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

Yanbing Shao
Northwestern Polytechnical University
Fengrui Jiang (jiangfengrui@nwpu.edu.cn)
Northwestern Polytechnical University
Jingnan Du
Northwestern Polytechnical University
Junchang Yang
Northwestern Polytechnical University
Quanmin Zhang
Xi'an Institute of Conservation and Archaeology on Cultural Heritage

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Abstract

In this study, the brass wires in the coronet excavated from M2 tomb in Xi'an, Shaanxi, dating back to Sui-Tang-dynasty were probed via portable X-ray fluorescence spectrometry (XRF) and scanning electron microscopy in combination with energy dispersive spectrometry (SEM-EDS) techniques. The wires were found to be composed of 83 wt% of copper, 12 wt% of zinc, and 3 wt% of tin. According to the metallographic analysis, the wires were formed by integral hot forging, and were then installed on the coronet after surface cold shaping, via cutting and hammering during the production of the support parts. It indicated that the composition of brass was evenly distributed without obvious composition segregation, revealing the features of the second stage of brass smelting in ancient China, which may prove brass had appeared and brass smelting technology had been mastered in the Sui-Tang-dynasty in the Central Plains of China. In addition, the use of brass in the coronet was in accorded with the hierarchical symbol given to the material by the feudal society. And the selection of brass was based on the dual combination of the excellent mechanical properties and the golden surface of brass. Thus, brass in the Sui-Tang-dynasty historical period was the tangible evidence of the development level of metallurgical technology, and also reflected the artistic and social attributes given to materials by different stages of social development.

1 Introduction

Copper and copper alloys as the earliest metals in human history have been of great significance to human civilization, representing a significant transition from the Neolithic to the Bronze Age and reflecting the social development influenced by the productive forces and production relations [1, 2]. In the literature, copper and copper alloy smelting techniques are widely emphasized as the evidence of the origin of human civilization [3]. The basic development route of copper metallurgy is from natural copper to smelted red copper and copper alloys. The breakthrough in copper alloy technology first led to a wide spreading of arsenic-copper alloys in West Asia due to their faster hardening during forging than pure copper [4]. However, arsenic-copper alloys were afterwards replaced by the tin-bronze composites owing to the good casting properties and better hardness of the latter [5, 6]. Among all kinds of ancient copper alloys, special attention was paid to zinc-based brass. Despite brass became available much earlier (4700 BC) than bronzes (2800 BC) and arsenic-copper alloys (4100 – 3900 BC), brass smelting was considered to emerge later than the other two [7]. This was mainly because the prehistoric brass artifacts were speculated to be acquired occasionally by smelting of copper-zinc ores [8, 9]. Therefore, they did not evidence the invention of zinc-copper alloy. Moreover, the historical beginning of the conscious production of brass in China has been unknown up to date, making it important to study the ancient Chinese alloying technique of zinc-copper composites.

According to the data about unearthed cultural relics, the brass wares with a zinc content from 10 to 32 wt % appeared occasionally as small ornaments in the prehistory, but disappeared in the middle of the Shang dynasty period (the 8th century BC) [10–12]. In turn, no artifacts that might be identified as brass had been found yet in the Han dynasty epoch (the 9-12th centuries AD) [13]. Due to the scarcity of excavated brass artifacts, the research on the brass history in China has mainly relied on the study of ancient literature records [11, 14]. The first explicit record of brass smelting was referred to a historical period of Song dynasty (960–1279 AD) [15], but the smelting technology of elemental zinc was traced back to the Ming dynasty (the 16th century AD) [16, 17]. Before the invention of zinc smelting technology, brass was obtained by smelting copper-zinc symbiotic ore, copper-zinc mixed ore or copper with zinc oxide ore, which had been demonstrated by simulation experiments [9, 18, 19]. Thus, brass appeared earlier than elemental zinc became technically feasible. Unfortunately, neither the extensive usage nor the physical evidence of brass was documented until the Ming dynasty. Therefore, based on the brass coins as the archaeological finds [20–23], the commercialization of brass in China was concluded to emerge in the Ming dynasty epoch with the mature zinc smelting technology as the technical support. As a result, the information about how brass has been discovered and utilized in ancient China remains controversial.

The purposeful smelting of brass originated in India in the second half of 1000 BC worldwide [24]. In 45 BC, the copper-zinc alloy produced by calcining red copper (with 71.1wt % of copper, 27.6 wt% of zinc) was already used in the casting of brass coins in ancient Roman Empire [5, 25]. Later, the brass smelting technology was spread to Persia with the Roman Empire, expanding to the Upper Mesopotamia in the 2nd century AD[25]. Brass smelting technology also had the possibility developing with the trade between China and Persia, which began no later than the 2nd century AD. So, it was generally believed that the Chinese people began to use zinc and brass in the last quarter of the 3rd century BC (Han dynasty) [26]. Some clues and evidence for this view were found from Chinese ancient documents. Brass had a "golden color" surface which was recorded during the Three Kingdoms period (228–280 AD). During the Sui-Tang-dynasty epoch, brass was called "*Toushi*". Moreover, brass was used by Persia to pay tribute to the Sui empire (581-618AD), as reported in the “*Sui Shu* (Book of Sui Dynasty)”. Later, according to the “*Tang Shu-Yu Fu Zhi* (Book of Tang Dynasty)” (619–907 AD), the officials were pledged to wear gold, silver, or "*Toushi*" belt according to their ranks, whereas the civilians were only allowed to wear copper or iron belt. Brass, because of its color, had become a status symbol in the Sui-Tang dynasty along with gold and silver. Moreover, there was plenty of brass coins in circulation as documented in the "*Tang Shu-Shi Huo Zhi* (Book of Tang Dynasty)". Therefore, being a valuable metal in that period, brass in the Tang dynasty served not only for higher-grade decorations, but also for casting coins. Recently, some brass artifacts dating from the 4th to 9th centuries have been unearthed in *Xinjiang*, Inner Mongolia, and *Qinghai* [27]. Some scholars put forward that brass was introduced into China with western Buddhism two thousand years ago [19, 28]. And relying on the ancient documents analysis, they believed that brass artifacts discovered on the Silk Road were the most evident physical pieces [25]. According to this point of view, China began to use brass in the late 3rd century BC, and the brass smelting process in China had already emerged during the Sui-Tang-dynasty period (581–705 AD). To sum up, the disputes about the earliest brass products and the origin of brass smelting technology refer to the historical period from the Han to a Ming dynasty [25, 29], thus the research of brass products dated to this epoch is expected to fill in some of the blanks in the Chinese brass history.

