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Archaeometallurgical Investigations of the Early Iron Age Casting Workshop at Kamieniec. A Preliminary Study

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Abstract

This preliminary study characterizes the bronze metalworking on a defensive settlement of the Lusatian culture in former Kamieniec (Chełmno land, Poland) as it is reflected through casting workshop recovered during recent excavations. Among ready products, the ones giving evidence of local metallurgy (e.g. casting moulds and main runners) were also identified. With the shrinkage cavities and dendritic microstructures revealed, the artifacts prove the implementing a casting method by the Lusatian culture metalworkers. The elemental composition indicates application of two main types of bronzes: Cu-Sn and Cu-Pb. Aside these main alloying additions, some natural impurities such as silver, arsenic, antimony and nickel were found which may be attributed to the origin of the ore and casting technology.
The collection from Kamieniec was described in terms of its structure and composition. The investigations were made by means of the energy dispersive X-ray fluorescence spectroscopy (ED-XRF), scanning electron microscopy (SEM) coupled with an energy dispersive X-ray analysis system (EDS) and optical microscopy (OM). In order to fingerprint either local or non-local profile of the alloys, the ED-XRF data-set was statistically evaluated using a factor analysis (FA).

Keywords: Non-destructive testing, Investment casting, X-ray fluorescence spectroscopy, Archaeometallurgy, Lusatian culture

1. Introduction

During excavations made in 2007 and 2012 by the Institute of Archaeology of Nicolaus Copernicus University on a defensive settlement in former Kamieniec, (currently in Czarnowo, Toruń county) the casting workshop of the Lusatian culture was recovered. It has preserved in a form of a roofed construction with a dome kiln and blacksmith stone inside. Among ready products, the ones giving evidence of local bronze metallurgy (e.g. destructs of casting moulds, and main runners) were also identified. Due to the works made in the 30' of 20th c. by J. Delekta (Toruń Town Museum) it became clearly that the workshop at Kamieniec was directed at manufacturing band ornaments in an investment casting method. According to the archaeological data obtained so far, the workshop was founded between 6th and 5th c. BC and started its activity, just after the settlement had been destroyed during the armed aggression [1, 2].

The lost-wax casting method was designed not only to manufacture small objects such as arrowheads but also to cast the ones more advanced in shape like decorative ornaments. Nowadays, this method is commonly applied to jewellery, implantology as well as mining, automotive, aviation, military and energy sectors [3-8]

2. Materials and methods

2.1. Materials

The majority of investigated here artifacts (Fig. 1) were recovered during excavations made in 2007 and 2012. Among ready products (applications, arrowheads, necklace, chain and socketed axe), semi-products (main runners, rods and wires) and bronze scrap (destructs and bronze drops), the ones indicative of technological process (destructs of clay casting moulds and slags) were also selected.

To contrast a manufacturing profile of the casting workshop, the investigated collection was completed by the band ornaments and main runners excavated from the settlement at Kamieniec in the interwar period [2].

Fig. 1. The investigated collection (the band ornaments and main runners by courtesy of the Toruń District Museum)

2.2. Methods

The elemental composition was established by means of the X-ray fluorescence spectrometry with energy dispersive X-ray fluorescence (ED-XRF) spectrometer Spectro Midex equipped with a molybdenum X-ray lamp of an excitation energy of 44.6 kV and a Si Drift Detector (SDD) with a resolution of 150 eV. The mechanical removal the corrosion products reaching the metallic core level was prior to ED-XRF investigations.

The microstructure was observed with a SEM microscope Hitachi S-3400N equipped with the EDS spectrometer Thermo Noran. For the casting moulds and slags the EDS investigations were made by a spectrometer Quantax 200 with XFlash 4010 detector (Bruker AXS) coupled with the SEM microscope LEO 1430VP (Zeiss). The EDS investigations were performed in semi-quantitative, surface and standardless mode using a BSE detector.

The macrostructure observations were made using a NIKON SMZ 745Z stereoscopic microscope equipped with a Nikon Digital Sight DsFi1 microscopic camera.

The investigations were realized at AGH - University of Science and Technology in Kraków and Nicolaus Copernicus University in Toruń.

3. Results

The results were divided into sets containing ready products, semi-products and bronze scrap and the ones indicative of technological process: casting moulds and slags.

