Research Article

Preliminary Study of Corrosion Status on Bronzes Excavated from Qin Dynasty Tombs at Xinfeng Town in China

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From 2007 to 2008, many bronze wares of Qin Dynasty were excavated from tombs at Xinfeng town. Being an important finding, these bronze wares attracted people's attention, especially for their conservation. Therefore, the corrosive products were explored by using Scanning Electron Microscope with Energy Dispersive X-ray Detector (SEM/EDS), X-Ray diffraction (XRD), and Raman spectroscopy (RM), which provided much valuable information on the conservation of these bronze wares. According to tested results, the corrosive products of bronzes were found to be comprised of cuprite (Cu_2O), covellite (CuS), lead carbonate (PbCO_3), and malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). Meantime, the multilayer corrosive structure was found in some samples due to the cracks in Cu_2O layer which had formed many microchannels to promote the material migration.

1. Introduction

From 2007 to 2008, about six hundred Qin Dynasty tombs were unearthed by archaeologists at Xinfeng town in Xi'an city, Shanxi province, China. It was reported as a significant archaeological excavation to dig out the largest number and scale of the Qin tombs in the central Shaanxi plain [1].

The site located south shore secondary tableland of Wei He River which was a domicile named as "Xiyi" where ceramics craftsman had once lived to build Qin Shi Huang Mausoleum [2].

A lot of bronzes were unearthed from these tombs, such as bronze ding tripod, bronze dou, bronze hu, and arrow, many of which were broken and in severe corrosion [2]. The bronzes are ternary alloy with the element of Cu, Sn, and Pb that would be in different corrosive situation after a long buried time [3]. In general, people had always research the corrosive mechanism of ancient bronze by analyzing on corrosive products or doing the simulated experiments [4, 5]. The analysis of corrosive products will supply important information to protect them and also provide important

reference to research their corrosive mechanism. This paper studied the corrosive products from the bronze fragments by Scanning electron microscope with energy dispersive X-ray detector (SEM/EDAX), X-Ray diffraction (XRD), and Raman spectroscopy (RM) and revealed the corrosive situation and mechanism on them.

2. Samples and Methods

2.1. Test Samples. In this paper, eight samples from different bronzes were studied, as shown in Table 1. All of them were collected from bronze fragile pieces, whose section was dealt with coarse grinding and polishing before the experiment.

2.2. Instrumentation. The cross-section morphologies were examined by a digital optical microscope (Keyence, VHX-600 K, Japan), which has large depth of field and was equipped with a 3CCD camera about 54 million pixels. X-ray diffraction (XRD) was obtained in a Rigaku D/Max-3C X-ray diffractometer, equipped with a Cu $K\alpha$ radiation

TABLE 1: The record of test samples collected from bronze fragile piece at Xinfeng town.

Number	Tombs/Implements	Sample site	Time	Location
Sample 1	M274/bronze <i>hu</i>	Abdomen	Qin	Xinfeng town
Sample 2	M83/bronze <i>ding</i>	Bottom	Qin	Xinfeng town
Sample 3	M691/bronze <i>ding</i>	Bottom	Qin	Xinfeng town
Sample 4	M301/bronze <i>ding</i>	Bottom	Qin	Xinfeng town
Sample 5	M55/bronze <i>ding</i>	Bottom	Qin	Xinfeng town
Sample 6	M268/bronze <i>hu</i>	Abdomen	Qin	Xinfeng town
Sample 7	M04/bronze <i>hu</i>	Abdomen	Qin	Xinfeng town
Sample 8	M256/bronze <i>pen</i>	Edge	Qin	Xinfeng town

FIGURE 1: Section photomicrograph of bronze samples.

source ($\lambda = 0.154056 \text{ nm}$) in the 2θ range from 10° to 70° , tube voltage 40 KV, current 40 mA. A FEI-Quanta 200 environment scanning electron microscopy (SEM) equipped with an X-ray energy dispersive spectroscopy (EDS) was used to research samples, which were examined in the high-vacuum mode and low high-vacuum mode at an accelerating voltage about 20 kV. Roman spectra were attained by a microscopic confocal Raman Spectrometer (Renishaw in via Plus, England) employing a 514 nm laser beam excited by argon ion laser with information collection time about 10 s and accumulation time about 3~5 s.