In 2007, a tomb of the late Sui dynasty in Xi'an (Shaanxi province) 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 gold surface, probed via portable XRF, SEM-EDS, and metallographic analysis techniques, were confirmed to be copper zinc alloy, namely brass. Recall that, because of the lack of archaeological evidence, the historical phase in which Chinese ancient brass products might have employed for the first time remains controversial. Prehistoric brass was believed to have been acquired accidentally. No other ancient brass wares, except for prehistoric brass, were found in the Central Plains of China. Therefore, the brass of late Sui dynasty discovered in Xi'an was momentous and has aroused attention. Since brass artifacts of the Sui-Tang-dynasty are rarely reported, the discovery of this compound in present study not only fills the gaps in the knowledge about the Sui-Tang-dynasty, but also brings important information about the development of ancient Chinese society and the history of art.

2 Materials And Methods

2.1 Materials

In 2007, an ancient tomb was unearthed at the *Kun Lun* Company in the eastern suburb of Xi'an, Shaanxi province. The tomb numbered M2 was a single-chamber earth cave tomb with a long ramp tomb passage. Archaeological excavations revealed that M2 was a joint burial, and a series of ornaments was found around the head of the female tomb owner. Judging from the shape and structure of the tomb and the unearthed artifacts, this might be related to a Sui dynasty or at least not later than the early Tang dynasty period (the 9th century) [30].

The metal ornaments in the shape of wings (Temples) and apricot leaves (Dian) enabled one to suggest that these were the ornamental components of a coronet. And the number of ornaments (eight Dian ornaments and two Temples) indicated the coronet as the personal adornment of high-ranking females in the hierarchical system during the Sui and Tang dynasty epochs (Fig. 1a) [31]. 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 subjects to nondestructive analysis and hereinafter labeled TBB1, TBB2, SD1, SD2, and SD3. Among these, TBB-1 and TBB-2 were the metal wires on the back of the Temples, whereas SD1, SD2, and SD3 were the metal wires on the back of the Dian ornaments. To acquire the information about composition and processing of the metal wires, sampling analysis was performed. Samples with length less than 5 mm were intercepted at the ends of TBB-1, TBB-2, and SD-2 in better preservation condition, and labeled S-1, S-2, and S-3 respectively (Fig. 1b).

Figure 1 (a) Temples and Dian ornaments of the ceremonial coronet; (b) TBB1, TBB2, SD1, SD2, and SD3: the metal wires on the back of the ornaments; S-1, S-2, and S-3: three experimental samples intercepted at the end of the wires.

2.2 Methods

2.2.1 Microscopic analysis

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

2.2.2 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 accurate composition information as much as possible, the supporting components labeled TBB1, TBB2, SD1, SD2, and SD3 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 S1, S2 and S3 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.

2.2.3 Metallographic investigation

The S1, S2 and S3 samples were cold-mounted, ground, and polished following the standard metallographic procedure. The polished sections were etched with alcoholic ferric chloride solution ($FeCl_3 + HCl + C_2H_6O$) to reveal their metallographic structures, and were then examined and photographed with a ZEISS optical microscope.

3 Results And Discussion

3.1 Results

3.1.1 The discovery of brass

Table 1 Chemical composition of supporting components of Temples and Dian ornaments, obtained using the portable XRF spectrometer.

Table 1
Chemical composition of supporting components of Temples and Dian 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.

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 Dian ornaments labeled TBB1, TBB2, SD1, SD2, and SD3 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, being 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 [32]. The iron concentration was found to be less than 2 wt%, which might have come from soil elements or impurities of raw ore during smelting. However, zinc was very rare in ancient metalworks. According to the literature, zinc smelting technology was first dated to only the Ming dynasty epoch in China, condensing that the appropriate equipment hadn't been invented before this historical period. Although brass was discovered earlier than elemental zinc and thus became technically feasible[33], the method of smelting brass with copper and zinc in China had been unknown until the Ming dynasty period, according to the unearthed relics [34]. Up to now, only a few brass products related to a historical period of the Sui to Tang dynasty have been found in the Central Plains. Therefore, the presence of zinc in metal wares of the late Sui dynasty in Xi'an was unexpected, and further research was needed to verify whether this element was indeed making part of the above relics.

3.1.2 The determination of brass

To obtain the internal composition information about the copper alloy, the cross-sections of S1, S2, and S3 were probed via SEM-EDS technique.

Figure 2 (a) Cross-sectional BSE images of S1 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.

Table 2 Cross-sectional EDS results for S1 sample.

Table 2
Cross-sectional EDS results for S1 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								
B (Fig. 2c)	82.4	84.2	12.1	12.0	4.2	2.3	1.3	1.5								
C (Fig. 2e)	82.2	83.8	12.6	12.5	3.4	1.8	1.2	1.4								
D (Fig. 2f)	83.8	85.4	12.0	11.8	3.6	2.0	1.6	1.9								
E (Fig. 2a)	80.7	82.8			8.6	4.7	10.7	12.5								
F (Fig. 2b)	92.2	94.9			6.5	3.6	1.4	1.6					22.5	54.3	0.5	0.5
G (Fig. 2a)	2.9	0.8											90	95.8	7.1	3.4
H (Fig. 2d)	15.1	21.8							68.1	30.1	16.9	48.2				
I (Fig. 2e)	6.8	18.7	1.1	2.9					92.2	78.3						
J (Fig. 2f)	87.1	89.3	6.4	6.4	5.4	3.0	1.1	1.3								

Cross-sectional BSE images of the S1 sample and the corresponding EDS results are shown in Figs. 2a-2f and Table 1. 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 [35]. 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 [36]. 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. And their main elements were copper, iron, and tin. Zinc was not detected in these areas as compared to the central part of the cross-section. In the long-term burial environment, the metallic elements in cultural relics had been undergoing electrochemical reactions, leading to selective corrosion of the components, and the active elements in the alloy were more likely to be corroded and dissolved [37]. In brass, zinc is easy to be dissolved by preferential corrosion [38]. Therefore, E and F areas were formed by dezincification corrosion. With the increase of corrosion rate, tin was also corroded and dissolved. Finally, only the residual copper corrosion products (oxides and chlorides of copper) were detected in region D. Furthermore, compared with a central region of the cross-section under examination, the dezincification corrosion led to zinc depletion at the grain boundary marked J in Fig. 2f. Therefore, 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 [39].

