

Study on the Materials Characteristics of Microstructure and Component Analysis of Bronze Artifacts Excavated from the Jeonju and Wanju Innovation City

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Abstract

The current study analyzed microstructure and chemical components of five bronze artifacts excavated in Jeonju and Wanju Innovative City ruins. An extremely small quantity of samples was collected from the five artifacts to execute metallographical microstructure analysis experiment, whose results were compared to understand the similarities and differences in terms of material characteristics and manufacturing methods. The results of the analysis showed that bronze spearheads and axe heads contained high proportion of Sn and low amounts of Pb, which fits the profile of these types of artifacts, which makes the weapons strong enough to easily pierce objects and withstand repeated shocks. In addition, the two pieces of bronze knife heads were manufactured only via casting process, without artificial thermal treatment or processing, and displayed high strength and hardness required for cutting and trimming objects. The single piece of bronze mirror excavated at the site contained 27.84% of Sn and 4.56% of Pb, an optimal composition ratio which creates an especially high hardness and a reddish white to white color as well as superior gloss. The mirror,

however, can break easily due to high hardness, which was the state in which it was discovered at the time of excavation. Based on these results, the current study concluded that the five bronze artifacts excavated in Jeonju and Wanju Innovation City ruins were manufactured with bronze alloy containing Sn and Pb, and that residents of the ruins were a group that used bronzeware that were not processed with heat or otherwise after the items were cast.

Key Words : Bronze spearhead, Bronze knife, Bronze mirror, Bronze axe head, Microstructure, Chemical component.

1 INTRODUCTION

Bronze, the first metal used in the human history to manufacture proper tools. is an alloy that contains more than ten percent of tin in the copper base, with a high proportion of zinc added. The proportion of tin in bronze differs depending on the type and use of the resulting bronzeware: Those with a tin component of twenty-five percent or higher are called nickel, used to manufacture mirrors and ceremonial utensils, and those containing a larger amount of zinc are brass, which takes a golden color that is adequate for making ornaments 1. Bronzeware was widely used in Korea during Bronze Age, beginning in late 2000s BC, into Early Iron Age in fourth to third century BC, during which iron and bronze were used in parallel. Korean bronzeware, found on the Korean Peninsula and in Manchuria, are mainly weapons such as daggers, spearheads, axe heads, and arrowheads, with some remains of various items including production equipment, household items, ornaments, and harnesses that were manufactured and used during those eras. Geometric patterns are predominant decorations on these artifacts 2.

One of the earliest researches on natural scientific aspect of bronzeware artifacts was conducted by Chung Gwang-yong, who used metallographic methodologies on bronze artifacts excavated in Mireuksa Temple Site in Iksan to understand the characteristics of such items 3. In addition, the researcher studied the development of bronzeware manufacturing technology shown in bronze artifacts unearthed at Silla Wanggyeong Capital Region site in order to reveal more about the level of Korean bronzeware technology

at the time 4. Park Jang-sik studied the system of bronzeware manufacturing technology displayed by artifacts excavated in Seolbongsanseong Fortress in Icheon, ultimately suggesting a possible process in which Korean bronzeware technology developed and was distributed 5. In more recent years, Han Wu-rim conducted a research project to understand the technologies used to manufacture bronze artifacts excavated in Pungnapdoseong Earthen Fortification and estimate the production site of copper materials contained in them, which adds to the effort in the Korean archeological community to understand the properties and the origin of ingredients of Korean bronzeware 6.

As such, the current study aims to utilize results from before-mentioned studies to make a scientific analysis on bronze artifacts excavated in Jeonju Wonjang-dong ruins, which was discovered by Jeonbuk Cultural Artifact Research Institute. The excavated bronze artifacts such as bronze spearheads, knives, mirror, and axe head were discovered in Early Iron Age pit tomb located at Wonjang-dong Site G 7. Among these artifacts, Bronze spearhead, bronze knife (A), bronze mirror, and bronze axe head were excavated from Pit Tomb No. 1, and bronze knife (B) was found in Pit Tomb No. 5. An extremely small quantity of samples was collected from the five artifacts to execute metallographical microstructure analysis experiment, whose results were compared to understand the similarities and differences in terms of material characteristics and manufacturing methods. Although only five pieces of artifacts were analyzed, the researcher of the current study intended to record the results of this research to be used as a valuable data point on technical aspect of Korean bronze artifacts because there is an absolute dearth of bronze artifact samples excavated on the Korean Peninsula, with even a smaller number of analyses available on such excavated bronze artifacts.

