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Characterisation of Passive Layers of Bronze Patinas (Cu-Sn Alloys) in Relation with the Tin Content of the Alloy

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Abstract

In order to develop our knowledge of the relations between the high degree of protectiveness of passive layers and their composition, corroded archaeological bronzes of Bronze Age (1500-950 BC) have been characterised by different methods of analysis. Results reveal that the passive layers have a bilayer structure and are due to the selective dissolution of copper from the copper solid solution of the alloy to the electrolyte. For all of the objects, the ratio $[(\text{Sn}/\text{Cu})_p / (\text{Sn}/\text{Cu})_a]$, with p for the outermost passive layer and a the alloy, has about the same value. Sn concentration within outermost passive layers is discussed in relation with the theoretical implications of the Kirchheim model.

1. Introduction

Corrosion studies on passive films are mostly concerned with processes occurring during short periods of time, *i.e.* often less than a hundred of hours. This paper is focused on the study of ancient metallurgical materials which have reached a stationary state after several hundreds of years.

Often, antique bronzes (Cu-Sn alloys) reveal 'uniform' surfaces which preserve the original surfaces, *i.e.* decor or polishing traces are still visible. This case of passive surface, known in the literature as 'noble patina' [1,2], is a typical example of the protection of an alloy for more than several millennia.

Little is known about the nature of these passive surfaces and the processes of their formation. External aspect, composition and microstructure of passive layers in natural conditions will be discussed in this paper from results obtained on a corpus of Bronze Age objects (1500-950 BC). Then the results will be related to the Kirchheim model describing passive films formed on homogeneous alloys in the quasi stationary condition.

2. Experimental Method

2.1 Description of the samples

The samples are 13 archaeological artefacts – pins, bars, needles, rings dated from about 1500 to 950 BC

and discovered in an important Bronze Age metallurgical centre (Fort-Harrouard, France). They have been described in detail elsewhere [3]. The archaeological soil is representative of a moderately aggressive oxygenated soil [4]. All these objects were not restored. The objects are Cu-Sn alloys with a Sn content from 4 to 14% by weight. They contain minor elements such as Ni (from 0.1 to 1% by weight), As (0.1-0.35%), Fe and Ag and Sb (0.03-0.25%), Zn and Co (0.003-0.01). Three objects have a lead content of more than 1%. However, lead is not miscible in the alloy and does not modify the nature of the copper solid solution.

2.2 Characterisation of the surfaces

The passive surfaces were analysed by energy dispersive spectrometry (EDS) on areas of *ca.* 0.1 to 0.01 mm². Each artefact was introduced directly into the chamber of a scanning electron microscope (SEM) without any preparation to keep it intact. In another part of the work, corrosion products were scraped-off from the surface before being analysed by X-ray diffraction and by infrared spectrometry.

Three objects, considered as representative of the whole corpus, with different tin contents, were sectioned transversally and longitudinally for metallographic examinations and characterisation of the internal microstructure. They were homogeneous single phase alloys with an annealing structure and contained numerous copper sulphide inclusions due to the ores used [5].

3. Principal Component Analysis (PCA)

The PCA method was applied in order to interpret the EDS analyses of the patinas. The method allows [6], first, a description of the variations of the p analysed chemical elements (here Si, P, Cl, Fe, Ni, Cu and As) and, secondly, a representation of the whole analytical results in a different reference system with p -coordinates defined as the main axes. Each new D_i axis ($i=1, \dots, p$) is defined by an eigenvector U_i which corresponds to the eigenvalue λ_i of the diagonalised correlation matrix between the p chemical elements. So the p eigenvectors (principal components) are expressed as a linear combination of the previous variables (Si, P ...). The eigenvectors U_i are classified by decreasing order of the eigenvalues to obtain the best representation of the results for the first principal axes.

In our case, the analytical results were pretreated first by dividing each analytical point by its Sn value to have independent values, and then by scaling each variable by the standard deviation of the analysed points. This procedure allows giving an equal weighing for each value in the data matrix.

