

RESEARCH ARTICLE

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Brass products in the coronet excavated from an M2-numbered Sui-Tang-dynasty tomb situated in Kun Lun Company in Xi'an, Shaanxi

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Abstract

Ancient Chinese brass smelting technology has promoted the invention of zinc smelting, thus becoming an important part of the metallurgical history. However, the information concerning its origin and development is still controversial. In that regard, thorough analysis of composition and structure of the early brass is crucial for studying various stages of the ancient brass smelting technology history. This study aimed to investigate brass artifacts from *Kunlun* M2 tomb in *Xi'an, Shaanxi*, dating back during Sui to early Tang Dynasty (581–712 AD). The composition and metallographic characterization of the materials was performed using XRF, SEM–EDS and metallographic analysis. According to the results, brass was composed of 83 wt% of copper, 12 wt% of zinc, and 3 wt% of tin. Furthermore, its microstructure consisted of α -isometric single crystals with some slip lines and a few twinned grains. This indicated that brass was obtained by melting an appropriate mixture of zinc ores and copper ores at a temperature above 920 °C. Furthermore, brass support components were installed on the coronet after integral hot forging and partial cold shaping. Besides, the use of brass in the coronet was in conformity with the social hierarchy of that historical period, and also reflected the attention paid to the properties of materials.

Keywords: Brass, Coronet, Sui-Tang-dynasty, XRF, SEM–EDS

Introduction

Copper and copper alloys as the earliest metals in human history have been of great significance to human civilization [1–3]. In various historical records, copper and copper alloy smelting techniques have been widely emphasized as the evidence of the origin of human civilization [4, 5]. Ancient Chinese brass smelting technology has promoted the invention of zinc smelting, thus becoming an important part of the metallurgical history. Notably, among all kinds of antique copper alloys, zinc-based brass is widely used in the modern materials.

However, the origin and development stages of Chinese brass smelting are still controversial, which has aroused great interest of scientists [6].

So far, a total of more than 40 pieces of brass artifacts from 5000 BC to the early 2000 BC had been found across the world, being especially frequent in the Aegean Sea, the Two River Basin, and the Persian Gulf, as well as in Iran, Central Asia, and China. Among them, the plate and pipe, found at *Jiangzhai* (姜寨) site dating back to the early *Yangshao* (仰韶) Culture (about 4000–4700 BC), were the earliest brass products in the human history [7, 8]. However, the prehistoric brass was speculated to be acquired occasionally by smelting of copper–zinc ores according to its technological characteristics [9]. The purposeful smelting of brass was believed to originate in India in the second half of 1000 BC worldwide [10]. In 45 BC, the copper–zinc alloys produced by calcining red copper were used

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in the casting of brass coins in ancient Roman Empire [6]. Later, the brass smelting technology was spread to Persia with the Roman Empire, expanding to the Upper Mesopotamia in the second century AD [11]. The emergence of this technology in China might be throughout the trade between China and Persia, as early as the third century AD [12].

However, based on numerous excavations, the mass manufacturing of brass products and brass coins could have occurred in China not earlier than in the fifteenth century, though According to scientists, Chinese brass technology could have become widespread during the Ming Dynasty (明) epoch [13]. Although the appearance of elemental zinc metal in China is also dated back to the Ming Dynasty period [14, 15], brass could be obtained by smelting copper–zinc symbiotic ore, copper–zinc mixed ore or copper with zinc oxide ore earlier [12, 16, 17]. Various new studies revealed that almost certainly brass was employed much earlier. In particular, the records about the use of brass were found in the ancient books from the Three Kingdoms period to the Sui-Tang-dynasty epoch. For example, officials were pledged to wear gold, silver, or “*Toushi*” (鍮石, the Chinese name of brass during the Sui-Tang-dynasty epoch) belts according to their ranks. The relevant information was documented by “*Yu Fu* (輿服)” in “*Old Tang Shu—volume 45, zhi25: Eighth grade and ninth grade officials were recognized by wearing dark cyan or light cyan uniforms and Toushi belts* (唐书-卷45, 志第25, 輿服: 八品服深青, 九品服淺青, 並鍮石帶)”. In addition, more tangible evidences highlighting the application of brass have been found recently. Among these, brassware dating back to the fourth–ninth century had been unearthed in *Xinjiang* (新疆), Inner Mongolia, and *Qinghai* (青海) areas along the Silk Road [18–20]. However, some scholars considered those utensils as imported brass that was introduced into China from the West along the Silk Road [2, 21]. Then, twenty one local brass products originating from the mid-late Jin Dynasty epoch (金1189–1217 AD) were unearthed in *Hebei* (河北) Province, which proved that diffusion and localization of brass cementation technology occurred in Northern China during the twelfth–thirteenth centuries AD [22]. Recently, low concentrations of zinc (2–4 wt%) were found in some Southern Song coinages (南宋1127–1279 AD), which reflected the sporadic input of recycled brass Buddha statues into the raw material melts [23]. Based on the above studies, Chinese brass technology dates back to at least the twelfth century. Moreover, it believes that, with the discovery of archaeological objects and their further research, the history of the smelting and use of brass in China would become more and more transparent. Thus, a thorough analysis of early brass products is of great significance for the Chinese brass history.

