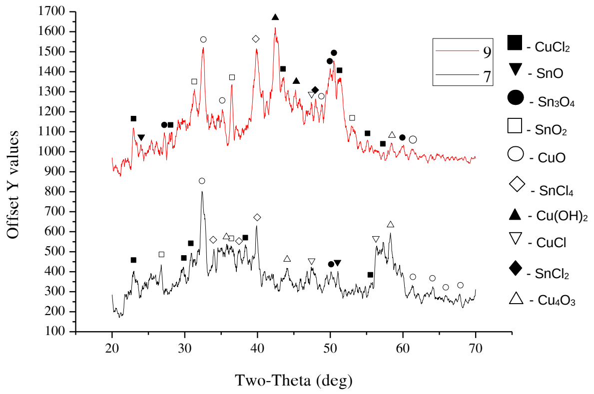


*Figure 5:* The X-ray pattern of the surface of the specimens 9 and 7 after corrosion test

Zn increases the corrosion resistance of alloy and can replace tin, so the phenomenon such as dezincification can reduce the corrosion resistance of alloys [5, 6]. When Zn gets out, it will form the holes in alloy. These holes will create the spaces for the ionization solution to penetrate inward and cause the corrosion developed, but the effect of dezincification is remarkable only if the concentration of Zn in alloys is more than 15 %. Sn is a right element which prevents the dezincification [6, 7], therefore, the corrosion rate of alloys 8 and 9 is the lowest due to the higher Sn concentration (≈ 9 %).

SEM images (Fig. 2) and the results of the composition analysis in different regions (table 3) of specimen 9 after 70 soaking days in the saline solution are shown that the black regions (regions 2

~ 6) have the high content of O and Cl contents, while light region 1 has almost no O and Cl. It proves that the black regions at the specimen outer edge were formed after soaking in the saline solution. This corrosion product layer has a thinness of about 10 µm and is very tight which forms the aforesaid passive protective layer inhibiting the corrosion process.

*Table 3:* The elemental elements in the different regions on section of specimen 9

| Region | % elemental mass | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cu | Sn | Zn | Pb | O | Cl | Na |
| 1 | 83.96 | 11.46 | 1.99 | 0.48 | 0.67 | 0.68 | 0.76 |
| 2 | 43.14 | 13.90 | 2.08 | 2.76 | 26.07 | 10.36 | 1.69 |
| 3 | 46.28 | 10.30 | 1.35 | 4.35 | 22.76 | 14.96 | - |
| 4 | 29.33 | 10.13 | 1.84 | 14.06 | 18.81 | 25.69 | 0.14 |
| 5 | 49.53 | 9.56 | 1.86 | 6.74 | 17.99 | 12.88 | 1.44 |
| 6 | 37.65 | 7.07 | 1.20 | 9.83 | 24.65 | 19.01 | 0.59 |

## 4. CONCLUSION

The study on the corrosion of the copper alloys in the strong corrosive environment shows that the corrosion rate reduces to small value and becomes unchanged as the tight passive film forms and remains stable.

The data of the loss mass and the corrosion rate shows that the alloy 9 (Pb-Zn-Sn-Cu: 0.72-1.60-9.68-88.00 %wt.) is the best against the corrosion in the strong corrosive environment. The corrosion product layer after immersion in the saline solution for 70 days has a thinness of about 10 µm and is very tight, protecting the internal alloy from further corrosion. Moreover, the low lead content (≈ 1%) in this alloy reduces the toxicity during melting process so is more environmentally friendly.

Sn decreases the corrosion rate by formation of SnO and $SnO_2$ oxides. More than that of restricts a phenomenon such as dezincification which makes the alloy more sensitive to corrosion attack.

## REFERENCES

1. Carol Powell, Peter Webster. *Copper Alloys for Marine Environments*, Copper Development Association, 2012.
2. Harold Anderson. *Centrifugal pumps and allied machinery 4th edition*, Elsevier Advanced Technology, 2007.
3. V. Alar, I. Stojanovic, B. Zidov, F. Ivusic, Corrosion Resistance of Highly Alloyed Materials in 3.5% NaCl solution at elevated temperature, *Int. J. Electrochem. Sci.* 8, 2013.
4. Trinh Xuan Sen. *Corrosion and protection of metals*, Vietnam National University Press, 2006.
5. A. Galerie, Nguyen Van Tu. *Corrosion and protection of materials* , Science and Technics Publishing House, 2008.
6. S. D. Cramer, B. S. Covino. *ASM Handbook Volume 13 Corrosion*, ASM International Handbook Committee, 1992.
7. C. D. S. Tuck, C. A. Powell, J. Nuttall. *Corrosion of Copper and its Alloys*, 2010.

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