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Full Length Article

# Formation of black patina on an ancient Chinese bronze sword of the Warring States Period

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ABSTRACT

In general, black patina is formed upon the surface of the ancient bronze mirrors. Recently, a kind of black patina is found on an ancient bronze sword, which was made 2500 years ago during the Warring States Period of China. In this paper, chemical compositions and microstructures of the black patina were characterized by using instruments including optical microscope (OM), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD) and Raman spectrometer (Raman). The results revealed that the formation of the black patina on the bronze sword is due to two reasons: (1) high tin (Sn) content reaches to 22.92 wt%; (2) damp, wet and acid burial environment. Therefore, it conforms to the natural corrosion formation mechanism, i.e., after selective dissolution of elements Cu and Pb from the matrix, element Sn was oxidized and then, the gel-like $SnO_2{\cdot}xH_2O$ filled the vacancies left by the selective corrosion of Cu and Pb. This work will be helpful for better restoration and preservation of the bronze cultural relics.

## 1. Introduction

Black patina is a kind of film with a glossy and smooth crystal jade texture, which usually exists on the surface of the unearthed ancient Chinese bronze mirrors. In general, patina exhibits excellent corrosion resistance. Many studies have been conducted on the formation mechanism of black patina, and current theories can be divided into two categories, i.e., natural corrosion mechanism [1–3] and artificial treatment mechanism [4,5]. Focus of the debate is whether this Sn-rich corrosion resistant layer was formed by artificial tinning treatment or selective corrosion in natural environments.

According to the natural corrosion mechanism [1–3], the patina formation is a process from outside to interior of an ancient bronze mirror. In burial environment metal copper (Cu) and tin (Sn) were firstly oxidized into cuprite ($Cu_2O$) and tin dioxide ($SnO_2$). Because $Cu_2O$ was prone to dissolve in the soil, and then the selective corrosion occurs, while $SnO_2$ stably remains, which resulted in formation of a dense $SnO_2$ layer, and can protect the bronze mirrors from further corrosion. In addition, the gel-like hydrated stannic oxide ($SnO_2{\cdot}xH_2O$) filled the vacancies in time, which were left by the selectively corroded metal Cu, and finally formed a dense Sn-rich black patina layer [1,3,6–8].

However, some researchers proposed a different point of view, i.e., for purpose of beauty, the ancient Chinese bronze mirrors will be firstly tinned for getting a silvery color, and then the patina was formed due to the further natural corrosion during long-time conservation. This is the so-called artificial treatment mechanism [4]. This mechanism is based upon a viewpoint that after the Warring States Period of China, most of the bronze mirrors generally had a tinning treatment on the surface, because Sn exhibits a silver and sparkling color. It is believed that mercury amalgam tinning method has been used for this treatment. The possible tinning process includes: (1) cleaning the mirror surface; (2) preparing the tin amalgam according to a formula and applying to the surface; (3) heating for vaporizing mercury and at last polishing the surface. When these mirrors underwent a natural corrosion in a long conservation or buried time, the superficial metal Sn was oxidized and formed a dense Sn-rich patina layer. Consequently, tinning and further natural corrosion are the two basic factors of this mechanism.

Huanggang City is located in the eastern part of Hubei Province, south of the Dabie Mountain and on the north bank of the middle reaches of the Yangtze River, China. As a historical and cultural city, it has been defined by its multi-culture. Therefore, it is of special significance to study the ancient bronze wares unearthed in this area. In this paper, the formation mechanism of black patina on the surface of a bronze sword was studied, and its chemical compositions, microstructures and morphologies were characterized systematically. Due to

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**Fig. 1.** Image of the bronze sword.

different fabrication processes, black patina on this ancient bronze sword exhibits different formation mechanism from the bronze mirrors. And it will also provide a proof for solving the dispute over the formation mechanism of black patina on the ancient bronze mirrors. Furthermore, it will be of significance for archaeology and protection of the ancient bronze swords.

## 2. Materials and methods

Fig. 1 shows the sword with black patina on the surface. It was excavated from No.14 tomb of Wangjiachong, Huangzhou district, Huanggang city, Hubei province, China. According to archeological typological comparison and coexistence relationships of the other artefacts, it is considered to be fabricated during the Warring States Period (453-221BCE) of China. However, this bronze sword looks distinctly different from the other ordinary bronze swords in the same period. It is covered with a smooth, transparent and jade-like film and exhibits black color with gloss, which is the typical patina characteristics.

The cross-section sample was cut along the edge of the sword fragment, and then mounted, grounded, and polished according to standard metallographic procedures. Microstructural observations and chemical composition analysis were carried out by using optical microscope (Leica DVM6, Germany) and scanning electron microscope (SEM, Phenom XL, Netherlands), which is equipped with an energy disperse spectroscopy (EDS), and operated at 15 kV. The crystalline phases were measured by using a X-ray diffraction spectrometer (XRD, D8 Advance XRD, Bruker AXS, Germany) with Cu Kα source and scanning speed 4°/min in a range of 20–90°, and Raman spectrometer (LabRAM HR, Horiba Jobin Yvon, France) with conditions involving 1000× objective lens, spot size 1 μm in diameter of the laser at the sample, 488 nm laser excitation, 10mW laser power and 300 μm slits.