4. Results

The passive 'surface' of the bronzes appears as a shiny lustrous surface (Fig. 1) keeping the limit of the original surface. It is characterised by a two-layer structure (Fig. 2):

- An homogeneous outermost layer, around 5 to 40 μm deep, about the size of a metallic grain, and with different possible colours (green, dark grey, blue or bright grey). Copper sulphide inclusions from the alloy are still visible in the outermost layer. Outer crusts, sometimes observed on this layer, result from the precipitation of copper cations in the soil.

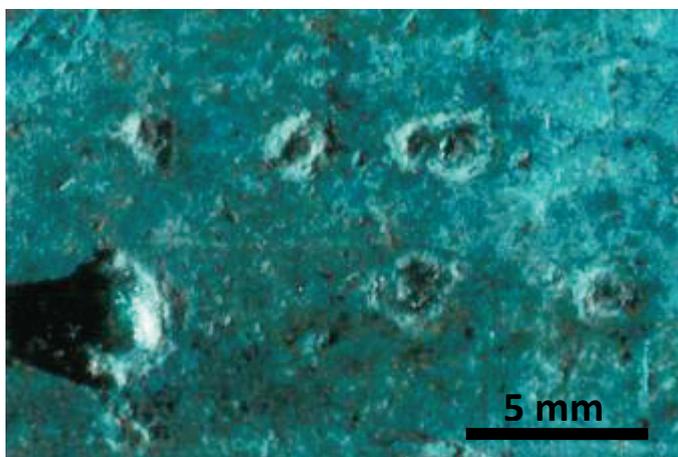


Fig. 1 Macroscopic view of a passive patina with re-passivated pits. Bronze Age bar (1250-1050 BC).

- An internal grey-brown layer, whose thickness may vary between 1 and 30 μm . Intergranular attack is occasionally encountered at the boundary of the alloy.

From the microstructural examinations, it can be concluded that the passive structure has grown from the original surface to the alloy without apparent volume change.

A typical example of the distribution of the chemical elements is given in the Fig. 3.

The outermost layer is rich in tin, oxygen and soil elements (mainly Si, Al, P, Ca, Fe and Cl). The soil elements show significant variations in composition for the same object, and also from one object to another. Only the Sn-content in the outermost layer was found roughly constant in a given patina, yet it varied from one sample to another. Ratios $(\text{Sn}/\text{Cu})_p$ and for the bulk alloy $(\text{Sn}/\text{Cu})_a$. The ratio between the two quantities,

$$\beta = \frac{\left(\frac{\text{Sn}}{\text{Cu}}\right)_p}{\left(\frac{\text{Sn}}{\text{Cu}}\right)_a} \quad (1)$$

was found to be $\beta = 18 \pm 4$ for all of the samples. Similar values had been obtained in the literature [7-9]. So it appears that a general behaviour exists for objects buried in moderate aggressive soils (loam or dry or calcareous soil) for different metallurgical and historical periods (from 1000 BC [8, 9] to 1000 AD [7]). The internal layer contains lower tin amounts than the outermost layer and no soil components. In this layer, the Sn/Cu varies strongly from one point to another.

Little information could be obtained from X-ray diffraction and infrared spectrometry results. The out-

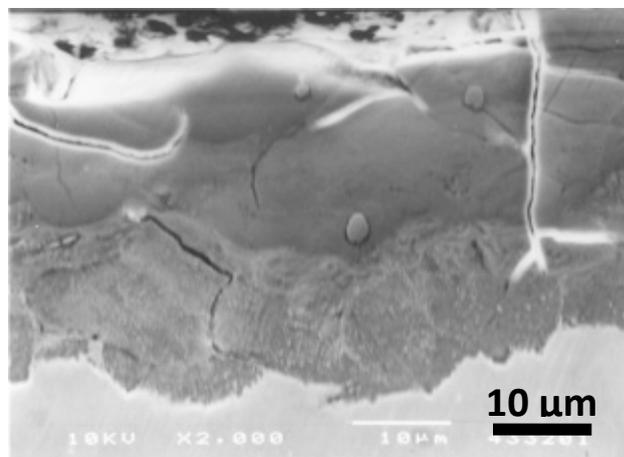


Fig. 2 Transversal microstructure of the passive layers. Inclusions within the passive layers and the alloy are copper sulphide inclusions (SEI). Bulk alloy is in bottom.

