Copper and Arsenical Copper During Eneolithic in Metallographic and Mechanical Properties Examination

A. Garbacz-Klemeka a∗, J. Kozana a, M. Piękoś a, W. Cieślak a, M. Perek-Nowak b, Ł. Kowalski c, K. Adamczak c, J. Łoś d

a AGH-University of Science and Technology, Faculty of Foundry Engineering, Historical Layers Research Centre
Reymonta 23, 30-059 Kraków, Poland
b AGH-University of Science and Technology, Faculty of Non-Ferrous Metals, Mickiewicz 30, 30-059 Kraków, Poland
c Nicolaus Copernicus University, Institute of Archaeology, Szosa Bydgoska 44/48, 87-100 Toruń, Poland
d Leon Wyczółkowski Bydgoszcz District Museum, Gdańska 4, 85-006 Bydgoszcz, Poland

*Corresponding author. E-mail address: agarbacz@agh.edu.pl

Received 20.11.2015; accepted in revised form 29.12.2015

Abstract

Arsenical copper has been used since 5th millennium cal.BC, later exchanged by application of Cu-Sn alloys in metallurgy. This work presents the results of metallographic and mechanical properties studies performed on two flat axes connected with local Eneolithic societies (4500-3000 cal.BC). The axes are one of the oldest metal artifacts from Polish land. Originally they were made from Cu-As alloy, and their chemical composition was established by X-ray fluorescence spectroscopy (XRF). Their microstructure was analysed using optical microscopy (OM) and scanning electron microscopy conducted with energy-dispersive X-ray spectroscopy (SEM-EDS). The macrostructure analysis (OM) of the axes was performed as well. On the basis of the results, the alloys used in the Eneolithic to cast the axes were reproduced in lab. In order to achieve the characteristics of the alloys, their mechanical properties including ultimate tensile strenght (UTS), hardness (HB), microhardness (HV0,1) and ductility were examined. The solidification process was studied by means of thermal analysis.

Keywords: Non-Destructive Testing, Copper, Arsenical Copper, Archaeometallurgy, Casting, Metallography, Eneolith

1. Introduction

The information on material structure and production technology of the prehistoric metal artifacts can throw light on when they were made, where they originate and their probable destination. Microstructure research is relevant for documentation of the prehistoric alloys, determining the condition of cast artifacts and designing the program of their conservation and protection. The elements that remain in the alloy as the consequence of copper smelting are relevant for researching the alloy’s origin; the following elements are common in such alloys: Fe, Co, Ni, Zn, As, Ag, Sn, Sb, Pb and Bi. It means, that the ratio of concentration of these elements to copper in the copper ore and concentration in the final product makes their correlation possible [1].

Prehistoric artifacts were obtained by casting and forging. Reforging of an already cast object could happen in order to change its shape or improve its mechanical properties.

Arsenical copper has been used since 5th millennium cal.BC, later exchanged by application of Cu-Sn alloys in metallurgy. Arsenic was an element naturally introduced to alloys with no control in concentration as it was incorporated in minerals, arsenides of copper: Cu₃AsS₄ (enargite), Cu₁₂As₄S₁₃ (tennantite), Cu₃As (domeykite) or Cu₅.2-8As (algodonite) [2]. Today, an attempt is analysis and made towards reproduction of those earliest Cu-As alloys basing on the careful analysis of their composition. [1, 3-6]
Arsenic is an impurity difficult to remove from liquid copper in the metallurgical process [7-8]. It has detrimental effect on both electrical and thermal conductivity of copper [9]. The addition of arsenic can also lower plastic properties of copper thus worsening the plastic properties of the material. But in some cases arsenic is considered to be an advantageous alloying additive [10]. In copper it improves the resistivity of alloys to corrosion [9]. Copper with the content of 0.3-0.5% As is used nowadays for chemical equipment and also in some appliances resistant to oxidation in increased temperatures [11]. Mechanical properties of alloyed copper are shaped respectively by heat treatment and plastic working.