Many bright white particles denoted I in Fig. 2e were observed in the cross-section. The main components of the particles were copper and lead, with a small amount of zinc, indicating that the lead existed in the alloy in the form of particles. The gray-white agglomerations marked H in Fig. 2d were accumulated at the corroded grain boundaries of the sample, being composed of mainly copper, lead, and sulfur. Presumably, the brass contained trace amounts of sulfur, and lead aggregated near the copper-zinc sulfide in the form of particles[28]. When brass was corroded, the zinc in the copper-zinc sulfide was lost due to dezincification corrosion. And in the oxygen-free state, the affinity of lead to sulfur was greater than that of copper to sulfur, so the gray-white lead sulfide was formed and accumulated near the corrosion products.

Figure 3 Cross-sectional BSE images for: (a), (b) S2 and (c), (d) S3 samples.

Table 3 Cross-sectional EDS results obtained on S2 and S3 samples.

Table 3
Cross-sectional EDS results obtained on S2 and S3 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						
B (Fig. 3b)	83.4	84.9	12.0	11.9	3.4	1.8	1.2	1.4						
C (Fig. 3c)	84.0	85.7	10.7	10.6	4.0	2.2	1.4	1.6						
D (Fig. 3d)	82.8	84.2	12.4	12.2	3.2	1.8	1.6	1.9						
E (Fig. 3c)	98.5	97.3											1.5	2.7
F (Fig. 3c)	91.2	93.8			6.6	3.6	2.2	2.6						
G (Fig. 3d)	92.8	94.0	3.7	3.6	2.9	1.6	0.7	0.8						
H (Fig. 3d)	9.9	14.9	1.6	2.4	3.2	2.6			69.4	32.3	15.9	47.9		
I (Fig. 3b)	13.3	32.4	2.0	4.6					84.7	78.3				

Figure 3 and Table 3 display the SEM-EDS results acquired on the cross-sections of S2 and S3 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, S2 and S3 were made of tin brass, which was consistent with S1 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. Moreover, the brass products exhibited their uniform composition without obvious segregation, which might be the new evidence that brass smelting technology was at a stage of steady development in the Sui-Tang-dynasty epoch.

3.1.3 Production process

Figure 4 Optical micrographs and SEM images showing the cross-sectional metallographic structure of S1 sample. (a) The structure consisting of twinned α-grains. (b) Grains at the edge filled with numerous slip lines, indicating that the sample was given multiple mechanical treatments. (c) Lead particles and lead sulfide (PbS). (d) Slip lines.

The metallographic structure was obtained, as shown in the Fig. 4. The zinc content of brass was stable at 12 wt%, and the microstructure of brass at room temperature was composed of single-phase α-copper-zinc solid solution (see in Fig. 4a), consisting exclusively of twinned α grains, which was an unmistakable indication of thermomechanical treatment applied to the sample [40]. α-phase brass had excellent mechanical properties due to its good plasticity and ability to withstand hot and cold processing. 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 [41]. Lead particles were randomly distributed in the cross-section, and lead sulfide (PbS) emerged at the Cu-Zn grain boundaries where the dezincification corrosion occurred [42]. The brass was assumed to be 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.

3.2 Discussion

3.2.1 Speculative reasons for the use of brass

The coronet was found to be made of two different materials. While ornamental components of the coronet were fabricated of gilding cooper, supporting components were composed of brass. The choice of various materials was justified by the two following reasons.

The first is the difference between the properties of both materials. Pure copper enables gilding, whereas brass has the better mechanical characteristics. Multiple gilding leaf-ornaments are only 200 μm thick, and are hung on the coronet by numerous gilding filaments with diameters less than 1 mm. Since pure copper is soft and plastic, it allows one to make such decorations. Moreover, pure copper ensures a much easier gilding than other copper alloys, thus being suitable for decorative components in terms of material modeling and gilding process. In turn, the brass possesses excellent strength characteristics that become even better with the increase of zinc content. The room temperature microstructure of copper-zinc alloy with zinc content less than 39 wt % is composed of single-phase α-Cu-Zn solid solution that is called α-brass. In turn, the microstructure of brass with a zinc content in the range of 39–45 wt% is the combination of α-Cu-Zn solid solution and β'-Cu-Zn electron compound solid solution, which is related to a two-phase brass. Once the amount of zinc covers the range of 45–50 wt%, the microstructure of brass exhibits a single-phase β'-Cu-Zn electron compound solid solution defined as β-brass. In particular, the best plasticity of brass can be achieved at a zinc concentration of 30 wt%, whereas its maximum strength is obtained at a zinc quantity of 46 wt% (Fig. 5 [43]). Recall that the zinc concentration in brass of the coronet was found to be about 12 wt%, and the microstructure of brass at room temperature was composed of a single-phase α-Cu-Zn solid solution, the above-mentioned α-brass. This type of brass exhibits outstanding plasticity, can withstand hot and cold processing, and has good corrosion resistance and cold deformation ability. 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 weighs more than 50 g and a Dian ornament's weight is more than 15 g. The use of brass instead of pure copper in the supporting components reflects deep understanding and rational utilization of the mechanical properties of this compound by the craftsmen in the Sui-Tang-dynasty epoch.

Figure 5 Effect of zinc content on mechanical properties of copper-zinc alloy. [43]

Here, σ_b is the tensile strength; δ is the elongation; HBS is the Brinell hardness.

The second reason may be the “golden-like” surface of the brass [44, 45]. 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”. Moreover, the modern brass materials H80 and H90 also have a single-phase α-Cu-Zn solid solution in their structure and are known as golden brass because of their golden yellow surfaces [46]. It is noteworthy that the brass in the coronet has the same structure as modern materials H80 and H90 with the intermediate zinc content. By analogy with the chroma of H80 and H90, the original color of the brass related to a Sui-Tang-dynasty might be golden yellow before corrosion. After polishing, the brass used in the coronet together with gilding copper ornaments, which could basically be disguised as gold. The golden surface of brass in the coronet was also demonstrated in the super depth of field image. Even though the brass had suffered the environmental erosion for more than 1,400 years, the golden surface of the brass wire could still be observed (Fig. 6). Therefore, based on the rational use of the excellent mechanical properties of brass, and considering the decorative properties of golden surface of brass at the same time, the presence of brass supporting components in the copper gilded ornaments is the result of double consideration of the mechanical properties and decorative properties of the material.