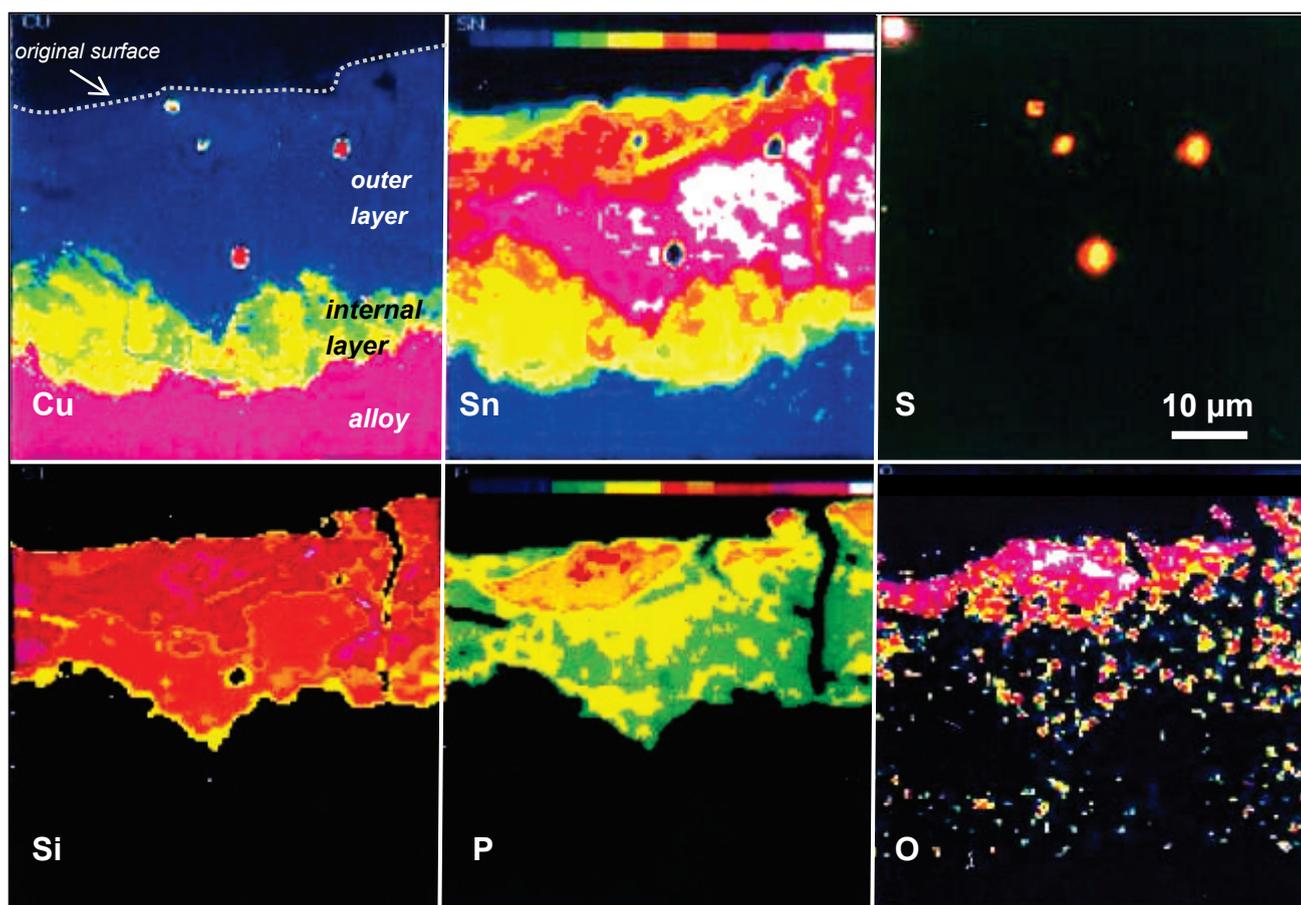


Fig.3 X-ray maps of the centre of the Fig. 2 (EDS: TRACOR™ – Ultrathin window)

ermost layer was amorphous and contained principally phosphate, silicate and hydroxyl groups under a non identified form. The products of the internal layer were difficult to isolate and no significant result could be interpreted. For both layers, it could only be assumed that the tin compounds are mainly amorphous hydrated tin oxides. It is known that tin (IV) oxide is thermodynamically stable over a large range of pH and potential values [10]. The copper compounds could not be identified as well-classified products, such as malachite, chrysocolle, libethenite..., as often encountered for corrosion copper products in bronzes [1,2,7,8].