2. Materials for research, methodology and experiments

2.1. Materials

Two Eneolithic flat axes are the object of this study. The first of them was discovered about 1890 in Augustowo, gm. Krajenka, pow. Złotów (refer to Fig. 1a; stored in the Bydgoszcz District Museum under ACCN: MOB/A-374) [12-14]. The second one was obtained about 1909 in Jezuicka Struga, gm. Rojewo, pow. Inowrocław (Fig. 1b; stored in the Bydgoszcz District Museum under ACCN: MOB/A-375) [14,15]. According to A. Szpunar the axe from Augustowo is of Bytyń A type while the axe from Jezuicka Struga is of Strzelin B type [14]. Having no archaeological context, both axes should be treated as single finds. Due to their typological features they may be placed arbitrarily in the period of 4500-3000 cal.BC and must be considered as imports.

![Fig. 1. The Eneolithic flat axes: (a) Bytyń A type; (b) Strzelin B type](image)

2.2. Experimental metod

The quantitative determination of the elemental composition was performed by X-ray fluorescence spectrometry (XRF) with energy dispersive X-ray fluorescence spectrometer SPECTRO Midex. The objects were prepared by the removal of the corrosion products.

The macrostructure analysis was performed using a NIKON SMZ 745Z stereoscopic microscope with a Nikon Digital Sight DsFi1 microscopic camera and a Nis-Elements BR picture analysis system. The macrostructure of the artifacts was observed with respect to the state of preservation and surface quality.

Their microstructure was analysed using a NIKON ECLIPSE LV150 optical microscopy (OM) and scanning electron microscopy (SEM, Hitachi S-3400N) equipped with energy-dispersive X-ray spectrometer (EDS Thermo Noran). The macrostructure analysis (OM) of the axes was performed as well. On the basis of the quantitative analysis, the alloys used to cast the axes in the Eneolithic period were reproduced in laboratory.

The foundry mixture was prepared from pure components (Cu, As). The successive four melts were obtained in an induction furnace, in a chamotte melting pot: (0) Cu, (1a) Cu+0.5% As, (1b) Cu+0.6% As, (2) Cu+1.8% As. The pouring temperature fell within the range 1200 – 1280°C. The oxygen concentration was assessed based on the Leco system. In order to achieve the characteristics of the lab alloys, their mechanical properties including ultimate tensile strength (UTS), hardness (HB), microhardness (HV0.1) and ductility were examined. The solidification process was studied by means of thermal analysis.

The impact of arsenic on copper was analysed in four stages: I – as cast (C) II – after casting and heat treatment in the temperature of 950°C 1h and 500°C 0.35h with water cooling and with 500°C 2h furnace cooling (C+HT) III – as cast and after plastic deformation by cold forging (C+F) IV – as cast, after cold plastic deformation and heat treatment, subsequently in the temperatures of 300°C, 400°C and 500°C for two hours and slow cooling (C+F+HT).

At every stage the material hardness was controlled (HB and HV0.1). The microstructure character was analysed using optical microscopy (OM) and Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS).

3. Results description

3.1. Research of artefacts

The analysis of chemical composition showed that both copper and arsenical copper were applied in manufacturing of the flat axes (Tab.1). Table 1 presents the results of elemental composition taken from quantitative analysis of the axes including the results obtained for the flat axe from Augustowo published in 1924 by Kostrzewski [13].

Having a content of mercury (Hg) below a detection limit (<0.001 wt%) together with a higher levels of cobalt (Co) and nickel (Ni), the chemical profiles suggest that the axes were made of recast copper ores [16]. The average iron (Fe) content in the objects did not exceed 1 wt% which seems to be typical for the Eneolithic and the Early Bronze Age artifacts [17].

The major contribution in the chemical profile of the axes was made by copper (Cu) and in both cases it was completed by arsenic (As), although the major secondary element contribution in Strzelin B type profile was made by antimony (Sb).

The macroscopic observations confirmed the presence of the casting defects on the surfaces of both axes. They were identified as the gating system (Fig. 3b) and cast seams pointing to mould parting line (Fig. 2a). Slag inclusions were present on the surface of the Strzelin B type axe. Such structures allow us to assume that both axes were cast in two-part closed moulds. Surface defects indicate the reactions taking part at the metal and mould boundary, resulting from the presence of moisture in mould and oxygen in metal. The macroscopic observation pointed out the usage traces on the Bytyń A type axe’s blade which probably resulted from its usage in the prehistory. The plastic forming of both axes was also recognized. For improving the metal structure and refining their shapes the axes were probably cold hammered just after being cast.
Table 1. The elemental composition (wt%) of the axes.