In addition, according to the ancient literature, brass, because of its color, had become a status symbol in the Sui-Tang-dynasty. Based on the results of the present work, the addition of brass in the coronet was aimed at referring to a certain hierarchy of Sui-Tang-dynasty. The number of Temples and Dian ornaments on the ceremonial coronet was configured according the rank; for instance, nine Dian ornaments and two Temples corresponded to the highest rank [31]. Eight Dian ornaments and two Temples indicated at least the second rank, which also allowed the use of brass in the ornaments. Therefore, the presence of brass in coronet reflected the social attributes given to the material by the feudal society.

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

3.2.2 History of brass in China

Table 4 Prehistoric brass artifacts unearthed in China.

Table 4
Prehistoric brass artifacts unearthed in China.

No.	Name	Archaeological site	Date	Composition(wt%)		Manufacturing process
				Cu	Zn	
1	Round piece	Shannxi, Jiangzhai Yangshao culture	4700BC-4000BC	66.5	25.7	casting
2	Brass Ji	Shannxi, Weinan Yangshao culture	3000BC	-	32.0	forging
3	Cone	Shandong, Jiaoxian Longshan culture	2300BC-1800BC	- -	20.1–26.4*	forging
4	Cone	Shandong, Jiaoxian Longshan culture	2300BC-1800BC	- -	20.1–26.4*	forging
5	Arrowhead	Shandong, changdao	1046BC-771BC	84.4	10.9	-
6	Arrowhead	Shandong, changdao	1046BC-771BC	82.1	11.8	-

Brass wares unearthed in China were traced back to two historical eras, namely, the prehistoric period and the 4th to 9th centuries AD. Among seven pieces of prehistoric brass artifacts, i.e., the plate and the pipe, found at the *Jiangzhai* site dating back to the early *Yangshao* Culture (about 4000–4700 BC), were the earliest brass products in the world [7]. All the prehistoric brass vestiges were small wares with diversified categories, scattered throughout various locations. These were found to have nothing in common with copper-zinc binary alloys, but contained lead and tin and exhibited uneven structure and large composition segregation, meaning that the raw materials used were cogeneration ores of multiple metals [9, 11, 47]. The development of Chinese brass smelting technology had experienced three stages: (1) occasional synthesis of brass by doping copper-zinc symbiotic ore during copper smelting; (2) combined smelting of calcite and pure copper; (3) pure copper and elemental zinc smelting. The smelting method of prehistoric brass before 1000 BC was relatively primitive, corresponding to the first stage. Thus, the appearance of prehistoric brass was accidental [48–50].

Table 5 Ancient brass artifacts unearthed in China.

Table 5
Ancient brass artifacts unearthed in China.

No.	Name	Archaeological site	Date	Composition (wt%)		Manufacturing process
				Cu	Zn	
1	Ring	Xinjiang, Yingpan	The 4th century	-	□20	-
2	Earrings	Xinjiang, Yingpan	The 4th century	-	□20	-
3	Bracelet	Xinjiang, Yingpan	The 4th century	-	□20	-
4	Ring	Neimeng, Qilangshan	The 4th century	92	7.3	Forging
5	Copper Decoration	Neimeng, Qilangshan	The 4th century	72.8	18.3	Forging
6	fragments	Xinjiang, Xiaohe	The 4th century	79.2	19.5	Hot forging
6	Copper bar	Qinghai, Dulan	The 9th century	63.2	29.2	Hot-working
7	Copper hook	Qinghai, Dulan	The 9th century	71.5	21.6	Hot-working
8	Bull nose ring	Qinghai, Dulan	The 9th century	71	19.5	Hot-working
9	Copper ring	Qinghai, Dulan	The 9th century	70.1	22	Casting
10	Buckle	Qinghai, Dulan	The 9th century	75.1	17.8	Casting

In addition to the prehistoric brass, 11 pieces of historical brass products had been unearthed in China by far, which were dating back to the 4th to 9th centuries AD (Table 5). They were unearthed in *Xinjiang*, Inner Mongolia and *Qinghai* that were the compact communities with the ethnic minority populations. Brass products of the 4th century AD unearthed from *Yingpan*, *Xiaohe*, *Xinjiang* and *Qilangshan* sites in Inner Mongolia shared common characteristics. And they were all small ornaments with relatively high zinc contents (above 20 wt%) and few impurities. Based on these characteristics of all brass products found at the Silk Road, elevated zinc concentration in them was considered to be one of the features of western brass smelting techniques. According to the data given in Table 5, the brass products of this historical period were believed to have been introduced from the West to the Central Plains of China via the Silk Road [51]. In that period, the Chinese brass products indeed were rich in zinc and impurity-depleted, which was associated with the second stage of Chinese brass smelting technology based on zinc ore and pure copper smelting.

It was worth noting that most of the unearthed brass artifacts dating back to the 4-9th century were ornaments such as rings, earrings, buckles, and so on [52–54]. It can be speculated that, with the progress of metallurgical technology and social development, the demands for materials in the Sui-Tang-dynasty were much more diversified. Different from arsenic-copper and tin-bronze compounds that were used due to their mechanical properties, brass in that period had the meaning of status and rank symbol owing to its decorative color, thus attracting attention in terms of the aesthetics [4]. During the Sui-Tang-dynasty, brass was not only a reflection of metallurgical technology progress but also a symbol of the stringent requirements for the science and art. Independent of whether brass smelting technology had been invented in the Sui-Tang-dynasty epoch or not, the discovery of this compound made an important contribution to the study of Chinese brass history, art history, and ancient society system.

