Basic Structure of Passive Layers of Cu-Sn Alloys Applied to Patinas of Archaeological Bronzes

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1. INTRODUCTION

The passive bronze corrosion structures have been characterized on numerous single-phase archaeological bronzes from Late to Early Bronze Age period (1500-900 BC), from metallographical examinations of cross-sections of artifacts. This paper focuses on the microstructure and the elementary composition of the passive patinas by SEM and EDX analysis (ultrathin window). A basic structure of the protective patinas is first described, then, deviations to the standard model are given. This model of passive structure and its deviations well agree with observations of archaeological bronzes stemming from other historical and geographical periods (Swann et al. (1992), Meeks (1993)).

2. BASIC STRUCTURE OF THE PASSIVE PATINA

In natural aqueous corrosive environments (pH between 3.5 to 9, redox potential in the range of -200mV to +400mV/ENH), Cu-Sn alloys can form a passive corrosion structure which preserves the limits of the original bronze surface (Robbiola et al. (1993)). The external aspect of such a protective patina is a shiny lustrous surface with different possible colours (blue, grey, dark-green...).

From cross-section examinations, the structure is a two-layer one, whose thickness may vary between 5 and 70 µm (Fig. 1):

- an outermost layer, characterized by high Sn/Cu ratios and by the presence of elements from the corrosive environment such as O, Si, Al, P, Fe, Cl and Ca,
- an internal layer in contact with the alloy, irregular in shape and thickness, which has lower Sn/Cu ratios than in the outermost layer, but higher ratio than in the alloy and only oxygen element. From microstructural examinations, it appears that the passive structure has been formed without apparent volume change. In accordance with previous results (Robbiola et al. (1994)), the process of formation can be attributed to internal oxidation of tin in relation with copper selective dissolution. Furthermore, tin atomic fraction in the outermost layer seems to depend on the aggressive character of the corrosive environment and on the Sn/Cu ratio of the alloy .

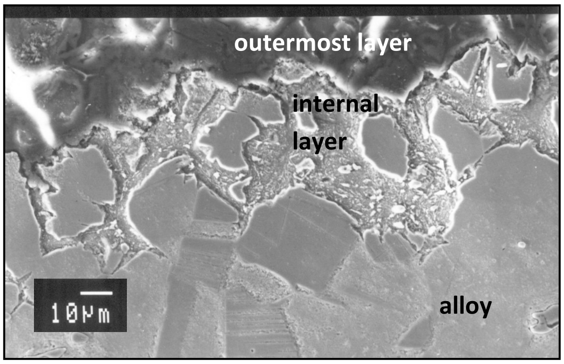
3. DEVIATIONS FROM THE BASIC STRUCTURE

From metallographical examinations, sorne discrepancies between the basic model and observations may be encountered (Fig.2). These deviations can be classified into three groups which are summarized in Figure 3.

a° The first group of deviation is characterized by the presence of an outer crust or deposit (often more than 300 µm thick) on the outermost layer. Analysis of deposits mainly revealed copper corrosion products such as cuprous oxide (cuprite) and/or cupric compounds (such as hydroxycarbonates or hydroxysilicates). The deposit formation can be related to the stabilization of copper products on the surface following the leaching of the copper ions from the alloy, in relation with the environment composition.

b° The second type of deviation corresponds to a modification of the corrosion layers due to localised extension of internal layer into the alloy or internal cracks. The extension of the internal layer is accompanied by the presence of corrosive species, notably chloride anion which are known to be important in localised corrosion. The cracks could be related to numerous factors such as internal stresses inside the corrosion layers, ageing of the corrosion compounds ... Furthermore, they may, in some cases, go in contact with the corrosive environment (aqueous electrolyte) giving rise to localised breakdown of the outermost layer.

c° The third type of deviation corresponds to an attack at the layer/alloy interface, due to an internal or transgranular attack strongly related to an internal oxidation process (diffusion short-circuits).



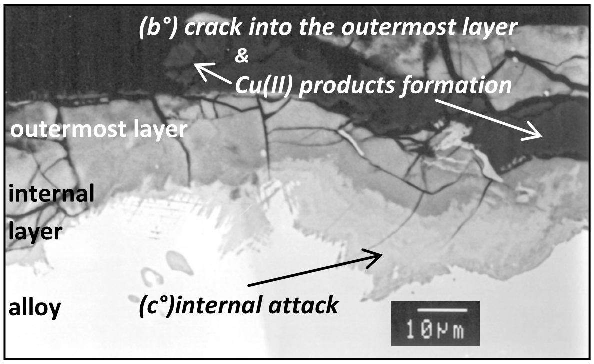


Figure 1 (Left): Bronze Age needle, structure of a protective patina (etched cross-section - SEM examination) - the alloy is at the bottom, the outermost layer above)
Figure 2 (right): Cross-section of a Bronze Age pin, internal attack inside a protective patina.

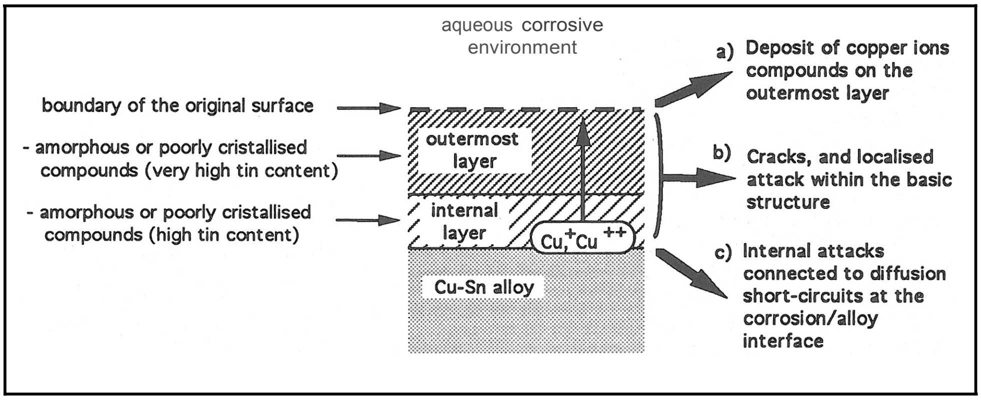


Figure 3: Schematic representation of the passive structure of bronze artifacts with the three groups of structural deviations: a) crusts or deposit on the outermost layer, b) internal localised attacks within the passive layers and c) attack at the corrosion layers/alloy interface.

Meeks N. (1993) Metal plating and patination (Butterworths-Heinemann, Oxford) pp 247-275.
Robbiola L., Fiaud C. (1993) Control of Copper oxidation (Ed. de Revue Métallurgie, Paris) pp 157-162.
Robbiola L., Fiaud C., Harch A. (1994) Modifications of passive films (Institute of Materials, London) pp 150-154.
Swann C., Fleming S., Jaksic M. (1992) Nucl. Instr. and Meth. B64, 499-504.