

Fabrication, microstructure and corrosive behavior of different metallographic tin-led bronze alloys part II: Chemical corrosive behavior and patina of tin-led bronze alloys



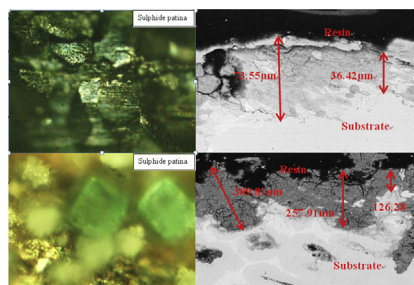
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HIGHLIGHTS

- Chemical formed patina on Cu–Sn–Pb bronze are characterized.
- Surface morphologies of cracks, pits and corrosion depth of multicolor patina are revealed.
- Different corrosion behavior and deterioration rate by aggressive environments are discussed.
- Schematic sketch/model to elaborate corrosion phenomenon is investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 July 2015

Received in revised form

25 October 2015

Accepted 26 November 2015

Available online 10 December 2015

Keywords:

Alloy

Corrosion

Raman spectroscopy

Powder diffraction

SEM

EDAX

ABSTRACT

This paper presents the chemical corrosion behavior and surface morphologies including cracks, pits and corrosive-depth of “patina” in the different metallographic Cu–Sn–Pb bronze alloys by the trace amounts of S^{2-} , SO_4^{2-} , NO_3^- , Cl^- and CO_3^{2-} aggressive environments. Typical patinas have been formed as brochantite patina ($Cu_4SO_4 \cdot (OH)_6$) by SO_4^{2-} solution with 46–144 μm corrosion depth, atacamite patina ($Cu_2(OH)_3Cl$) by Cl^- solution through many subsequent “dissolution-ion pairing-precipitation” steps with 15–70 μm corrosion depth, gerhardite patina ($Cu(NO_3)(OH)_3$) by NO_3^- solution with 0.3 μm corroded layer, gerhardite or lead nitrate ($Pb(NO_3)_2$) or malachite ($Cu_2(OH)_2CO_3$) patina by CO_3^{2-}/NO_3^- solution as 390 μm depth of corrosive layer, atacamite $Cu_2Cl(OH)_3$ along with cuprite (Cu_2O) and cersite (SnO_2) patina with 11–390 μm multilayered corrosive crust by CO_3^{2-}/Cl^- solution, and a mixed black patina of brochantite, brendtite (SnS_2), roxbyite (Cu_7S_4) by S^{2-} solution with 34–256 μm corrosive depth. Among all environments, the deterioration rate is evaluated as order of $S^{2-} > CO_3^{2-}/Cl^- > Cl^- > CO_3^{2-}/NO_3^- > SO_4^{2-} > NO_3^-$. The minor bronze disease is observed in highly tin-contained alloys (>19%), while the amount of lead in alloy exhibits no specific role in corrosion. Based on these results, the phenomenological models of corrosion behavior due to an internal oxidation, ionic migration and de-alloying of “a protective barrier” are proposed.

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1. Introduction

Bronze is one of the most metallic alloys for manufacturing historical monuments or used in architectural elements [1]. Tin is used to increase the hardness while lead is used to increase

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pourability. However, bronze often gets corroded in an aggressive environment after a long time burial to form a colored crust [2], and generally appears as a brownish-green or greenish-blue crust, which is normally defined as “patina” or called as “bronze disease” [3]. Actually, the corroded ancient bronze-made artifacts often hide peculiar degradation processes and corrosive phenomenon symbolized as the first visual clue to the metal type and the chemical environment [4]. It is reported that the main constituents of the green-colored patina are copper salts, such as malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ (in soil), brochantite $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_3$ (in the atmosphere) or atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (in sea-water), covering a red cuprous oxide layer in contact with the metal core of the alloy [5,6]. The tone of green is darkened by the presence of copper sulphide or lead but lightened by lead carbonate or tin-oxide [7]. Furthermore, in a Cu–Sn bronze, especially in the comparative tin-rich bronze, the brownish patina is confirmed to be more stability than greenish patina due to the low solubility and high stability of tin species letting the tin ions to linger in the patina [6]. Both chemical methods (in a sulphate solution and a chloride one) and electrochemical process (in a sulphate/carbonate solution) can produce bluegreen patina. The sulphate patina is composed essentially of brochantite $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_3$ or $\text{Cu}_4\text{SO}_4 \cdot (\text{OH})_6$ [7–10], the chloride patina of atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, and the electrochemical patina of malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$. All three patinas have also a smooth part of surface consisted of cuprite Cu_2O [11].