The brass products in this study were for the first time discovered in the Central Plains of China and dated back to the Sui-Tang-dynasty period. This was the tangible evidence that brass was widely used in the Sui-Tang-dynasty after being introduced from the west. A thorough analysis of the brass wares proved that the composition of the brass wares was evenly distributed without obvious composition segregation, revealing the features of the second stage of brass smelting in ancient China, in which brass was obtained via zinc ore and pure copper smelting [9]. A purposeful brass smelting began as brass production entered into the second stage. Based on the facts described in the corresponding historical sources, the brass detected in the coronet was locally manufactured and processed, meaning that brass smelting technology had been not only mastered but also developed steadily in the Sui-Tang-dynasty in the Central Plains of China.

The elemental analysis of the coronet attributed to the Sui-Tang-dynasty enabled one to conclude that the decorative parts were made of gilded copper, while the supporting compositions were of brass. Presumably, with the progress of metallurgical technology and social development, the demands for materials in the Sui and Tang dynasties became more diversified. The use of brass in that epoch was mainly due to its decorative color in terms of status and rank as well as artistic aesthetics. Therefore, brass in the Sui-Tang-dynasty history was not only a reflection of metallurgical technology but also a symbol of the diversified demands for science and art.

4 Conclusions

The brass products in this study were for the first time discovered in the Central Plains of China and dated back to the Sui-Tang-dynasty period, which was an important discovery in Chinese metallurgical archaeology. The coronet supporting metal wires with 2 mm diameters were examined using portable XRF and SEM-EDS appliances. Their composition was found to be the brass composed of 83 wt% of copper, 12 wt% of zinc, and 3wt% of tin. According to the metallographic analysis data, the brass wires were formed by integral hot forging, and were afterwards installed on the coronet after surface cold shaping such as cutting and hammering during the production of the supporting parts. A thorough analysis of the brass wares proved that the composition of the brass wares was evenly distributed without obvious composition segregation, revealing the features of the second stage of brass smelting in ancient China, in which brass was obtained via zinc ore and pure copper smelting. Perhaps these can prove brass smelting technology had been not only mastered but also developed steadily in the Sui-Tang-dynasty in the Central Plains of China.

In addition, the presence of brass in the copper gilded ornaments was the result of double consideration of the mechanical properties and decorative properties of the material, and accorded with the social attributes given to the material by the feudal society. Presumably, with the progress of metallurgical technology and social development, brass in the Sui-Tang-dynasty historical period was not only the tangible evidence of the development level of metallurgical technology, but also reflected the artistic and hierarchical symbol given to materials by different stages of social development.

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.

Declarations

Availability of data and materials

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

Competing interests

The authors declare that they have no competing interests.

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Authors' Contributions

Yanbing Shao: Methodology, Validation, Investigation, Data analyses, Writing—original draft, Writing—review & editing.

Fengrui Jiang: Methodology, Project administration.

Jingnan Du: Writing—review & editing.

Junchang Yang: Methodology, Project administration.

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Figures

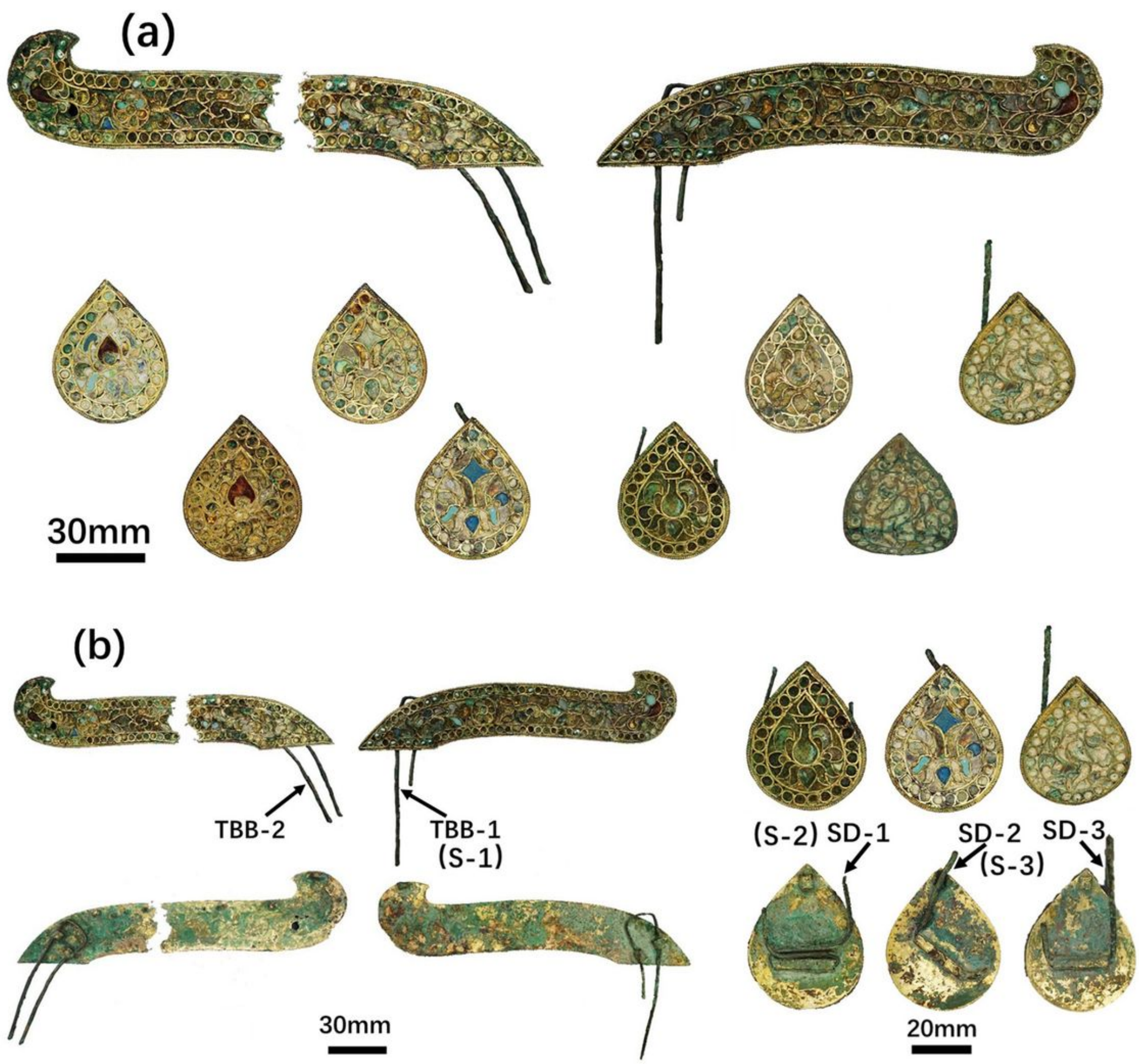

Figure 1

(a) Temples and Dian ornaments of the ceremonial coronet; (b) TBB1, TBB2, SD1, SD2, and SD3: the metal wires on the back of the ornaments; S-1, S-2, and S-3: three experimental samples intercepted at the end of the wires.