<table>
<thead>
<tr>
<th>Axe type</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Se</th>
<th>Ag</th>
<th>Sn</th>
<th>Sb</th>
<th>Te</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Bytyń A (2015)</td>
<td>0.032</td>
<td>0.048</td>
<td>0.064</td>
<td>99.1</td>
<td>0.77</td>
<td>0.0032</td>
<td>&lt; 0.020</td>
<td>&lt; 0.051</td>
<td>&lt; 0.051</td>
<td>0.00091</td>
<td>&lt; 0.020</td>
<td>0.012</td>
</tr>
<tr>
<td>The Bytyń A (1924)</td>
<td>-</td>
<td>N/A</td>
<td>+</td>
<td>99.2</td>
<td>0.51</td>
<td>N/A</td>
<td>N/A</td>
<td>0.05</td>
<td>-</td>
<td>N/A</td>
<td>+</td>
<td>N/A</td>
</tr>
<tr>
<td>The Strzelin B</td>
<td>&lt; 0.025</td>
<td>0.045</td>
<td>0.073</td>
<td>99.7</td>
<td>0.020</td>
<td>0.0072</td>
<td>0.0096</td>
<td>&lt; 0.051</td>
<td>0.055</td>
<td>0.0010</td>
<td>&lt; 0.020</td>
<td>0.015</td>
</tr>
</tbody>
</table>

3.2. Discussion

Due to the fact that Kostrzewski did not specify the applied analytical method [13], the comparison of the chemical profiles of the flat axe from Augustowo encountered some difficulties, nevertheless, both profiles correspond quantitatively to each other.

The macrostructure of the Bytyń A type axe, suggesting the application of plastic deformation after casting, is presented in Figure 4. In the microstructure of Strzelin B axe (0.02wt% As) copper grains were observed, which underwent deformation. In the microstructure of Bytyń A axe (0.77wt% As) the outlines of a solid solution of arsenic crystallites were noticed, as well as numerous impurities coming from ores (Fig. 5-6).

Additionally, marks of plastic deformation as well as corrosion changes were observed (Fig. 6). Microhardness tests for both axes yielded the same value of 76HV0.1
3.3. Results and discussion

Based on the research of the prehistoric axes, the experiment of recreating the model alloys with a variable arsenic content and the evaluation of arsenic impact on the material properties. The chemical content was controlled after the melt (Tab. 2).

It follows from the Cu-As phase diagram (Fig. 7), that the maximum solubility of arsenic in copper equals 7.96 wt% in the temperature of 685 °C and it decreases in step with decreasing the temperature. Arsenic additives influence slightly but noticeably the decrease of crystallization temperature, which is confirmed by both the Cu-As phase diagram and by the cooling curve recorded for the materials tested during the experiment (Fig. 8).

The conducted thermal analysis made it possible to register the characteristic transformations taking place during the solidification of the materials tested. In the case of pure copper solidifying at the temperature of \( T_1=1084 \) °C, it is worth pointing to the temperature of \( T_2=1066 \) °C, characteristic for the crystallisation of oxygen eutectic (Fig. 9).

This eutectic disappears after adding arsenic, which is confirmed by the decreased oxygen content in Cu-As in comparison to Cu (Tab. 3).

Changes in crystallising conditions caused by the arsenic additive determine the microstructure character. Already with 0.5% As content (CuAs-1a) in as-cast condition (Stage I Casting) the dendritic structure of solid solution is formed \( \alpha_{\text{Cu}(\text{As})} \) (Fig. 10-11).

Arsenic locates itself at farther distances from the main dendrite axes and in interdendritic spaces, which is confirmed by chemical content analysis in microareas (Fig. 11). The structure of the other samples, where the arsenic content was 0.6% (CuAs-1b) and 1.8% (CuAs-2) is similar.

Mechanical properties: ultimate tensile strength \( R_m \), hardness HB and microhardenss HV0.1 of the as-cast material, independent of the arsenic content, are similar (Figs 12-14). However, the arsenic addition decreases the plasticity of the material.