The averaged and normalized results concerning the elemental composition of the 21 metal artifacts (representing ready products, semi-products and bronze scrap), determined with ED-XRF are summarized in Table1.

Table 1.
The elemental composition (wt%) of the metal artifacts by means of the ED-XRF

Signature	*Artifact*	Fe	Co	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi
Kam_1	*Band ornament*	< 0.025	0.056	0.53	90	0.13	0.96	0.76	2.4	2.1	3.4	0.034
Kam_2	*Band ornament*	0.38	0.094	0.43	89	0.14	0.97	0.68	3.6	1.7	3.4	0.043
Kam_3	*Band ornament*	< 0.025	0.056	0.66	93	0.14	0.98	1.1	0.76	2.3	1.1	0.044
Kam_4	*Socketed axe*	< 0.025	0.059	0.11	96	0.074	<0.00051	0.21	2.8	0.50	0.16	< 0.0010
Kam_5	*Necklace*	< 0.025	0.064	0.042	90	0.029	0.78	1.2	3.7	2.4	2.2	< 0.0010
Kam_6	*Arrowhead*	< 0.025	0.092	0.28	87	0.031	0.066	0.20	5.0	0.34	6.7	< 0.0010
Kam_7	*Arrowhead*	< 0.025	0.061	0.079	87	0.040	1.0	1.5	0.12	4.9	5.2	< 0.0010
Kam_8	*Application*	< 0.025	0.13	0.62	83	0.019	1.4	2.2	5.7	6.8	0.41	< 0.0010
Kam_9	*Application*	< 0.025	0.080	< 0.015	84	0.029	0.65	1.9	9.0	4.4	0.41	< 0.0010
Kam_10	*Application*	< 0.025	0.058	0.64	85	0.032	2.6	1.5	0.46	4.2	6.0	< 0.0010
Kam_11	*Chain*	0.026	0.056	0.45	95	0.12	0.13	0.47	2.1	1.1	0.87	0.0069
Kam_12	*Main runner*	< 0.025	0.059	0.13	93	0.021	0.55	1.1	1.3	2.2	2.0	< 0.0010
Kam_13	*Main runner*	0.13	0.22	0.67	87	0.12	1.1	0.72	2.7	3.7	3.2	< 0.0010
Kam_14	*Main runner*	< 0.025	0.050	0.58	91	0.16	1.0	0.88	1.8	2.0	2.1	0.037
Kam_15	*Main runner*	0.20	0.090	0.36	92	0.14	0.90	0.46	3.3	1.3	1.1	0.068
Kam_16	*Rod*	< 0.025	0.089	0.055	96	0.050	0.014	0.20	2.6	0.43	0.13	< 0.0010
Kam_17	*Rod*	< 0.025	0.13	0.46	84	0.14	0.14	0.029	15	0.20	0.073	0.026
Kam_18	*Wire*	0.11	0.14	0.46	84	0.13	0.14	0.023	15	0.19	0.12	0.019
Kam_19	*Destruct*	0.026	0.056	0.45	95	0.12	0.13	0.47	2.1	1.1	0.87	0.0069
Kam_20	*Bronze drop*	0.051	0.058	0.20	93	0.13	0.12	1.9	2.5	1.1	0.47	0.035
Kam_21	*Bronze drop*	< 0.025	0.072	0.12	82	0.14	0.029	0.10	17	0.10	0.42	0.020

3.1. Ready products

The arrowheads both exhibit a microstructure with dendrites, which is typical for cast structures (Fig. 2).

The dendritic phase in the Kam_6 arrowhead is the solid solution α of copper and tin with lead appearing as precipitates in the interdendritic spaces. The dark fields are due to increasing Cu weight fraction reaching a value of 100wt%.