## 3. Results and discussion

### 3.1. Microstructures of the black patina

Fig. 2 shows optical metallographic images of the sword. Obviously, the sword body was of typical casting microstructures, i.e., it was mainly composed of fine α dendrites with many (α + δ) eutectoid structure which were homogeneously existed between the dendrites and the isolated Pb particles [9]. Some very small black dots were porosities which were generated during casting.

Fig. 3 shows the cross-section optical microstructures of the patina layer. It could be seen that the black patina consisted of two layers: (1) a completely mineralized outside layer with approximately 100–150 μm thickness; (2) a partially mineralized intermediate transition layer with approximately 60–80 μm thickness. This patina morphology was similar to the observations of the ancient bronze mirrors [8,10]. In the transition zone, it was found that the α dendrites had been completely corroded and transformed into a kind of green corrosion product, while the δ phases were remained un-attacked. In addition, adjacent to the matrix of the sword body, there were some corrosion products of orange. Further SEM observations revealed that at the interface between the intermediate transition layer and the sword origin matrix, the α phases (low Sn content) were corroded firstly and then the corrosion moved forward along the α phases to the sword body matrix, as shown in Fig. 4.

Table 1 lists the chemical compositions within each zone and portion. The results indicated that: (1) The bronze sword was made of Cu-Sn-Pb alloy; (2) Besides the main alloys, the completely mineralized outside layer also contained impurity elements including O, C and Si, etc.; (3), In the intermediate transition layer, it was found that the replacements of α phase and δ phase exhibited quite different compositions, i.e., the replacements of α phase contained high level Sn, and its atomic ratio of elements Cu, C and O is close to the corrosion product malachite ($CuCO_3{\cdot}Cu(OH)_2$), while Sn content in the replacements of δ phase is 35.9 wt%, which is close to its original value [11]; (4), Along the cross section, the Sn content increased gradually from the inside to the surface, while the Cu content showed an opposite variation, as shown in Fig. 5; (5) The decrease speed of the Cu content and the increase speed of the Sn content in the α phase was faster than that in the δ phase, as shown in Fig. 6.

XRD measurements revealed that the main phases in the patina including tin dioxide ($SnO_2$), malachite ($CuCO_3{\cdot}Cu(OH)_2$), lead oxide (PbO), and the residual δ phase, as shown in Fig. 7. The weak diffraction peaks illuminated low crystallization degree of theses phases. Further quantitative analysis indicated that the black patina contained 49.43 wt% $SnO_2$, 38.15 wt% $CuCO_3{\cdot}Cu(OH)_2$, 5.97 wt% PbO and 6.45 wt% δ-bronze, which were almost coincident to the EDS data. According to the Scherrer formula at diffraction angle 26.6° with a 1.5° half-width, the $SnO_2$ grain size was 5.4 nm, which was in good consistent with TEM observation of bronze mirrors by Wang et al. [12].

Fig. 8 illustrates the Raman spectra of different zones within the black patina. The results displayed that: (1) In the completely mineralized layer, the peak of the nano-sized $SnO_2$ was appeared at 572 $cm^{-1}$ [13–15], as shown in Fig. 8(a). Its wide and asymmetric peak shape was related to the impurities or defects. (2) In the orange area adjacent to the sword matrix, the peaks at 50 $cm^{-1}$, 217 $cm^{-1}$, 397 $cm^{-1}$, and 630 $cm^{-1}$ were attributed to $Cu_2O$ [16,17] , as shown in Fig. 8 (b). (3) In the intermediate layer, the peaks at 154 $cm^{-1}$, 180 $cm^{-1}$, 219 $cm^{-1}$, 270 $cm^{-1}$, and 432 $cm^{-1}$ came from the vibration of Cu—O bond; the peaks at 1493 $cm^{-1}$, 1100 $cm^{-1}$, 1067 $cm^{-1}$, 1367 $cm^{-1}$, and 750 $cm^{-1}$ belonged to the carbonate ($CO_3^{2-}$), and the peaks at 3313, 3378 $cm^{-1}$ were due to the stretching of O—H bond in the replacements of the α phase [18] , as

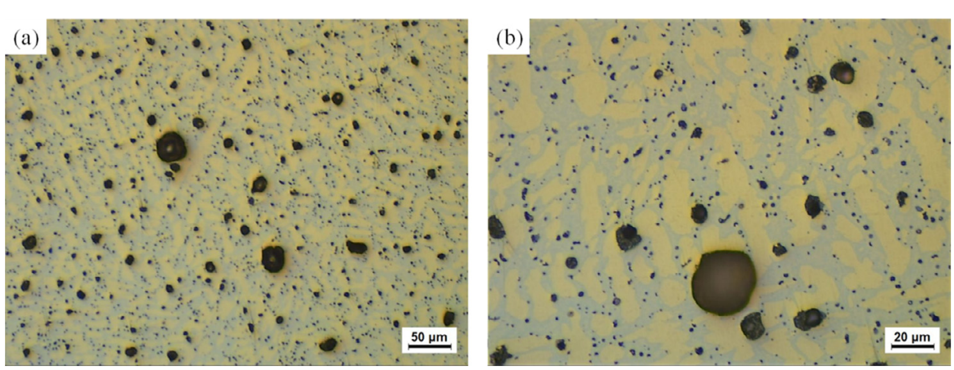


**Fig. 2.** Optical microstructures of the sword body: (a) low magnification; (b) high magnification.