Analysis of a Castings Quality and Metalworking Technology. Treasure of the Bronze Age Axes

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Abstract

Cast axes are one of the most numerous categories of bronze products from earlier phases of the Bronze Age found in Poland. They had multiple applications since they were not only used objects such as tools or weapons but also played the prestigious and cult roles. Investigations of the selected axes from the bronze products treasure of the Bronze Age, found in the territory of Poland, are presented in the hereby paper. The holder of these findings is the State Archaeological Museum in Warsaw. Metallurgical investigations of axes with bushing were performed in respect of the casting technology and quality of obtained castings. Macroscopic observations allowed to document the remains of the gating system and to assess the range and kind of casting defects. Light microscopy revealed the microstructure character of these relicts. The chemical composition was determined by means of the X-ray fluorescence method with energy dispersion (ED-XRF) and by the scanning electron microscopy with X-ray energy dispersion analysis in micro-areas (SEM-EDS). The shape and dimensions of cores, reproducing inner parts of axes were identified on the basis of the X-ray tomography images. Studies reconstructed production technology of the mould with gating system, determined chemical composition of the applied alloys and casting structures as well as revealed the casting defects being the result of construction and usage of moulds and cores.

Keywords: Non-destructive testing, Archeometallurgy, Tin Bronze, X-ray spectroscopy, Castings defects

1. Introduction

Cast axes belong to the most often found category of bronze products, from the younger phases of the Bronze Age, in the present territory of Poland. Discussions concerning the function of socketed axes are still being continued since these axes had various applications. They were not only used as tools and weapons, but most probably, played certain prestigious and cult roles. Cast axes are interesting not only for their usage and symbolism but also because of their casting technology. Moulds, crucibles and production waste are helpful in the recreation of former metallurgical and casting processes [1]. The
reconstruction of casting techniques, including the structure of the mould with gating system analysis, is possible due to traces of production processes, visible on defected and not worked castings. They constitute a characteristic feature of the local casting production.

Decorations and tools, in the Bronze Age were cast in clay moulds by the investment casting method [2-4], as well as in permanent moulds [5]. Larger products such as axes, razors, knives, etc., were the most often cast in stone moulds. Moulds were made very carefully and precisely with taking into account mutual joining of both halves. Moulds for casting of axes had to have the core for the bushing reproduction. Articles cast in stone moulds required often more work at their finishing e.g. removal of flashes called also foundry seams, marking the dividing plane of casting in the contact place of both halves. Mould parts were joined and heated before pouring to remove the humidity residue, which could cause the metal gasification during pouring. Stone moulds, after being used for a long time, become less tight and finishing of castings required more work. Stone two-part moulds for casting axes, with a bushing and a lug (Fig. 1), were found in the Legnica cemetery in foundryman graves (Lower Silesia, Poland) [5]. Accessories related to the foundryman work, including foundry moulds, are known from other places too [6-8].

Current investigations indicated various solutions of introducing metal - along the core into the mould cavity, including the use of two or four channels of various cross-sections (Fig. 2) [5, 9-10]. Using the analytical methods and the reverse engineering in investigations of the found moulds allows to reconstruct the technology of casting of axes (Fig. 3) [5].

2. Issues and research methodology

The research covers selected elements of the treasure from the Bronze Age, found in Central Poland. The State Archeological Museum in Warsaw is the authority responsible for these findings. Up to the present, a part of the findings from Nowa Góra (West Warsaw district) was subjected to analysis. The majority of axes were determined as Danubian type imports (typologically older specimens), while the remaining finds are Lusatian forms, known from Silesia and Wielkopolska, determined as Lusatyc type [11-12]. The treasure from Nowa Góra is preliminarily dated to 900-1000 BC [12].

Modern analytical methods allow to assess the surface and microstructure of old metal products, as well as the chemical composition and structure of castings [13-14]. The state of preservation and corrosion processes assessment is also important [15]. Analysis of defects resulting from the production process can be made by using non-destructive testing [16-17].

