www.czasopisma.pan.pl PAN www.journals.pan.pl

ARCHIVES
of
FOUNDRY ENGINEERING
DOI: 10.24425/122496
Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (2299-2944)
Volume 18
Issue 2/2018

21 – 26

4/2

DSC Application for Microstructure Investigations of Medieval Cu Alloys

J. Konieczny [a, *], K. Labisz [a], K. Głowik-Łazarczyk [b], S. Surma [a], Ł. Wierzbicki [a], S. Jurczyk [c]
[a] Department of Railway Transport, Faculty of Transport, Silesian University of Technology,
Krasińskiego 8 Str., 40-019 Katowice, Poland
[b] CHEMET S.A. Company, Sienkiewicza 47 Str., 42-600 Tarnowskie Góry, Poland
[c] Institute for Engineering of Polymer Materials and Dyes, Paint & Plastics Department in Gliwice
Chorzowska 50A Str., 44-100 Gliwice, Poland
* Corresponding author: E-mail address: jaroslaw.konieczny@polsl.pl

Received 27.12.2017; accepted in revised form 30.03.2018

Abstract

Archaeometallurgical investigations presented in this work focus on analysing the microstructure as well as mechanical properties of artefacts from the17th in form of findings performed from cast iron as well as copper casts. The presented research results extend the up-to-date knowledge and present the analysis of structural compounds found in the microstructure of the artefacts from the time dating back to the late Middle Ages in the region around Czestochowa, Poland. The tested samples were found in earth in the city centre under the present marketplace. The excavation works were carried out in summer in the year 2009, and have resulted in the excavation of artefacts in form of copper block of the weight of several kg. The excavation action was led by a group of Polish archaeologists collaborating with the local authorities.

The performed pre-dating of this element determines the age of the artefacts as the 17th century AD. The excavations that have been taking place since 2007 have widened the knowledge of the former Czestochowa. Historians of this town have suggested, that the found weight and traces of metallurgical activity suggest that the exposed walls were an urban weight. The weight is visible on the 18th century iconography. What was find on the Old Market indicates that there was a lush economic life before the Swedish invasion in this part of Poland. Some buildings lost their functions or were changed, others died in fires, but new places developed.

To describe the microstructure, with its structural components, research was done using microscopy techniques, both of the light as well as electron microscopy (SEM), also chemical composition analysis was carried out using the EDS technique, as well as tool for phase analysis were applied in form of X-Ray Diffraction (qualitative analysis), especially for the reason to describe the phases present in the excavated material. This research will help to obtain new information in order to investigate further archaeometallurgical artefacts, extending the knowledge about middle age metallic materials its usage and manufacturing.

Keywords: Scanning calorimetry DSC, Archaeometallurgy, Copper alloys, Microstructure, Excavations, Phase analysis

1. Introduction

Metallurgical activities were encouraged - not only in Poland – for the reason of production of diverse elements used in everyday human activities, mainly for economical or military purpose. One of them was trade and market activities where copper was applied for example for weights or shawls for weighting goods [1-6].

Based on this background, in this paper are presented extending investigations of previous research [2], showing results concerning microstructural investigation of the excavated artefact. The investigated object was a heavy block of copper/copper alloy, probably used for measuring (weighing) with a weight o 2-3 kg. It was found in the ground by an archaeologist group, led by Iwona Młodkowska-Przepiórowska – a local archaeologist during excavation works done under the Czestochowa marketplace in 2009. The copper object had a solid form and was shaped in form of a bell, named kettlebell.

The performed pre-dating of the kettlebell allows to determine the age of the bell as the seventeenth century, which is in accordance with classical works [3-6], where similar artefacts produced ca 400 years ago of Fe and Cu casts are described and investigated. For determining the microstructure, as well as the microstructure compounds, its chemical composition, size, distribution or homogeneity, as well as impurities, electron microscopy methods were applied [10-21].

The main objectives and achievement of this project are, that the achieved results deliver new information and thorough new light about early manufacturing technique used for production of metallic artefacts in the old ages. This is also a multidisciplinary undertaking, linking specialists from different research branches, like: archaeology, material engineering or metallurgy, allowing a wide collaboration between specialists.

