Corrosion of bronze by acetic and formic acid vapours, sulphur dioxide and sodium chloride particles

Korrosion von Bronze durch Essig- und Ameisensäuredämpfe, Schwefeldioxyd und Natriumchloridpartikel

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This paper studies the corrosion of patinated and unpatinated bronze by acetic and formic acid vapours, sulphur dioxide and sodium chloride salt particles, at 100% relative humidity. Weight loss, X-ray diffraction, infrared and scanning electron microscopy were the techniques used. Acetic and formic acid vapours, sulphur dioxide and sodium chloride produce a high corrosion rate on bronze. In general, no protective effect was found by the patina on bronze. The principal compounds identified were Cu_2O , Cu_2S , $Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O$, $Cu(CH_3CO_2)_2 \cdot XH_2O$ and $Cu(HCO_2)_2$.

Vorliegende Arbeit behandelt die Korrosion von Bronze mit und ohne künstlicher Patina durch Essig- und Ameisensäuredämpfe, Schwefeldioxyd und Natriumchlorid bei relativer Luftfeuchtigkeit von 100%. Die eingesetzten Verfahren waren Gravimetrie, Röntgenstrahlenbeugungsanalyse, Infrarotanalyse und Rasterelektronenmikroskopie. Wie Schwefeldioxyd und Natriumchlorid erzeugen auch Essig- und Ameisensäuredämpfe auf Bronze eine starke Korrosion. Die wichtigsten identifizierten Bestandteile sind Cuprit, Kupferschwefel, hydratisiertes Kupfersulfat, Kupferazetat und Kupferformiat.

1 Introduction

Vapour phase corrosion (VPC) phenomena in metallic materials have been observed for a long time [1-3]. Trace amounts of volatile contaminants can accelerate metal corrosion and certain organic acids are corrosive to metallic materials [4-7]. This effect is known as "bronze disease", caused, for example, by acetic acid emissions from wood shavings used as packing materials or by volatile acids in oak beams which deteriorate lead used in church roofs [3, 8].

It is known that bronze monuments installed in marine atmospheres are often subject to severe corrosion if proper measures are not taken to counter the effect of NaCl salt particles on patina composition [1]. Sulphur dioxide is an accelerating factor of bronze corrosion in urban and industrial atmospheres [9, 10].

The aim of this paper was to study the corrosion of bronze, with and without patina, by acetic and formic acid vapours, sodium chloride salt particles and sulphur dioxide contami-

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nants. Special attention was dedicated to designing experimental methods which accurately recreate the corrosive atmospheres.

2 Experimental method and materials

Two bronze materials were used with the following percentage chemical compositions (in mass-%), Bronze A: 87 Cu, 8 Sn, and 5 Pb. Bronze B: 4.76 Sn, 4.58 Pb, 4.35 Zn, 0.16 Sb, 0.13 Fe, 0.13 Al, 0.13 Mn, 0.88 Ni, 0.003 P, 0.081 S, and remainder Cu. The bronze ingots were cut into 4 cm \times 3 cm \times 0.3 cm samples.

Two bronze surface preparations were tested. (i) Unpatinated bronze: mechanically polished samples were prepared by hand-polishing with different grades of emery paper (down to 2/0) and pressure air dried. (ii) Patinated bronze: following treatment (i) samples were further chemically etched in a 10% HNO₃ aqueous solution for 10 min, rinsed in distilled water, heated in an oven (Selecta Mod. 210) at 160 °C for 1h and, finally, the samples were covered with patina by dipping in a 10% potassium sulphide solution, held at 70 °C, for 3 min. This process is called artificial patination of bronze.

The corrosive atmospheres were generated in a tight-closed desiccator-type container of about 2.4 litre volume. The relative humidity (RH) of approximately 100% was obtained by placing 350 ml of distilled water in the bottom of the container. The temperature was maintained at 30 °C for all measurements by immersing the containers in a thermostatically controlled water bath.

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A 3 mm diameter hole was made in the bronze samples to allow them to be suspended by a nylon fibre below a flat 12 cm \times 6 cm plastic cover with four legs 7 cm high. This additional device was used to prevent droplets of condensation dripping onto the bronze samples.

