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RESEARCH

Transmission and innovation on gold granulation: the application of tin for soldering techniques in ancient China

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Abstract

Granulation, an ancient metal processing technique mainly applied to gold, has originated from West Asia, and later appeared at many different archaeological sites across the Eurasia. The distribution of granulated gold ornaments bearing diverse soldering techniques reveal the long-distance human interaction across the Eurasia. This paper presents the scientific analysis of the surface morphology and elemental composition of two granulated gold ornaments from Tushan Tomb No.2 pit in Xuzhou, Jiangsu Province, which approximately dated to the first century CE of Han Dynasty. Multiple non-destructive analytical methods including Ultra-Depth Three-Dimensional Microscope, Energy dispersive X-ray fluorescence spectrometer (XRF) and Scanning electron microscope with energy dispersive X-Ray spectrometer (SEM-EDS) were conducted to obtain analytical data. The result indicates that tin-participated soldering technique has been adopted to accomplish the granulation. Although the usage of tin has been mentioned in a former study as "a secret of Etruscan granulation", the lack of quantitative analyses leaves this assumption unconvinced. Our findings on Tushan ornaments throw light on this issue by illustrating the regular distribution pattern of the tin content at the joints, which appears to be intentionally added for certain amount. Although tiny in size, the gold granules record the secret of soldering techniques used in China and many other regions across the Eurasia during the ancient time, complementing the study of granulation techniques and reflecting the transmission and innovation along with the technological and cultural contacts.

Keywords: The Tushan Tomb, Han Dynasty, Gold ornaments, Granulation, Soldering techniques

Introduction

Gold was worshiped in widely separated parts across the Eurasia in ancient times. Among the fabulous techniques employed by ancient goldsmiths revealed by archaeometallurgy, granulation appeared to be very intriguing for its technical and aesthetic values.

Granulation is a fine gold processing technique to produce tiny granules and attach them to a gold substrate, constituting a brand-new decorative system originated in the Western Asia dated back to as early as the 3rd millennium BCE, where earlier metallurgy and metalworking on copper laid a solid foundation for the subsequent gold craftsmanship. Three major techniques of granulation have been defined and extensively discussed from analytical and metallurgical perspectives in former studies, including copper salt soldering, metal alloy soldering, and fusion welding [1–6]. Replication experiments were conducted and compared with archaeological materials for better understanding of these ancient techniques [2, 7]. This sophisticated soldering technique reached its peak in Etruscan craftsmanship, flourished in the Mediterranean world during the 1st millennium BCE, and diffused to the east and the north. Granulation technique was preserved and applied to silver ornaments in Early Medieval Europe [8, 9]. At the meantime, gold

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ornaments with granulation firstly appeared sporadically in the eastern part of the Eurasia. Granulated gold ornaments appeared in China since the Spring and Autumn period, developed during the period of warring states, and prospered in Han and Tang dynasty. As a relatively exotic technique, granulation provides a unique eyesight into the relationship between the east and the west.

The Tushan Tombs, dated to Han dynasty, were located at the north foot of Yunlong Mountain in Xuzhou, Jiangsu Province (Fig. 1). The Tushan complex comprises three tombs, among which Tomb 2 (Tushan Tombs' No.2 Pit) was in the middle and has been excavated for four times since 1977 by Xuzhou Museum and Nanjing Museum. It has been rewarded as one of China's Top 10 New Archaeological Discoveries of the year 2020. Till recently, more than 4850 artefacts were unearthed from Tomb 2, including 350 (sets) from the chambers, and more than 4500 artifacts from the mound. A corridor of 28 m long, 1.75 m wide and 3.8 m high, with brick laid in the middle of the ground surface, was found surrounding the rear chamber of Tomb 2. A single layer lacquered coffin made of ovate catalpa wood, with jade disks inlaid on the outer surface and lime covered the bottom, was found in the east corridor. Jade mat, gold ornaments, and organic artifacts made of bones and antlers were found inside the coffin. In this assemblage, a group of gold ornaments bearing granulation technique is of particular interest. Since Tomb 2 has been looted, there might be more gold artifacts, while only several pieces survived, and 6 pieces have been excavated till now. The excavation carried by Xuzhou Museum is still going on, and there might be more astonishing finds.

This research provides the first scientific study of the gold ornaments found in Tushan Tomb No.2 pit. Using multiple non-destructive analytical methods, namely, Ultra-Depth Three-Dimensional Microscope, Energy dispersive X-ray fluorescence spectrometer (XRF) and Scanning electron microscope with energy dispersive X-ray

Fig. 1 Map showing the location of Tushan Tomb

spectrometer (SEM-EDS), we investigated the detailed surface morphology and elemental composition, thus analyzed the manufacturing technique, especially soldering technique of the gold artefacts unearthed from Tomb 2. Furthermore, the extensive technological and cultural interactions regarding gold craftsmanship across the ancient Eurasia, as well as the localization of a particular technique in East Asia are archaeologically described.

Samples and methods

Description

Two representative samples (Fig. 2) were selected from the 6 gold artefacts excavated from Tushan Tomb No.2 pit for in-depth analysis. These objects were very likely to be decorative ornaments once attached to clothing, considering that they were tiny in size, perforated in the middle and carefully decorated. Sample No.1 is geometrically lozenge in shape, and symmetric both vertically and horizontally. It measures 27.15 mm in length, 13.33 mm in width and 0.59 mm in thickness, with a round hole of about 1 mm in diameter perforated in the middle. Single linear granulation constituted by about 260 granules with an average diameter of 0.3–0.4 mm (Fig. 3a) are arranged along the convex lines shaped to the substrate previously. Sample No.2 is damaged and deformed under external force, the reserved part measuring 12.42 in length and 7.92 in width. The granules, the diameters of which range between 0.25 and 0.35 mm (Fig. 3b), are averagely smaller than those on Sample No.1 and less in number.

Analytical methods

Ultra-depth three-dimensional microscope

Preliminary observations on surface details and microstructures of the two samples at the Xuzhou Museum were conducted using a microscope (Keyence VHX-7000 series with high-resolution lenses, a 4K CMOS, and high-performance lighting), thus gain a basic knowledge of the technological features, including the size and distribution of the granules, as well as the possible joining method of granulation. Through carefully observing and recording, we located some typical areas for s further analysis.

Energy dispersive X-ray fluorescence spectrometer (XRF)

Preliminary qualitative analysis of the elemental composition of the samples were conducted using a XRF (Skyray EDX3600H with UHRD/SDD detector of amtek). The software used is EDX2.0 of Tianrui Company. Standard gold standard sample GBW02751-GBW02753 was used for curve correction before analysis. During operating, the voltage and current applied were set at 45 kV and 150 μA respectively, the collimation hole was φ2mm, and the test time was 200 S.