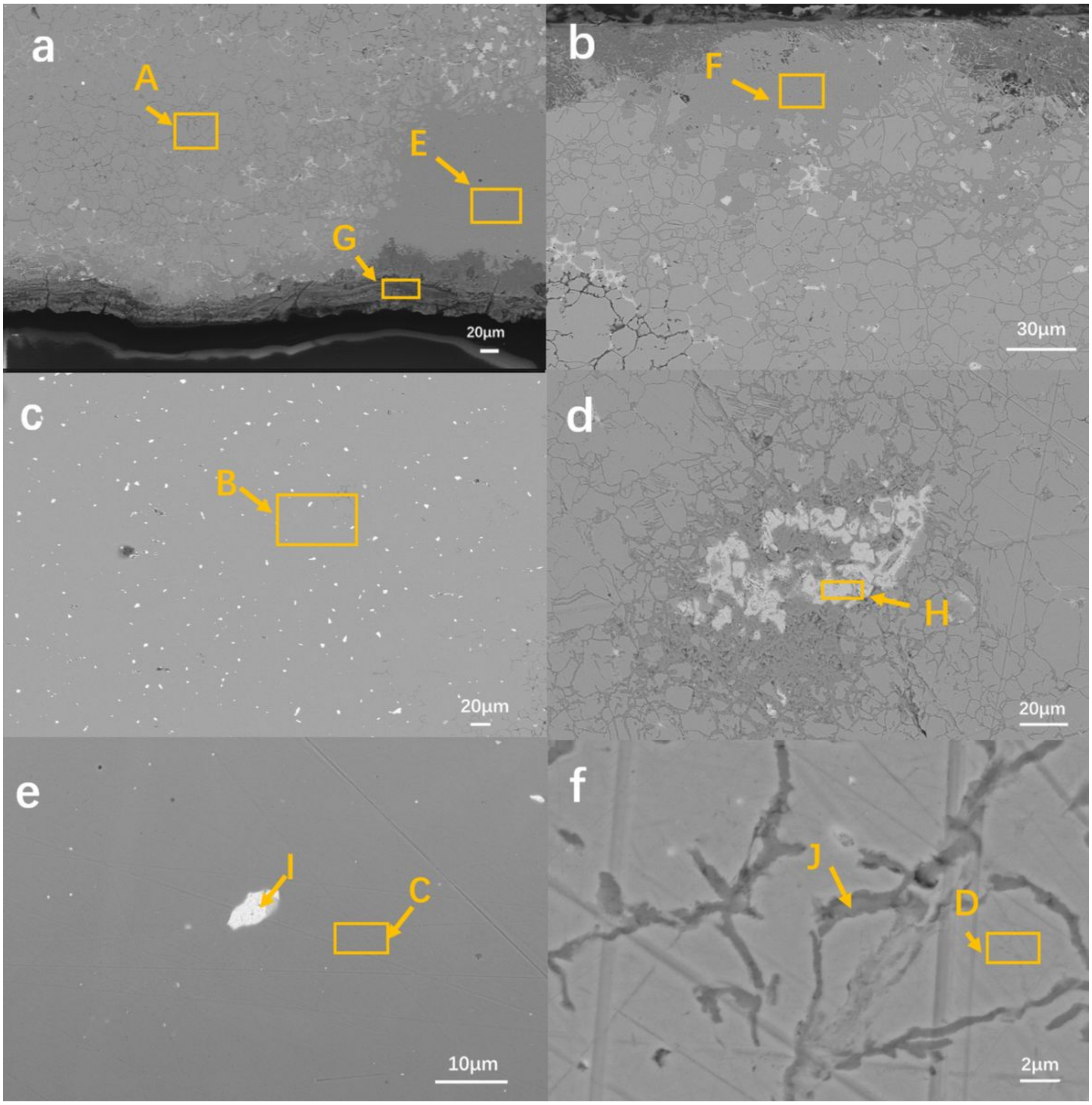

Figure 2

(a) Cross-sectional BSE images of S1 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.