In 2007, a tomb of the late Sui Dynasty (隋) in *Xi'an* (西安), *Shaanxi* (陕西) province, China was unearthed to reveal a batch of exquisite ornaments. After cleaning the relics, the supporting parts on the back of the ornaments were found to have a gold-like surface with no traces of gold-plated coating, which was assumed to be brass. The metal wires with golden surface, probed via portable X-ray fluorescence spectrometer, scanning electron microscope with energy spectrum analyzer, and metallographic analysis techniques, were confirmed to be of copper–zinc alloy. Since no other ancient brass, except for prehistoric brass, was found in the Central Plains of China by far, it was assumed that the appearance of brass in China could be advanced to the sixth–eighth centuries AD. Furthermore, the detailed study of brass can furnish more information for brass metallurgical technology and expand a database of the Chinese brass history.

Materials and methods

Materials

The tomb numbered M2 and unearthed at the *Kun-Lun* (昆仑) Company in the eastern suburb of in *Xi'an*, *Shaanxi* province, China was a single-chamber earth cave with a long ramp passage. Archaeological excavations revealed that M2 was a joint burial with a total of 20 groups of cultural relics. A series of ornaments was arranged neatly around the head of the female tomb owner. Judging from the shape and structure of the tomb and the unearthed artifacts, this could be related to a Sui Dynasty or at least not later than the early Tang Dynasty period (the ninth century) [24].

The metal ornaments in the shape of wings (temples) and apricot leaves suggested that these were the ornamental components of a coronet. Moreover, the number of ornaments (eight apricot-leaf ornaments and two temples) indicated the coronet as the personal adornment of high-ranking females in the hierarchical system during the Sui-Tang-dynasty epochs (Fig. 1a) [25]. The main body of ornaments was gilded on the surface and inlaid glass, pearl, and semi-precious stone. While the supports and link wires on the back of the ornaments had the golden-like surfaces with no traces of gold. The wires with a golden-like surface were within the scope of this work.

The metal wires on the back of the ornaments were the supporting components subjected to nondestructive analysis and hereinafter labeled TBB-1, TBB-2, SD-1, SD-2, and SD-3. Among these, TBB-1 and TBB-2 were the metal wires on the back of the temples, whereas SD-1, SD-2, and SD-3 were the metal wires on the back of the apricot-leaf ornaments. To acquire the information about composition and processing of the metal wires, samples with the length less than 5 mm were intercepted at the