Fig. 2 Gold granulated ornaments found in Tushan Tomb No. 2 Pit. (Left top: Sample 1; Right bottom: Sample 2)

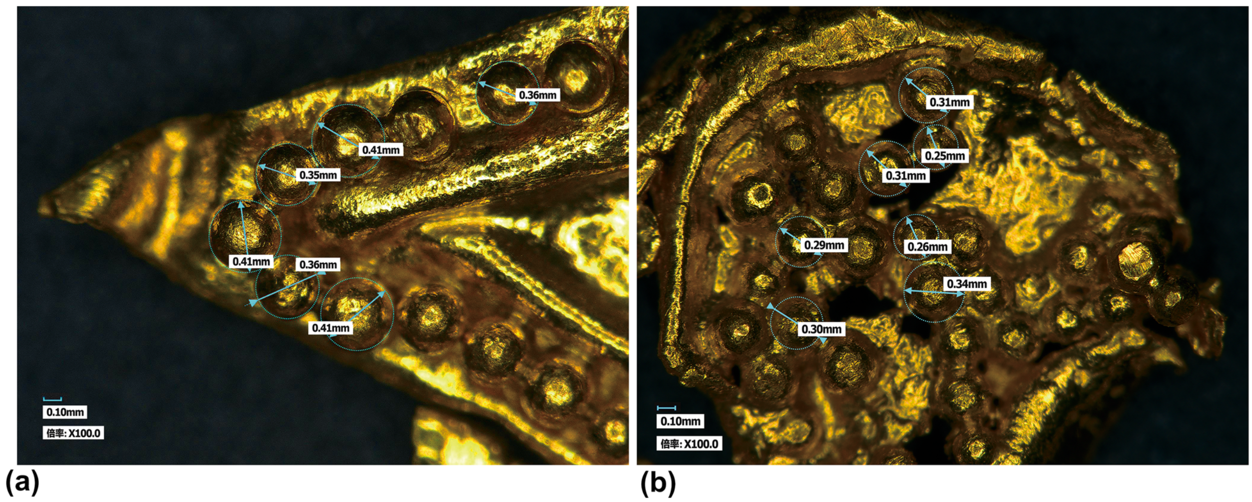

Fig. 3 **a** Dimension of the granules along the edge of sample 1; **b** dimension of the granules on sample 2

Scanning electron microscope with energy dispersive X-ray spectrometer (SEM-EDS)

The morphology analyses revealing details of the manufacturing process using a SEM (ZEISS GEMINI460, Germany), and the composition analyses providing information of elemental composition of different areas using an EDS (Oxford Instruments Ultim Max100/X4 processor/AZt.Ec operation software) were combined for a better understanding of the craftsmanship. Before analytical data collection, quantitative analysis of standard samples is carried out in Aztec software. During analytical data collection, the SEM-EDS operating conditions were in spot scanning, line scanning and mapping modes with 20 KV acceleration voltage, 500 pA probe current, and a SEM working distance of 8.5 mm. The spot scanning (quantitative analysis) was conducted in the collection mode "the total number of sets reaches 500,000 counts", with the number of channels up to 2048, and the processing time set to 5. Line-scan was operated in the collection mode "until stop", with the number of channels up to 2048, and the processing time set to 5. Mapping was conducted in the collection mode "until stop", with pixel resolution set at 1024, the number of channels up to 2048, and the processing time set to 5.

Results

The SEM-EDS analysis provides information on both the morphological features and elemental composition of the two samples.

Morphological observation

The morphological observation using ultra-depth microscope and SEM reveals detailed tool marks and surface features on the two samples, constituting their smart designs and highly skilled craftsmanship.

The substrate of sample 1 is prepared with concave-convex line decorations, and the arrangement of granules largely correspond with the surface pattern, along the convex lines (Fig. 4a, b) that seem to be the baselines to assist in placing the granules in a previously determined layout. A set of cutting marks could be observed (Fig. 4c, d) passing though the granules and the joints between granules near the zigzag edge. It is intriguing that the orientations of the cutting lines are consistent with the edges, which indicates that the lines might be cut accidentally when shaping the edge. Meanwhile, the outward sides of some granules along the edge are smoothed into a flat surface (Fig. 4e), which might be formed together with the cutting marks along the edges. This suggests that sample 1 might be cut to shape after the surface granulation. More strikingly, fine lines with slightly different microstructure could be observed at the joints between the granules (Fig. 4f), which indicates possible compositional changes within the soldering zones.

Besides the linear granulation along the edge (Fig. 5a), field granulation is applied adapted to the concave pattern previously shaped to the substrate of sample 2 (Fig. 5b). Comparing to the granules on sample 1, which are more isolated and distinct to each other, granules on sample 2 are tightly adhere to the substrate, some of

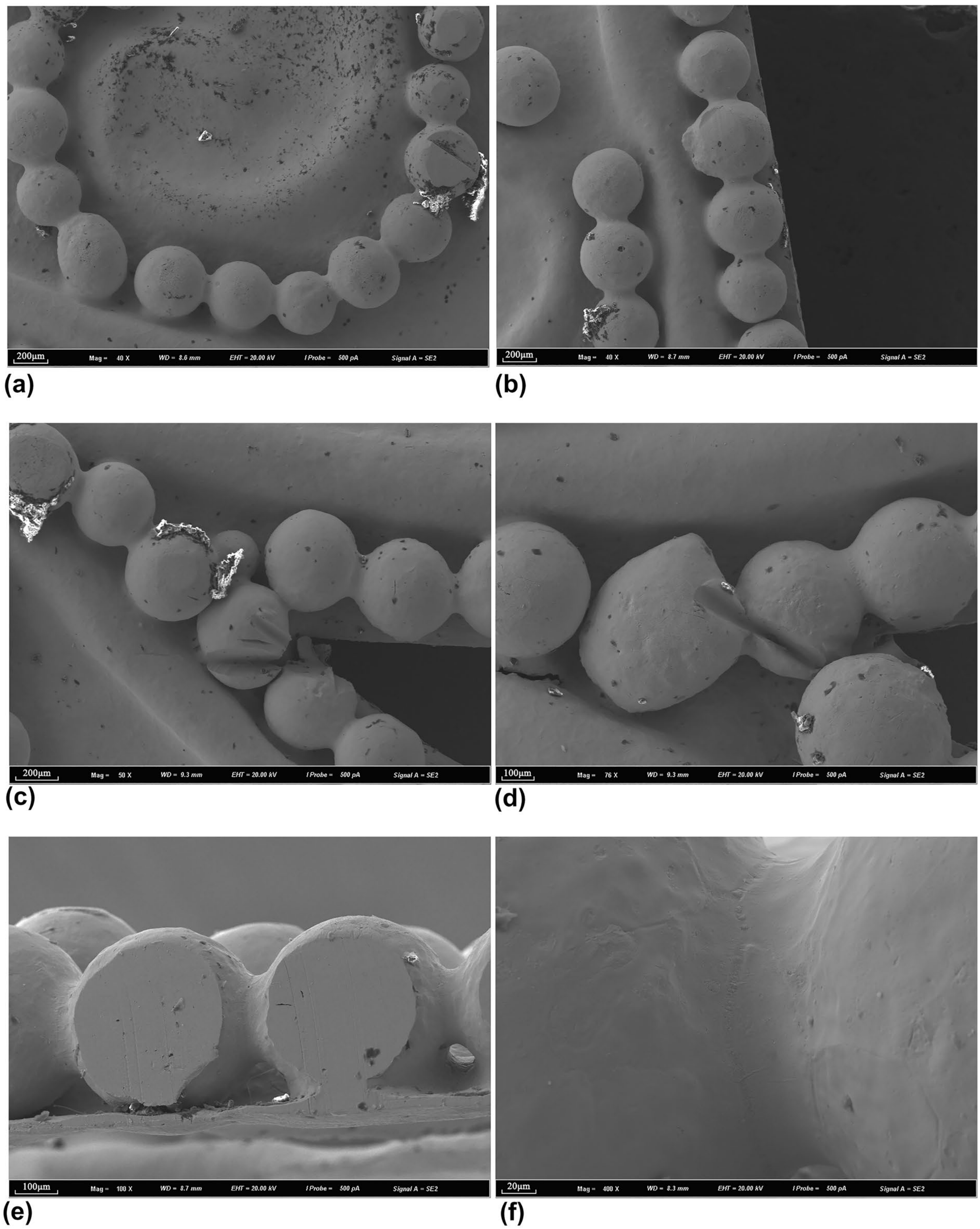

Fig. 4 SEM images of sample 1. **a** The arrangement of granules along the meandered grooves on substrate; **b** the arrangements of granules along the edge; **c** the granules bearing cutting marks; **d** the granules bearing cutting marks; **e** the smooth surface of the granules along the edge; **f** the joint between granules