Carried out analyses and interpretations of the results help also to modify and create new methodological assumptions for investigations of next archeometalurgical elements, widening the knowledge of past ages metallic artefacts.

2. Material and methodology

For investigations there was used the excavated object presented in Fig. 1, this kettlebell was formed in a bulk, bell-like shape. It was defragmented in several parts due to numerous breaks in its surface layer, as visible in Fig. 1b).

Downside, the bottom of the kettlebell with a diameter of 130 mm reveals a circular cavity with a diameter of: Ø = 40 mm in its centre, with a depth reaching 10 mm. On the weight cross-section the shape is ellipsoid with a clipped, blunt end, reaching 90 mm in height. In the middle there occurs a small recess and a sign is visible, probably a craft sign of the licensee in form of a number "4".

The research was performed using the following investigations methods and tests:

- Light microscopy investigation of the micro- and macrostructure using a Leica device, with images analysis software. Analyse and observations were carried out in the bright field image technique.
- Surface preparation was made using a standard procedure in form of:
  - grinding with SiC paper,
  - polishing with 1µm Al_2O_3 polishing paste
  - drying,
  - mounting in thermally-hardened resin,
  - etching in 5% Nital at room temperature for individually chosen time.
- Scanning calorimetry tests were done using the DSC (Digital Scanning Calorimetry) model 822e/700 Mettler-Toledo. Specimens with a weight between 20-22 mg were heated in the temperature range 0ºC to 600ºC at an increasing rate of 5ºC/min. The cooling process was set with the same rate of 5ºC/min in nitrogen gas with a flow rate of 60 ml/min. The specimens were hermetically closed in DSC capsules made of aluminium with a volume of 4 ml. For analyses of the DSC data was used the dedicated STARe Mettler-Toledo software.
- Analysis of the chemical composition (EDS Energy-dispersive X-Ray spectroscopy) as well as analysis of the microstructure were carried out using scanning electron microscope (SEM) - Zeiss Supra 35, on accelerating voltage equal 20 kV.
- Crystallographic investigations including phase composition analysis were carried out using X-Ray diffractometer PANalytical X'Pert equipped with a copper anode and an angle range 20º-140º, with 0.05 º step.
- Vickers microhardness (HV) was measured on cross-section plain designated as x-plane by applying a load of 300 g for 15 s using Vickers hardness tester.