Macroscopic observations were performed by means of the stereoscopic microscope NIKON SMZ 745 with a digital camera and a system for image analysis Nis-Elements. The chemical composition was assessed on the basis of the X-ray fluorescence spectrometry using the energy dispersion spectrometer (ED-XRF), Spectro Midex with X-ray tube, Mo anode and a semiconductor SDD (Silicon Drift Detector). The microstructure and chemical composition analysis in the micro-areas was performed by means of the scanning electron microscope (SEM) Hitachi S-3400N with Energy-Dispersive X-ray Spectrometer (EDS) by Thermo Noran. Tests of non-destructive materials were conducted by means of X-ray imaging (RT) with YXLON MU2000 systems. They were performed in order to check the casting insides, in respect of shape and the core size and also in respect of defects in the casting structure.

3. The results of observations and analytical research

Microscopic and electronic observation methods and digital methods of X-ray representation were applied in the research
as well as analytical methods for the chemical composition analysis in macro and micro-areas. The obtained results are presented below.

3.1. Macroscopic observations

The gating system with introducing channels is the waste product, usually subjected to remelting. The snap-off or cut-off by means of sharp tools from the rough casting left traces on the axe circumference. Observations revealed various shapes and placements of gating channels (Figs. 4, 5). Usually there were two channels of the same cross-section, which were symmetrically leading from the gating tank cone to the casting edge. There were also overflow channels assuring the proper mould filling and the removal of gases and the metal excess from the mould.

Numerous surface defects were noticed on castings. There were flashes along the line joining the mould, being a result of not sufficient fitting of mould halves, which were not removed during the surface treatment (Figs. 6b, 7b). Another typical casting defects, deciding on the castings quality are mainly external bubbles and incomplete fillings – called in the foundry environment as misrun (Fig. 6a). External bubbles are formed when gases and air bubbles cannot get out, since the mould has too low permeability [18-21]. Low permeability together with insufficient flowing power can bring the misrun occurs on the cast surface, as observed on figures 5 and 7a.

3.2. X-ray tests and observations

Issues of casting defects and the size and shape of casting cores was considered on the basis of digital X-ray images of cast axes. The analyzed images indicate that two types of cores were applied in production: 1 – a long core nearly reaching the blade (Fig. 8), or a short spherical core ending in the middle of the axe (Fig. 9). In the first case casting defects are much wider and apart from numerous short runs are seen while these tools are lighter and less raw material was used for their production. In the second case the casting in its lower part is without defects, while defects concentrate in the upper part, near the core. The applied maximal parameters of the X-ray analysis (160 kV, 11 mA) did not allow to identify the smallest defects and structure discontinuities (< 2 mm).
In both cases a significant material discontinuity was seen near the core. In the remaining parts of castings the defects were insignificant. That could be identified defect mainly provoked with high humidity of core.

3.3. Tests of chemical composition

The melting process and structure formation of copper castings is strongly related to their chemical composition [22]. The concentration of metallic elements in the alloy was determined by means of the X-ray fluorescence analysis (ED-XRF). The chemical composition of eight selected axes is presented in Table 1. Each of raw materials belongs to the tin bronzes group, however the tin content varies strongly from 1.2 wt% (NG25) to 15.6 wt% (NG9). Only in one case (NG21) an increased lead content was seen (2.7 wt%), which indicates its deliberate introduction into bronze. The highest silver content (0.25 wt%) is in axes NG9 axe. The highest nickel (1.35 wt%), arsenic (0.34 wt%) and antimony (0.09 wt%) content was found in NG7 sample.

3.4. Analysis of microstructure by SEM-EDS

Microscopic investigations were performed by using the Scanning Electron Microscopy (SEM). During observations, shape and composition of precipitates were determined; besides internal defects were reported.