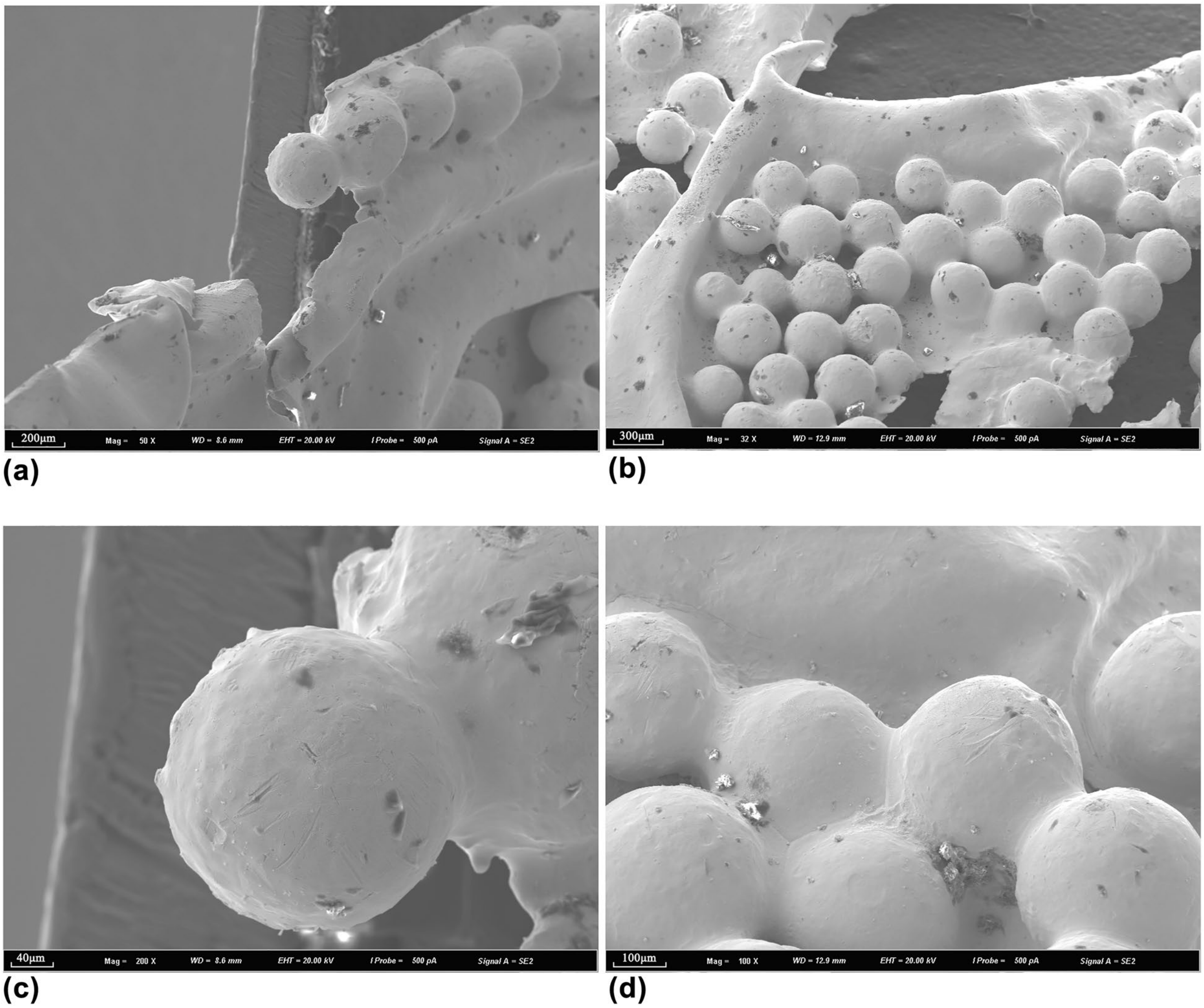

Fig. 5 SEM images of sample 2. **a** The arrangement of granules along the edge; **b** the granules spread on the substrate; **c** the granule along the edge with a hemispherical shape; **d** the joints between granules

which appear to be hemispherical in shape (Fig. 5a, c); and to each other, with attaching necks of larger diameters between granules (Fig. 5d). This indicates slight difference in soldering techniques the two samples, which is proved by the EDS analyses.

Compositional characteristics

The analytical data obtained by XRF indicates that the concentrations of Au ranges between 95 and 98wt.%, Ag fluctuates between 2 and 5 wt%, and other elements below 0.1 wt%. No differences were observed in the composition between the obverse and the reverse of the objects, hence the marked elements are not included in the solder mixture.

SEM-EDS analysis of sample 1

Towards a better understanding of the joining technique, SEM-EDS analyses were carried out at multiple joint areas on sample 1. Remarkably, compositional changes were observed at the joints between granules, as well as between granules and substrate.

Joints between granules and substrate

As mentioned above, the outward sides of some granules along the edge are smoothed into a flat surface (Fig. 4e), where the inner contents of the joints were exposed to be examined. The EDS results of different areas are consistently like each other, and the full results of two selected areas are presented below (area 1, area 2).

Table 1 SEM–EDS spot scanning results of Sample 1, Area 1 (Wt%, normalized to 100%)

Area	No.	Metal elements (wt%)		Area	No.	Metal elements (wt%)			Area	No.	Metal elements (wt%)		
		Au	Ag			Au	Ag	Sn			Au	Ag	Sn
Granule	77	98.04	1.96	Joint	83	94.06	3.06	2.88	Substrate	88	94.52	4.02	1.46
	78	97.69	2.31		84	96.36	3.64	0		89	91.35	2.74	5.91
	79	97.85	2.15		85	96.53	3.47	0		90	95.49	3.76	0.75
	80	97.79	2.21		86	96.30	3.70	0		91	96.43	3.57	0
	81	97.68	2.32		87	95.43	3.45	1.12		92	96.16	3.84	0
	82	97.92	2.08							93	94.84	4.25	0.91
										94	96.23	3.77	0
										95	95.25	4.75	0