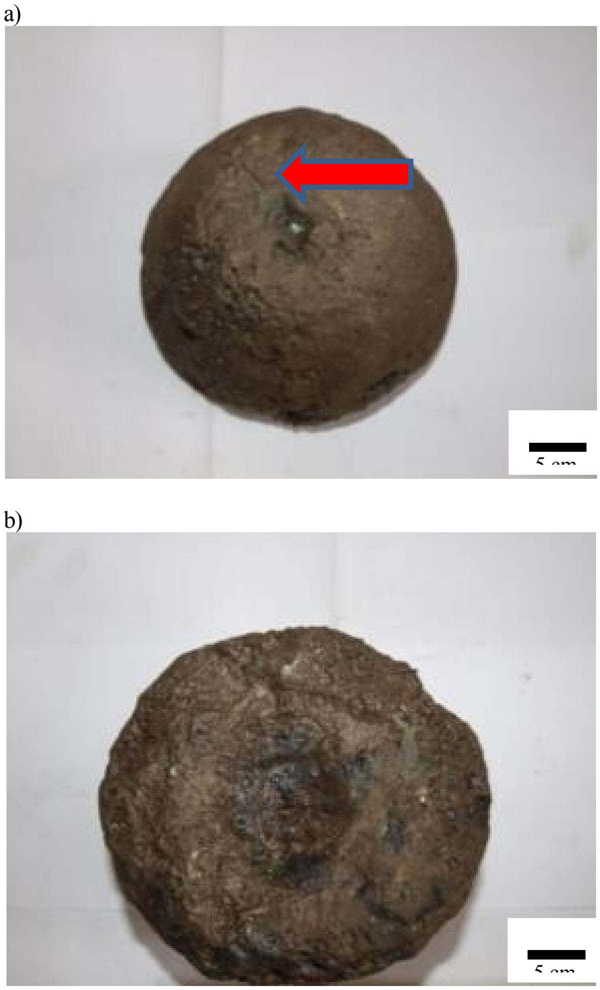

Fig. 1. The kettlebell used for investigations a) top view, b) bottom view

3. Investigation results

Macrostructure investigations

On the surface of the weight a numerous small holes and perforations were discovered (Fig. 1b). Probably they are a result of air bubbles, which are released by the carried out casting process. This is a well-known defect occurring during cast coming into occurrence due to the lack of knowledge of the foundry-men to outlet the diverse gas types (O_2, N_2, H_2) from the melt.

X-Ray Diffraction

For analysing the structure of the phase X-Ray Diffraction (qualitative) was carried out for determining the phases, formed during the casting process of the weight - providing indirectly proof concerning the technologies used by foundry-men in those age. The presented in Fig. 2 X-Ray Diffraction confirms, that Cu is the basic compound in the weight structure. Copper crystallises there in the A1 lattice, typical for $Cu_α$.

It were also confirmed other phases present in the matrix, like:

- arsenopyrite - FeAsS, crystallising in monoclinic system, with the following lattice parameters - a = 5.7412 Å, b = 5.6682 Å and c = 5.7704 Å, for β = 111.93°,
- copper sulphide - Cu_2S and CuS_2,
- copper chloride - CuCl and $CuCl_2$.

Arsenopyrite (FeAsS) and copper sulphide are recognised probably as the remaining phases coming from the ores of which the artefact was produced.

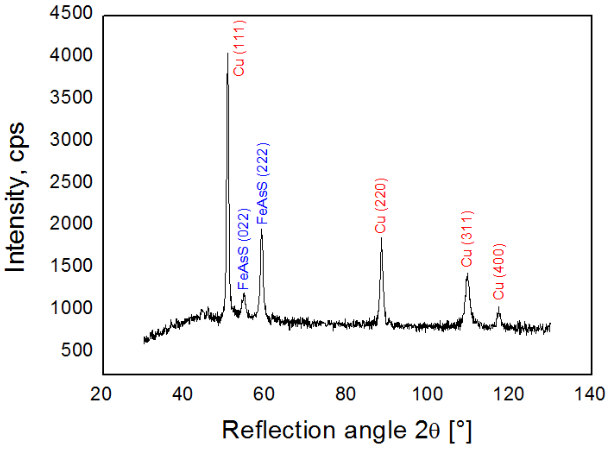

Fig. 2. Phase analysis performed using X-Ray diffraction [2]

Microstructure investigations (LM)

The investigated material was tested also metalographically, especially revealing its microstructural features and compounds, the investigations were carried out on a light microscope, and the micrographs are presented in Fig. 3.

In the analysed material can be found a relatively fine-grained microstructure (Fig. 3a) involving the $Cu_α$ matrix with three intermetallic phases inside. Also lot of voids as well as impurities is also present (Fig. 3b). The intermetallic phases occur in form of large spherical-shaped precipitates, numerous low-sized precipitations (light colour) as well as a number of voids can be also found (Fig. 3c). The voids appeared probably as a not perfectly done casting process, or a lack of sulphur removing technology in those ages.

