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ARCHAEOMETRIC STUDY ON UNEARTHED WARRING STATES BRONZE 'FU' EXCAVATED FROM PUJIANG, CHENGDU, CHINA

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ABSTRACT

In this study, metallurgical microscope, scanning electron microscope in combination with energy dispersive X-ray analysis (SEM-EDS), Raman spectrometer and X-ray diffractometer (XRD) were used to analyze the craft, alloy composition and corrosion products of the Warring States bronze vessel "Fu" excavated from Pujiang county, Chengdu city of China (the Warring States period lasts from 475 BC to 221 BC). The results showed that the bronzes were casted and made of lead-tin bronze, the content of tin and lead were relatively high. The corrosion products of the bronzes are mainly cassiterite, malachite, hematite and lead ore. This article provides a scientific basis for the study of ancient bronze culture and for the conservation of such cultural relics.

KEYWORDS: The Warring States, Cemetery, Bronze, Vessel, Craft, Alloy composition, Corrosion product

1. INTRODUCTION

A Warring States' cemetery with plenty ship-shaped coffins was discovered in Pujiang county, Chengdu city of China in 2016. The cemetery was located in the livable area between mountain and river. The excavation was conducted with more than 400 artifacts unearthed. The unearthed bronzes could be divided into weapons and vessels, a small amount of bronze vessels were identified as "Fu" (Liu et al., 2017). The cemetery with ship-shaped coffins has been reported excavated alongside the river since the 1950s in Sichuan area. Some of the coffins are incomplete due to the degradation (Feng et al., 1958). Buried in a ship-shaped coffin is a popular funeral custom in ancient Sichuan area from the Warring States to Han dynasty, as well as among other riverside residents in ancient China. However, inhumation with soil on land in ship-shaped coffin is quite unique in ancient Sichuan area (Duan et al., 2002).

The bronze manufacturing in Sichuan area has a long history. Binary alloy and ternary alloy were discovered at the early stage. The content of Sn experienced a significant increasing in the Warring States(Sichuan Provincial Museum, 1993; Yao et al., 2004). Bronzes could be grouped into different categories, as a typical type of bronze vessel, "Fu" is frequently decorated with geometrical patterns and was used together with "Zeng"(甑), for steaming or cooking food. Such vessels have been discovered in several regions of China(Ma et al., 1998). According to the excavated Warring States' cemetery in Pujiang county and surrounding area, bronze "Fu" was found in more than 50% of the cemetery, indicating it was widely used in such area (Jiang et al., 2002; Jiang et al., 2002; Chen et al., 1985).

Scientific analysis has been applied to the study of Warring States' bronzes in Sichuan area. Cu-Sn-Pb ternary alloy was identified, the detection of a tin-rich layer with special pattern on the surface of bronze weapons indicates a mature bronze manufacturing of ancient people. The characteristic Bashu bronze culture was formed in Warring States and has achieved great prosperity, despite it was far fall behind central China (Li et al., 2002; Yao et al., 2007). SnO_2 was determined as main corrosion product, especially for the bronze with a tin-rich layer (Xiao et al., 2006). Seldom research of bronze vessel has been reported. In this study, metallurgical microscope, SEM-EDS, Raman spectrometer and XRD were used to analyze the craft, alloy composition and corrosion products of bronze vessel "Fu", providing a scientific basis for the study of ancient bronze culture and for the conservation of such cultural relics. Considered as effective methods, such techniques were also applied in the study of ancient lead-copper alloy of Byzantine Age in Egypt, for the characterization of alloy and corrosion products (Salem et al., 2021).

2. MATERIAL AND METHODS

2.1. Material

Six (6) bronze "Fu" were unearthed, they were in poor condition because of the severe corrosion. 12 fragments with full structure were carefully selected under microscope as samples, among which, 6 samples are from the matrix and 6 samples are from the corrosion product. The basic information of the bronzes and samples are shown as Table 1.

Table 1. This is an automated table caption.

Sample No. (Matrix)	Sample No. (Corrosion Product)	Size（cm）	Weight（g）	Condition	Photo
PJ1	PJ2	–	596.7	Fragments with corrosion	
PJ3	PJ4	–	1353.5	Incomplete bronzeware with corrosion	

PJ5	PJ6	–	245.2	Fragments with corrosion	
PJ7	PJ8	length:21.4 width:14.6 height:16.0	7909.0	Incomplete bronzeware with corrosion	
PJ9	PJ10	–	–	Incomplete bronzeware with corrosion	
PJ11	PJ12	–	2007.4	Fragments with corrosion	

2.2. *Methods*

2.2.1. Microscopic Analysis

Observation of the samples was conducted by two microscopes (Axio Scope A1 equipped with ICCS optical system, Zeiss Ltd., Germany and a three-dimensional digital microscope VK-X250, Keyence Corporation, Japan) with the magnification from 50-200 X and 20-200 X.

2.2.2. Metallographic Analysis

The metallographic observation was conducted on 6 samples collected from the matrix of the vessels. Samples were embedded by a metallographic inlaying machine (CitoVac, Struers Ltd., Denmark), ground and polished by a Tegramin-20 automatic grinding and polishing equipment (Struers Ltd., Denmark) according to the standard metallographic procedures to achieve the cross-section of the samples. A polarizing microscope (Axio Scope A1, Zeiss Ltd., Germany) was used to observe the cross-section before and after etching with aqueous ferric chloride alcohol solution with the magnification from 50-200 X. All solvents were purchased from Sinapharm Chemical Reagent CO., analytical grade. The corrosion products were observed directly under microscope. SEM-EDS analysis was conducted with a FEI Verios 4G SEM coupled with an Oxford X-max 20 EDS analyzer to obtain secondary electron (SEM) images and backscattered electron (BSE) images for phase studies. The embed samples with cross-section were analyzed before etching. Samples were analyzed with10-20 kV acceleration voltage and 8-9 mm working distance.