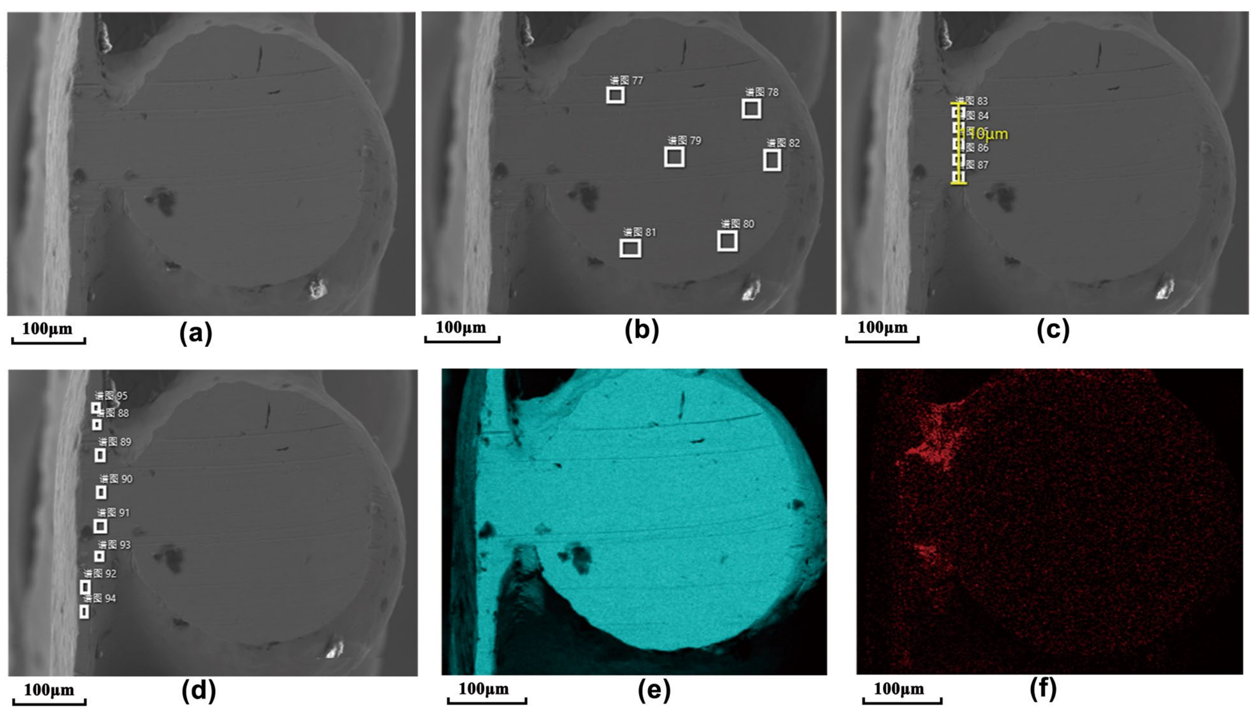

Fig. 6 Spot scanning and elemental maps obtained by SEM-EDS, sample 1, area 1. **a** The smoothed surface for scanning; **b** spots on the smoothed surface of the granule; **c** spots at the joints between granules and substrate; **d** spots on the substrate; **e** Elemental map of Au; **f** Elemental map of Sn

Firstly, in area 1 (Fig. 6a), spots were selected on the cross section of the granule (Fig. 6b), the joint (Fig. 6c) and the substrate (Fig. 6d) for scanning. The SEM-EDS results of elemental composition are presented in Table 1. The EDS analyses demonstrate the content of gold (97.68-98.04wt.%) for the cross section of the granule are slightly higher than those of the joint and substrate, which contained 94.06–96.53 wt% and 91.35–96.43 wt% respectively. Strikingly, the content of tin was detected at both the joint and substrate, and the distribution of tin element largely concentrated at the outer surface of the joint, and the surrounding areas on the substrate. (Table 1) We further conduct surface mapping for elemental distribution of this area (Fig. 6e, f). The elemental map of tin element (Sn) illustrates the concentration of tin at the outer surface of the joint (Fig. 6f), which corresponds with the result of spot scanning.

The elemental map of Sn is even more representative in area 2 (Fig. 7a), the cross section of another granule, with

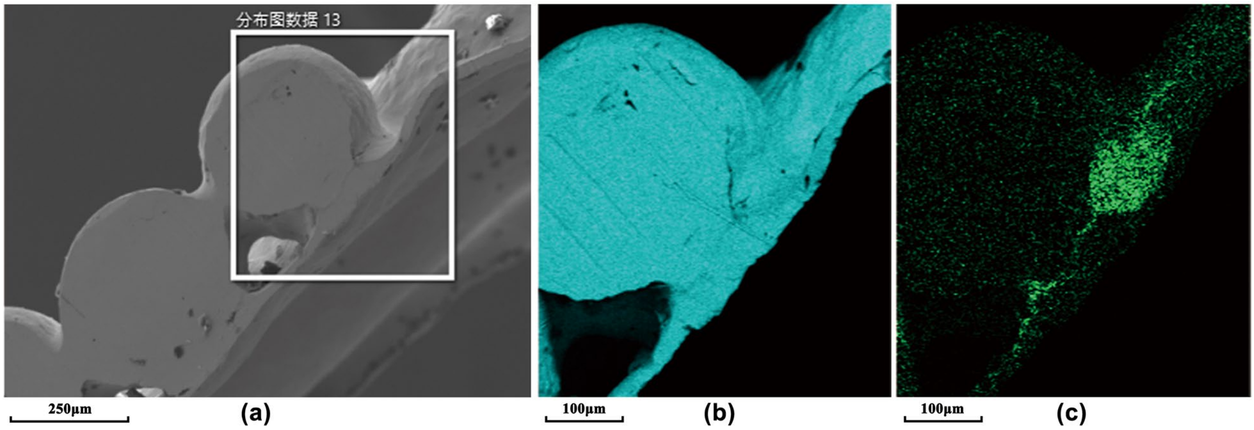

Fig. 7 Elemental maps obtained by SEM-EDS, sample 1, area 2. **a** The smoothed surface for scanning; **b** Elemental map of Au; **c** Elemental map of Sn

its joint and the corresponding area of substrate. Similar to area 1, tin element distributed at the joint between granule and substrate, concentrating at the outer surface (Fig. 7c). In this case, small amount of tin could be seen inside the joints.

The analogous elemental composition of different areas indicates that the small amount of tin content for the joints might be the "secret" of granulation for this Tushan ornament. The difference between area 1 and area 2, namely, the existence of absence of tin inside the joints, is possibly caused by the depth of outer surface grinding, that area 1 is smoothed deeper inside the joint and the granule than area 2. The deeper inside the joints, the less amount of tin left, and eventually disappeared.

Joints between granules

To examine the employment and effect of tin in the soldering process of the granules, a number of joints between granules were selected for analysis, three of which (area 3, area 4, and area 5) are presented in detail below.

Area 3 is located to the left of area 1, where a fine line with slightly different microstructure could be observed at the joint between granules (Fig. 8a), as mentioned above, this indicates possible compositional changes. 19 spots were scanned within this area, which could be divided into 3 groups according to the content of tin. Spots 112, 113, 114, 115 and 116 constitute group 1, containing 6.24 wt%, 5.92 wt%, 4.96 wt%, 5.76 wt% and 6.02 wt% tin respectively. A declined amount of tin, ranged between 1 wt% to 1.33 wt% were detected at spots 117, 118, 120, 121, and 122, as group 2. There was no tin content detected at spots 123–130, as group 3. Surface mapping illustrates the distribution of tin content correspond with both the morphological analysis and the spot scanning result. The tin content concentrated along the fine line with slightly different microstructure, where group 1 spots contain 4.96 wt% to 6.24 wt% tin. The content of tin declined in group 2 area and vanished in group 3.