2 ARTIFACTS AND ANALYTIC MET-HODOLOGY

A. Analyzed Artifacts

A. a. Bronze Spearhead

The bronze spearhead was excavated with one slender bronze

dagger at the top part of soil filling the Pit Tomb No. 1. The spearhead was placed diagonally, with the blade pointing to the bottom. The the whole shape of the artifact was well-preserved, and the stem was in a square shape with concaved bottom part. The cross-section is flat in a slender rectangular shape. In addition, the bottom part is sloped, with two holes having a diameter of 0.9 centimeters punched with 1.7 centimeters of each other. A spinal form can be seen at the center of the spearhead, with the spinal column making the cross-section take an octagonal form. Grooves for catching blood can be found on both sides of the spinal column, which do not come together at the blade and runs separately. Without a separate part, the entire spearhead body forms a triangular cross-section. The body and the spinal column show signs of polishing, while the blade is not sharp due to rusting, and the groove showing remnants of wooden materials(Figure 1).

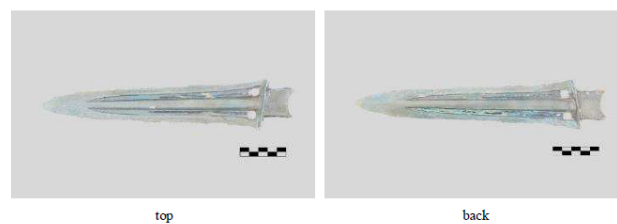


Fig. 1. Photos showing the appearance of the Bronze Spearhead excavated from Wonjangdong at Jeonju.

A.b. Bronze Knife Head(A)

This bronze knife was excavated at the top of soil filling the pit tomb, along with a pommel. The knife was in many pieces on initial discovery, and was since restored. The blade and the body remains in the body, with the blade processed to be sharp, and the body having a slender rectangular cross-section and a spinal column protruding from the center. The edge is only formed at the blade portion, and shows signs of polishing. The knife has a cross-section with a convex front and a concaved back(Figure 2).

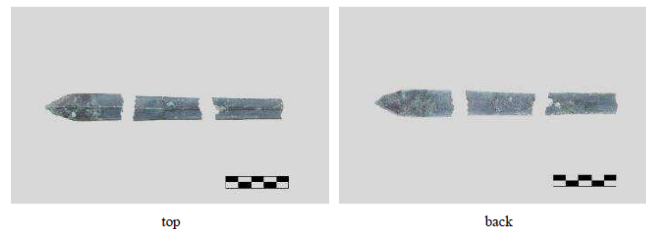


Fig. 2. Photos showing the appearance of the Bronze Knife Head(A) excavated from Wonjangdong at Jeonju.

A.c. Bronze Axe Head

The axe head was excavated in the soil filling the pit tomb, slightly above the coffin. Only a part of the blade was lost from this axe head, overall showing adequate preservation. The cross-section of the body is in a drum shape, with the blade and the spinal portion widening at the center. The axe is single-sided, with only one side featuring the blade. The edge of the spinal portion features four pivots. The spinal portion has the wooden materials remaining, which is thought to be the handle(Figure 3).



Fig. 3. Photos showing the appearance of the Bronze Axe Head excavated from Wonjangdong at Jeonju.

A. d. Bronze Mirror

The mirror was excavated above the slender bronze dagger, at the center of the inside of the wooden coffin. At the time of initial excavation, the mirror side was facing up, with some rust in on the surface and the parts of the edge cracked, showing decent state of preservation overall. The mirror surface is slightly concaved, but

was mostly flat, and the cross-section of the edge is a semicircular shape. Slightly above the center of the back of the mirror is two parallel semi-ring shaped attachments. The left attachment is not in a complete form because the liquid metal was not supplied well at the time of casting(Figure 4).