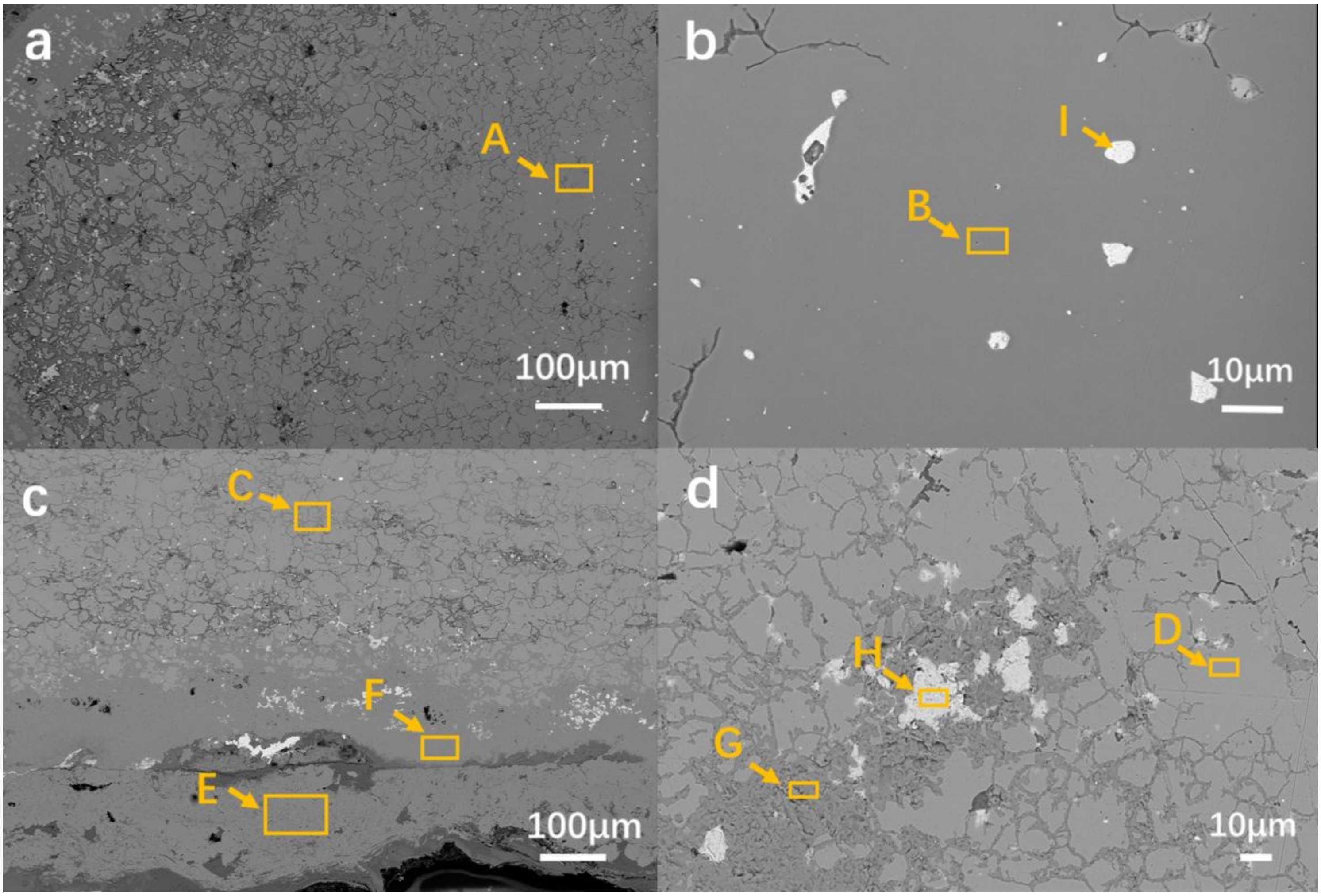

Figure 3

Cross-sectional BSE images for: (a), (b) S2 and (c), (d) S3 samples.

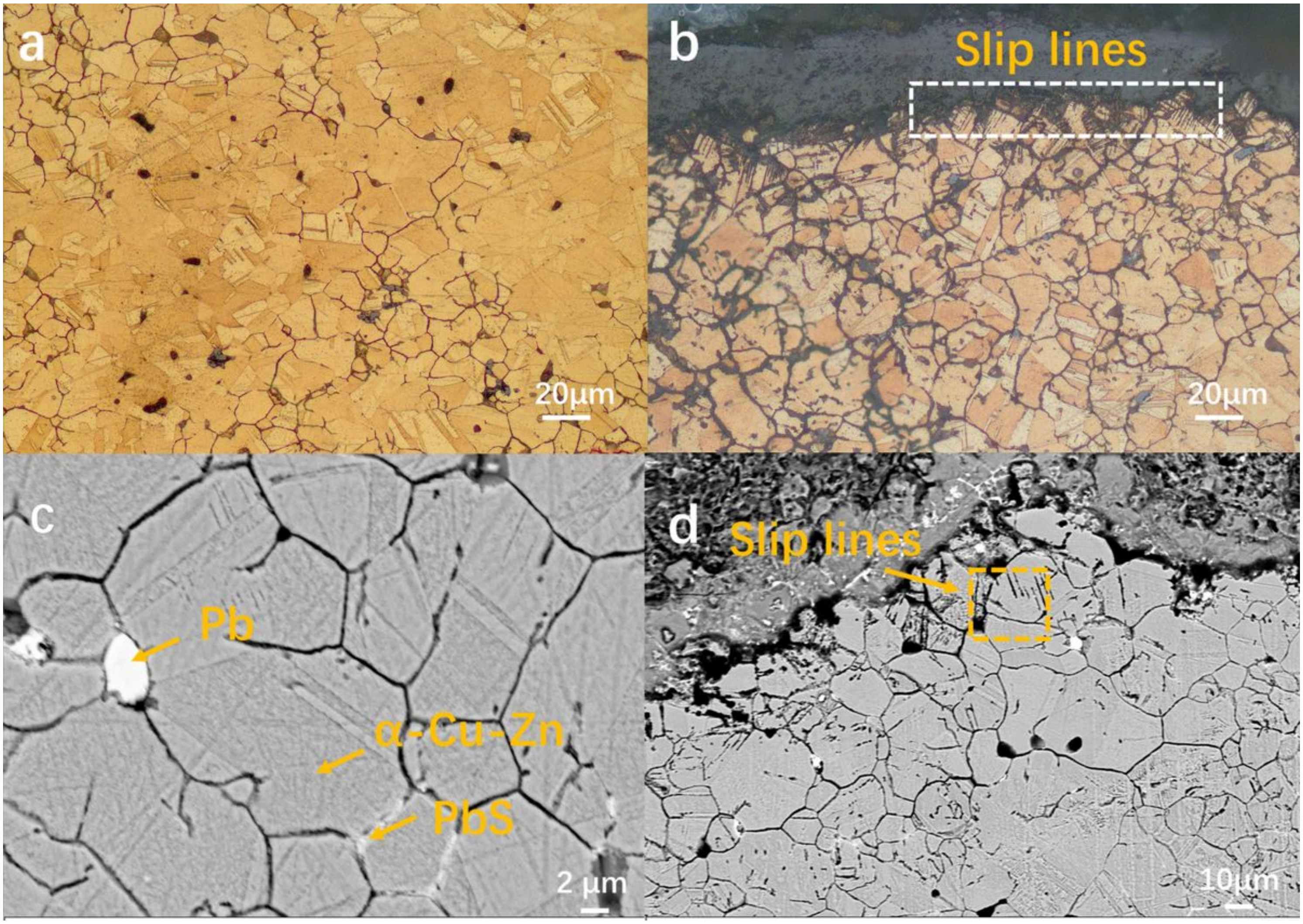

Figure 4

Optical micrographs and SEM images showing the cross-sectional metallographic structure of S1 sample. (a) The structure consisting of twinned α-grains. (b) Grains at the edge filled with numerous slip lines, indicating that the sample was given multiple mechanical treatments. (c) Lead particles and lead sulfide (PbS). (d) Slip lines.