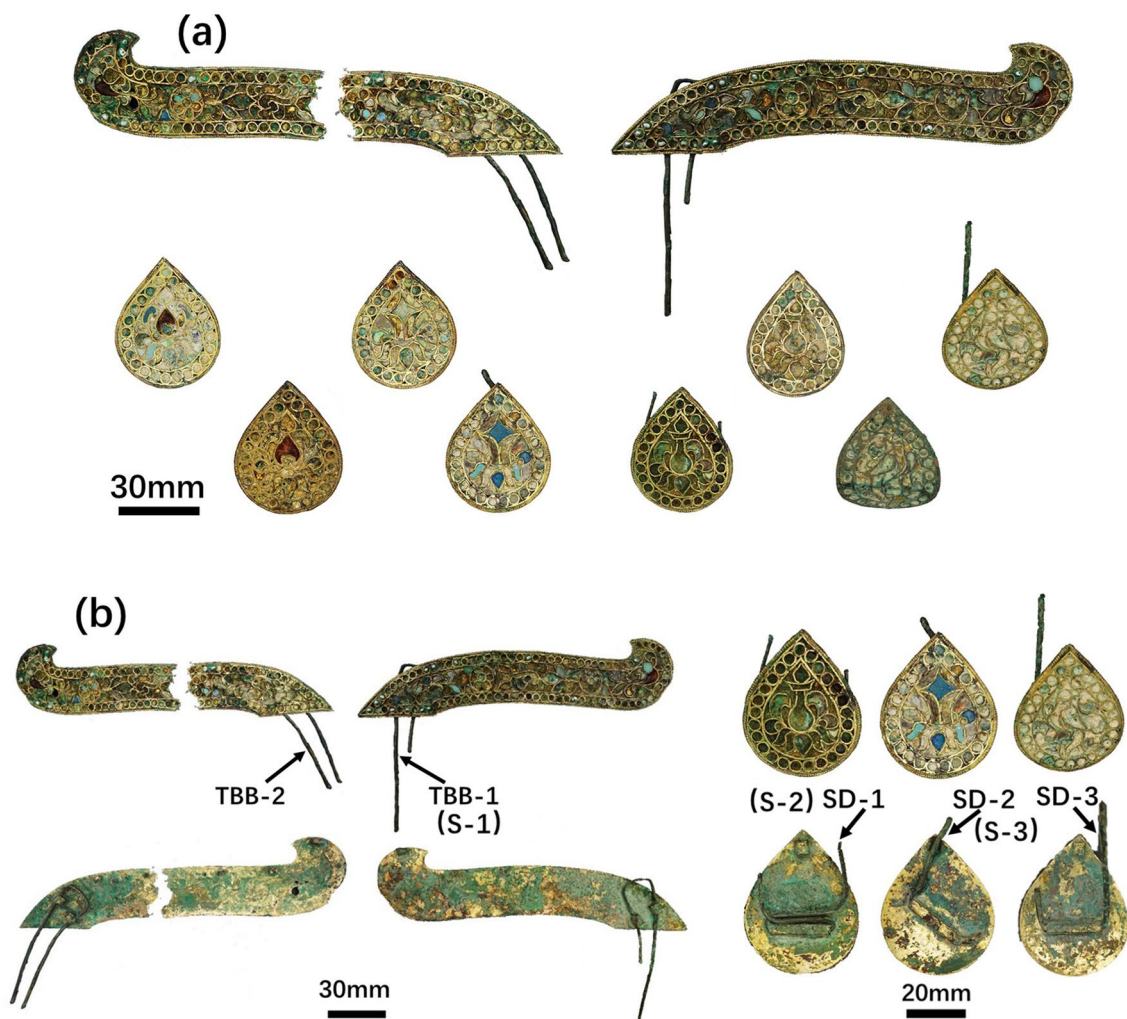


Fig. 1 **a** Temples and apricot-leaf ornaments of the ceremonial coronet; **b** TBB-1, TBB-2, SD-1, SD-2, and SD-3 are the metal wires on the back of the ornaments; S-1, S-2, and S-3 are experimental samples intercepted at the end of the wires

ends of TBB-1, TBB-2, and SD-2 under the best preservation conditions, and labeled S-1, S-2, and S-3, respectively (Fig. 1b).

Methods

Microscopic analysis

The supporting components of the coronet were investigated using an ultra-depth field microscope (KEYENCE VK-X250, Japan) and a VH-Z20R objective lens with 20–200× magnification and a field depth ranging from 34 to 0.44 mm.

Compositional analysis

After a long period of erosion in the buried environment, all the coronet ornaments evidenced varying

degrees of damage and were covered by soil and rust. To obtain as much accurate composition information as possible, the supporting components labeled TBB-1, TBB-2, SD-1, SD-2, and SD-3 were mechanically cleaned to remove surface contaminants, and then analyzed by a handheld portable X-ray fluorescence (XRF) spectrometer (p-XRF, Thermo Niton XL3t800, USA) equipped with a silver anode X-ray tube operating at 2 W and 50 kV. The alloy testing was performed with respect to the three modes according to certain elements: a Precious Metals mode, a Standard Alloy mode, and an Electronics Alloy mode whose effective testing diameters were 8, 3, and 3 mm, respectively. Notably, the Standard Alloy mode was employed to conduct 3–5 measurements on each sample, and the valid data were incorporated into the final reported result. The

acquisition time for each analyzed spot was 60 s and the collected elemental data were afterwards normalized.

The S-1, S-2, and S-3 samples intercepted at the ends of TBB-1, TBB-2, and SD-2, were cold-mounted, ground, and polished following the standard metallographic procedure. Their cross-sections were then examined and photographed with a ZEISS EVO MA 25 SEM microscope equipped with an Oxford X-max 20 EDS console to obtain secondary electron (SEM) images, backscattered electron (BSE) images, and alloy composition information. The experiments were done at an accelerating voltage of 20 kV and a working distance of approximately 8–9 mm. The ESD data were acquired by standardless analysis method according to Chinese national standard GB/T 17359-2012, and industrial copper reference sample was used for calibration and optimization. During the measurements, each micro-area was analyzed at least three times, and the results were averaged and normalized.

Metallographic investigation

The S-1, S-2, and S-3 samples were cold-mounted, ground, and polished following the standard metallographic procedure. The polished sections were etched with alcoholic ferric chloride solution ($\text{FeCl}_3 + \text{HCl} + \text{C}_2\text{H}_6\text{O}$) to reveal their metallographic structures, and were then examined and photographed with a ZEISS optical microscope.

Results

The discovery of brass

Based on the rarity of cultural relics, the nondestructive XRF method was first selected for their analysis. In particular, all the metal wires on the back of the temples and apricot-leaf ornaments labeled TBB-1, TBB-2, SD-1, SD-2, and SD-3 were scanned using a portable XRF spectrometer. The surface chemical composition of all the samples was similar in component proportions, and the results are given in Table 1. Among all the components, the copper content was predominant, accounting for more than 78 wt%, followed by zinc (5.2–7.7 wt%). In addition, other elements such as tin, lead, and iron were detected on the surface of the wires. Among these elements, copper, tin and lead were the main components of Chinese ancient bronze wares, making part of Chinese ancient metal relics [26]. However, zinc was very rare in antique metalworks, and its presence in metal wares of the late Sui Dynasty in *Xi'an* was unexpected, so that the further research was needed to verify whether this element was indeed making part of the above relics.

Table 1 Chemical compositions of supporting components of temples and apricot-leaf ornaments, obtained using the portable XRF spectrometer

Sample	Composition (wt%) ^a				
	Sn	Pb	Zn	Cu	Fe
TBB-1	4.8 ± 0.1	3.1 ± 0.1	5.6 ± 0.1	80.3 ± 0.2	1.6 ± 0.3
TBB-2	5.2 ± 0.1	3.0 ± 0.5	7.7 ± 0.4	78.2 ± 0.4	1.7 ± 0.2
SD-1	4.0 ± 0.1	3.5 ± 0.3	5.2 ± 0.1	86.3 ± 0.2	1.2 ± 0.2
SD-2	4.2 ± 0.1	5.5 ± 0.7	6.2 ± 1.0	79.0 ± 1.9	0.8 ± 0.1
SD-3	4.2 ± 0.4	1.8 ± 0.1	5.4 ± 0.3	83.6 ± 2.3	0.8 ± 0.1

^a The average value of multiple test values due to the systematic error of the portable XRF device

The determination of brass

To obtain the internal composition information about the copper alloy, the cross-sections of S-1, S-2, and S-3 were probed via SEM–EDS technique.