![Fig. 7. Copper-arsenic phase diagram [18]](image)

**Table 2.** The elemental composition (wt%) of the alloys.

<table>
<thead>
<tr>
<th>Elements (wt%)</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Zn</th>
<th>Ag</th>
<th>Sn</th>
<th>Sb</th>
<th>Te</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-0</td>
<td>&lt;0.025</td>
<td>0.04381</td>
<td>0.0596</td>
<td>99.62</td>
<td>0.00273</td>
<td>0.1155</td>
<td>0.0057</td>
<td>&lt;0.051</td>
<td>&lt;0.051</td>
<td>0.00100</td>
<td>&lt;0.020</td>
<td>&lt;0.0010</td>
</tr>
<tr>
<td>CuAs-1a</td>
<td>&lt;0.025</td>
<td>0.0432</td>
<td>0.0616</td>
<td>99.04</td>
<td>0.5051</td>
<td>0.1407</td>
<td>0.1446</td>
<td>&lt;0.051</td>
<td>&lt;0.051</td>
<td>0.00092</td>
<td>&lt;0.020</td>
<td>0.0093</td>
</tr>
<tr>
<td>CuAs-1b</td>
<td>&lt;0.025</td>
<td>0.04830</td>
<td>0.0615</td>
<td>99.02</td>
<td>0.6438</td>
<td>0.1283</td>
<td>&lt;0.020</td>
<td>&lt;0.051</td>
<td>&lt;0.051</td>
<td>0.00096</td>
<td>&lt;0.020</td>
<td>&lt;0.0010</td>
</tr>
<tr>
<td>CuAs-2</td>
<td>0.1095</td>
<td>0.0451</td>
<td>0.631</td>
<td>97.80</td>
<td>1.771</td>
<td>0.1515</td>
<td>0.0739</td>
<td>&lt;0.051</td>
<td>&lt;0.051</td>
<td>0.00095</td>
<td>&lt;0.020</td>
<td>&lt;0.0010</td>
</tr>
</tbody>
</table>

![Fig. 8. Thermal characteristics of copper with As additives: for Cu \( T_1=1084\) °C; \( T_2=1066\) °C, for Cu+0.6%As \( T_1=1079\) °C, and for Cu+1.8%As \( T_1=1070\) °C.](image)

![Fig. 9. Copper-oxygen phase diagram [19].](image)

**Fig. 7.** Copper-arsenic phase diagram [18]

**Fig. 8.** Thermal characteristics of copper with As additives: for Cu \( T_1=1084\) °C; \( T_2=1066\) °C, for Cu+0.6%As \( T_1=1079\) °C, and for Cu+1.8%As \( T_1=1070\) °C.

**Fig. 9.** Copper-oxygen phase diagram [19].
Table 3. Oxygen content in copper and alloying copper

<table>
<thead>
<tr>
<th>Sample</th>
<th>As content (wt%)</th>
<th>O₂ content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-0</td>
<td>0.0</td>
<td>340</td>
</tr>
<tr>
<td>CuAs-1b</td>
<td>0.6</td>
<td>160</td>
</tr>
<tr>
<td>CuAs-2</td>
<td>1.8</td>
<td>150</td>
</tr>
</tbody>
</table>

Fig. 10. Microstructure of alloy Cu0.5As (OM)

Fig. 11. Microstructure and chemical composition (wt.%) of Cu0.5As alloy (SEM-EDS)

Fig. 12. Influence of As additive on strength and deformation of Cu and CuAs as-cast structure

At the II stage the influence of heat treatment on copper with arsenic additives was tested (C+HT). Soaking at 500°C with successive slow cooling in the furnace and quick water cooling, caused, in each case, lowering of the material hardness. The soaking temperature of 950°C with quick cooling causes hardness increase in the sample with 0.6 wt% As (Fig. 13). Since the arsenic atomic radius is smaller than the corresponding radius in copper, it should be concluded that in these conditions arsenic strengthens the copper structure.

During the III stage of work, the material cast earlier (C+F) was plastically deformed by cold hammering. This process significantly increased the material hardness in step with higher arsenic content (Figs 13-14). During the IV stage, which was based on heat treatment of the cast and forged alloy (C+F+HT) soaking at the temperature range of 400-500 °C caused a distinct increase in hardness with the addition of 0.5 wt.% As (CuAs 1a) as well as a change in microstructure in comparison to the as-cast structure of the material (Figs. 15-16). This effect did not take place at the temperature of 300 °C.