2.2.3. Compositional Analysis

SEM-EDS analysis was conducted with a FEI Verios 4G SEM coupled with an Oxford X-max 20 EDS analyzer, which was also hired for the characterization of chemical composition. Matrix (cross-section) and corrosion samples were analyzed with 10-20 kV acceleration voltage and 8-9 mm working distance. Industrial copper reference sample was used for calibration and optimization before analysis. Mapping scanning was adopted during element analysis by EDS in order to minimize the detection error. The area with Pb particle and corrosion were avoided while selecting the detection zone. For the EDS analysis of inclusions and special phase, dot scanning was preferred for accurate results. Each sample was analyzed for three times, the elemental results detected were averaged and normalized.

XRD was performed by a X'Pert Pro MPD diffractometer (Philips, Netherlands) equipped with a Cu-Ka radiation source (λ= 0.15418 nm) in the range of 5-95°, with a tube voltage of 40 kV and a current of 200 mA at a scan rate of 10°min^{-1}. Corrosion samples were ground into powder for analysis. XRD spectra was analyzed and matched by JADE.

A Renishaw inVia RM200 Raman spectrometer coupled with microscope was used for analysis. Measurements were performed using an argon gas laser at 532 nm with the range 100-3000 cm^{-1}. The detection temperature is 25 °C with the humidity lower than 50%. The spectral resolution was 0.6 cm^{-1}. The laser power was approximately 0.5 mW, which ensured that good quality spectra was recorded. Corrosion samples were placed directly under microscope for the selection of certain corrosion product before detection.

3. RESULTS AND DISCUSSION

3.1. Metallographic Analysis

Analysis of 6 matrix samples are shown as Fig.1-6. Metallurgical observation of the samples is shown as Fig.1a-6a (before etching) and Fig.1b-6b (after etching). SEM image is shown as c and d in Fig.1-6. Metallurgical observation of the cross-section presents typical casting microstructure, further processing during manufacturing didn't appear according to the metallographic analysis, which is different from the weapons in ancient Chengdu Plains (Li et al., 2020). Among the samples, PJ1 is fully mineralized with little casting microstructure remained, which is the characteristic of severe corrosion. Metallurgical observation shows α solid solution (zone A) with segregation. The (α+δ) eutectoid (zone B) was uniformly distributed among the dendritic microstructure, similar to bronzes along Xia River (Zeng et al.,1992; Yao et al., 2005). Lead inclusions (zone C) distributed dispersively among the samples, together with a few blue-grey inclusions (zone D was identified as sulfide and zone E was identified as chloride). The shape, size and distribution of Pb particles were influenced by the ratio of Pb and the manufacturing craft. The inclusions with Cu and S are frequently distributed as particles in the cast structure (Tian et al., 2014).