Cross-sectional BSE images of the S-1 sample and the corresponding EDS results are shown in Fig. 2a–f and Table 2. Since the area marked G in Fig. 2a was found to be composed of copper, chlorine, and oxide, this indicated that it was seriously eroded by soil elements under a long-term burial environment, and the corrosion products were mainly chlorides and oxides of copper [27]. To eliminate the influence of soil elements, the central regions labeled A, B, C, and D of the cross-section were analyzed. The components of A, B, C, and D were consistent with each other, being copper, zinc, tin, and a small amount of iron. The content of zinc was 12 wt% and that of tin was 3–4 wt%, meaning that the copper wire had a tin brass structure [28]. The iron content was stable across different areas, arising presumably from impurities in the smelting ore raw material.

Several grey regions (denoted as E in Fig. 2a and F in Fig. 2b) located between the severely corroded parts and the center of the cross-section were also examined [29]. In brass, zinc was easily dissolved by preferential corrosion [30], so that E and F areas were formed by dezincification corrosion [31]. With the increase of corrosion rate, tin was also corroded and dissolved. Thus, only the residual copper corrosion products (oxides and chlorides of copper) were detected in region D. The elemental analysis of J, E, and F areas suggested that the corrosion of the cross-section diffused from the surface to the interior along the grain boundaries [32].

The main components of the bright white particles were copper and lead with a small amount of zinc, indicating that lead existed in the alloy in the form of particles (I in Fig. 2e) aggregated near the copper–zinc sulfide [31]. As soon as brass was corroded, zinc in the

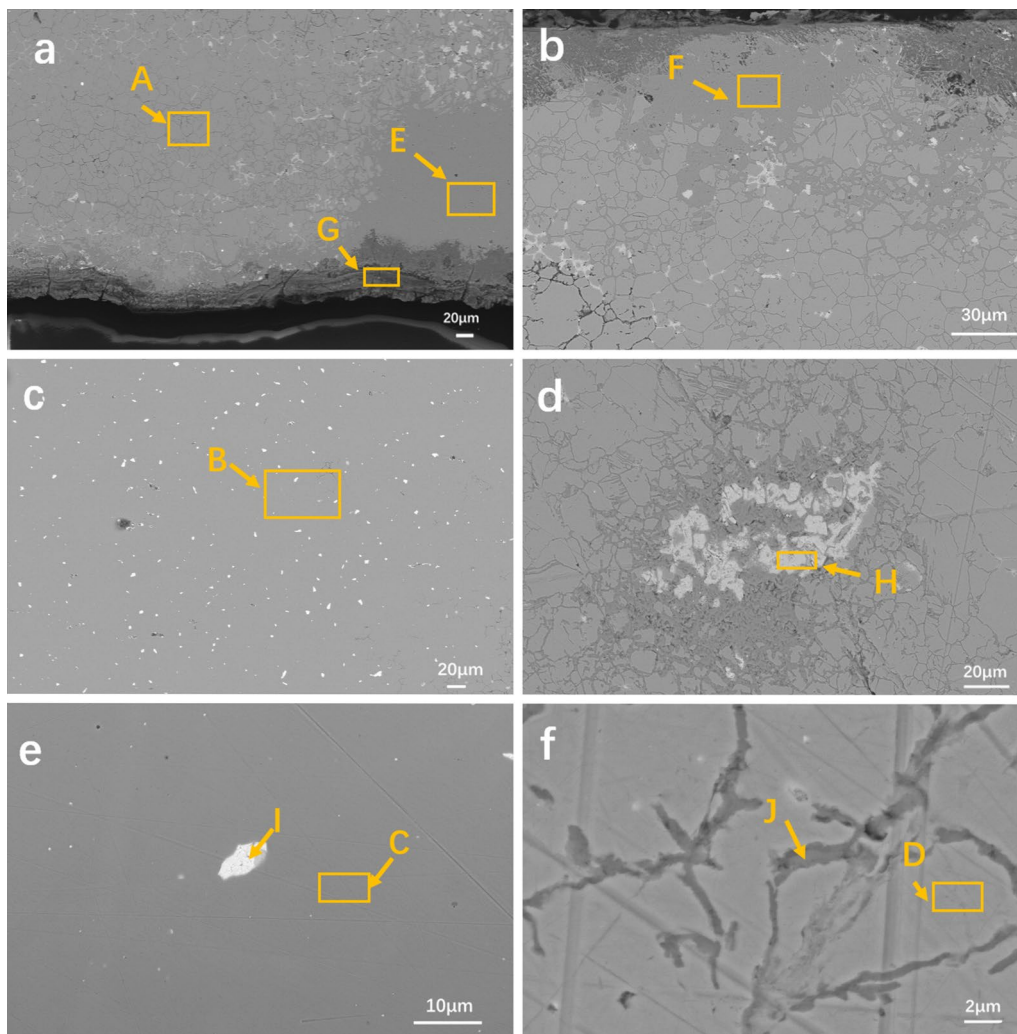


Fig. 2 **a** Cross-sectional BSE images of S-1 sample. **b** Severe corrosion area at the edge of the cross-section. **c** Environmentally unaffected area at the center of the cross-section. **d** Grayish-white agglomeration areas in the cross-section. **e** Bright white particles in the cross-section. **f** Corrosion grain boundaries in the cross-section

copper–zinc sulfide was lost due to dezincification corrosion. Besides, the affinity of lead to sulfur in the oxygen-free state was greater than that of copper to sulfur, which allowed the gray-white lead sulfide particles to form and accumulate near the corrosion products (H in Fig. 2d).