Fig. 4. Photos showing the appearance of the bronze mirror excavated from Wonjangdong at Jeonju.

A.e. Bronze Knife Head(B)

This knife was excavated with slender bronze knife, stuck to the northwestern wall of the Pit Tomb No. 5, broken into many pieces. The knife has been since restored. This artifact has blade and body portions remaining, with a sharp blade portion. The body part is in a slender rectangular shape, with a spinal column protruding from the center. The edges are only formed at the blade portion, with signs of polishing. The knife has a cross-section with a convex front and a concaved back(Figure 5).

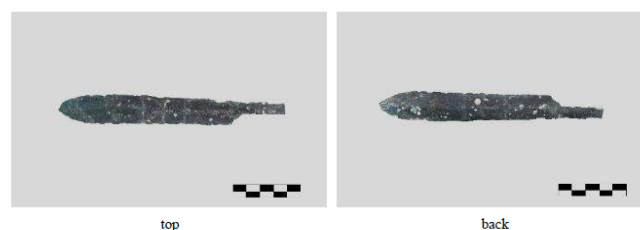
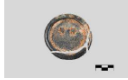


Fig. 5. Photos showing the appearance of the Bronze Knife Head(B) excavated from Wonjangdong at Jeonju.

B. Analytic Methodology

The parts colored in red in Table I show the locations from which an extremely small quantity of analysis samples were collected in the process of preservation. The samples, after going through grinding and rusting, were used for structural analysis using optical microscopes and scanning electron microscopes (SEM). The chemical components of the samples were measured with the energy dispersive spectrometer (EDS) attached to the SEM.

Table I . Photo showing the locations where samples were taken.

No	Artifacts	Findspot	Site analysis	Method analysis
1	Bronze Spearhead			
2	Bronze Knife Head(A)	Remains G, Togwangmyo		Microstructure and Component analysis
3	Bronze Axe Head	No.1		
4	bronze mirror			
5	Bronze Knife Head(B)	Remains G, Togwangmyo No.5		

3 RESULTS OF THE ANALYSIS

A. Bronze Spearhead

This artifact has a well-developed dendrite structure, which is shown typically from bronze casting process. Overall, heterogeneous α phase is well developed in the dendrite, with $\alpha + \delta$ phase showing

in between. Pb particles are distributed overall in the sample, with some having rusted in clusters. In addition, air bubbles and heterogeneous segregates are scattered throughout the sample (Figure 6). An analysis with EDS detected 76.27% Cu, 21.56% Sn, 2.8% Pb, 0.33% as, and 0.4% S (Table II). This result contradicts a research that concluded that bronze spearheads have a chemical component similar to that of bronze swords, with relatively higher Pb component than bronze arrowhead 8. Instead, the analysis in the current study shows that Pb contents in this bronze spearhead is similar to that of typical alloy composition of bronze arrowheads (12 - 20% of Sn and less than 5% of Pb), in order to make it harder. In addition, the results of this analysis reveal that as commonly discovered in ancient bronzeware was not deliberately added. Rather the chemical element, which was included in the ore, likely remained in Cu in the process of smelting. The small amount of S is an inclusion that is a sulfide. In addition, large amounts of Pb can be seen in spectrums 8 - 10, which seems to be lead segregates that were not filtered out during casting.

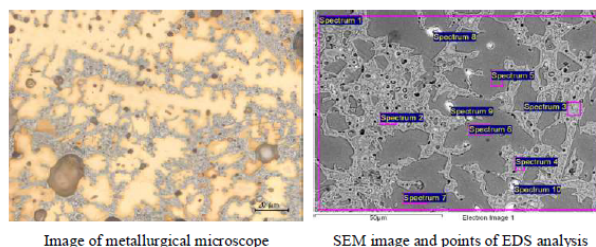


Fig. 6. Microstructure of Bronze Spearhead.