Fig. 13. Influence of As additive on copper hardness HB of the as-cast structure and after heat treatment

Fig. 14. Microhardness of axes Bytnia A and Strzelin B and the influence of As addition on the microhardness HV0.1 of plastically formed copper

Fig. 15. Arsenic influence on the microstructure of Cu after Casting and Forging (C+F) (a) and after Casting, Forging and Heat Treatment 400°C (C+F+HT) (b)
950 °C and then it is water cooled. A significant hardness increase properties of the material was assessed. Regarding the material working when making them. Both axes were made from copper: a relatively pure copper Strzelin B type and copper with arsenic Strzelin A type. The arsenic content in one of them made designing the experiment possible.

During the experiment the influence of arsenic on mechanical properties of the material was assessed. Regarding the material hardness, this influence is relevant, providing the soaking temperature is 950 °C and then it is water cooled. A significant hardness increase caused by an arsenic addition also takes place with plastic working of an already prepared cast. This effect disappears after the heat treatment at 500 °C and slow cooling, which results from copper recrystallization. The microstructure and microhardness analysis (76HV0.1), conducted for the prehistoric axe containing arsenic (Btyty A), point to the process of casting and forging the tool, which caused the increase of its properties in comparison to the cast material, as well as the recrystallization process, which lowered the properties with respect to the forged metal. In pure copper no change in mechanical properties is visible as the result of plastic working and heat treatment. That is why plastic working and, possibly, heat treatment of the copper Strzelin A axe influenced permanently the microstructure but not the material properties.

Also, the influence of arsenic on copper deoxidation was confirmed, which impacts both the microstructure and eliminates the surface defects of the cast. It can be also observed in analysis of prehistoric axes: Btyty A with 0.77wt% As shows much less surface defects than Strzelin B with low As content. Arsenic copper is also characterized by better fluidity what improves a casting process.

Based on the results of studying the real casting of the flat axes, an attempt towards characterization of the used alloys with regard to their microstructure and mechanical properties was undertaken. The analyses involved three different states of material: as-cast, forged (plastic working) and heat-treated states. A change in mechanical properties was observed.

It is likely that prehistoric smiths in the Eneolithic were conscious of mechanical properties limitations of the alloys they used for manufacturing metal objects. The forming technique (cold or hot forging) was a deliberate treatment used for improving properties of the cast objects.

The obtained results contribute to a better understanding of metallurgy, casting and forging techniques during the Eneolithic on Polish land.

4. Conclusions

The obtained research results allowed to determine the chemical composition and microstructure of the prehistoric axes, which made it possible to draw conclusions on utilizing casting technology and plastic working when making them. Both axes were made from copper: a relatively pure copper Strzelin B type and copper with arsenic Strzelin A type. The arsenic content in one of them made designing the experiment possible.

During the experiment the influence of arsenic on mechanical properties of the material was assessed. Regarding the material hardness, this influence is relevant, providing the soaking temperature is 950 °C and then it is water cooled. A significant hardness increase caused by an arsenic addition also takes place with plastic working of an already prepared cast. This effect disappears after the heat treatment at 500 °C and slow cooling, which results from copper recrystallization. The microstructure and microhardness analysis (76HV0.1), conducted for the prehistoric axe containing arsenic (Btyty A), point to the process of casting and forging the tool, which caused the increase of its properties in comparison to the cast material, as well as the recrystallization process, which lowered the properties with respect to the forged metal. In pure copper no change in mechanical properties is visible as the result of plastic working and heat treatment. That is why plastic working and, possibly, heat treatment of the copper Strzelin A axe influenced permanently the microstructure but not the material properties.

Also, the influence of arsenic on copper deoxidation was confirmed, which impacts both the microstructure and eliminates the surface defects of the cast. It can be also observed in analysis of prehistoric axes: Btyty A with 0.77wt% As shows much less surface defects than Strzelin B with low As content. Arsenic copper is also characterized by better fluidity what improves a casting process.

Based on the results of studying the real casting of the flat axes, an attempt towards characterization of the used alloys with regard to their microstructure and mechanical properties was undertaken. The analyses involved three different states of material: as-cast, forged (plastic working) and heat-treated states. A change in mechanical properties was observed.

It is likely that prehistoric smiths in the Eneolithic were conscious of mechanical properties limitations of the alloys they used for manufacturing metal objects. The forming technique (cold or hot forging) was a deliberate treatment used for improving properties of the cast objects.

The obtained results contribute to a better understanding of metallurgy, casting and forging techniques during the Eneolithic on Polish land.

Acknowledgements

The financial support of the State Committee for Scientific Research of Poland under the grant numbers 11.11.170.318 – 11.

References