For better illustrating the compositional changes at the joints between granules, line scanning in both transverse and longitudinal orientations were operated at area 4 and area 5 (Fig. 9).

The line scanning of area 4 (Fig. 9a) shows the increasing amount of tin content at the middle of the joint, where the fine line with microstructural difference located, and the gradual decrease and vanishment on the surface of granules at both sides (Fig. 9b). This corresponds with morphological analysis, spot scanning, and surface mapping.

Area 5 is a cross section of the joint between granules on the smoothed outer surface (Fig. 9c). Line scanning through the joint indicates that the tin content, consistently concentrating at the outer surface, extend inward for about 4 microns at the joints, without obvious distribution of the tin content inside the joint (Fig. 9d).

SEM-EDS analysis of sample 2

Compared with the sample 1, the granules on sample 2 are relatively unevenly distributed and deformed in shape, which indicates possible differences in the granulation technique.

Being damaged and deformed, a granule was mostly exposed at the broken edge (Fig. 5c). EDS scanning at multiple spots was operated in this area (area 1, Fig. 10a, b). Nevertheless, all the spots, including those at the joints, are mainly composed of gold (96–97.5 wt%) and silver (2.5–4 wt%), without other

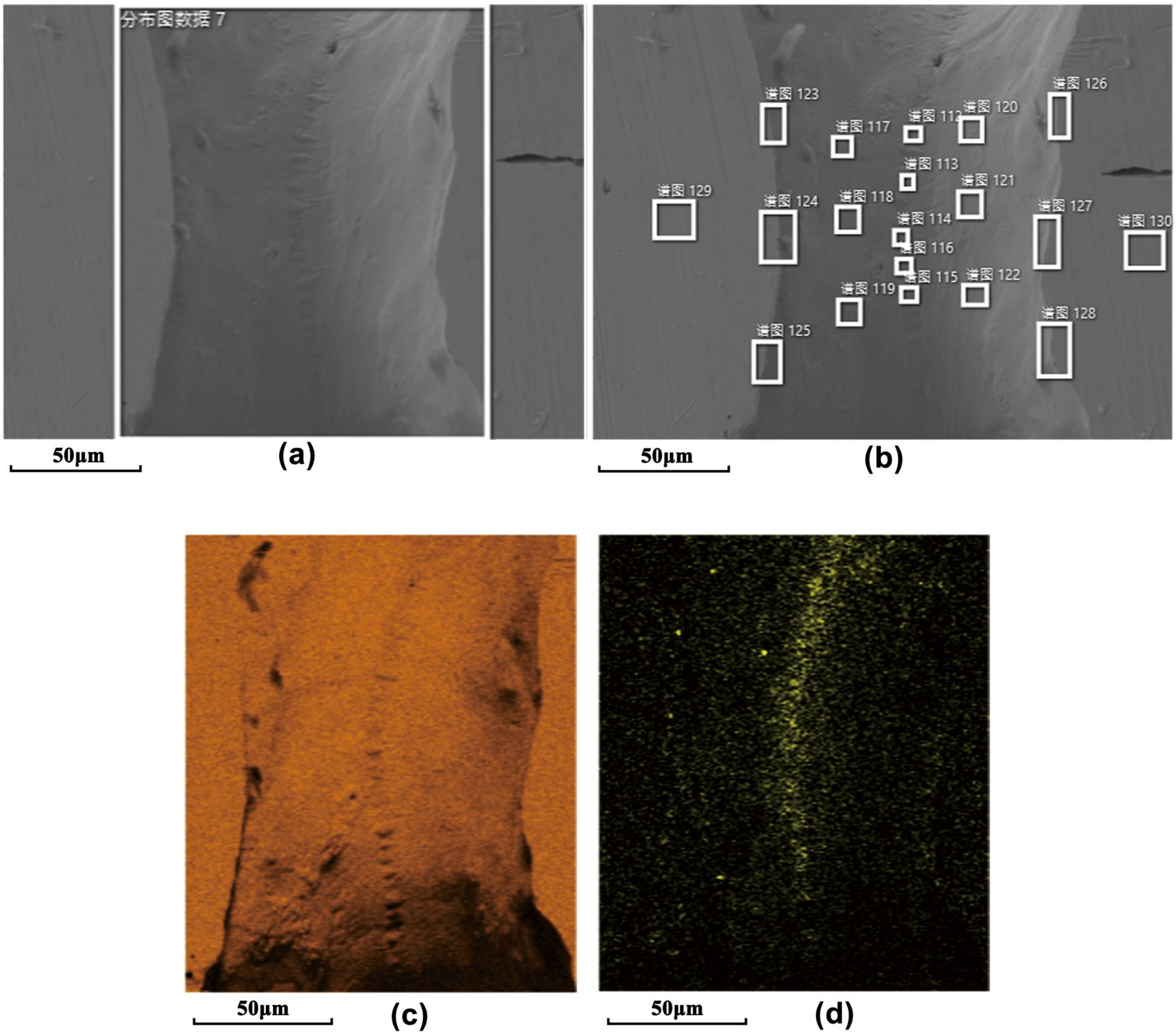

Fig. 8 Spot scanning and elemental maps obtained by SEM-EDS, sample 1, area 3. **a** The joint between granules with a fine line of slightly different structure; **b** spots for scanning; **c** elemental map of Au; **d** elemental map of Sn

components found. Most of the other granulated areas are consistently the same, except several spots in area 2 (Fig. 10c).

A joint in area 2 shows distinct pattern, where the tin content is detected at 7 spots (Table 2) along the joints. The tin content ranges between 0.77 and 4.68 wt%, but mostly around 1 wt%. The unevenness in distribution and variation in amount indicates that tin seems to appear randomly on sample 2, without a stable pattern, unlike sample 1, where tin is found regularly at the joints.

Discussion

Technological features of the Tushan gold ornaments

The analytical data of the two samples reveals a remarkable technological feature, namely, the participation of tin in the joining process. It is likely that small amounts of tin were added intentionally to assist the fusion by lowering the melting points at the joints. However, the obvious difference in soldering techniques between the two samples is noteworthy.