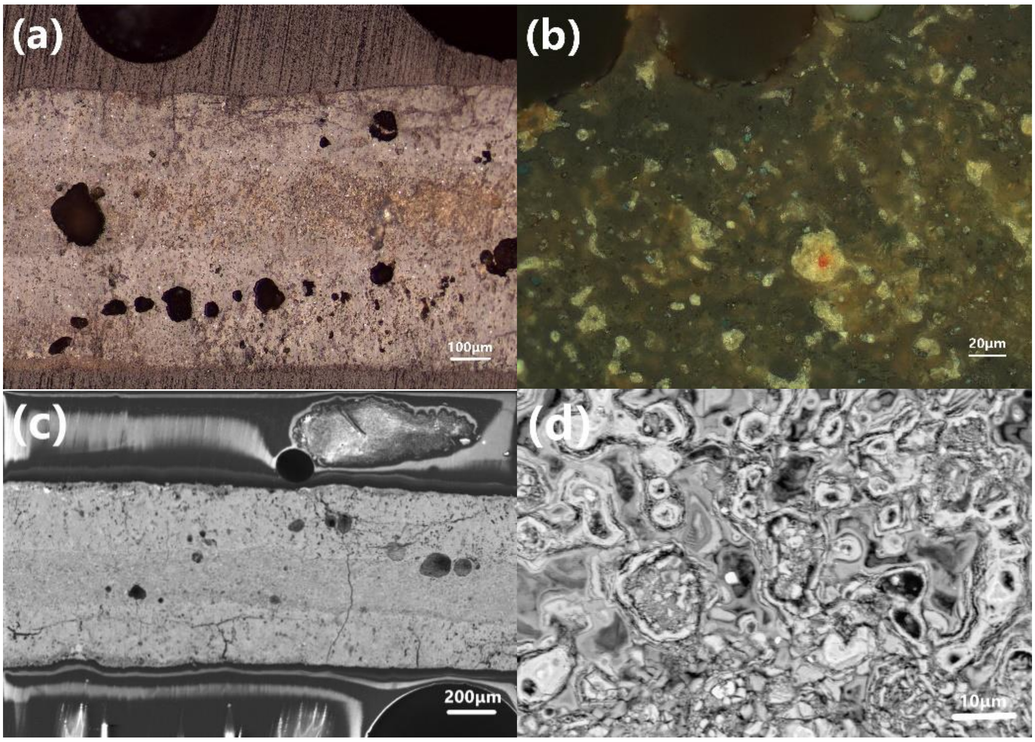

Figure 1. Metallographic analysis of PJ1

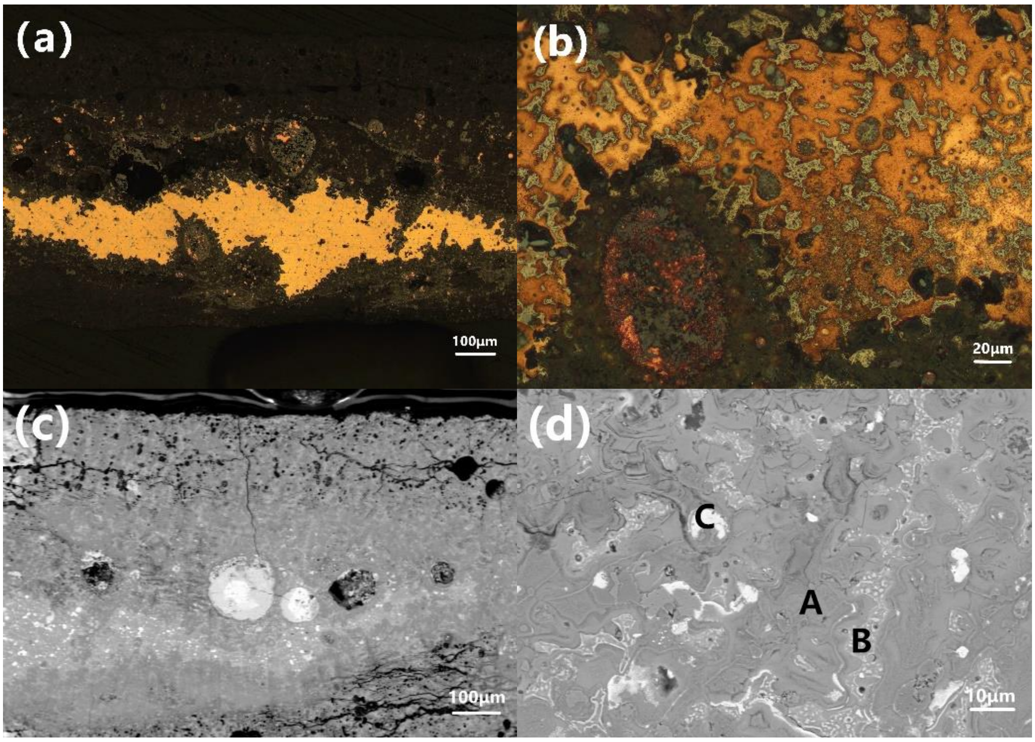

Figure 2. Metallographic analysis of PJ3

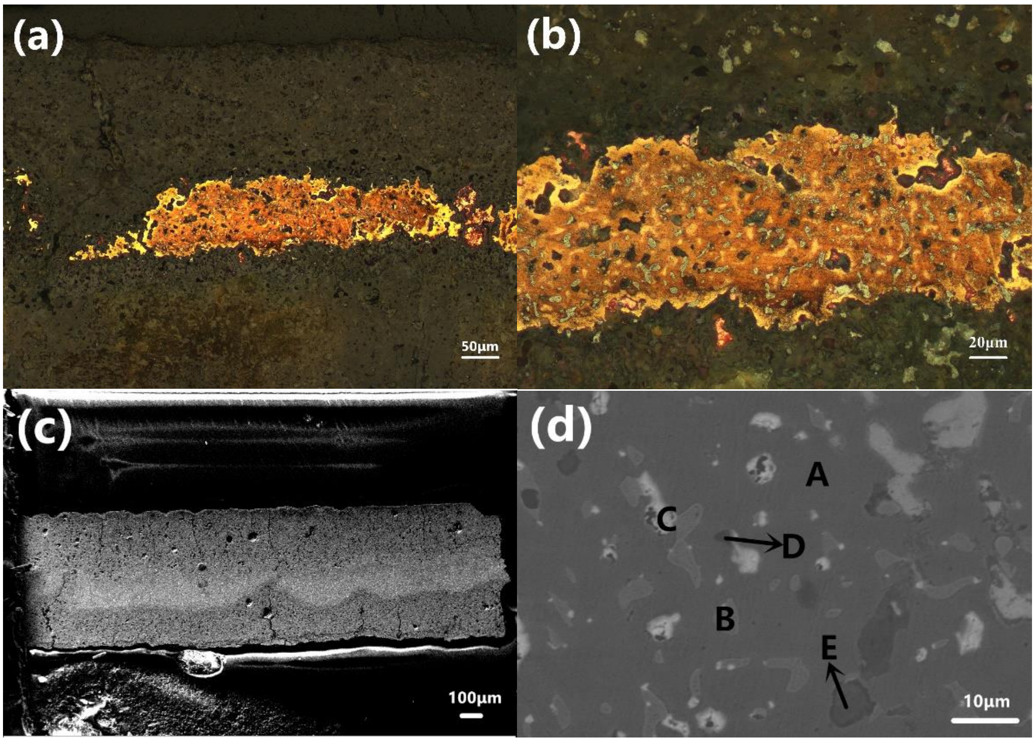

Figure 3. Metallographic analysis of PJ5

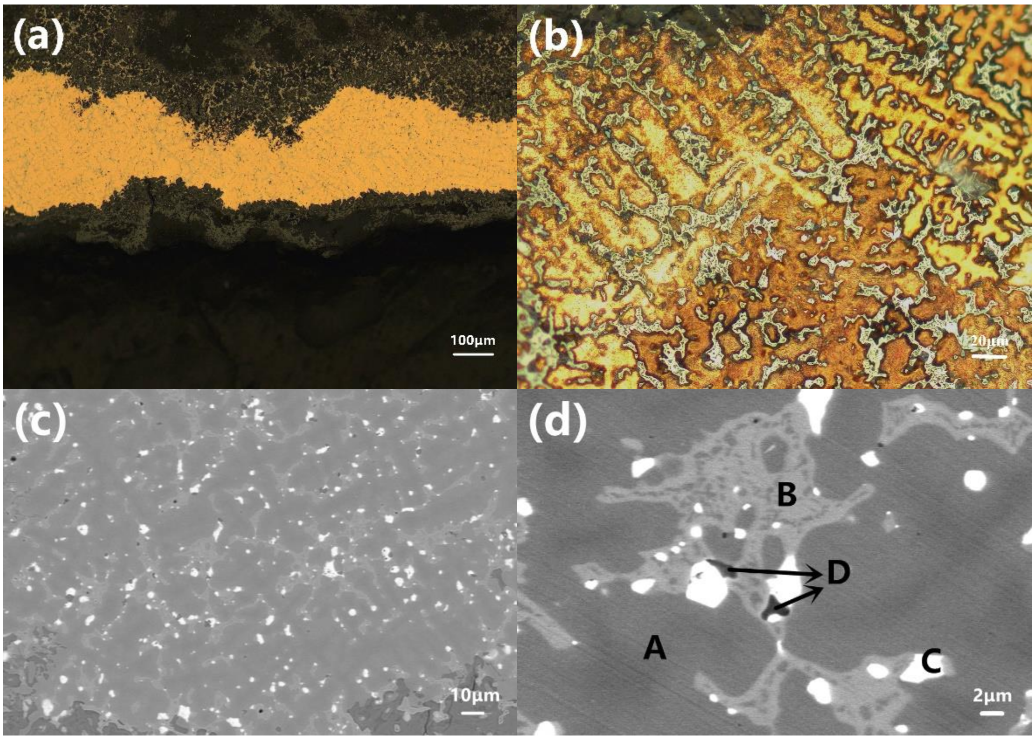

Figure 4. Metallographic analysis of PJ7

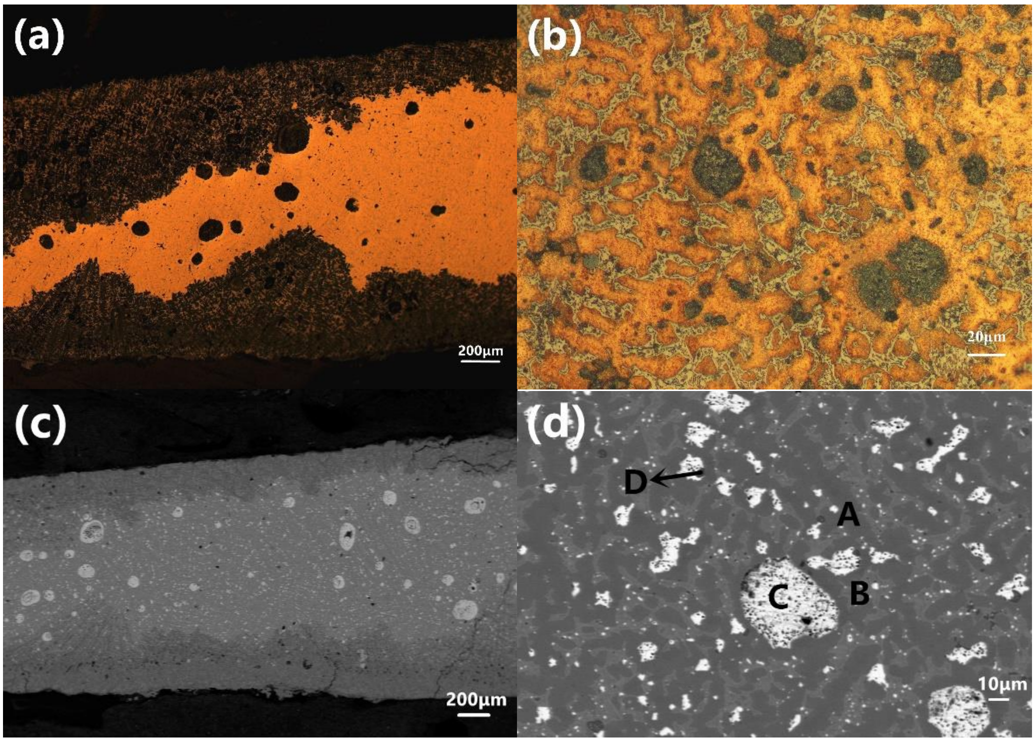

Figure 5. Metallographic analysis of PJ9

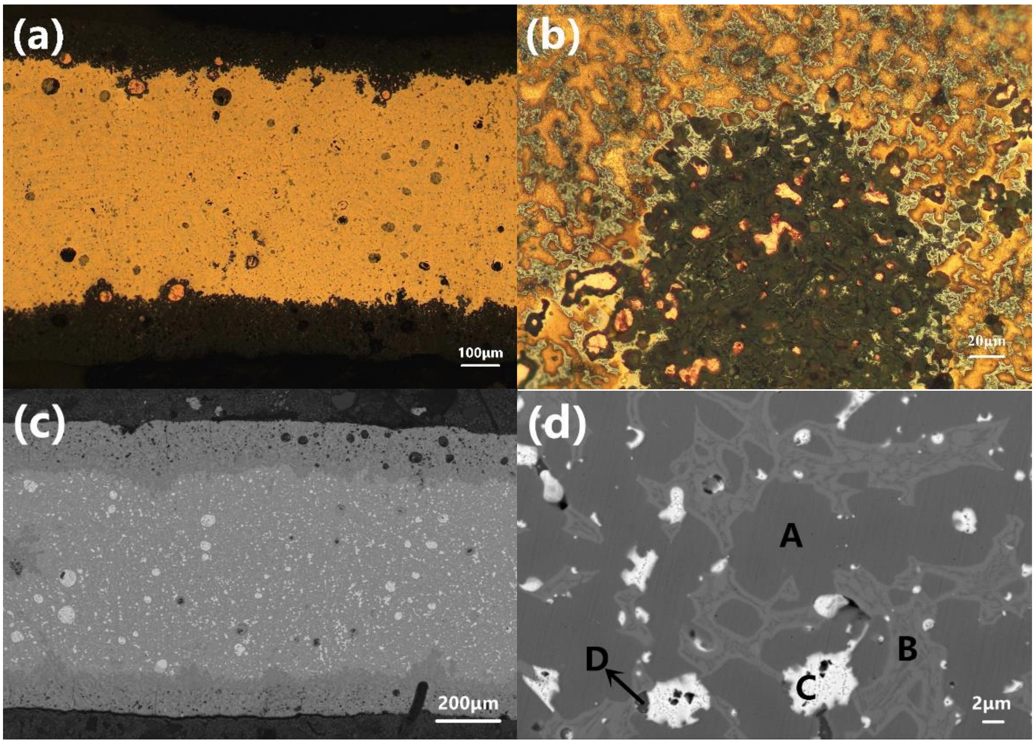

Figure 6. Metallographic analysis of PJ11

3.2. SEM-EDS Analysis

3.2.1. Analysis of the Alloy

The composition of the alloy is shown as Tab.2, the data has been treated with main elements for comparison. It has been generally recognized tin bronze refers to a copper-based alloy containing 2% tin or over, a Cu–Sn–Pb ternary alloy contains both tin and lead at the level of 2% or more (Mei et al., 2009). A relatively high content of Sn (exceeds 16%) was identified, the data is even more than 20% in PJ17 and PJ11. Therefore, the excavated bronzes are tin-lead bronze with the proportion of Cu and Pb from 63-76 % and 7-17 %.