The PCA on the outermost layers analysed by EDS is given in Fig. 4 for the two first principal components (72% of the PCA representation). PCA allows to attribute a relative weight to each participant (Si, P ...) to the growth of the layer. If the chemical species are in the same region of the diagram, they can be supposed to have the same contribution to the growth of the passive layer. Figure 4 reveals different groups of chemical elements. The group of the incorporated soil elements (Si, P, Fe and Cl) are in the same region of the diagram and are strongly correlated, *i.e.* these ele-

ments have a similar contribution to the elaboration of the outermost layer. For the constituents of the alloy, copper is unrelated as well as As and Ni, showing that the basic element of the alloy does not have the same contribution as the minor or traces elements in the formation of the protective layer.

The presentation of the results in the Fig. 4 shows different classes of analytical points which correspond more or less to the amounts of soil elements (Si, P, Cl, Fe) in the patinas. We can remark that the classes are related to the different colours of the outermost layer. The largest amounts of soil elements are encountered in the blue patinas, whereas bright grey surfaces have a higher copper content than the others. The exact nature of the species in which the soil elements are incorporated has not been investigated and remains an open question.

Consequently, there exist very important variations in soil species from one kind of patina to another. The soil compounds maintain the electroneutrality but anions and minor contents or traces of metallic cations do not directly interfere in the relative enrichment of the tin cations in the passive layers. The reaction between the soil products and the metallic cations is

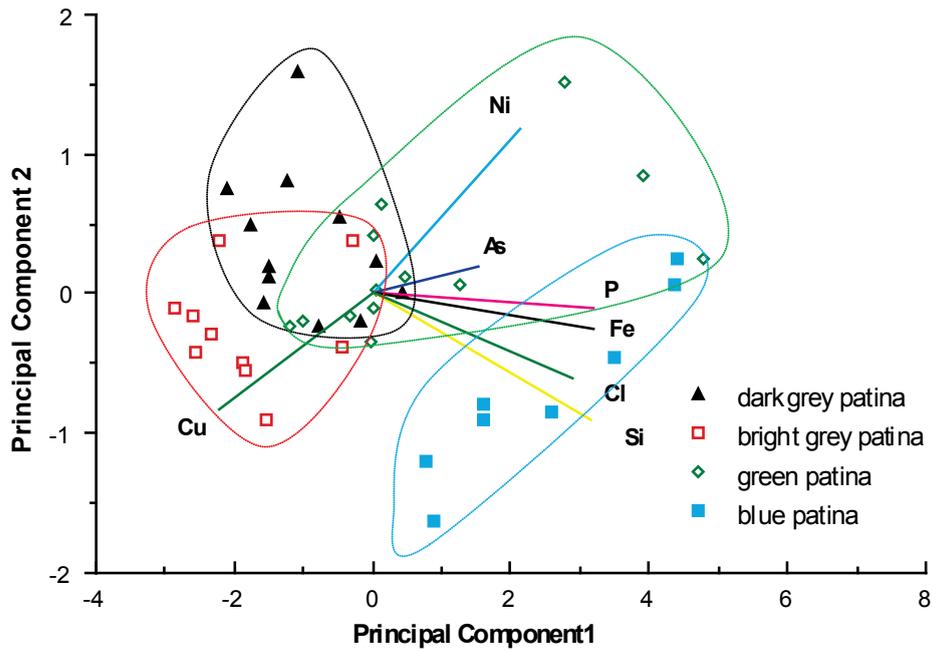


Fig. 4 Representation of the chemical variables and of the analysed points of the outermost passive layers. Principal components analysis.