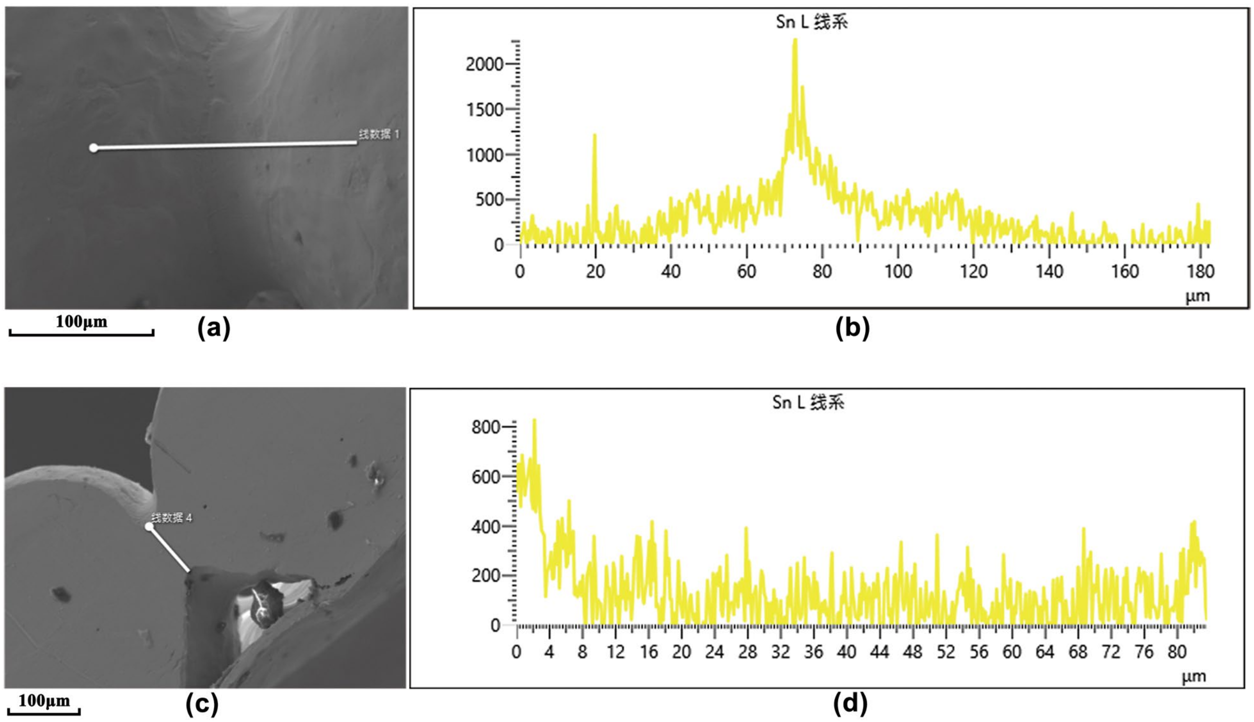

Fig. 9 Line scanning obtained by SEM-EDS. **a** The scanning path, area 4, sample 1; **b** elemental line of Sn, sample 1, area 4; **c** the scanning path, sample 1, area 5; **d** elemental line of Sn, sample 1, area 5

The tin content appears to be consistently and regularly concentrated at different joints of sample 1, indicating that flux containing tin might be applied to the joints before heating. During heating, the content tin played an important role to lower the melting point at the joints, and then overflowed with the increasing temperature precisely controlled by skilled craftsmen, which resulted in the regular distribution of the tin content between granules and substrate, as well as between granules, concentrating at the outer surface of the joints and decreasing gradually inwards. However, there are still questions unanswered. For instance, how was tin added to the joints, and how it worked during the heating. Whether tin powder or tin ore powder were used? If small amount of tin was added to a certain kind of flux, what else ingredient might constitute the recipe. Moreover, how did ancient craftsman managed to control the amount of tin and the heating temperature. Further replication experiments are required for a better understanding of the process.

Table 2 SEM–EDS spot scanning results of sample 2, area 2 (Wt%, normalized to 100%)

Sample	Area	Spot	Metal elements (wt%)		
			Au	Ag	Sn
2	2	267	95.9	3.33	0.77
		268	95.99	3.27	0.74
		269	95.61	3.34	1.05
		270	95.55	3.15	1.31
		273	95.8	2.99	1.21
		274	93.03	2.29	4.68
		275	95.4	3.31	1.29

The technological feature is very different on sample 2, where the tin element seldomly appears at few joints, without regular patterns. This indicates that most of the granules on sample 2 are soldered without any additional elements by directly heating the surfaces to the melting point to be joined, without reaching the bulk melting point. This may explain the morphological difference possibly caused by excessive heat during the soldering, that the granules are unevenly distributed, tightly adhered at the joints, and mostly deformed, sometimes even hemispherical in shape. This could be considered as tin-participated fusion welding technique.

Ancient soldering technique undoubtedly requires extraordinary skill. Different from standardized industrial production in the modern world, the selection and application of soldering flux was influenced by the knowledge and experience of the craftsman, the availability to raw

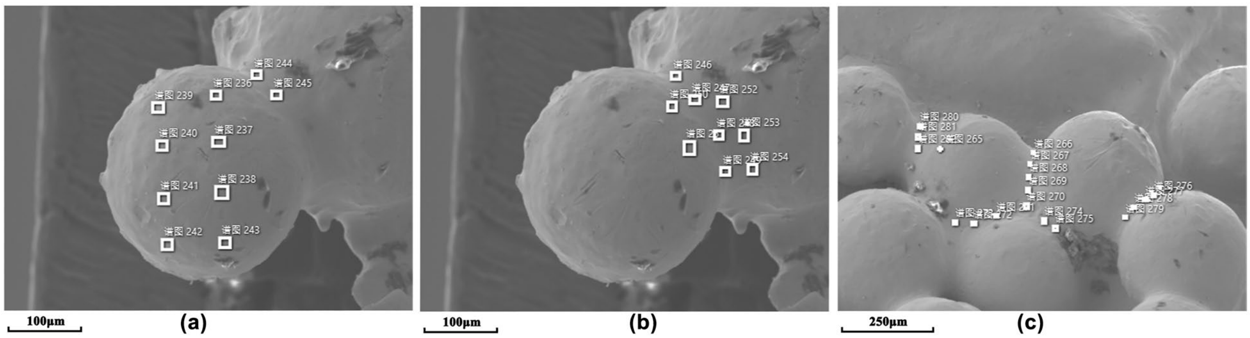

Fig. 10 Spots scanning obtained by SEM-EDS. **a** Spots on the surface of a granule, sample 2, area 1; **b** Spots at a joint between granules, sample2, area 1; **c** spots at the joints between granules, sample 2, area 2

material, as well as the sociocultural habitus. The similarities and differences between sample 1 and sample 6 indicates that they were probably from the same workshop but crafted by different craftsmen. As discussed above, it is very possible that a particular kind of flux containing certain amount of tin was used for granulation on these two ornaments, especially sample 1. Nevertheless, there has yet to be a comprehensive understanding of the ingredients and how it works, where further replication experiments needed.

Types of the joining method of granulation

As mentioned above, three major techniques of granulation have been defined and extensively discussed from analytical and metallurgical perspectives in former studies, namely, copper salt soldering, metal alloy soldering, and fusion welding.

Copper salt soldering

Both filigree and granules of various sizes could be soldered to substrates as a decoration by copper-salt solder, composed of mineral powders of copper compounds such as copper sulfate ($CuSO_4$) and copper carbonate (such as powders of malachite, $CuCO_3$ $Cu(OH)_2$), as well as gelatin of fish (or deer) [5]. This technique creates tiny and fine joints and perfect surface, being considered as an innovation of Syrian, Anatolian (Trojan) and Mesopotamian craftsmen [10] and reached its peak in the hands of the Etruscans in northern Italy from 8th to 4th Century BCE. Copper salt granulation was also found on