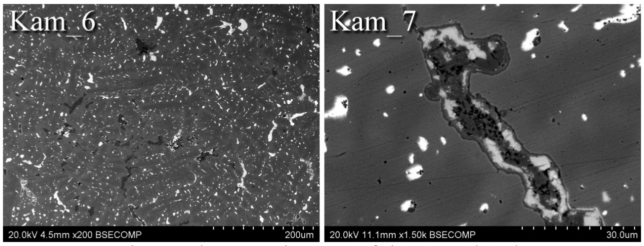

Fig. 2. The SEM images of the arrowheads

The Kam_7 arrowhead exhibits the dendritic α-phase containing lead precipitates. Low-melting Pb-rich eutectics are appearing white. Having been found in the interdendritic phase, the antimony-arsenic-silver inclusions are likely to be remnants of the ore [9]. Pores seen as dark spots can be attributed to the imperfect melting and smelting practice and also to degrading corrosion process.

When looking at the macrostructure of the arrowheads, it is evident that a difference between them lies in the manufacture quality (Fig. 3). While the Kam_7 arrowhead is fine-shaped with regular and smooth lobes, the Kam_6 exhibits many surface casting defects such as blows and drops what might be due to the improper pattern design and imperfect melting and casting practice, in particular. Hence the Kam_6 arrowhead may be seen as local imitation of the steppe-styled weapon [1, 2, 10], however it should be rather considered as failed attempt.

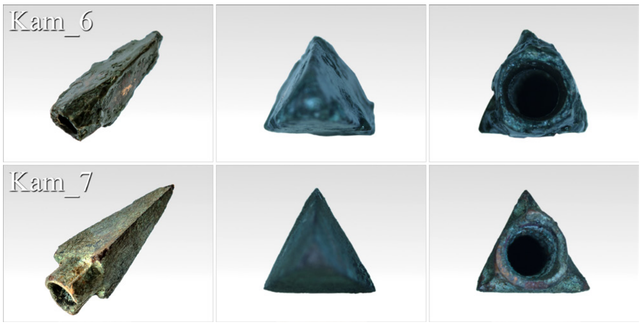

Fig. 3. The macrostructures of the arrowheads

The band ornaments exhibit a microstructure typical for cast structures with dendrites and well-developed grain boundaries, partially degraded already by the corrosion (Fig. 4 and Tab. 2).

The dendritic phase in the Kam_1 band ornament is the α-copper with lead appearing as white particles in the interdendritic phase and also with antimony seen throughout this substructure. Arsenic and nickel inclusions can be also found in the interdendritic phase.

The Kam_2 band ornament was cast in tin-lead bronze with natural inclusions of antimony and nickel. The microstructure exhibits the dendritic phase containing the α-copper with lead precipitates appearing white in the interdendritic phase between the solid dendrites.

The Kam_3 band ornament was cast in lead bronze. Among the dendritic α-phase with low-melting intercrystalline phases the Pb-rich and silver inclusions are appearing white.

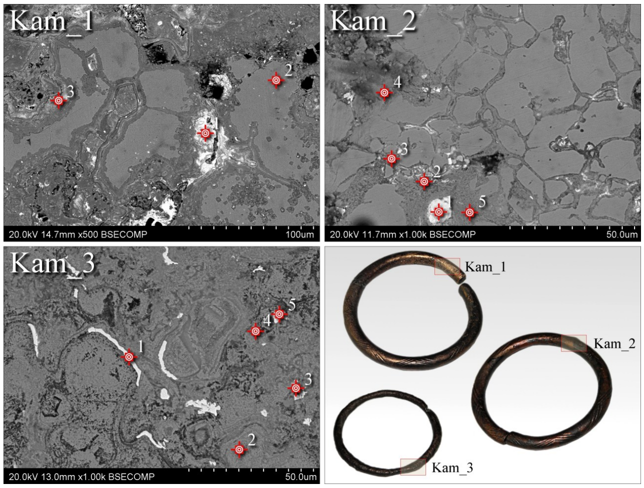

Fig. 4. The SEM images of the band ornaments with the EDS microareas spots and analytical macroareas marked by the rectangles

Table 2.
The elemental composition (wt%) of the band ornaments by means of the SEM-EDS