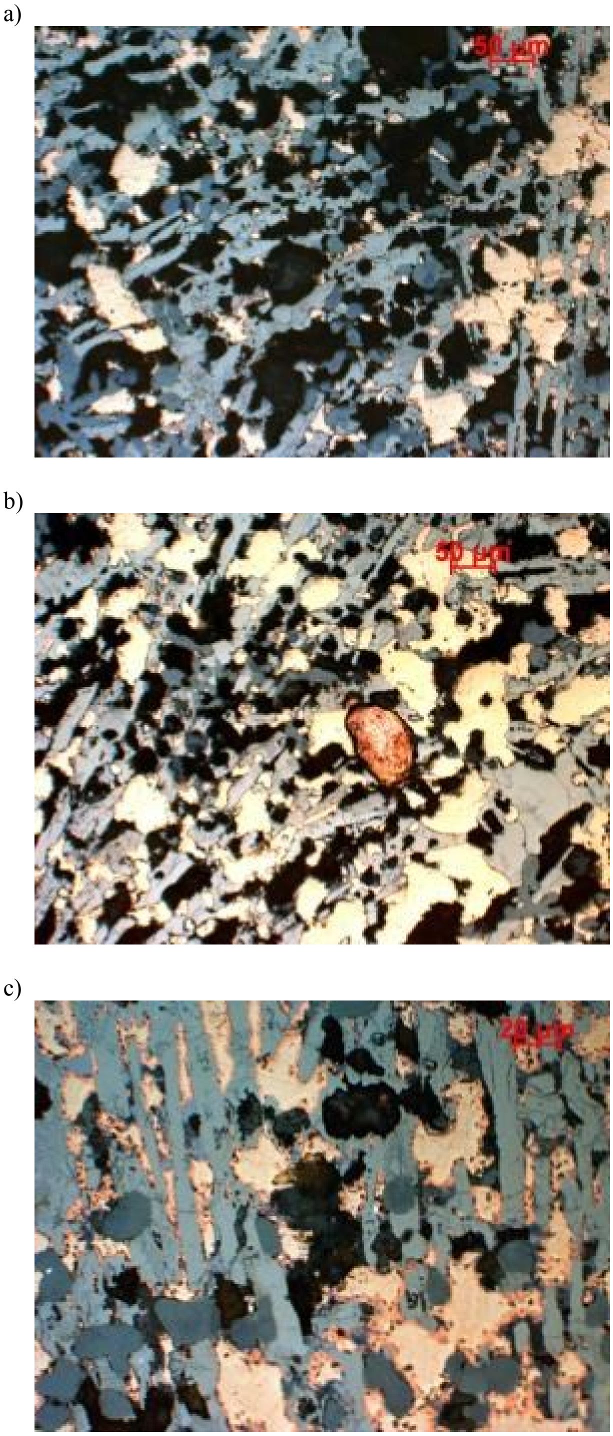

Fig. 3. Kettlebell microstructure, a) fine grains, b) inclusions, c) intermetallic phases, LM

Chemical composition analysis, carried out in works [2, 3] reveals, that the main element occurring in the investigated kettlebell is copper, with an amount more than 94%. Occurrence of arsenic with 3.7 mass % was also discovered. The chemical composition analysis of the spherical-shaped particles, reveals that Cu is its main chemical element - occurring in a concentration of ca. 64.6 mass. %.

Based on the EDS chemical composition analysis also the presence of the following elements was confirmed:

- sulphur with a concentration of ca. 25 mass. %,
- iron, with a content of ca. 9 mass. %,
- cobalt, in an amount lower than 1 mass. %.

DSC analysis

The DSC analysis was performed in the temperature range between 0°C and 600°C, with a tempering time of 5 min between the cooling and heating process at the temperature of 600°C. A nitrogen flow rate 60 ml/min was also set, further parameters are showed in Table 1.

Table 1.
Parameters of the DSC investigation

Temperature range	Heating/ cooling rate	Nitrogen flow rate
0 - 600 °C	5.00 °C/min	N_2 60 ml/min
600 °C	5.00 °C/min	N_2 60 ml/min
600- 0 °C	5.00 °C/min	N_2 60 ml/min

The resulting DSC curves from the heating and cooling with its peak transitions temperatures are presented in Fig. 5. This investigations have allow to determine the melting temperature of sulphur (S) with a peak value of ca. 104°C. At higher temperature values, in the range of 120°C-170°C there occurs diffusion transitions, which is related with solution of alloy components in copper during annealing, as well as with phases transitions of alloy impurities. At a range between 320°C-460°C there occurs temperature interval connected with recrystallization annealing of alloy. On the heating part of the diagram curve there occurs a distinct melting peak, with a peak value of ca. 518°C, where the phase of copper sulphide crystallises.