Figure 3 and Table 3 display the SEM–EDS results acquired on the cross-sections of S-2 and S-3 samples. The four BSE images in Fig. 3 include the matrix regions corresponding to the uncorroded zone, the section with copper corrosion products formed by the environmental corrosion, the dezincification area, and the lead sulfide accumulated domain, respectively. The central area of the copper wire, which was less affected by the environment,

was composed of copper, tin, zinc, and lead particles. According to these data, S-2 and S-3 were made of tin brass, which was consistent with S-1 sample. Therefore, the supporting parts of the coronet were all of brass which was the first confirmation of the brass application in the Central Plains during the Sui-Tang-dynasty period.

Production process

The metallographic structure was obtained, as shown in Fig. 4. The zinc content of brass was stable at 12 wt%, and the microstructure of brass at room temperature was presented by the α -copper–zinc solid solution (see Fig. 4a), consisting exclusively of twinned α grains, which was an unmistakable indication of

Table 2 Cross-sectional EDS results for S-1 sample

Analyzed area	Average composition															
	Cu		Zn		Sn		Fe		Pb		S		O		Cl	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
A (Fig. 2a)	83.7	85.3	11.3	11.2	3.8	2.1	1.3	1.5	N	N	N	N	N	N	N	N
B (Fig. 2c)	82.4	84.2	12.1	12.0	4.2	2.3	1.3	1.5	N	N	N	N	N	N	N	N
C (Fig. 2e)	82.2	83.8	12.6	12.5	3.4	1.8	1.2	1.4	N	N	N	N	N	N	N	N
D (Fig. 2f)	83.8	85.4	12.0	11.8	3.6	2.0	1.6	1.9	N	N	N	N	N	N	N	N
E (Fig. 2a)	80.7	82.8	N	N	8.6	4.7	10.7	12.5	N	N	N	N	N	N	N	N
F (Fig. 2b)	92.2	94.9	N	N	6.5	3.6	1.4	1.6	N	N	N	N	22.5	54.3	0.5	0.5
G (Fig. 2a)	2.9	0.8	N	N	N	N	N	N	N	N	N	N	90	95.8	7.1	3.4
H (Fig. 2d)	15.1	21.8	N	N	N	N	N	N	68.1	30.1	16.9	48.2	N	N	N	N
I (Fig. 2e)	6.8	18.7	1.1	2.9	N	N	N	N	92.2	78.3	N	N	N	N	N	N
J (Fig. 2f)	87.1	89.3	6.4	6.4	5.4	3.0	1.1	1.3	N	N	N	N	N	N	N	N

N the element was not detected

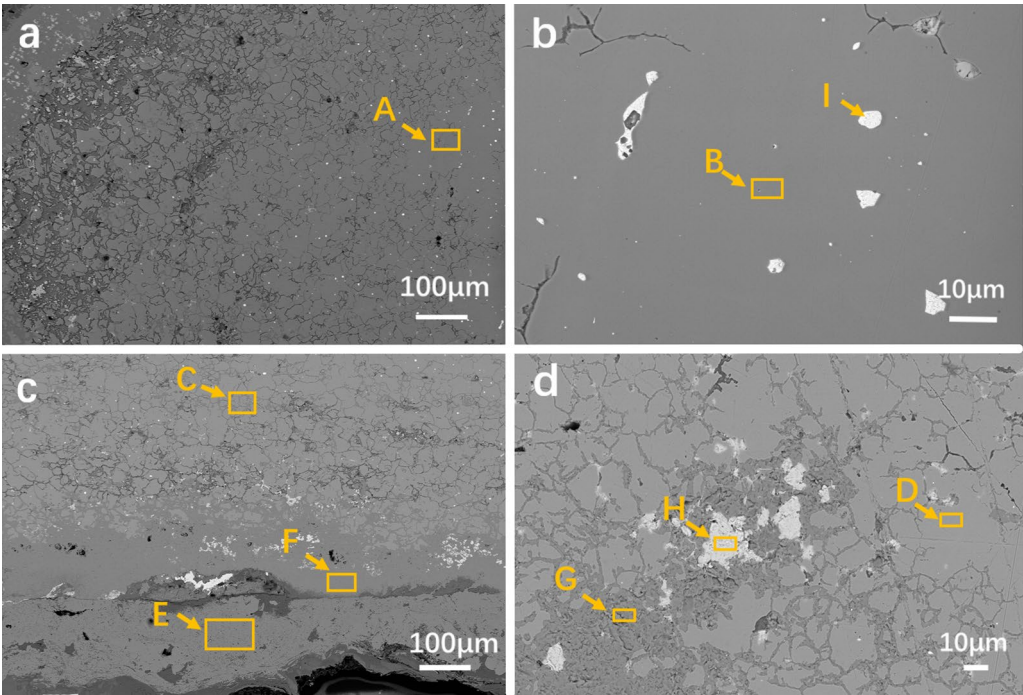


Fig. 3 Cross-sectional BSE images for: **a, b** S-2 and **c, d** S-3 samples

thermomechanical treatment applied to the sample [33]. In Fig. 4b, grains at the edge of the sample were filled with numerous slip lines in different directions, which indicated that the sample underwent multiple cold processing in different directions. Lead particles were randomly distributed in the cross-section, and lead sulfide (PbS) emerged at the Cu–Zn grain boundaries [34].