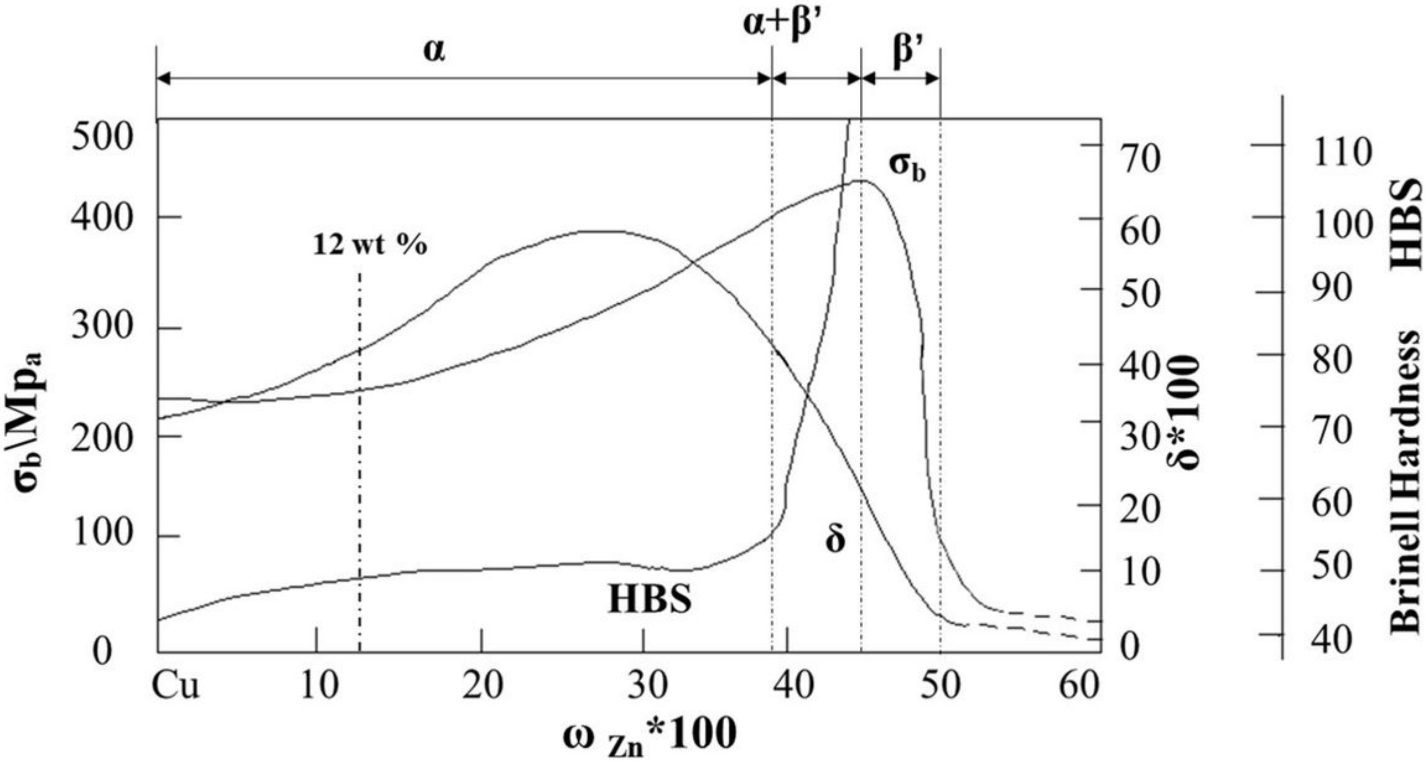

Figure 5

Effect of zinc content on mechanical properties of copper-zinc alloy. [43] Here, σb is the tensile strength; δ is the elongation; HBS is the Brinell hardness.

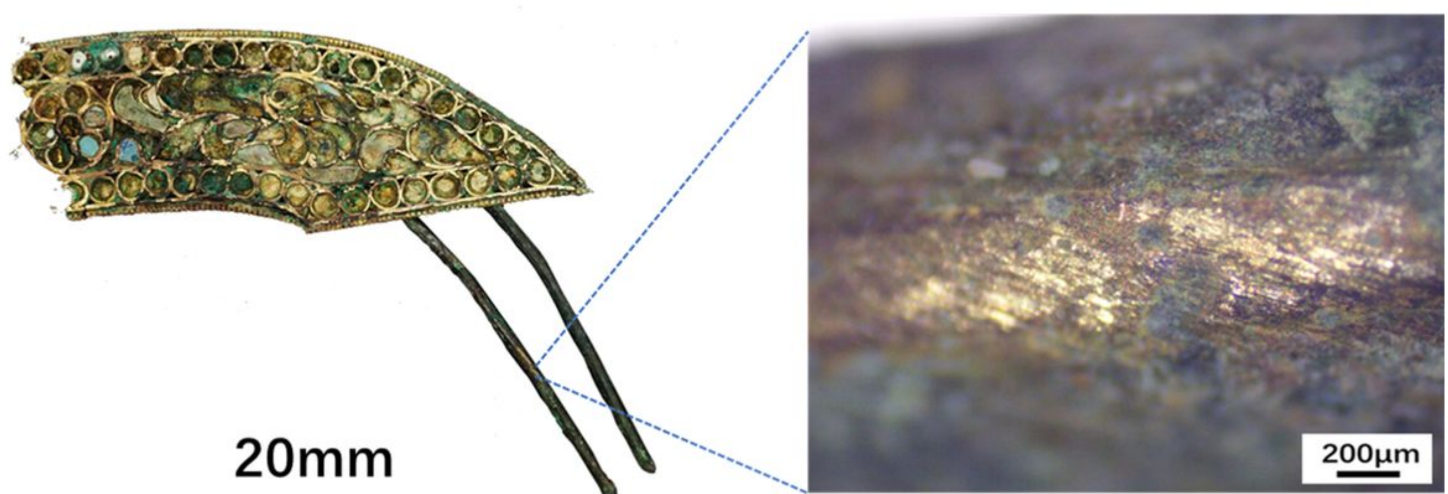

Figure 6

Super deep depth of field image of the brass wire.