The DSC cooling curve (Fig. 5b) allows to determine the crystallization transition temperature of copper sulphide, with a peak value of ca. 521°C. At a temperature range between 330°C and 270°C a peaks value was determined of solid-state diffusion transitions of alloy components. The lowest transition peak value equal 74°C is related to the sulphur crystallization.

Investigations of the microstructure using scanning electron microscope (SEM)

Based on SEM investigations four phases occurred in the microstructure of the investigated material are confirmed, with a huge difference in its amount:

- Cu_{α} phase, observed as the alloy matrix, #1 in Fig. 4a.
- FeAsS phase observed as dark blue or black (after etching) particles, occurring as oval dot-like shapes on phase boundaries, #2 in Fig. 4b.
- CuS phase, observed like black particles (after etching) occurring as irregular-shaped patches, #3 in Fig. 4b.
- Light blue phase (after etching), rich on Cu and Cl, revealing a mass ratio of $\frac{Cu}{Cl} \approx \frac{65}{35}$, visible as bulk areas, #4 in Fig. 4c.

EDS analysis reveals further the presence of antimony (Sb) with a concentration of 67.6 mass % as well as nickel (Ni) with a concentration of 32.4 mass%. However it is not clear, it these elements are solute in the Cu matrix or does they build any fine dispersed or rarely distributed intermetallic phases. In area #4 the highest mass concentration of 90 mass. % has lead (Pb). Besides lead also the presence of oxygen with a concentration of 8 mass. % and ca.2 mass. % aluminium was found.

Vickers hardness measurement

For hardness tests, three sets of 10 measurements were performed, placed on the surfaces from internal kettlebell material weight (Table 2). Analysing the 30 measurement points it can be stated, that the lowest value is159.6 HV and the highest 227.3 HV, with an average value of 186 HV and 9.7% standard deviation, revealing its huge stability along the analysed object.

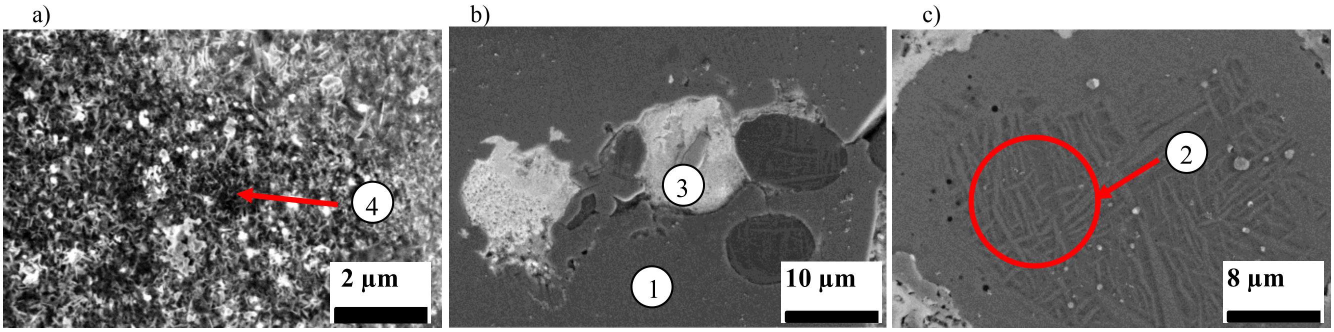

Fig. 4. Microstructure of the investigated alloy, a) Cu_{α}, b) FeAsS phases, c) Cu and Cl containing phase, SEM

Table 2.
Measured microhardness of the kettlebell alloy [2]

series 1	series 2	series 3	total	measurement
188	179	190	186	average [HV]
24.4	12.6	15.3	18.2	standard dev.
13%	7%	8%	9.7%	average standard dev