The elemental distribution of different phases was also detected, taken PJ11 as an example (Fig. 7 and Tab. 3), α phase (spot-1), δ phase (spot-2), inclusion (spot-3) and light white particle (sopt-4) were detected. The content of Cu in spot-1 (86.42%) is higher than spot-2 (72.32%), both phases are composed of Cu and Sn. As an important maker of alloy properties, the number and status of inclusions matters significantly (Morcillo et al., 2017). In some cases, inclusions are also served as raw material which could be used for geographical origin traceability. Inclusions in PJ11 were found among α solid solution or attached around white particles and (α+δ) eutectoid with an irregular shape. Cu and S were found in the inclusion (spot-3) with the proportion of 59.32% and 24.86%. Such inclusions were also found in other matrix samples. According to the binary equilibrium diagram, the eutectic reaction happens at 1067 ℃ with Cu_2S and Cu-S solid solution, resulting in the existence of Cu_2S in the area with the content of S exceeds 0.75% (Yuan et al., 2017). The white particle consists of Pb (91.26%), Cu (6.28%) and O (2.45%). It was reported that Pb plays an important role in the bronzes, the fluidity of melting metal increased with the adding of Pb. The optimal fluidity appears with the proportion of Pb from 10-15% and decreases when the data was over 15%, such raw material is suitable for casting (Su et al., 1995; Han et al., 2002).

Table 2. Alloy composition of the matrix

No.	Composition (wt %)				Alloy
	Cu	Sn	Pb	As	
PJ1	–	–	–	–	–
PJ3	70.01	16.89	13.10	–	Cu-Sn-Pb
PJ5	76.46	16.08	7.46	–	Cu-Sn-Pb
PJ7	64.88	27.73	7.05	0.34	Cu-Sn-Pb
PJ9	65.44	17.45	17.11	–	Cu-Sn-Pb
PJ11	63.71	24.01	12.28	–	Cu-Sn-Pb

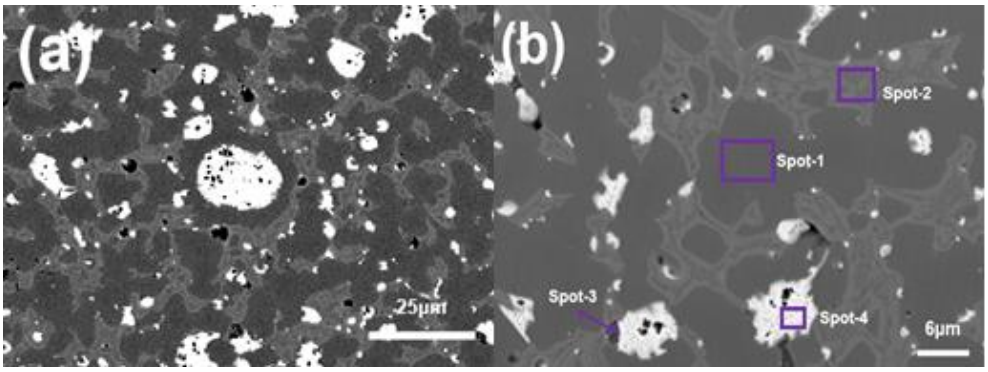

Figure 7. SEM image of PJ11

Table 3. The elemental distribution of PJ11

	Elemental Distribution（wt%）				
	Cu	Sn	Pb	S	O
Spot-1	86.42	13.58	–	–	–
Spot-2	72.32	27.68	–	–	–
Spot-3	59.32	2.29	14.53	24.86	–
Spot-4	6.28	–	91.26	–	2.45

3.3. *Analysis of the Corrosion Products*

Different corrosion products were discovered, appeared as green, white and red mineral. The XRD analysis of the corrosion products was shown as Fig.8, peaks at 14.8°, 17.6°, 24.0°, 24.3°, 31.1° and 35.6° are attributed to malachite (PDF#72-007, $Cu_2CO_3(OH)_2$. The characteristic signal of SiO_2, Cu_2O and SnO_2 were also detected (PDF#87-2096, SiO_2, PDF#78-2076, Cu_2O, PDF#72-1147, SnO_2).