Fig. 11 Gold ornaments from Arzhan II, Tuva, after Chugunov, 2017

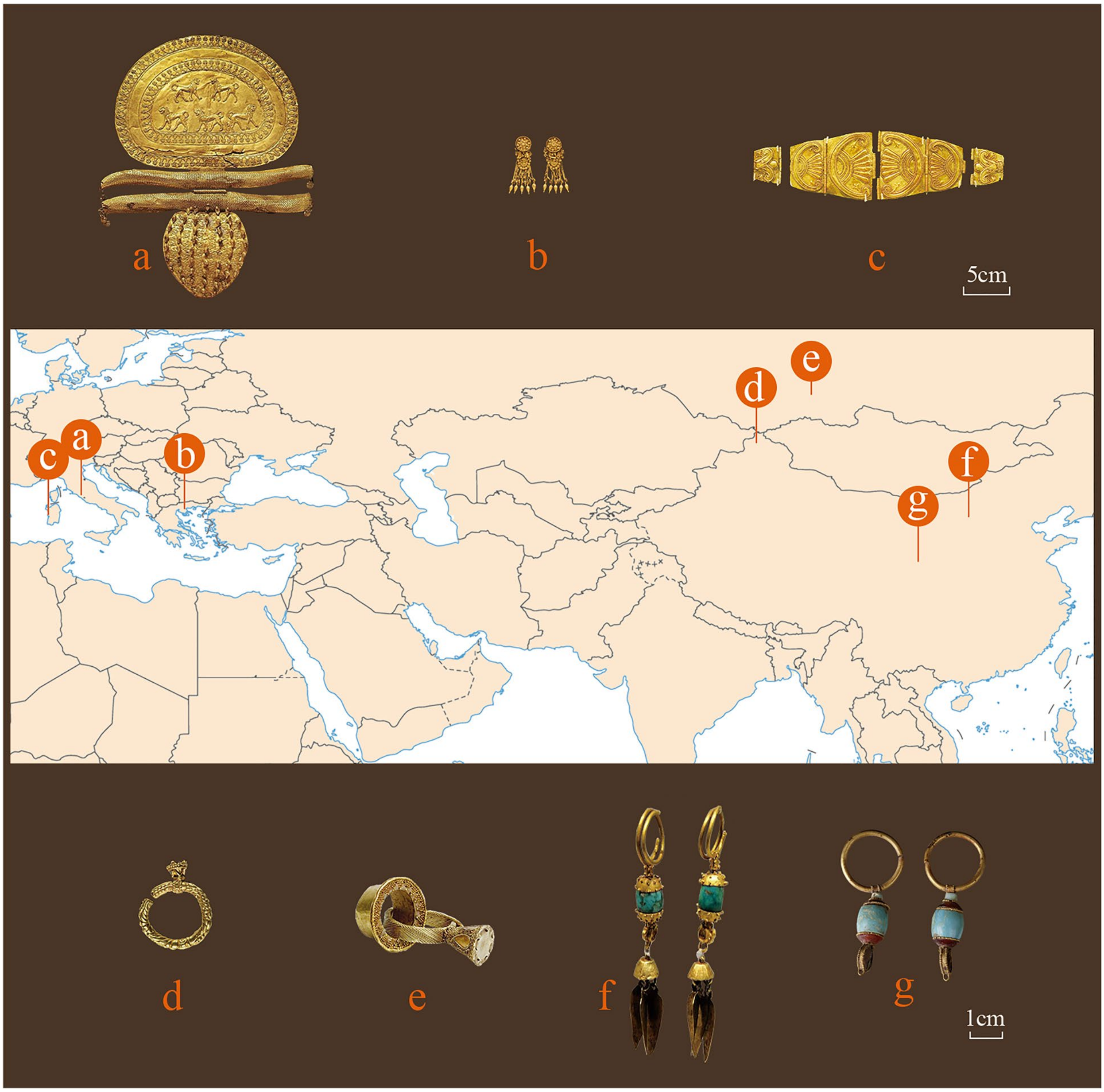

Fig. 12 Map showing the geographical distribution of gold artifacts with granulation from different archaeological sites across the Eurasia, the 1st millennium BCE. **a** Large parade fibula, 670-650BCE, Vatican Museum **b** gold earrings with disk and boat-shaped pendant, 300BCE, Metropolitan Museum of art; **c** phoenician gold diadem, Tharros, 7th-6th century BC, British Museum; **d** ring, Dongtalud Cemetery of Haba River County, Xinjiang, the Spring and Autumn Period, Xinjiang Institute of Cultural Relics and Archaeology; **e** gold ornaments decorated with granulation, Arzhan II royal cemetery in Tuva, 7th century BC. **f** ear rings, Aluchaideng, Inner Mongolia, late Warring State Period; **g** earrings, Majiayuan cemetery in Gansu, the Warring states Period, Gansu Provincial Institute of Cultural Relics and Archaeology

the ornaments decorated with granulation unearthed in Boma site, Xinjiang, China, 3rd to 5th CE [11].

Metal alloy soldering

Gold-silver-copper alloy, as another kind of solder, works in a similar mechanism with copper salt, but more frequently employed for bonding gold structural components [10]. Residues of metal alloy solder were found on several gold ornaments unearthed from Arzhan, 7 century BCE, showing that the craftsmen had mastered the skills of using alloy solders with lower melting points comparing to the bulk [12]. The solders usually contain more copper or silver than the bulk.

Fig. 13 Necklace decorated with granulation, unearthed in Majiayuan, Gansu Provincial Institute of Cultural Relics and Archaeology

Fusion welding

The last method is fusion welding, which means soldering without any additional elements, directly heating the surfaces to the melting point to be joined, without reaching the bulk melting point. This method does not produce any compositional changes at the joints, that is to say, no composition difference would be found between the joints and substrates, as we found at some scanning areas of sample 2. On a gold belt buckle with dragon pattern unearthed from the Western Han Period tomb 2003M76 in Yingchengzi Block, Dalian, Liaoning Province, fusion welding method is found, which is the first discovery of fusion welding granulated artifact in China [13].

Tin-participated soldering

Scholars has suggested the intentional addition of small amounts of tin as the "secret" of Etruscan granulation [14]. This opinion was not widely accepted because of the lack of quantitative data and the absence of tin in the granules [15]. Nevertheless, the analytical data of sample 1 and 2, that the tin content appears consistently or seldomly at the joints between granules as well as granules and substrates, sheds new light on this issue. Tin-contained flux soldering and tin-participated fusion welding, corresponding with sample 1 and sample 2 respectively, could be defined as two newly recognized soldering techniques once used for granulation in ancient China.

Tin has been known, acquired, and used for a long time across the ancient Eurasia. The tin bronze foil from the site of Pločnik, a Vinča culture site in Serbia, is the earliest known tin bronze artefact [16]. This securely contextualised find comes from a single undisturbed occupation horizon dated to c. 4650 BCE [17]. The Afanasievo culture (3500BCE), where nearly 100 metal artifacts (most made of copper and few made of gold and silver) were found, and its successor the Okunev culture (2500BCE) in the Minusinsk Basin [18] had deep interaction with the people from the west, who mastered metallurgical knowledge. They adopted the exotic technologies and discovered abundant resource of copper and tin in the Altai region, based on which the alloy technology of tin bronze [19] flourished and spread across the ancient Eurasia. In ancient China, tin has long been used in welding bronze wares. The solders for welding bronze transformed from lead or tin in the late Western Zhou Dynasty and the Spring and Autumn Period, to lead-tin alloy of lower melting point during the Warring States period [20]. This may have laid the technical foundation for the use of tin-participated technique in gold soldering in Han dynasty.

Despite the evidently wide distribution of ancient metallurgy involving tin, there has yet to be a comprehensive understanding of tin-participated soldering. When and where did this technique origin and how did it disperse across the Eurasia? Our knowledge about the long-distance human interaction is still insufficient, where more work needed to be done.

A summery on granulation techniques

To finish the soldering without reaching the bulk melting point, ancient craftsmen managed to use solders for lowering the melting point at the joints[10].