Discussion

Technical features of brass in the coronet

According to the results, the brass with a zinc content of 12 wt% had a single α -phase microstructure with the evenly distributed composition in the uncorroded area. These characteristics are similar to a certain stage of the development of brass smelting technology in Ancient China. The development of Chinese ancient brass

Table 3 Cross-sectional EDS results obtained on S-2 and S-3 samples

Analyzed area	Average composition													
	Cu		Zn		Sn		Fe		Pb		S		Cl	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
A (Fig. 3a)	83.6	84.9	12.5	12.3	2.9	1.6	1.0	1.2	N	N	N	N	N	N
B (Fig. 3b)	83.4	84.9	12.0	11.9	3.4	1.8	1.2	1.4	N	N	N	N	N	N
C (Fig. 3c)	84.0	85.7	10.7	10.6	4.0	2.2	1.4	1.6	N	N	N	N	N	N
D (Fig. 3d)	82.8	84.2	12.4	12.2	3.2	1.8	1.6	1.9	N	N	N	N	N	N
E (Fig. 3c)	98.5	97.3	N	N	N	N	N	N	N	N	N	N	1.5	2.7
F (Fig. 3c)	91.2	93.8	N	N	6.6	3.6	2.2	2.6	N	N	N	N	N	N
G (Fig. 3d)	92.8	94.0	3.7	3.6	2.9	1.6	0.7	0.8	N	N	N	N	N	N
H (Fig. 3d)	9.9	14.9	1.6	2.4	3.2	2.6	N	N	69.4	32.3	15.9	47.9	N	N
I (Fig. 3b)	13.3	32.4	2.0	4.6	N	N	N	N	84.7	78.3	N	N	N	N

N the element was not detected

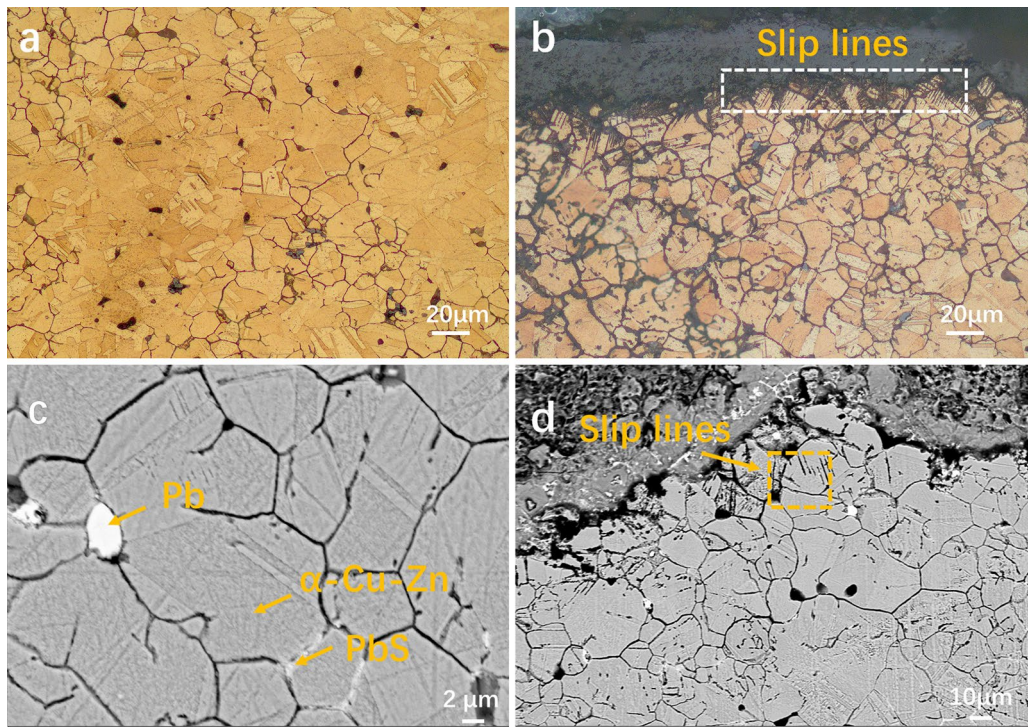


Fig. 4 Optical micrographs and SEM images showing the cross-sectional metallographic structure of S-1 sample. **a** The structure consisting of α -isometric single crystals with twinned grains. **b** Grains at the edge filled with numerous slip lines, indicating that the sample has undergone multiple mechanical treatments. **c** Lead particles and lead sulfide (PbS). **d** Slip lines

smelting technology had experienced three stages. In the first stage, brass was manufactured using a “solid-state reduction” technique at the temperature of 800–900 °C or “melting” over 920 °C [12, 34]. In addition, the raw materials could be copper ore with zinc ore or pure copper with zinc ore. In the second stage, cementation technology, taking its origin from the west at around 1400