2.1 Acetic and formic acid vapours

Three acetic acid vapour levels (25, 83, and 225 ppm) and three formic acid vapour levels (50, 157, and 314 ppm) were studied. In order to obtain a vapour concentration of acetic and formic acid in equilibrium with the aqueous concentrations of these acids, it was assumed that in an acetic or a formic dilute solution the vapour pressure, P, is proportional to the molfraction, χ , of the solvent present in the solution

$$\mathbf{P} = \chi \mathbf{P}_{\mathbf{o}} \tag{1}$$

which is the expression of Raoult's law [11], where P_0 is the vapour pressure of a pure acetic or formic acid.

The ppm of acetic or formic acids can be written as

$$ppm = 10^6 \frac{P/760}{29} P_m = 45.37 P P_m$$
(2)

where P_m is the acetic or formic molecular weight; and 29 is, approximately, the molecular weight of air.

If G is the acetic or formic number of grammes in a 1000 ml aqueous solution, the χ can be written as

$$\chi = \frac{G/P_{\rm m}}{1000/18} = 1.8 \ 10^{-2} \ G/P_{\rm m} \tag{3}$$

Taking into account equations (1), (2) and (3), it is possible to write

$$ppm = 81.7 \ 10^{-2} \ G \ P_o \tag{4}$$

therefore,

$$G = 1.224 \text{ ppm/P}_{o} \tag{5}$$



Fig. 1. Dependence of vapour pressure on the reciprocal of the absolute temperature of acetic and formic acids [12]

Abb. 1. Abhängigkeit des Dampfdrucks von der reziproken Absoluttemperatur von Essig- und Ameisensäure The P_o value was obtained from literature [12] using the Claussius-Clapeyron equation: $\log p_o = -a/T + b$ (Fig. 1).

The vapour level of acetic or formic acid was obtained by replacing the 350 ml of distilled water at the bottom of the tight-closed container with a solution containing the appropriate amount of glacial acetic acid (Merck) or 85% formic acid (Merck), according to equation (5). In order to obtain a constant level of acetic or formic acid during the experiments, both atmosphere and solution were replenished once a week for 30 days.

2.2 Surface contamination with NaCl particles

Four NaCl contamination levels (0.1, 1, 5 and 10 mg/m²/ day) were tested. The contamination was simulated by surface deposits of NaCl salt particles. 250 mg of NaCl (Merck) was dissolved in 125 ml of distilled water and 375 ml of methyl alcohol (Merck). Every two days for 30 days the specimens were removed from the tight-closed container and the appropriate amount of NaCl was deposited on the metal surface using a pipette and spread with a glass rod. Methyl alcohol was used to facilitate the evaporation of the solvent. Thus, when the samples were returned to the tightclosed container the bronze surface was dry.

2.3 Presence of SO₂ contaminant

Twelve SO₂ contamination levels (0.02, 0.04, 0.07, 0.10, 0.23, 0.51, 1.07, 2.13, 4.07, 7.30, 12.68 and 35.39 ppm corresponding to pH values: 8.2, 8.0, 7.9, 7.8, 7.6, 7.4, 7.2, 7.0, 6.8, 6.6, 6.4 and 6.0, respectively) were studied. SO₂ contamination was simulated by replacing the 350 ml of distilled water at the bottom of the tight-closed container with a solution containing 50 ml of a 0.2 M potassium dihydrogen orthophosphate (Merck) solution and 16.78 g/200 ml of sodium sulphite (Merck) [13]. The pH values were obtained by adding a fixed quantity of a 0.2 M NaOH solution.

When SO₂, a partially soluble gas, is dissolved in water sulphurous acid is formed: SO₂ + H₂O \Leftrightarrow H₂SO₃ (K₁ = 1.76). Considering the dissociation constant of sulphurous acid: H₂SO₃ \Leftrightarrow H⁺ + HSO₃⁻ (K₂ = 2.19 10⁻²), and the dissociation constant of hydrogen sulphite: HSO₃⁻ \Leftrightarrow H⁺ + SO₃²⁻ (K₃ = 7.9 10⁻⁸), it is deduced from these equilibriums that the partial vapour pressure of sulphur dioxide, Pso₂, is given by:

$$P_{SO_2} = \frac{\text{Total } SO_3^{2-}}{K_1} \frac{[H^+]^2}{K_2 K_3 + K_2 [H^+] + [H^+]^2}$$
(6)

Thus, due to this dependence on pH and using equation (6), it was possible to calculate the SO₂ vapour parts per million (vpm) level. The vpm was then converted to ppm using: 1 vpm SO₂ = 2.21 ppm SO₂. In order to obtain a constant level of SO₂, both atmosphere and solution were replenished once a week for 30 days.