The dendritic structure, indicating the as-cast state without traces of plastic working, was noticed. The presence of micro-porosity and occurrence of numerous fine precipitates was documented (Figs. 10-11).

Dendrites of solid solution α of tin dissolved in copper, eutectoid in interdendritic zone and other precipitates in the microstructure were identified on the basis of the X-ray fluorescence analysis in micro-areas (SEM-EDS). The phases containing copper, tin, silver and nickel were observed on the microstructures (Figs. 12-13). In addition, the lead phases were separately crystallized in the structure (Fig. 12, Table 2). Precipitates of copper sulphides Cu$_2$S indicate that sulphur was not completely removed during roasting (Fig. 13, Table 3).

Table 1.

<table>
<thead>
<tr>
<th>No of Artifact</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>NG7</td>
<td>0.686</td>
</tr>
<tr>
<td>NG9</td>
<td>1.037</td>
</tr>
<tr>
<td>NG13</td>
<td>0.255</td>
</tr>
<tr>
<td>NG15</td>
<td>0.249</td>
</tr>
<tr>
<td>NG21</td>
<td>0.601</td>
</tr>
<tr>
<td>NG24</td>
<td>0.605</td>
</tr>
<tr>
<td>NG25</td>
<td>0.323</td>
</tr>
<tr>
<td>NG26</td>
<td>0.259</td>
</tr>
</tbody>
</table>
Fig. 12. The SEM images of the axe (NG21) microstructure with the EDS micro-areas spots (refer to table 2)

Table 2.
The elemental composition (wt%, at%) of the axe (NG21) by means of SEM-EDS (Fig. 12)

<table>
<thead>
<tr>
<th>Point</th>
<th>Cu</th>
<th>Ag</th>
<th>Sn</th>
<th>Pb</th>
<th>Cu</th>
<th>Ag</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>pt1</td>
<td>9.14</td>
<td>-</td>
<td>-</td>
<td>90.86</td>
<td>24.69</td>
<td>-</td>
<td>-</td>
<td>75.31</td>
</tr>
<tr>
<td>pt2</td>
<td>75.31</td>
<td>14.24</td>
<td>10.45</td>
<td>-</td>
<td>84.34</td>
<td>9.39</td>
<td>6.27</td>
<td>-</td>
</tr>
<tr>
<td>pt3</td>
<td>98.41</td>
<td>-</td>
<td>1.59</td>
<td>-</td>
<td>99.14</td>
<td>-</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>pt4</td>
<td>95.25</td>
<td>-</td>
<td>4.75</td>
<td>-</td>
<td>97.40</td>
<td>-</td>
<td>2.60</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 13. The SEM images of the axe (NG26) microstructure with the EDS micro-areas spots (refer to table 3)

Table 3.
The elemental composition (wt%, at%) of the axe (NG26) by means of SEM-EDS (Fig. 13)

<table>
<thead>
<tr>
<th>Point</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>S</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>pt1</td>
<td>4.77</td>
<td>-</td>
<td>77.12</td>
<td>18.11</td>
<td>-</td>
<td>5.89</td>
<td>-</td>
<td>83.61</td>
<td>10.51</td>
<td>-</td>
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<tr>
<td>pt2</td>
<td>6.47</td>
<td>0.97</td>
<td>73.27</td>
<td>19.29</td>
<td>-</td>
<td>8.00</td>
<td>1.14</td>
<td>79.64</td>
<td>11.22</td>
<td>-</td>
</tr>
<tr>
<td>pt3</td>
<td>2.72</td>
<td>-</td>
<td>87.04</td>
<td>10.23</td>
<td>-</td>
<td>3.24</td>
<td>-</td>
<td>91.03</td>
<td>5.73</td>
<td>-</td>
</tr>
<tr>
<td>pt4</td>
<td>-</td>
<td>-</td>
<td>79.05</td>
<td>-</td>
<td>20.95</td>
<td>-</td>
<td>-</td>
<td>65.56</td>
<td>-</td>
<td>34.44</td>
</tr>
<tr>
<td>pt5</td>
<td>-</td>
<td>-</td>
<td>94.10</td>
<td>5.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>96.75</td>
<td>3.25</td>
<td>-</td>
</tr>
</tbody>
</table>