Microarea	Ni	Cu	Sn	As	Ag	Sb	Pb
Kam_1 (1)	…	10.28	…	…	…	…	89.72
Kam_1 (2)	0.74	98.33	…	0.93	…	…	…
Kam_1 (3)	…	72.51	…	6.23	…	2.79	18.47
Kam_2 (1)	…	5.83	2.67	…	…	…	91.50
Kam_2 (2)	…	87.93	…	…	…	…	12.07
Kam_2 (3)	…	89.64	3.49	…	…	…	6.88
Kam_2 (4)	…	43.10	8.06	…	…	3.58	45.26
Kam_2 (5)	0.79	93.88	3.38	…	…	1.33	…
Kam_3 (1)	…	8.37	…	…	…	…	91.63
Kam_3 (2)	…	100.00	…	…	…	…	…
Kam_3 (3)	…	23.50	…	7.91	…	68.59	…
Kam_3 (4)	…	95.73	…	2.36	…	1.91	…
Kam_3 (5)	…	4.98	…	…	95.02	…	…

3.2. Semi-products and bronze scrap

As the main runners recovered from the settlement had been broken off the ready products, they directly confirm the composition of the cast made in the workshop.

The funnel-shaped main runners exhibit the surface of a free solidification and shrinkage cavity both indicative of the cast areas solidifying at the end (Fig. 5).

Fig. 5. The macrostructures of the main runners

The Kam_14 main runner exhibits a dendritic α-phase containing tin and lead in a solid solution with copper. The inclusions brought to the microstructure by lead and silver were captured in the interdendritic phase (Fig. 6).

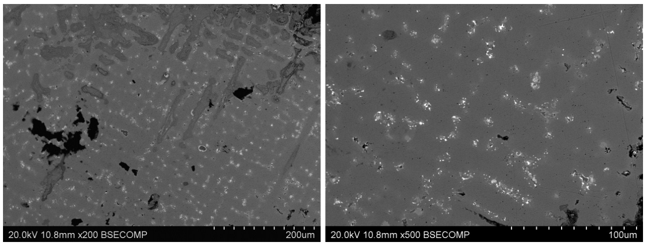

Fig. 6. The SEM images of the Kam_14 main runner

Having been discovered in the vicinity of the workshop, mainly within the range of mud floor, both the semi-products (main runners, wires and rods) and the bronze scrap (destructs and bronze drops) prove that the casting was done on the spot [1].

3.3. Casting moulds and slags

The lack of the stone moulds is indicating that the clay moulds only had been in use during the casting workshop activity. This may be also supported by the characteristics of the ready products, particularly the band ornaments (Fig. 7) carrying no casting seam usually left by a divided stone mould [11].

Fig. 7. The band ornaments with style- and shape-matching destructs of the casting moulds

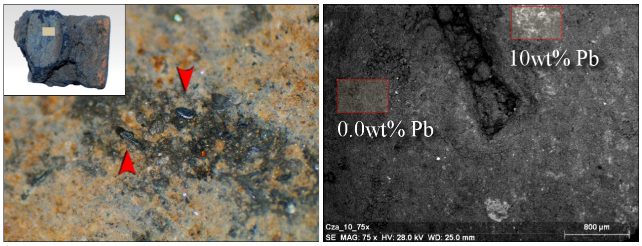

Fig. 8. The casting mould with the remnants of Pb adhered

Due to poor solubility of the copper-lead phase, the remnants of pure Pb had adhered to the inner part of a clay casting mould destruct (Fig. 8). The mould is shape- and style-matching some ornaments recovered and it is in a good relation to the band ornaments showing an emphasis on Pb-rich alloys (Fig.7).

Frequently occurring in the vicinity of the dome kiln, the slags composed of charcoal and copper drops incorporated to its surface, are another supportive indication for implementing a local casting (Fig. 9).

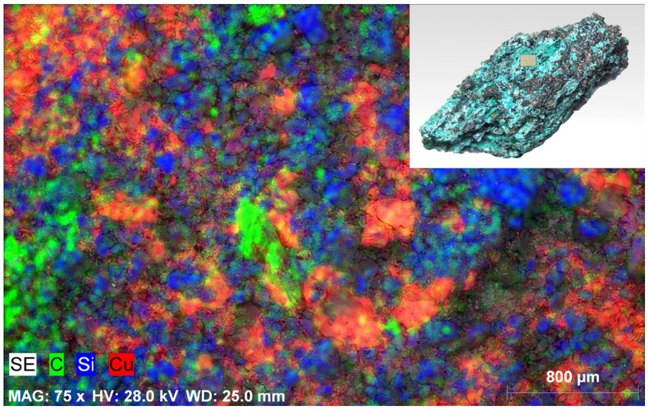

Fig. 9. The SEM-EDS mapping of the slag

4. Discussion

The elemental composition results lead to the conclusion that the workshop had been directed at casting in both tin- and lead-copper alloys (Table 3). A suggestive indication for the casting use lies in the dendritic microstructure. With different types of inclusions brought in, the microstructure is indicating that bronze had been molten and relatively rapidly solidified [9]. The alloys contained some impurities of nickel, arsenic, silver and antimony impacting on the technological properties. The impurities might be attributed to the origin of the ore used or the melting practice.