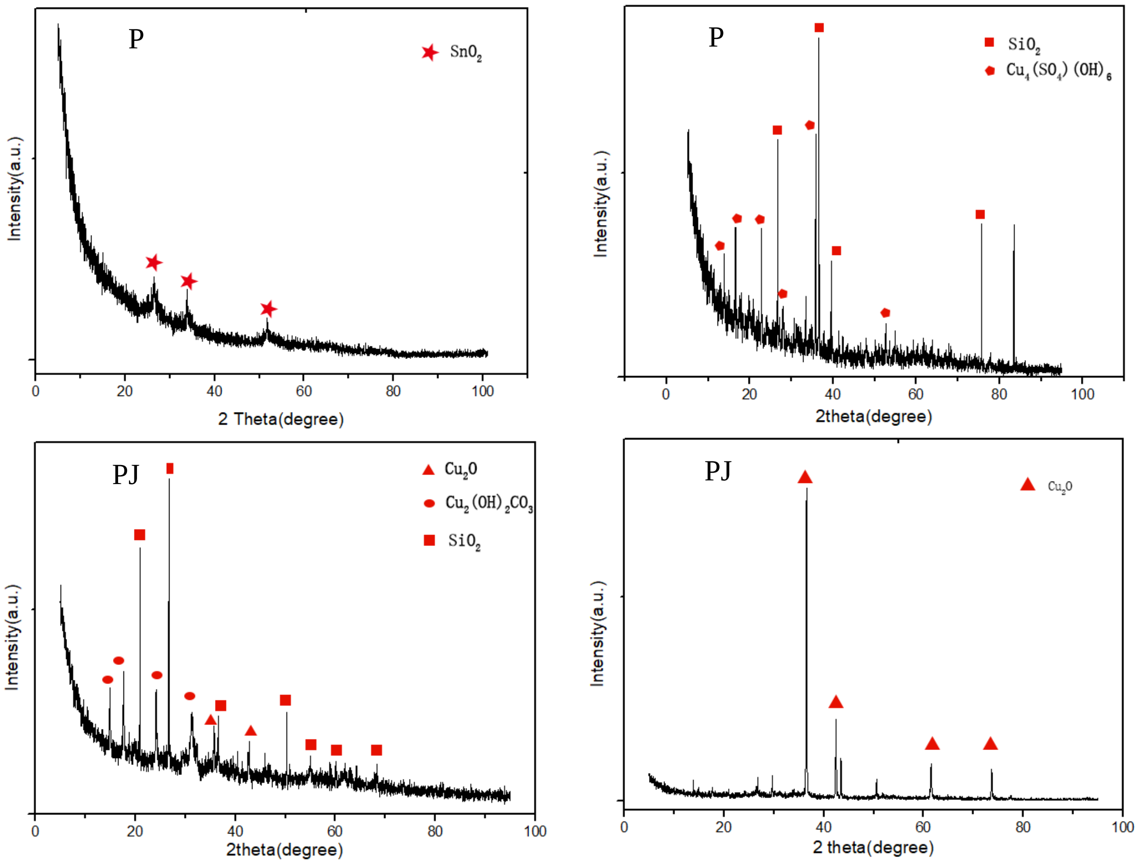

Figure 8. XRD of selected samples

The corrosion products with different color were also detected by Raman with spectroscopy (Fig.9), the green area was supposed to be $Cu_2CO_3(OH)_2$, peaking at 154, 181, 215, 268, 358, 434, 534, 720, 756, 1059, 1095, 1371, 1490 and 1595 cm^{-1} (Li et al., 2008). The reddish-brown mineral was attributed to Cu_2O with the characteristic peaks at 148, 218, 279 and 645 cm^{-1} (Zmuda et al., 2016). The white mineral was identified as $PbCO_3$ with the characteristic peaks at 153, 298, 394, 684, 1091, 1433 and 1590 cm^{-1} (Lowell et al., 1999).