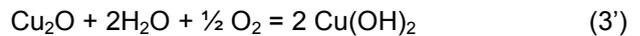
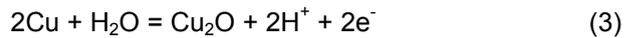
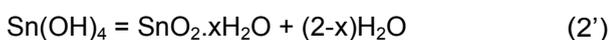
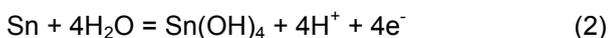
not the rate determining step in the attainment of the passive state.

5. Discussion

The excellent corrosion resistance of tin bronzes in moderately aggressive natural conditions can be attributed to the formation of highly resistant tin compounds. Hydrated tin oxides ($\text{SnO}_2 \cdot x\text{H}_2\text{O}$) are known to form amorphous gel like compounds. Furthermore, three important points appeared from the results:

- (1) The pseudomorphic replacement of the surface alloy by the passive layers,
- (2) The same β value (eq. 1) for all the patinas, and
- (3) The large variation of soil components in the passive outermost layers.

Consequently, the high Sn amount in the passive layers can only be explained by Cu selective dissolution (decuprification). The soil components (mainly silicates and phosphates) do not seem to affect directly the process of the selective dissolution of the copper and the relative tin enrichment: their incorporation into the patina could be a second step in the formation of the passive surface. It can be assumed that the process leading to the oxidation of tin and copper is:



The process involved is in fact an internal oxidation of tin and copper: the relative Sn enrichment in the outermost passive layer could be due to both the higher mobility of copper cations and the greater stability of the tin oxide in the layer.

For homogeneous binary alloys in the stationary state, the approach of Kirchheim offers to explain the atomic fraction of the components in the passive layer and in the alloy [11], assuming that the composition of the subsequent layers depends on the diffusivities of the cations. In the passive state the average atomic fractions of the components can be estimated from the following formula for a binary alloy A_xB_{1-x} [12]:

$$\frac{X_p}{1-X_p} = \frac{X_a}{1-X_a} \frac{D_B}{D_A} \exp \frac{(\alpha \cdot (Z_B - Z_A) \cdot s \cdot F \cdot E')}{R \cdot T} = \beta \frac{X_a}{1-X_a} \quad (4)$$

where X_p is the atomic fraction of the component in the passive layer and X_a in the alloy, D and Z are respectively the diffusivity and the valency of the cation components A or B. α is the transfer coefficient, s the jump distance of the cation and E' the electric field within the film.

In the case of bronzes, $A = \text{Sn}$ and $B = \text{Cu}$. Figure 5 shows the results of measurements of the average composition of the tin atomic fraction in the passivating patina $X_{\text{Sn},p}$ as a function of that in the alloy