Table II. EDS results of Bronze Spearhead(- : not detected).

Analysis Position	Composition(wt.%)				
	Cu	Sn	Pb	As	S
1	74.6	22.0	3.5	-	-
2	71.8	25.8	2.5	-	-
3	70.7	25.7	3.2	0.4	-
4	73.5	26.5	-	-	-
5	80.5	16.8	2.4	0.3	-

6	80.1	17.2	2.4	0.3	-
7	82.7	16.9	-	-	0.4
8	38.6	12.5	48.8	-	-
9	43.1	13.3	43.7	-	-
10	36.3	12.2	51.5	-	-

B. Bronze Knife Head (A)

Figure 7 is a picture of microstructure from knife head (A) excavated from Pit Tomb No. 1. Because the surface of the artifact is rusted, a thin, black layer can be observed. δ phase in fine line or particle shape are distributed within the metal structure, with $\alpha + \delta$ phase distributed among them. In addition, while δ phase has high strength and hardness, it can be easily broken due to fragility. The existence of δ phase is what makes bronze difficult to process in room temperature [9]. Microstructure is developed uniformly overall, which is because the molten metal was produced with high quality and even composition during the manufacturing process. Because there are no signs of artificial processing or thermal treatment, it can be determined that there were no additional processes after casting. An observation of SEM image revealed extremely small and circular particle phases were distributed all across the structure, between which were areas with dark and light portions. Multiple white inclusions and holes can be observed in the structure, and the background structure shows black inclusions. Composition analysis revealed that knife head (A) is a ternary alloy with 68.18% Cu, 25.98% Sn, and 5.85% Pb (Table III). Rather high quantity of Sn was detected because of the rust found on the artifact, and multiple Pb observed in spectrums 5 - 7 seems to be lead segregate that were not eliminated in the casting process.

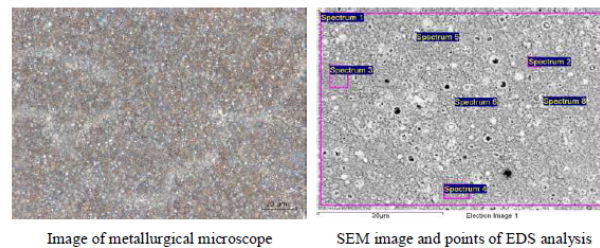


Fig. 7. Microstructure of Bronze Knife Head(A).

Table III. EDS results of Bronze Knife Head(A)(- : not detected).

Analysis Position	Composition(wt.%)				
	Cu	Sn	Pb	As	S
1	66.9	25.8	7.3	-	-
2	68.8	26.2	5.0	-	-
3	68.0	26.1	5.9	-	-
4	69.0	25.8	5.2	-	-
5	52.0	22.4	25.7	-	-
6	64.2	25.1	10.7	-	-
7	62.4	24.0	13.7	-	-

C. Bronze Axe Head

Circular particles of Pb segregates, heterogeneous segregates, and air bubbles are distributed among the sample. Well-developed dendrite structures typical of bronzeware can be observed, with heterogeneous α phase developed as dendrite, between which $\alpha + \delta$ can be observed (Figure 8). EDS composition analysis detected 71.89% Cu, 23.99% Sn, and 3.93% Pb (Table IV). This result indicates that the axe head was manufactured to be harder and more resistant to multiple shocks, which are inevitable when chopping objects with axes. In addition, the results of this analysis reveals that As, an element commonly discovered in ancient bronzeware which was detected in trace amounts of 0.45%, was not deliberately added, but rather what was included in the ore likely remained in Cu in the process of smelting. The small amount of S (0.5%) is an inclusion that is a sulfide. In addition, large amounts of Pb (52.73%) can be seen in spectrums 8 - 10, which seems to be lead segregates that

were not filtered out during casting.