However, the corrosion behavior of leaded-bronze alloys shows that the composition of patina depends on the concentration of Cu, Sn and Pb in each alloy, and the corrosion resistance decreases with decreasing copper content [12]. In the corrosion process of Cu–Sn–Pb bronze, tin has a prodigious influence by oxidizing firstly developing a passivating tin-oxide layer. This protective layer somewhat inhibits copper dissolution from the alloy, in comparison with pure copper [13,14]. Therefore, it has been concluded that a two-layer structure is mostly formed in the bronze patina: an outermost layer is generally consisted of Cu (oxide (copper (I) oxide, cuprite) and chlorides (atacamite)) and lead (Pb) compounds (oxide, sulphates and carbonates), and an inner layer is enriched in Sn products [15–17], as Sn is not dissolved in the environment and the tin-compounds remain in the inner layer as an insoluble product (like hydrates) while lead remains insoluble in the form of small globules [11,18]. It has been proved that the kinetics of bronze oxidation is governed by diffusion through a porous layer which forms at initial exposure and grows as time of exposure increases the bronze in an alternating immersion in artificial acid rain [19]. While, the kinetics of bronze oxidation for zinc-leaded bronze is governed by diffusion through a two-layer patina: an inner Sn-rich layer and an external Cu and Pb-rich layer [19]. The corrosion rate of the alloy decreases with time, but the dissolution of individual metals in the environment shows progressive patina destabilization. By comparison to the relative initial proportion of the metal elements in the alloy, Pb corrodes preferentially [19]. Sometimes, in the deeper part of corrosion layers, lead shows a great trend variability due to the different natures of the analyzed areas (greenish or brownish), tin concentrations seem to increase through the thickness of the patina and, on the contrary, copper concentrations assume an almost constant value [19]. A superficial soil derived crust may be cerussite (PbCO_3), cuprite (Cu_2O), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), litharge (PbO) and soil derived products (goethite ($\text{FeO}(\text{OH})$) and quartz (SiO_2) [20]. The corrosion behavior of high-leaded bronze of Chinese archaeological bronzes shows intermediate steps of degradation. The sequence leading to corrosion of lead globules consists in a direct substitution of lead corrosion products by cuprite [21]. It can be found that all above related researches are attempted to define the corrosion processes of bronze. But, up to now, there is still unknown about the actual nature of

corrosion and about the processes governing the formation of the corroded structures [8,9]. Therefore, it is essential to give a methodical study on different bronze alloys.

The aim of this paper is to recommend an appropriate procedure for the corroded surface study of binary (Cu–Sn) and ternary (Cu–Sn–Pb) bronze alloys, and to understand the corrosive behavior or growing pattern by focusing a deeper insight into the chemical patina. The corrosive products of “patina” by the trace amounts of S^{2-} , SO_4^{2-} , NO_3^- , Cl^- and CO_3^{2-} are investigated using optical microscopy (OM), scanning electron microscopy coupled with EDAX (SEM-EDAX), X-ray diffraction (XRD) and Raman spectroscopy (RS), in order to reveal which chemical ion ruins much to bronze, which patina has high corrosive rate to bronze, what is the real roll of lead (Pb) playing in corrosion process and which metallic composition leads to fatal erosion. On the other hand, the formation of a passive deposition due to an internal oxidation with a decuprification process, ionic migration in the substrate and de-alloying “a protective barrier” is discussed. Surface morphologies including cracks, pits and multicolor patina are revealed. Current investigation enabled us to describe the *multiplex* corrosion chemistry of binary Cu–Sn and ternary Cu–Sn–Pb alloys and to figure out the corrosion and deterioration mechanism in various aggressive environments.

2. Experimental

2.1. Preparation of bronze alloys

The binary (Cu–Sn) and ternary (Cu–Sn–Pb) bronze alloys of required quality were fabricated by using two novel approaches of argon purged furnace (APF) and plasma arc chamber (PAC) methods in order to avoid air impurities and the sojourn of the superficial oxide layering.

2.1.1. Plasma arc chamber (PAC)

PAC alloy was synthesized in a highly inert atmosphere controlled by high precision SCR (Silicon Controlled Rectifier) digital controller with accuracy $\pm 1^\circ\text{C}$ and 30 segments programmable up to 1700°C . The mixed elemental powders with definite weight ratios (total 8 APF alloys named as PAC 1–8, same of them were given in Table 1) in the ceramic crucibles were placed in the center of alumina tube furnace with constant argon purging. The maximum temperature of the furnace was set at 1150°C with a constant increment of 10°C per minute from its startup. It turned off automatically after staying 30 min at targeted temperature and cooled down slowly in the same inert atmosphere for 10–12 h in order to avoid bubbling during alloying.

2.1.2. Argon purge furnace (APF)

APF alloy was prepared in a constant stream of argon gas (Ar, 99.9999% purity) as plasma generating gas at the rate of $0.3\text{--}0.4\text{ mL s}^{-1}$. Plasma chamber (27.12 MHz) was used for melting of materials at $T_M < 3400^\circ\text{C}$ and 6500 K temperature. The mixed elemental compositions (total 9 PAC alloys named as APF 1–9, same of them were given in Table 1) were to put in numbered cuvettes of alloying plasma reactor. When the alloying chamber was cagily closed and degassed by a rotary vacuum pump, then argon gas was purged very slowly ($\sim 0.5\text{ Pa}$) and flushed out. This process was repeated thrice to ensure complete air evacuation. This was further vivified up to 10^{-4} to 10^{-5} Pa by using ultra-molecular vacuum pump for 1 h. Plasma arc holder was manually moved to each cuvette to fuse elemental specks mixture into a stunning alloy.

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