The first three granulation techniques could be distinguished according to the morphological features and elemental compositions of the granules. In copper salt joining, the copper atoms originated from the reduction of its salts diffused in gold, with little left at the joints, and formed fine meniscus to create the effect of the spheres perched on the substrate. Conversely, metal alloy with a lower melting point partially floods the granules, with the consequent loss of tridimensionality and design [3]. Copper content could be detected at the joints and the surrounding areas when the former two methods were adopted. In fusion welding which requires higher temperature, the granules tend to melt and collapse into the substrate support them if the heating is prolonged. Therefore experience and skillful craftsmanship is required to ensure the precise temperature control [13].

Based on morphological and elemental analyses, two different granulation techniques were applied to the Tushan samples. Tin-participated fusion welding could be seen on sample 2, indicated by deformed granules, thick joins, and the absence of compositional changes at most of the joints. Nevertheless, the seldom appearance of tin suggests that the secret of tin was known, but not mastered by the craftsmen. Sample 1 with more isolated granules and finer joints is granulated with the

Fig. 14 Map showing the geographical distribution of gold artifacts with granulation from the Tushan tomb and other archaeological sites in China. **a** Gold belt buckle, Heigeda Cemetery of Yanqi County, Xinjiang, Han Dynasty; **b** gold belt buckle, Tianshui, Gansu, Han Dynasty; **c** gold hearth, Lujiakou, Xian, Eastern Han Dynasty; **d** gold ornaments, Yuelongtai, Taiyuan, Western Han Dynasty; **e** gold animal, Dingzhou, Eastern Han Dynasty; **f** gold belt buckle, Yingchengzi, Dalian, Liaoning, Han Dynasty; **g** gold hearth, Juxian County, Shandong, Han Dynasty; **h** gold ornaments, Shizishan royal tomb of Chu State, Xuzhou, Jiangsu, Western Han Dynasty **i** gold ornament, Tushan Tomb, Xuzhou, Jiangsu, Han Dynasty; **j** gold ornament, Hanjiang, Jiangsu, Eastern Han Dynasty; **k** gold ornament, Hanjiang, Jiangsu, Eastern Han Dynasty; **l** gold belt buckle, Shouxian county, Anhui, Eastern Han Dynasty; **m** gold ornaments, royal tomb of Nanyue state, Guangzhou, Guangdong, Western Han Dynasty

participation of tin, which might be intentional added to certain kind of flux assisting the granulation.

Transmission and Innovation of Gold granulation

Clothing decoration tradition

The deliberately granulated Tushan gold ornaments with middle perforations are likely to be attached to clothing as decorations, which appears to be a tradition originated from the people in the northern Eurasian steppe mastering metallurgical techniques and developed by the pastoral and nomadic cultural groups. After 1000BCE, gold ornaments as clothing decorations were found in many different sites across the Eurasia, such as the Arzhan II in the Southern Siberia [12] (Fig. 11) the Bazerek culture in the Altai-Sayan region, the *Issyk Golden Man* in eastern Kazakhstan, the Scythian noble cemetery on the northern coast of the Black Sea, and the Dongtalede Cemetery, Haba River County, Xinjiang, China. These ornaments are often geometrical or animalized in shape, tiny in size and equal with each other, indicating that molds might be used for mass production.

Granulation, a new level of technical and artistic mastery

Different from the gold craftsmanship based on chasing and casting in the Chalcolithic Age, granulation, as a fine gold process, might be impulse by the new aesthetic value and decoration methods based on sociocultural contexts.

Furthermore, the consideration of economizing raw materials might also be a key factor. Although the Fertile Crescent is suitable for crop growth, the raw materials of precious stone and metal are of great scarcity, where the demand for gold relied on importation.

Last but not least, the technological innovation represented by the appearance of tiny granules and fine wares happened around 2500BCE, based on the long-time accumulation of practice and experience during the Chalcolithic and Early Bronze Age, as well as the invention of the solders such as copper salt and metal alloy to achieve firmness and aesthetic value at the same time.

Three waves of the eastward transmission of granulation

After 2000BCE the granulation technique started to spread across the Mediterranean world, while the eastward transmission of granulation and its intensive influence on East Asia after 1000BCE could be concluded to three waves, which are discussed below.

The First Wave After 1000 BCE, the earliest known granulated gold ornaments appeared in East Asia. From 61burials at Dongtalede (9th to 7th century BCE) in the Altai region of Xinjiang Province, massive (Fig. 11) artifacts including potteries, bronze wares, iron artifacts and gold artifacts were excavated, among which around 800 pieces of gold artifacts took the largest proportion. Granulation were found on an impressive gold ring (Fig. 12d) and some other gold ornaments from tomb 3 (M3), which yields abundant burial goods reflecting the higher social status of the individual [21]. About the same age, gold earrings with granulation were found from Arzhan II (7th Century BCE) (Fig. 12e). A few hundred years later, in the southeastern part of the Hexi Corridor, a large number of metal ornaments decorated on chariots and horses unearthed from the cemetery of the nomadic chieftains in Majiayuan, Gansu Province, dated to around 3rd century BCE. Among the assemblage, several pairs of earrings (Fig. 12g) appear to be similar to those found in Arzhan II of earlier age in style, whereas a necklace decorated with granulation, mainly constituting of turquoise and carnelian (Fig. 13), bears typical characteristics of Western Asian design and craftsmanship, which is very possible to be exotic, reflecting the long-distance human interaction. Similarly, another granulated earring from Aluchaideng Huns cemetery in Inner Mongolia is found with granulation, adding further evidence to this issue.

Nevertheless, the sporadic appearance of granulated gold ornaments is far from forming a prevailing technique in this area. Meanwhile, the transmission route of granulation technique is still blur where more field works need to be done.

The Second Wave The second wave for granulation in East Asia occurred during the late Hellenistic period, which was contemporaneous with Chinese Han Dynasty. Since the 4th century BCE, Alexander the Great has brought Greek arts including mental processing techniques from Mediterranean region to the hinterland of Central Asia, and the techniques were later introduced further into East Asia by the contact between difference groups of people. By Han Dynasty, 2nd century BCE, granulated gold ornaments flourished with its distribution covering most areas in China (Fig. 14), reflecting the interaction and localization of relatively exotic techniques in this period.

The third wave The third wave of granulation emerged in the Tang Dynasty, when this technique was widely applied on gold ornaments such as diadem decorations, clothing accessories and gold combs. Granulation, which became a symbol for both technical and aesthetic values, also appeared on metals other than gold in this period.

Conclusions

The identification of tin-contained flux soldering and tin-participated fusion welding through intensive investigation of the surface morphology and elemental composition of the granulated gold ornaments from Tushan tomb complements the research of soldering techniques and granulation. The distinctive soldering techniques in Tushan ornaments reveal the localization of relatively exotic techniques in Han China. Furthermore, the origination and transmission of granulation reflect the technological and cultural interactions within huge spatiotemporal scope in Eurasia. Nevertheless, there are still questions remaining unknown, such as the specific procedures of the tin involved soldering, as well as the origin and distribution of this tin involved soldering technique, where further experiments and studies are needed.

Abbreviations
XRF: Energy dispersive X-ray fluorescence spectrometer; SEM-EDS: Scanning electron microscope with energy dispersive X-Ray spectrometer.

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Competing interests
All authors declare that there are no competing interests.

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