4. Conclusion

Out of the analyzed deposit of bronze axes certain representative castings, selected in respect of the gating system structure and characteristic defects, were investigated and described. They were produced in permanent, supposedly stone moulds. Their chemical composition as well as shapes of castings and cores indicate that the deposit of axes is not a uniform collection and originates probably from various casting houses. Raw materials, of which they were cast, generally belong to the group of tin bronzes, in one case to tin-lead bronzes. Tin bronzes, being alloys of a wide range of solidification temperatures, indicate tendency to forming porosity scattered...
within the whole casting [23-24]. Several not intended additions such as silver, nickel, arsenic and antimony were found in investigated alloys. This indicates that they originated from polymetallic ores. Tests performed in micro-areas revealed the presence of sulphides, indicating the raw material quality. Sulphides retained in copper are a result of not sufficient roasting of raw materials at the stage of obtaining copper from sulphide ores.

Investigations of microstructure confirmed its dendritic character proving the as cast state. Traces of plastic working were not seen. however axes blades were often forged to achieve better mechanical properties.

Several defects in casting structures were noticed during X-ray flow detection tests. The core surroundings indicate significant discontinuity of the material, visible as a group of bubbles of spherical shapes and large diameters. Gases emitted from solidifying metal, originated from the reaction between liquid metal and a moisture content of moulds and cores, are the reason of these bubbles formation. Stone core, with too low temperature or clay core, not dried enough, mostly effect too high humidity insite the mould. In addition, too low temperature of liquid metal and small permeability of a stone mould could escalate this defect. From the other point of view, the reason of this defect could be also shifting of a core causing asymmetrical thickness of casting walls and the metal flow disturbance in a thinner wall.

Defects seen in upper parts of castings can be the result of too small cross-sections of the gating system elements. The aim of these channels was not only providing the mould cavity with liquid alloy, but they were also supposed to function as the feeder, which eliminates defects related to material shrinkage during the solidification process. The additional reason for this situation is probably a small castability and low temperature of casting alloy, which for tin bronzes containing app. 10% Sn should be: 1080-1120°C, while at lower tin content - as in the majority of discussed here cases - app. 1180°C.

The cores, them shape and size, are evince about local character of production. Axes, which core was reaching nearly up to their blades, were very light and probably acted more as representational tools than functional ones. Quite opposite was in case of more massive axes with short cores. Castings of decorative axes of thin walls and small weight constituted a challenge for casting houses and not always they were obtained without defects. The previous investigations testified the casting technology in the Bronze Age was advanced one, however defected castings attesting committed errors were occurred sometimes. Examples of defects appearing in the cast axes are documented and analyzed in the hereby paper.

On the artefacts apparent the gating system remains, which were not removed after successfully knocking out the casting, and it were also described in this paper. As were good known, metal and stone tools were used for castings treatments. Most likely, Casting defects may have been repaired in the Bronze Age by skillful pouring alloy to fill gaps. Macroscopic images revealed flashes along the mould partition line (also known as casting seam) and traces of feeding system. However, in the discussed cases, castings were not repaired and finished, and defects were not removed. Since defects were making castings less valuable, they were not polished and ground precisely as it was done with healthy ones. However the treasure of axes could have a great meaning as the treasure of bronze raw materials.

Objects found on present territory of Poland had multiple applications. Not only they were used in farming, but more and more often the military meaning is ascribed to them. They also played certain prestigious or cult roles [25-30]. Other bronze products dated as to the late Bronze Age were - so far - not found in this area [11]. Findings from the Nowa Góra stands out with the quantity of objects found, as well as the presence of basically one category of artefacts [11, 12].

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References

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