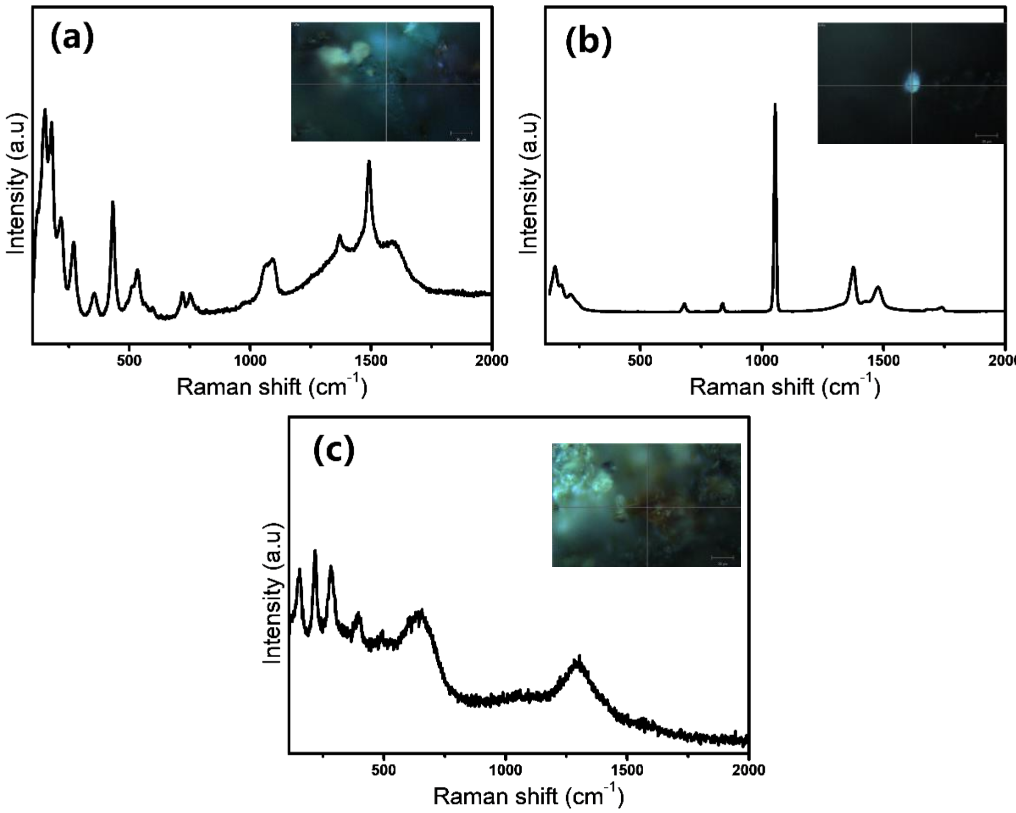

Fig. 9: Raman spectra of corrosion products
a: Green area-$Cu_2CO_3(OH)_2$; b: White area-$PbCO_3$; c: Reddish brown area-Cu_2O

Among the detected minerals, SiO_2 comes from the burial surroundings. The formation of Cu_2O was easily detected while the copper was placed with certain humidity and temperature, known as the bronze oxidation. The Cu_2O was also considered as noble patina for its dense structure will reduce future corrosion in some degree (Echavarria et al., 2009). Future contact with water and CO_2 contributes to the formation of malachite from Cu_2O. Basic copper carbonates malachite is typically part of the "vile patina"(Privitera et al., 2021; Ingo et al., 2019). It's a quite special feature by adding such amount of Pb in the manufacturing of ancient Chinese bronzes, especially in the Warring States. The Pb particle distributed as isolated phase along dendrite, and is easily suffered from corrosion after electrochemical reaction when exposed to CO_2, O_2, H_2O and sulphate (Mu et al., 2020).

4. COMPARATIVE STUDY OF THE EXCAVATED BRONZES IN PUJIANG

In order to get a better understanding of the bronze manufacturing in ancient Pujiang, the elemental composition of the 31 unearthed bronze vessels (including 'Fu' and 'Mou' (Liu et al., 2022)) were compared with bronze vessels unearthed in the surrounding area (Bashu district) of the Warring States (Fig.10). Few studies of the Warring States bronzes excavated from Bashu district have been reported, such as the bronze vessels from Xindu Majia, Emei and suburb of Chengdu. More than 5 types of bronze vessels were discovered in Xindu Majia, the concentration of Cu, Sn and Pb varies from 72-85%, 12-18% and 10%, respectively. One piece of bronze vessel was excavated from Emei, the concentration of Cu, Sn and Pb in 80%, 15.3% and 5.5%. Unlike the clustered data of Xindu Majia, the elemental composition of Feihu villiage has a fluctuation in a wider range, but one should also notice that the proportion of Cu has a relative concentration, indicating a mature bronze manufacturing of Bashu district in Warring States.