In order to fingerprint either local or non-local profile of the alloys, the ED-XRF data-set was statistically evaluated using a factor analysis (FA) with the maximum likelihood (ML) extraction method completed by the Varimax rotation with three factors to include in the model. Commonly considered as provenance markers, nickel, silver and bismuth were used to determine the FA model. Having both, in fact provenance and technology marking potential, cobalt, arsenic, antimony and lead were also included in the model [12]. The weights fractions below a detection limit were replaced by a value equal to its half.

Table 3.
The characteristics of the alloys used in the workshop

Artifact type	*Alloy*			
	Type	*%*	*Class*	*%*
Ready products	Cu-Sb	9	*Binary*	27
	Cu-Sn	18		
	Cu-Pb-Sb	9	*Ternary*	18
	Cu-Pb-Sn	9		
	Cu-Pb-Sb-As	9	*Complex*	55
	Cu-Sn-Sb-Ag	18		
	Cu-Pb-Sn-Sb	27		
Semi-products	Cu-Sn	57	*Binary*	57
	Cu-Pb-Sb	29	*Ternary*	29
	Cu-Pb-Sn-Sb	14	*Complex*	14
Scrap bronze	Cu-Sn	100	*Binary*	100

With a major contribution made by antimony and silver the first factor impact on a significant intergroup diversity within the military accessories and the rest investigated (Fig. 10, 11), however with an exception of the Kam_6 and K_10. Since no significant differences were found between the Kam_7, Kam_8 and Kam_9 they may be considered as non-local products. Perhaps they should be attributed to the armed groups who had destroyed the settlement at Kamieniec. The archaeological context makes such possibility more likely [1].

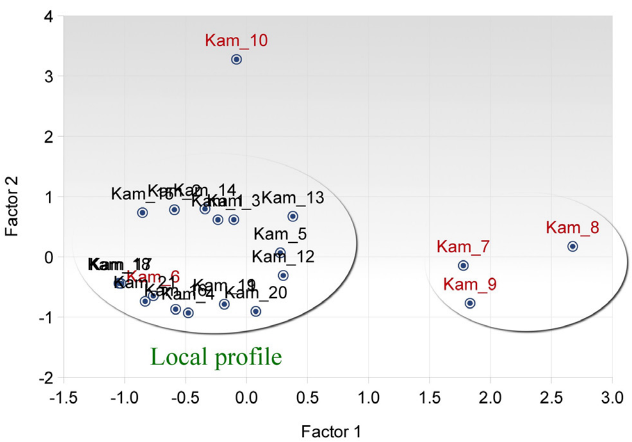

Fig. 10. The FA projection on a 1x2 factor plane with the military accessories marked red

Correlated strongly with the third factor, bismuth kept the Kam_13 main runner separated (Fig. 11). It may be explained by its stronger technological than provenance marking potential. With the main runners tend to share the FA space, the band ornaments (Fig. 12, 13) are more likely now to be cast on the spot.

It has been established that there is a strong alloy profile matching between the arrowhead Kam_6 and the objects directly associated with the workshop activity, such as semi-products and bronze scrap (Fig. 10-13). Despite the lack of the clay mould possibly used to cast the Kam_6, by combining the compositional, metallurgical and archaeological data it is clear that the Kam_6 was cast in the workshop at Kamieniec. Such observation provides valuable support to the conception referring to local imitating the steppe-styled arrowheads or, even more likely, steppe-styled accessories by the Lusatian culture metalworkers.