BC, became the standard method of brass production in China in the tenth century. According to this technology, copper sheets were mixed with zinc oxide or carbonate and charcoal in an unsealed crucible [22]. When heated, zinc ore was reduced to metallic zinc vapor and diffused into copper, forming brass then. Finally, in the third stage dated back to around the fifteenth century and with the

availability of zinc metal, brass could be obtained by smelting pure copper and metallic zinc [17]. Thus, the composition distribution and metallographic structure of the sample were consistent with brass prepared by smelting copper ore [35, 36] consisting in melting an appropriate mixture of zinc ore and copper ore over 920 °C [12, 22]. Furthermore, it could be inferred that brass in the coronet was obtained by purposeful smelting of zinc ore.

In addition, twinned α grains and slip lines in the microstructure were the unmistakable indications of thermomechanical treatment and multiple cold processing in different directions. The brass was processed by integral hot forging into brass wires with diameters of 2 mm, which were afterwards fixed on the crown after surface cold shaping such as cutting and hammering during the production of the supporting parts.

Rationality of brass in the coronet

The strict hierarchical system of feudal society gave materials with specific hierarchical attributes [37]. In particular, the coronet under consideration was found to be made of two different materials. While its ornamental components were fabricated of gilding copper, supporting components consisted of brass. Since there were a few brass products dating back before the fifteenth century AD, a lot of knowledge about brass came from the ancient documents. Moreover, before the tenth century AD, brass was a precious metal in China, being the second after gold and silver only, and was used exclusively by elites [22]. Judging from the shape and structure of the tomb and the unearthed artifacts, the male tomb owner

should be an official of rank five or higher. In addition, in the Sui-Tang-dynasty epoch, the number of temples and apricot-leaf ornaments on a ceremonial coronet was configured according to the rank. For instance, nine apricot-leaf ornaments and two temples corresponded to the highest rank [25]. Eight apricot-leaf ornaments and two temples on the coronet from *Kunlun* M2 were attributed to at least the second rank. Therefore, the use of gilding copper and brass in this coronet was in conformity with the social attributes given to the material by the feudal society.

In addition, the preference for brass over gilding copper in the supporting components was related to the properties of the material. Multiple gilding leaf ornaments were only 200 μm thick, and were hung on the coronet by numerous gilding filaments with diameters less than 1 mm. Such a decoration could be possible due to softness and plasticity of pure copper. In turn, the brass with a single α -phase structure (the so-called α -brass) possessed excellent strength characteristics that became even better with the increase of zinc content (Fig. 5; [38]). Thus, brass with a 12 wt% concentration of zinc exhibited outstanding plasticity and could withstand hot and cold processing due to good corrosion resistance along with cold deformation ability [39]. Eroded under a long-term burial environment, most of the inlay fell off, and the metal also deteriorated to a great extent. However, one temple weighed more than 50 g and the weight of one apricot-leaf ornament was more than 15 g. The use of brass as the supporting components reflected the rational utilization of the mechanical properties of this

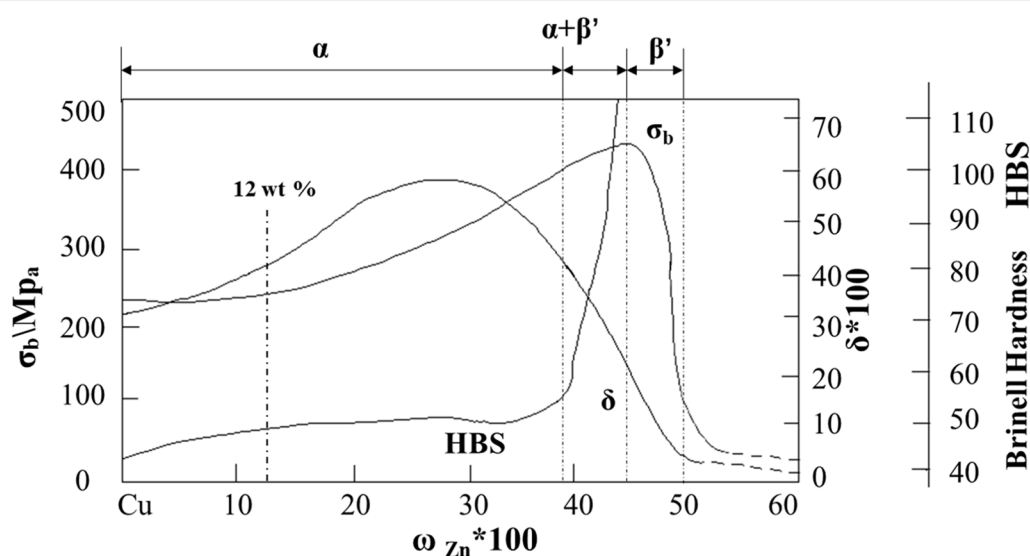


Fig. 5 Effect of zinc content on mechanical properties of copper–zinc alloy [38]. Here, σ_b is the tensile strength; δ is the elongation; HBS is the Brinell hardness