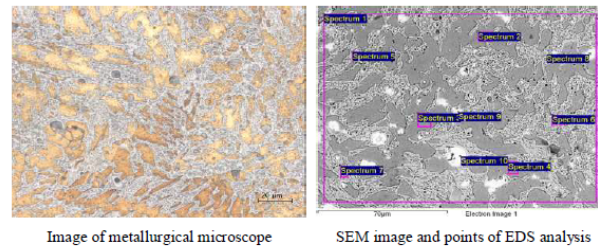


Fig. 8. Microstructure of Bronze Axe Head.

Table IV. EDS results of Bronze Axe Head(- : not detected).

Analysis Position	Composition(wt.%)				
	Cu	Sn	Pb	As	S
1	69.2	24.6	6.2	-	-
2	76.5	20.0	3.2	0.3	-
3	76.1	19.8	4.1	-	-
4	76.2	19.7	3.5	0.6	-
5	68.5	28.3	3.2	-	-
6	69.0	27.6	3.4	-	-
7	67.7	27.9	3.9	-	0.5
8	33.4	14.6	51.9	-	-
9	35.6	14.8	49.6	-	-
10	29.8	13.5	56.7	-	-

D. Bronze Mirror

Figure 9 is a microstructure photo of bronze mirror discovered in the Pit Tomb No. 1. Because the surface of the artifact is rusted, a thin, black layer can be observed. δ phase in fine line or particle shape are distributed within the metal structure. δ phase in fine line or particle shape are distributed within the metal structure, with $\alpha + \delta$ phase distributed among them. δ phase is generated in the intergranular form of γ phase initially generated, and forms

ultra-fine particles as it takes circular form around the lead particles 10. In addition, δ phase has high hardness and strength, but also has high fragility, making it vulnerable to breaking. Microstructure is uniformly developed overall in the sample, and no additional processing seems to have taken place, as there are no signs of artificial processing or thermal treatment. This is because there is no need to add extra processing or thermal treatment when manufacturing bronze mirrors, but the additional reason seems to be that processing is difficult because δ phase is highly brittle 11. In addition, multiple small air bubbles can be found in the structure, which is because the gas included in the molten metal which could not escape out of the mold was captured in the liquid during coagulation. However, no larger air bubbles, which are generated when external air is mixed into the molten metal during pouring, were not discovered. This is because the relatively simple form of the bronze mirror made the air escape the liquid more easily, and the molten metal was poured into the mold slowly enough to prevent the air from being mixed in 12. An observation of SEM image showed extremely small circular particles distributed along the structure, among which dark and light portions were observed. Multiple white inclusions and holes were observed in the structure, with black inclusions on the background structure. A composition analysis showed 67.46% of Cu, 27.84% of Sn, and 4.56% of Pb, which falls within the alloy composition range of typical bronze mirror group II (23 -30% of Sn and around 5% of Pb). The 0.2% of as, which is a trace amount, seems to have come from the original ore and remained in the Cu during the smelting process, rather than being deliberately added (Table V).

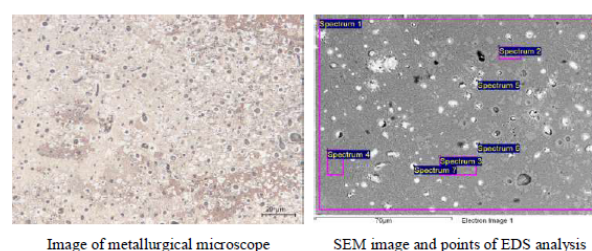


Fig. 9. Microstructure of bronze mirror.

Table V. EDS results of bronze mirror(- : not detected).

Analysis Position	Composition(wt.%)				
	Cu	Sn	Pb	As	S
1	66.1	27.4	6.5	-	-
2	68.3	27.7	4.0	-	-
3	68.5	27.8	3.7	-	-
4	68.0	27.8	4.0	0.2	-
5	55.4	23.3	21.2	-	-
6	53.8	23.3	22.9	-	-
7	66.4	28.9	4.6	-	-