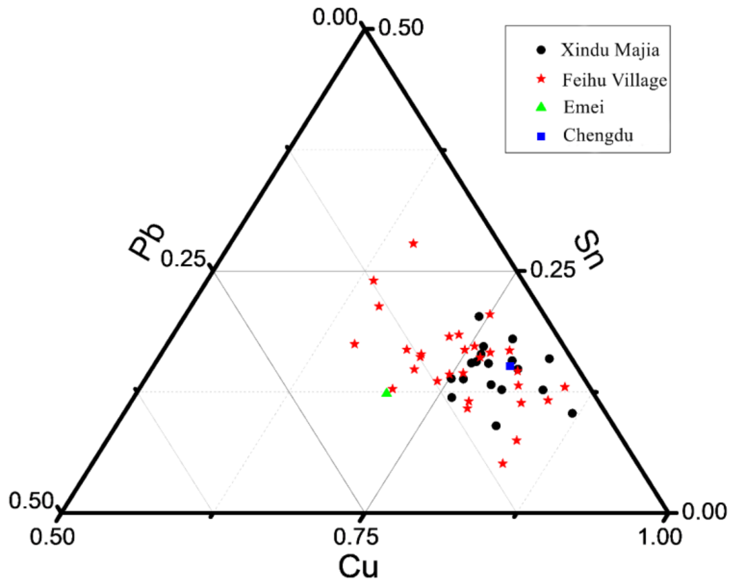

Figure 10. Elemental composition of the Warring States bronze vessels

5. COMPARATIVE STUDY WITH THE MEDITERRANEAN ANALOGUES

The evidence of smelting copper was found in Serbia and Iran in around 5000 BP and the technique was expended to central Europe, southeast Europe and west Asia (Radivojevic, 2010; Roberts, 2009). Any historical inspection will show the most evident parallels between ancient Mediterranean and especially Greece and ancient China at least during the 1st millennium BC. The Hellenic world was mostly made up of several city-states spanning the Black Sea and Mediterranean coasts in the 5th century BC. When we look at China at the same time, we see a vast geographical area separated into several small and big semi-independent kingdoms that are all nominally ruled by Zhou (since 1050 BC). Having the nobles Zhou stopped supporting the Zhou Dynasty, and Zhou's vassal states declared themselves independent from Zhou and fought for territory, they became kingdoms or warring states. It lasted 200 years of Zhou dynasty that the Warring States period developed metallurgy and the present bronze 'Fu' was under investigation. Yet Lewis (Lewis, 2000) view in ancient China is a 'city-state' culture (Hansen, 2000) and that the Hellenes as mariners and the Chinese as river revelers has interesting points connecting socio-political status. In this aspect we recall the essential difference between those people across the globe: the farmers of the Yangtze River delta and the islanders of the central Aegean Sea waterborne travel encouraged a culture of exchange, long-distance relationships, and maritime or riverine navigation. Despite structural similarities, both communities would have been perplexed at the alienness of the populous settlement of Liangzhu, "*…. Within the lush evergreen surroundings, the masterful jade craftsmanship, the network of Cycladic villages surrounded by meagre land from which a living was eked out and hard rocks mined for rare minerals, and the intrepid sailing of dangerous Aegean waters for trade, community, marriage, and war.*" (Liritzis and Westra, 2022).

In ancient Greece there seem to have workshops for making bronze and those for 'iron objects. (Gauthier, 1976, comments, 'Les chalkotypoi sont les artisans bronziers, les sidèreis sont les ferroniers.'). Chernykh (2009) calls technological "explosion" the invention of bronze metallurgy and this is noted in the European and Asian-Chinese regions.

The bronze objects are various in shapes and uses in both ancient Greece and ancient China. Copper was widely available in the ancient Mediterranean, most notably on the island of Cyprus. Tin was rare; and it was obtained from the East, in Anatolia, and in the distant West, in Spain and the British Isles. Herodotus, a Greek historian from the 5th century B.C., refers to the British Isles as the "tin islands" (*Histories* 3.115). The ratio of copper, tin, or lead and antimony and added materials can be manipulated to produce a range of aesthetic effects. Pliny in his *Natural History* (34:3), writes that bronze made in Corinth was particularly renowned for its fine coloring. Today, most surviving bronzes exhibit a green patina, but in their original form, bronze vessels would have had a golden sheen. (Diehl, 1964).

Bronze vessels were made in a wide range of shapes over a long period of time. Many of the earliest vessels, dating to the 9th and 8th centuries B.C., were tripods, which are three legged stands that supported large cauldrons; sometimes the two parts were made together in one piece. The cauldrons were originally used as cooking pots, but the tripods also were given as prizes for winners in athletic contests (see Museum of Delphi). The edges of the cauldrons and stands could be decorated with foreparts of animals or mythical creatures. The griffin—a fantastic beast with the body of a lion and the head of an eagle—and the sphinx—with a feline body and a human head—were favorite motifs (Rolley, 1986).

Water jars (hydriai) seem to have been a preferred shape in bronze. The characteristic shape of a hydria is well suited to its function, with a narrow neck for preventing spills, a rounded belly for holding water, a vertical handle for pouring, and two lateral handles for lifting. A long series of hydriai survive, spanning the Archaic, Classical, and Hellenistic periods. The vases from the late seventh and sixth centuries B.C. have heavy proportions, with a broad mouth, straight neck, and rounded belly. (Lamb, 1929). They often are decorated with geometric patterns, powerful animals, mythical creatures, and human figures, especially at the points at which the handles are attached to the body of the vase. In the 5th century B.C., the proportions are more harmonious, with a narrower mouth, curved neck, and full body. The finest examples received delicate chased decoration in low relief on the body. In the fourth century B.C., the shape becomes even lighter, with an elegantly curved neck and tapered body. The mouth, foot, and ends of the handles usually are decorated with geometric or floral patterns rendered in low relief. Below the vertical handle, an independently worked appliqué with mythological scenes appears, which was made using a repoussé technique that involves hammering the panel from the front and back to achieve different levels of relief within the composition. Bronze hydrae of the Hellenistic period (ca. 323–31 B.C.) tend to be slender and have minimal decoration. Several different vessels for wine were produced in bronze, which may have been reserved for sumptuous drinking parties, called symposia (Sowder, 2000).

On an analogue manner in ancient China 5th-3rd century BCE the carious bronze objects unearthed include various types, such as bowls, bells, drums, cups, axes, swords, spears, dagger-axes, knives, saw, stamps, and coins et. al. It has been found from archaeological excavations bronze artifacts decorated with designs of animals and designs of people playing musical instruments, made in Shang times long ago. (Li et al., 2020). Different bronze vessels were excavated, include ritual vessels and vessels for use. The vessels could be used for wine and food with different patterns.

6. CONCLUSIONS

The Warring States bronze vessel "Fu" excavated from southwestern China, presents compositional and metallurgical characters which enriches our knowledge of ancient bronze manufacturing. The study showed that the bronzes were casted and made of lead-tin bronze, the content of tin and lead was relatively high. The (α+δ) eutectoid was uniformly distributed among the dendritic microstructure. Lead inclusions was distributed dispersively among the samples, together with a few blue-grey inclusions.

The corrosion products of the bronzes are mainly cassiterite, malachite, hematite and lead ore. Unlike other clustered data of the Warring States bronze vessels, the elemental composition of Feihu village has a fluctuation in a wider range, but the proportion of Cu has a relative concentration, indicating a mature bronze manufacturing of Bashu district in Warring States. This article provides a scientific basis for the study of ancient bronze culture and for the conservation of such cultural relics.

AUTHOR CONTRIBUTIONS

All co-authors contributed equally in: Conceptualization, methodology, investigation, data curation, writing-original draft preparation, writing-review and editing, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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