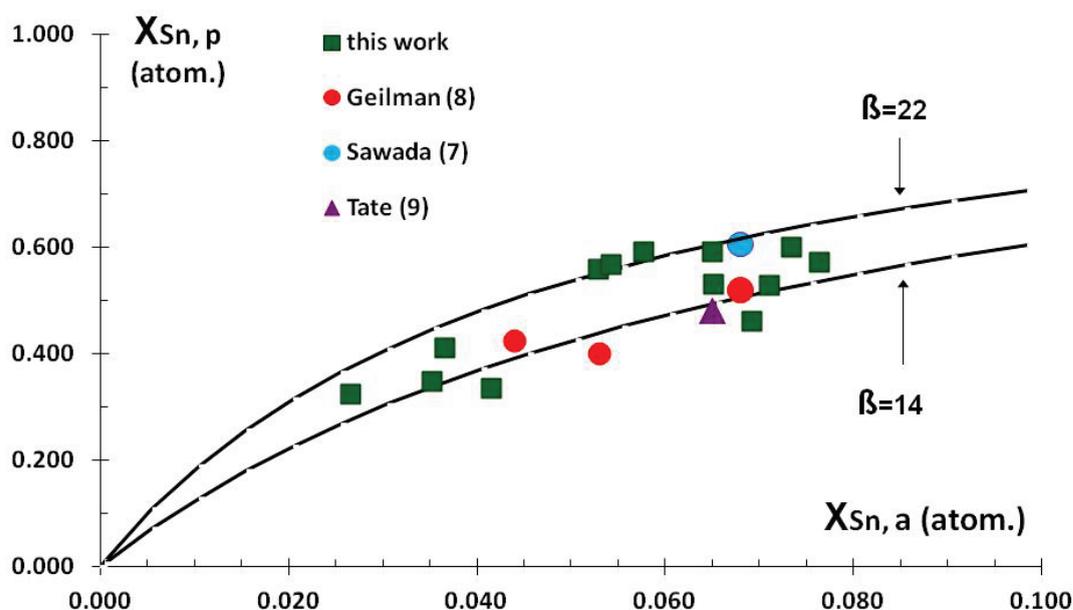


Fig.5 Fraction of tin cation in passivating film ($X_{Sn,p}$) as a function of the tin fraction in the alloy ($X_{Sn,a}$) for various studied bronzes. The solid lines are calculated using eqn (4) with $\beta = 14$ and $\beta = 22$.

$X_{Sn,a}$ using data from this work and from [7-9]. Assuming that the soil and minor metallic elements do not play a major role in the selective dissolution of copper, the atomic fraction X_{Sn} has been calculated as:

$$X_{Sn} = \frac{1}{1 + \frac{M_{Sn}}{M_{Cu}} \frac{Y_{Cu}}{Y_{Sn}}} \quad (5)$$

where Y_{Cu}/Y_{Sn} is the ratio of the mass percentages and M_{Sn} and M_{Cu} respectively the atomic mass of tin and copper.

The full lines in Fig. 5 give the theoretical curves corresponding to $\beta=14$ and $\beta=22$. The large relative Sn enrichment in the passive outermost layers is consistent and may agree with the Kirchheim's model for single phase alloys ($X_{Sn,a} < 0.085$).

In order to approximate the D_{Cu}/D_{Sn} ratio in the stationary state, we used $Z_{Cu} = +2$ and $Z_{Sn} = +4$, $\alpha = 0.5$, $s = 10^{-8}$ cm and $E' = 5.10^6$ V/cm which are in a range of reasonable values [12]. Equation (4) gives:

$105 < D_{Cu} / D_{Sn} < 170$, confirming a much higher diffusivity of copper cations than that of tin cations.

6. Conclusion

The excellent resistance of Cu-Sn alloys in a moderately aggressive soil is based on the beneficial role of tin in the alloy. The structure of the passive 'surface' is of the bilayer type. The microstructural characterisation and the elementary analysis indicated that the main corrosion effect is the selective dissolution of copper into the soil with a relative

enrichment in tin cations within the passive layers. The process is similar to an isomorphic one with internal oxidation. Tin atomic fraction within the outermost passive layer of archaeological bronzes was found to agree with the theoretical prediction of the Kirchheim model describing passive films formed on homogeneous alloys.

References

1. R. G. Gettens, 'Patina noble and vile' in Art and Technology: a symposium on classical bronzes, MIT Press, Cambridge MA, 1970, 57-72.
2. L. Soto, J. P. Franey, T. E. Graedel and G. W. Kammlott, Corros. Sci., 23, 241-250, 1983.
3. L. Robbiola, I. Queixalos, L. P. Hurtel, M. Pernot and C. Volfovsky, Stud. in Conserv., 33, 205-215, 1988.
4. M. Romanoff, Underground Corrosion, NBS Circular N° 579, Washington DC, 1957.
5. D. Hanson and T. Pell-Walpole, Chill Cast Tin Bronze, Edward Arnold & Co, London, 1951.
6. E. R. Minkowski, Factor Analysis in Chemistry, 2nd Edn, John Wiley, New York, 1191.
7. M. Sawada, in Bull. of the 30th anniversary, Nara Cultural Properties Research Institute, Japan, March 1983, 1221-1232.
8. W. Geilmann, Die Naturwissenschaften, 37, 97-102, 121-128, 1950.
9. J. Tate, Nucl. Instr. and Meth., 168, 20-23, 1986.
10. M. Dogrowska, H. Menard and L. Brossard, J. Appl. Electrochem., 21, 84-90, 1991.
11. R. Kirchheim, B. Heine, H. Fischmeister, S. Hoffman, H. Knote and U. Stolz, Corros. Sci., 29, 899-917, 1989.
12. M. Janik-Czachor, Corros. Sci., 33, 1327-1328, 1992.