Weight loss experiments were carried out taking measurements at the beginning of the experiments and at their end following removal of the corrosion products using a 10%H₂SO₄ aqueous solution, according to ASTM standard [14]. All the experiments were performed in triplicate.

3 Experimental results

Table 1 shows the effect of acetic acid vapour on the corrosion rates of Bronzes A and B, with and without patina. In patinated Bronze A the corrosion rate was higher than in unpatinated Bronze A. In Bronze B some protection by the patina can be observed.

Table 2 shows the effect of formic acid vapour on the corrosion rates of Bronzes A and B, with and without patina. As with acetic acid vapour (Table 1), the patina provides some protection to Bronze B. In patinated Bronze A no protection was provided by the patina.

Fig. 2 shows the corrosion rates of Bronzes A and B, with and without patina, contaminated with sodium chloride salt particles. The corrosion rates of both Bronzes A and B was higher in patinated than in unpatinated bronze.

Fig. 3 shows the corrosion rates of Bronzes A and B, with and without patina, in the presence of sulphur dioxide contaminant. In contrast with the results for Bronze A, the corrosion rate in patinated Bronze B was lower than in unpatinated Bronze B.

4 Discussion

High corrosion rates can be observed in Bronzes A and B by the action of acetic and formic acid vapours (Tables 1 and 2). X-ray diffraction analysis (XRDA) and infrared analysis (IRA) show Cu₂O (cuprite), Cu₂S (copper sulphide), SnS₂ (tin sulphide) and Cu (CH₃CO₂)₂ · XH₂O (copper acetate hydrate) for patinated bronze in the presence of acetic acid vapour. XRDA technique shows Cu₂O and Cu₂S in the presence of formic acid vapour. Finally, IRA shows Cu₂O and Cu(HCO₂)₂ (copper formate) in the presence of formic acid vapour. With both acetic and formic acid vapours the patina gives some protection in Bronze B. In contrast, the corrosion rate of patinated Bronze A is higher than for unpatinated Bronze A. This different behaviour may be associated with the different chemical compositions of the bronzes tested.

The high corrosion rate of bronze in the presence of acetic and formic acid vapours (Tables 1 and 2), is particularly marked with acetic acid vapour, implying that small quantities of acetic acid vapour are capable of producing a disproportionately large amount of corrosion [7]. At the same time, the relatively high acidity of formic acid ($pK_a = 3.75$) in the adsorbed water layer on the bronze surface could stimulate the corrosion process [12]. Finally, the reducing action of formic acid encourages the corrosion of bronze [5].

In the presence of formic acid vapour the corrosion product layer was a compact garnet deposit (cuprite) upon which adherent blue crystals (copper formate) grew. However, in the presence of acetic acid vapour the crystals formed on the corrosion product layer (garnet) were much greener in appearance, rich in blue crystals and of porous nature (copper acetate). This may also explain why acetic acid vapour gives higher corrosion rates than formic acid vapour (Tables 1 and 2). These results are in agreement with *Vernon* and *Donovan* [1, 15]. During the first week of experimentation, the blue crystals were surrounded by zones free of corrosion products which could act as cathodic areas [16]. After 20 days exposure all the bronze surface was covered with corrosion products. Visually the specimens appeared to be covered with a layer of non adherent solid corrosion products.

Fig. 2 shows the corrosion rates of Bronzes A and B contaminated with NaCl salt particles. The behaviour of both unpatinated Bronzes A and B is similar, with a corrosion rate close to 0.5 mdd. The corrosion rate is independent of the chloride content on the surface. It is known that NaCl is hygroscopic, promoting corrosion by favoring electrolyte formation at low RH [17]. In this study the RH was close to 100%.

Table 1. Corrosion rate, as mg/dm²/day (mdd), of Bronzes A and B, with and without patina, in the presence of acetic acid vapour **Tabelle 1.** Korrosionsgeschwindigkeit (mdd) der Bronzen A und B, mit und ohne Patina, in Essigsäuredämpfen

Acetic vapour contamination ppm	Corrosion rate, mo	ld	Corrosion rate, mdd				
	Bronz	e A	Bronze B				
	Without patina	With Patina	Without patina	With patina			
25	8.10	23.00	2.74	2.06			
83	27.34	53.62	10.07	6.42			
225	36.53	82.02	13.40	8.09			