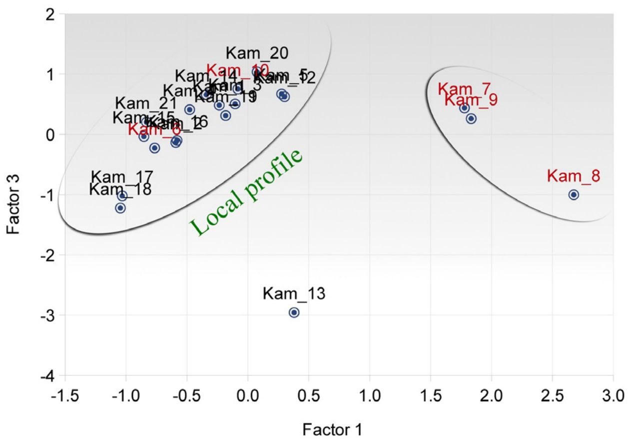

Fig. 11. The FA projection on a 1x3 factor plane with the military accessories marked red

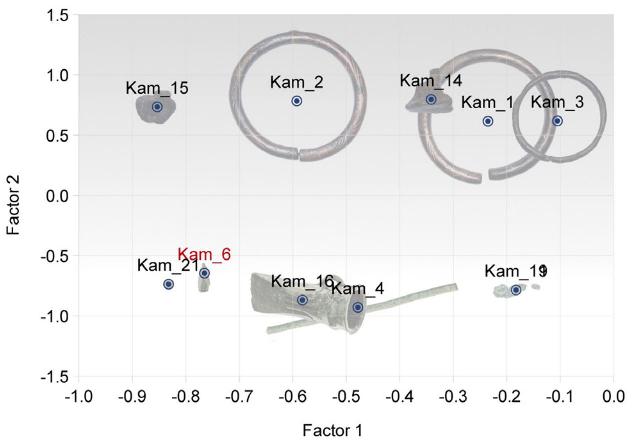

Fig. 12. The Kam_6 agglomeration close-up on a 1x2 factor plane

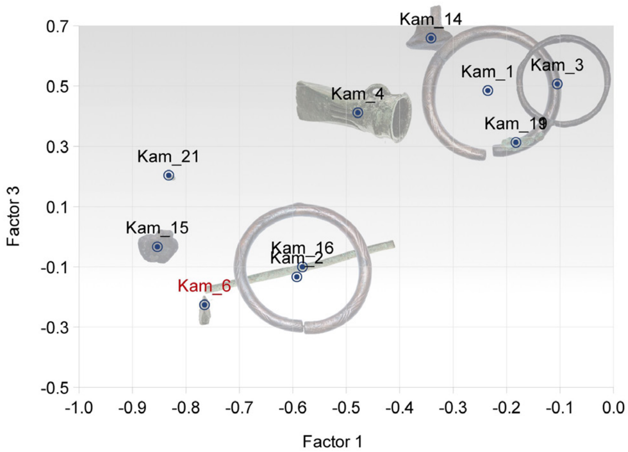

Fig. 13. The Kam_6 agglomeration close-up on a 1x3 factor plane

4. Conclusions

The results of the micro- and macrostructure analyses are supportive indication that the precision casting with application of lost-wax method and clay moulds was done on the spot. In particular, the objects cast in the workshop at Kamieniec show an emphasis on tin- and lead-based alloys as it has been confirmed by the composition of the semi-products and the scrap bronze recovered. It is also probable that antimony and lead were both used by the metalworkers to improve the technological properties of the products and therefore modifying the alloys made directly in the workshop.

Since the steppe-styled military accessories (arrowheads and applications), and to a lesser extent the ornaments (nail type earrings), are commonly thought to be indicative of the nomads penetration in Central Europe, the militaries excavated from Kamieniec may be found as a contributing factor towards the conception referring to local manufacturing of such accessories and also to the Lusatian culture in-fighting [1, 10, 13-15].

Notwithstanding that, it would be unwise to speculate now on the cultural origin of the groups responsible for destroying the settlement at Kamieniec, on the basis of the composition of the military accessories they had, perhaps left during the aggression, without reference to a wider data base.

While this preliminary study can only touch on the problems highlighted hereinbefore, integrated compositional, metallurgical and archaeological investigations made on the casting workshop at Kamieniec may provide a valuable contribution to the understanding of the Early Iron Age metallurgy organization and practice in this area.

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