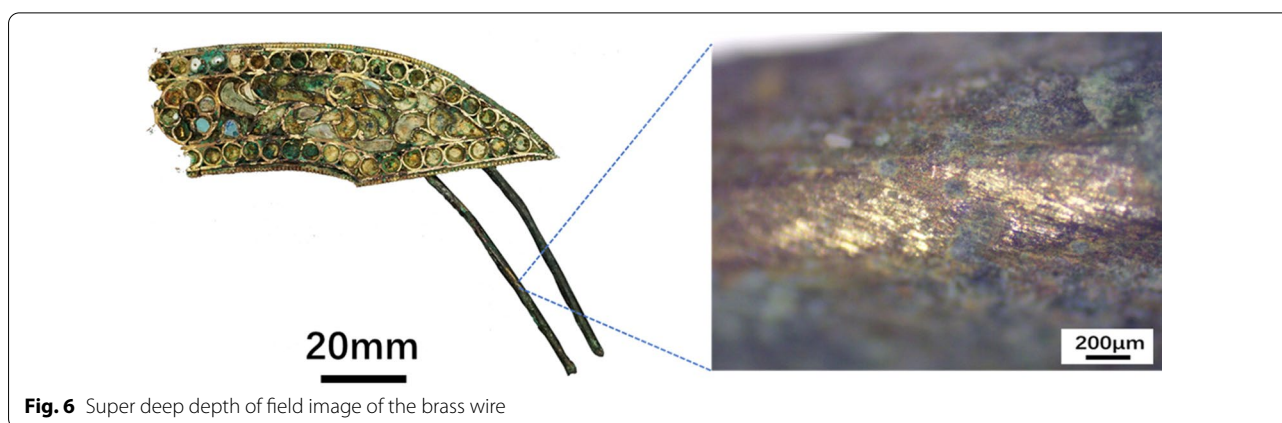


Fig. 6 Super deep depth of field image of the brass wire

compound by the craftsmen in the Sui-Tang-dynasty epoch. Furthermore, the decorative property of brass as a part of the coronet was also taken into account. During the Three Kingdoms period, brass was not recognized as an alloy, but served as a substitute for gold due to a quite similar luster. In that regard, brass was even called “fake gold”. By analogy with modern brass materials H80 and H90 (known as golden brass) [40], the brass in the coronet could be golden yellow before corrosion. After polishing together with gilding copper ornaments, it could basically be disguised as gold. Even though the brass had suffered the environmental erosion for more than 1400 years, the golden surface of the brass wire could still be observed (Fig. 6).

Being the second after gold and silver, the presence of brass in the coronet was in conformity with the social hierarchy of metal application in the Sui-Tang-dynasty. Besides, good mechanical properties and color similar to gold justified the choice of brass for supporting components. Presumably, with the progress of metallurgical technology and social development during the Sui-Tang-dynasty epoch, more attention was paid to the performance of materials. The craftsmen of that period were well aware of the properties of brass and used it accordingly.

Conclusions

Brass artifacts dating back to the Sui-Tang-dynasty epoch were for the first time discovered in the Central Plains of China, which enabled one to advance the Chinese brass history to the sixth–eighth century AD. The uniform composition distribution and the single α -phase microstructure of the products indicated that brass was obtained by purposeful melting of an appropriate mixture of zinc ores and copper ores at a temperature above 920 °C. The presence of brass in the artifacts not only was in conformity with the hierarchy of the related historical period, but also reflected the attention paid to the

properties of materials in the use of precious metals at that time. Presumably, craftsmen of the Sui-Tang-dynasty were able to master the characteristics of brass and apply it accordingly. Therefore, the findings of this study reveal tangible evidence of the production and use of brass during the Sui-Tang-dynasty epoch.

Abbreviations

p-XRF: Portable X-ray fluorescence; SEM-EDS: Scanning electron microscope with energy dispersive spectrometer; BSE: Backscattered electron; Cu: Copper; Zn: Zinc; Sn: Tin; Pb: Lead; Fe: Iron; S: Sulfur; O: Oxygen; Cl: Chlorine.

Acknowledgements

We would like to thank the Xi'an Institute of Conservation and Archaeology on Cultural Heritage for the samples. The authors are grateful to Ms. Xiaojuan Dang and Ms. Juan Ji from Shaanxi Institute for the Preservation of Cultural Heritage, for the support and help on the metallographic investigation, and SEM-EDS. Special thanks go to Dr. Yan Liu, Dr. Huan Yang, Dr. Dong Wang, Dr. Qingxing Xia, and Lifeng Jiang for suggestions on the manuscript. We also appreciate the valuable comments from the four anonymous reviewers, Editorial Board Member, and in-house Editor.

Authors' contributions

YS: methodology, validation, investigation, data analyses, writing—original draft, writing—review and editing. FJ: methodology, project administration. JD: writing—review and editing. JY: methodology, project administration. All authors read and approved the final manuscript.

Funding

The Project Supported by: (1) Natural Science Basic Research Program of Shaanxi (Program No. 2021JQ105). (2) The Humanities and Social Science Foundation of Ministry of Education of China (No. 21YJCZH050). (3) The Fundamental Research Funds for the Central Universities (Social Sciences), Northwestern Polytechnical University (No. D5000210802).

Availability of data and materials

The data and materials used during the study are available from the corresponding author on reasonable requests.

Declarations

Competing interests

The authors declare that they have no competing interests.

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Received: 30 June 2021 Accepted: 1 November 2021

Published online: 09 November 2021

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