3. Results

3.1. Optical Microscope Analysis. The cross section of samples indicated that these bronze fragile pieces were a serious corrosion, as shown in Figure 1. Many samples had similarly corrosive situation, such as sample 1, 3, 4, 5, 6, 7, and 8, which had outer green rust layer and inner red rust layer [6]. Specially, the section of sample 2 demonstrated a multilayer dust, which had the existence of alternate red and green corrosive product layer.

3.2. Backscattered Electron Phase and Component Analysis. After samples were inlaid into Acrylic resin, they were dealt with surface grinding and polishing. Then sample 1, 2, 3, and

6 were analyzed by SEM/EDS, whose electron images were attained by backscattered electron and elementary content were detected by X-ray energy dispersive spectroscopy (EDS), data as shown in Table 2.

There are four scanning area of sample 1, such as Area-1 to Area-4, as shown in Figure 2. The result indicates that Area-1 and Area-2 were outer layer of corrosion with complex component, especially with high content of C and O element, which revealed that the surface layer of sample had been corroded. Meantime, the backscattered electron images of Area-3 take on a white look which due to PbCO_3 according to the high content of some element as 20.53% C 12.4% O and 67.07% Pb. The analyzed Area-4 revealed that a significant amount of 83.63% Cu and 16.37% Sn, which should be remnant α -phase in bronze alloy.

For sample 2, four areas were analyzed about Area-5 to Area-8, as shown in Figure 2. The analyzed Area-5 is middle area of red corrosive product layer whose component is complex with 36.46% C, 43.55% O, 14.13% Cu, 5.29% Pb and 0.57% Si, which mean that the red corrosive product layer (Cu_2O) contains impurities. The complex composition of 27.48% C, 26.67% O, 3.74% Cu, and 42.11% Pb indicates that lead carbonate is main corrosive product in the other analyzed Area-6.

Five areas of sample 3 were analyzed, Area-7 is α -phase in bronze alloy with 86.61% Cu and 13.39% Sn; Area-8 is

TABLE 2: The content of composite element of samples (wt%).

	Element																
Area	C	O	Cu	Sn	Pb	Ca	Si	Al	S	As	K	Fe	Mg	Ni	Cl	Na	P
Area-1	18	52.79	26.08		2.67	0.46											
Area-2	19.17	31.19	18.46	22.35	7.15		1.25	0.42									
Area-3	20.53	12.4			67.07												
Area-4			83.63	16.37													
Area-5	36.46	43.55	14.13		5.29		0.57										
Area-6	27.48	26.67	3.74		42.11												
Area-7			86.61	13.39													
Area-8	8.69	5.86	54.28	31.17													
Area-9		20.07	79.93														
Area-10	16.61	6.08	57.82						19.5								
Area-11	11.34	22.08	27.26	16.55	16.66					2.42					3.69		
Area-12	26.07	4.77	69.16														
Area-13	15.82	45.55			2.04		21.79	7.94			5.89					0.97	
Area-14	23.24	34.74	5.99		24.49	1.47	4.43	2.11				1.57	0.63	1.34

FIGURE 2: SEM photograph of sample cross section and drawing of site of energy spectrum analysis area.

the remnant α - δ phase with 8.69% C, 5.86% O, 54.28% Cu, and 31.17% Sn; Area-9 is dull color area where is composed of 20.07% O and 79.93% Cu, which suggest the existence of copper oxide [7]; Area-10 is dark area with 19.5% S in which there are some copper sulfide; Area-11 shows white with complex composition and 16.66% Pb.