E. Bronze Knife Head (B)

Figure 10 shows microstructure of bronze knife head (B) excavated from Pit Tomb No. 5, with a layer of rust on the surface of the artifact. Coarse brass yellow particles can be observed throughout the structure, with borders of the particles showing webbed bright metal phases spread out. Inclusions which are thought to be lead segregates can be observed in multiple places in the structure; these inclusions seem to have had enough time to crystallize because they are coarser than those in other analyzed artifacts, Lead has a melting point of 327°C , which is lower than that of copper, at $1,084^{\circ}\text{C}$. Also, lead, unlike tin, does not melt into copper. As such, when molten bronze including lead cools, the lead crystallizes and develops first in the molten metal due to segregation phenomenon. Therefore, large clusters of Pb particles with a lower melting point are related to a slower cooling speed [13]. In addition, because no signs of deliberate heat treatment or processing were discovered, the artifact seems to have cooled without no further processing taking place after casting. EDS analysis showed a composition of 67.38% Cu, 26.23% Sn, and 5.95% Pb. Parts in which there is a lower Sn composition is estimated to be $\alpha + \delta$, while those with higher Sn composition seems to be a mix of δ and $\alpha + \delta$ phases, but additional analysis is required to determine the exact phase (Table VI). The 0.4% of As, found in trace amounts, seem to be from the original ore which remained in the Cu during the smelting process, rather

than being added deliberately in the manufacturing process, and the 0.55% of S shows that it is an sulfide inclusion.

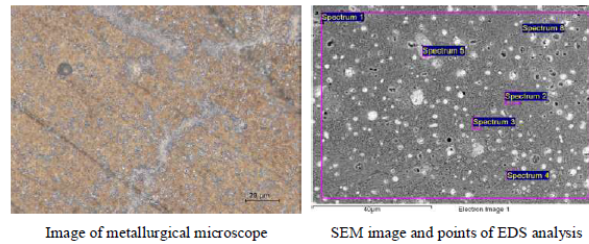


Fig. 10. Microstructure of Bronze Knife Head(B).

Table VI. EDS results of Bronze Knife Head(B)(- : not detected).

Analysis Position	Composition(wt.%)				
	Cu	Sn	Pb	As	S
1	65.6	25.7	8.8	-	-
2	68.0	26.2	4.8	0.4	0.6
3	68.2	26.5	5.3	-	-
4	67.7	26.5	4.9	0.4	0.5
5	56.2	22.7	21.1	-	-
6	54.2	21.9	23.9	-	-

4 CONCLUSIONS AND DISCUSSION

The following are the results of microstructure observation and composition analysis to understand the manufacturing technology of five bronze artifacts excavated in Jeonju and Wanju Innovation City site.

The analyses of bronze spearhead and bronze axe head that were excavated showed that they are dendrite cast structure with mixed yellow α phase and white $\alpha + \delta$ phase. A composition analysis revealed a smaller quantity of Pb, which falls under the range of typical bronze arrowheads' alloy composition (12 - 20% of Sn and less than 5% of Pb), which indicates that the spearhead and

axe head were manufactured to break through objects easily and withstand repeated shocks by adding more Sn and less Pb, making the products sturdier.

Observing the microstructures of the two bronze knife heads each discovered in Pit Tombs No. 1 and No. 5 revealed that they were manufactured only with casting process, without artificial heat treatment or processing. Composition analyses confirmed 5.85 - 5.95% of Pb content, which falls under the alloy composition range of typical bronze sword (6 - 20% of Sn and 5 - 10% of Pb). This composition was used in order to reduce brittleness caused by excess hardness, while maintaining adequate strength and hardness in the knives, which were required to cut and trim objects.

The bronze mirror excavated from Pit Tomb No. 1 contained 27.84% of Sn and 4.56% of Pb, with very high hardness and reddish white to white color that has outstanding gloss, making it optimal for use as a mirror. High hardness, however, makes the mirror easy to break, and the artifact was indeed laying broken to pieces when it was first discovered.

The results of the current study indicate that the five bronze artifacts discovered in Jeonju and Wanju Innovation City site used bronze alloy containing Sn and Pb, and that the group of people who manufactured them used bronzeware that were not put under artificial heat treatment or processing after casting.

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