Table 2.	Corrosion rate,	as mg/dm²/day	/ (mdd), o	f Bronzes	A and B.	, with ar	nd without	patina,	in the	presence	of formic	acid	vapour
Tabelle 2	. Korrosionsge	schwindigkeit (mdd) der	Bronzen A	A und B,	mit und	ohne Pati	na, in A	meisen	isäuredän	npfen		

Formic vapour contamination ppm	Corrosion rate, mo	ld	Corrosion rate, mdd				
	Bronz	e A	Bronze B				
	Without patina	With Patina	Without patina	With patina			
50	10.90	45.20	0.02	1.00			
157	15.01	71.29	3.70	1.50			
314	34.19	76.98	5.64	1.79			



Fig. 2. Corrosion rate against NaCl salt particles for Bronzes A and B, with and without patina.

Abb. 2. Korrosionsgeschwindigkeit als Funktion der NaCl-Konzentration der Bronzen A und B, mit und ohne Patina.



Fig. 3. Corrosion rate against SO_2 content for Bronzes A and B, with and without patina.

Abb. 3. Korrosionsgeschwindigkeit als Funktion der SO₂-Kontamination der Bronzen A und B, mit und ohne Patina.

When NaCl salt particles were deposited on unpatinated bronze surfaces a rather unevenly distributed red and green coating (with green crystals) appeared after a few days experimentation. Sometimes pitting was observed on the surface of the bronze under the green crystals. X-ray diffraction analysis shows only cuprite with a red colour. Similar green coatings obtained by spraying sea-water on copper have been reported in the literature and were associated to $CuCl_3 \cdot 3Cu(OH)_2$ (atacamite) [1]. This result suggests that though atacamite has not been detected by XRDA and IRA techniques its possible presence cannot been dismissed.

Pitting was observed mainly in the red zones. This behaviour may be interpreted as disruption of the non-homogeneous passive layer on the bronze surface by chloride ions.



Fig. 4. SEM micrograph for Bronze A after artificial patination process.

Abb. 4. SEM-Mikrogefügebild der Bronze A nach künstlicher Patinierung.

Thus, it may be concluded that in green zones the basic salts lead to the adsorption of passivating OH ions and some of the chloride ions become inactive.

No protective effect can be observed by the patination of Bronzes A and B (Fig. 2). Bronze A shows a high corrosion rate. Since the experimental conditions are identical for both Bronzes A and B this different behaviour may be due to the presence of zinc and lower percentage of tin in Bronze B compared with Bronze A.

Fig. 4 shows a micrograph obtained by scanning electron microscopy (SEM) for patinated Bronze A (Bronze B showed a similar micrograph). It can be seen that the layer formed on the bronze is very porous and not highly protective with a high apparent surface. For this reason chlorides may participate in the anodic mechanism.

Fig. 3 shows the corrosion rates of Bronzes A and B, with and without patina, in the presence of sulphur dioxide. As in the presence of acetic and formic acid vapours (Tables 1 and 2) the patina shows some protective effect on Bronze B. In the case of patinated Bronze A the corrosion rate is higher than in unpatinated Bronze A. This different behaviour may be due to the chemical composition of the two bronzes tested.

As the contamination level of sulphur dioxide was increased a higher corrosion rate was obtained (Fig. 3). At high contamination levels the corrosion rate was independent of the SO₂ concentration. This behaviour may be related to the formation of a basic copper sulphate hydrate, $Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O$.

Two main theories have been suggested to explain the mechanism of the accelerating effect of sulphur dioxide on metallic materials, one based on the cathodic process effect [18], and the other is associated with the anodic process and the formation of solid corrosion products [17]. The appearance of a plateau at high sulphur dioxide contamination levels suggests that the present data could be interpreted by the more widely accepted theory of anodic process and the formation of the copper sulphate hydrate solid product. Cu₂O may form and subsequently, due to the action of sulphur dioxide, oxygen and the water in the adsorbed layer, an insoluble basic sulphate which obstructs the corrosion process may appear.

5 Conclusions

The proposed experimental methods, based on the dissociation constants of the partially soluble gas SO_2 and on Raoult's law, provide a simple way of obtaining a specified concentration of sulphur dioxide and acetic and formic acid vapours, respectively.

Acetic and formic acid vapours, sulphur dioxide and sodium chloride produce a high corrosion rate on bronze. No protective effect was shown by patinating the bronze.

Cuprite, copper sulphide, basic copper sulphate hydrate, copper acetate hydrate and copper formate were found to be the principal compounds of the corrosion products.

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