Sample 6 was analyzed in three areas from Area-12 to Area-14, as seen in Figure 2. In the Area-14, the high content of 24.49% Pb element was detected by EDS which is more than that in Area-13. In fact, Area-13 has complex component of 15.82% C, 45.55% O, 2.04% Pb, 21.79% Si, 7.94% Al, 5.89% K, and 0.97% Na which means this area is soil. On the other hand, Pb element wasn't found in the analyzed Area-12. It could draw a conclusion that element Pb has the trend of migration from the bronze alloy to the circumambient soil.

3.3. Secondary Electron Image of Sample 2. The secondary electron image of sample 2 showed obviously multilayer structure about corrosive layer, as seen in Figure 3. The zonal cuprite could be seen in the SEM image in which many cracks also were observed clearly.

3.4. Analysis of XRD. The XRD pattern of sample (Figure 4) showed that the peaks at 29.6° , 36.5° , 42.4° , and 61.5° can be indexed to Cu_2O (JCPDS Card No. 77-0199). Other diffraction peaks at 23.4° , 25.5° , 29.7° , 34.5° , 36.7° , 43.3° , and 49.7° can be indexed to PbCO_3 (JCPDS Card No. 03-0358).

3.5. Raman Spectrum. Different color corrosive product of cross section of sample 2 and sample 6 was analyzed by Micro-Raman spectroscopy. Figures 5(a) and 6(a) show

FIGURE 3: Morphology photograph of cross section of sample no. 2.

FIGURE 4: X-ray diffraction pattern of sample 1.

Raman pattern of patina from two samples which displayed vibration peaks at 1493 cm^{-1} (vs), 1051 cm^{-1} (vs), 431 cm^{-1} (vs), 266 cm^{-1} (m), and 177 cm^{-1} (s) due to malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) [8]. The red corrosive product demonstrates Raman vibration peaks at 636 cm^{-1} (s), 413 cm^{-1} (m), 213 cm^{-1} (vs), and 146 cm^{-1} (m) corresponding to cuprous oxide (Cu_2O) [9], as shown in Figures 5(b) and 6(b). Figure 5(c) shows Raman pattern of blue corrosive product from sample 2 with a vibration peak at 472 cm^{-1} (vs) due to copper sulphide (CuS) [10, 11].

4. Discussion

The analytical result of XRD indicates that two kinds of corrosive products existed in most collected test samples, which are Cu_2O and PbCO_3 . Actually, the signal of patina was not detected by XRD, which was confirmed by Raman spectroscopy as malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$).

(a)

(b)

(c)

FIGURE 5: Raman spectrum of corrosion of sample 2: (a) green particle; (b) red particle; (c) blue particle.

Cuprite (Cu_2O) is one kind of common corrosive products of bronze wares that underground burial environment [12, 13] that would form a tough red layer on the surface of

FIGURE 6: Raman spectrum of corrosion of sample 6: (a) green particle; (b) red particle.

bronze wares, which is regarded to delay corrosion of bronze alloy by keeping the harmful ion out [6, 14] and primary electrochemical reaction as follow.

Negative pole:

Positive pole:

Actually, transverse cracks observed in Cu_2O layer of cross section of sample 2 formed a free migrating pathway between the bronze alloy and the burial circumstance. The cracks in Cu_2O layer are likely to be a lot to produce along with the gradual corrosion of bronzes, its mechanism required further study.

Lead carbonate (PbCO_3) was confirmed by XRD that was a common lead corrosive phase in bronze wares [15].

Generally, the reaction of Pb to PbCO_3 will occur in burial environment as follow [16]:

By the result of SEM image and chemical element distribution, the sample 6 showed the migration out of Pb element from bronze alloy.

5. Conclusion

Photograph of cross section and component element data indicates that bronze substrate has been corroded severely, which must be consolidated before its restoration. The SEM image revealed transverse cracks in Cu_2O layer in sample 2 which had provided the pathway for element diffusion between the bronze alloy and the burial circumstance.

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