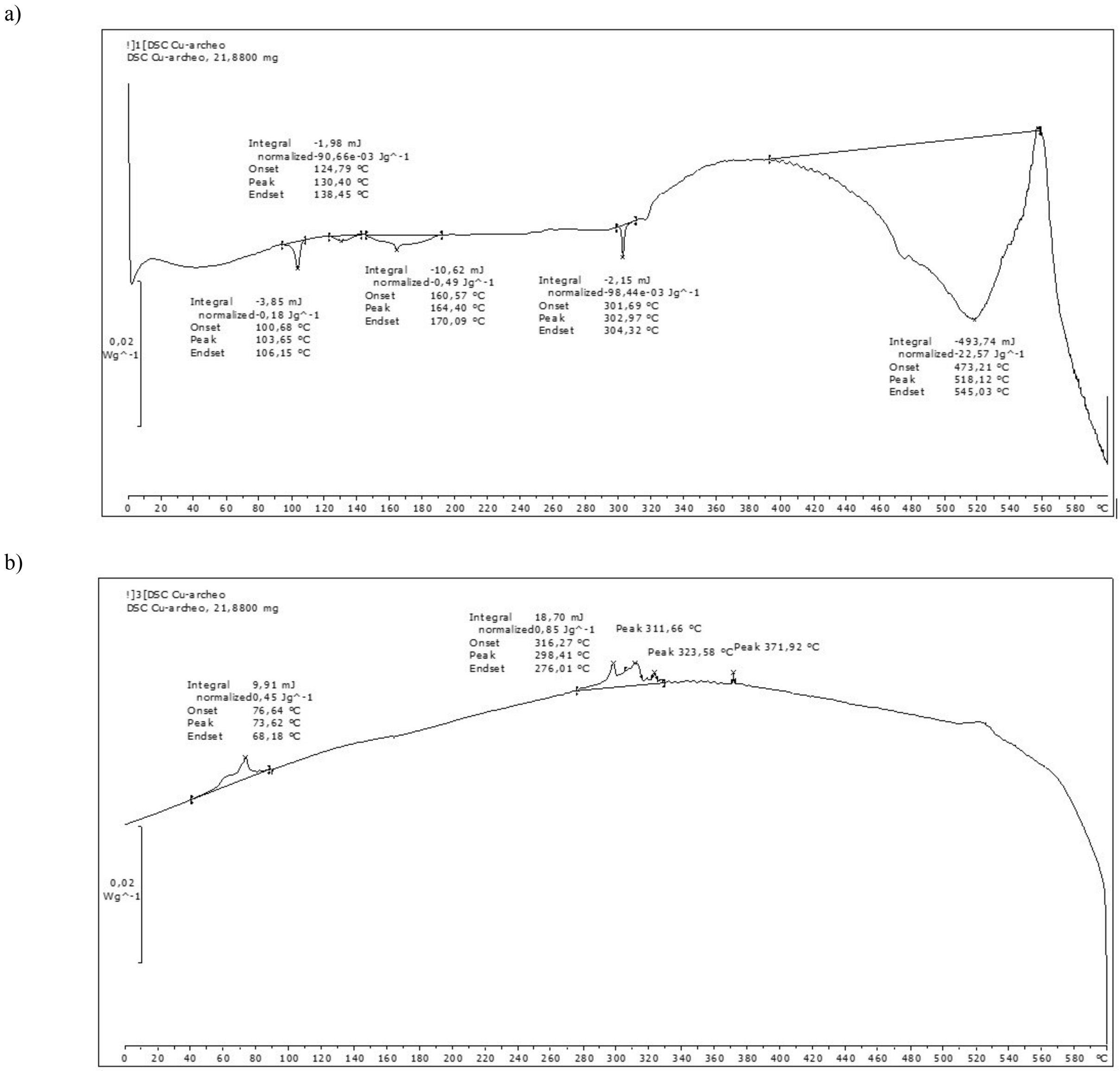

Fig. 5. DSC analysis, a) heating, b) cooling of the investigated material

Moreover, the EDS analysis of the entire measured micro-area also confirms also other elements like:

- oxygen (O), occurs in copper ores as cuprite (Cu_2O),
- silicon (Si, SiO_2), very popular in the Earth's crust, in very pure form of mainly sand or sandstone,
- sulphur (S), because sulphur is present in Poland in diverse copper ores like: chalcocite, copper glance (Cu_2S), chalcopyrite ($CuFeS_2$), covellite (CuS) or bornite (Cu_3FeS_2),
- chlorine (Cl),
- iron (Fe) because like oxygen, occurs in copper ores as cuprite (Cu_2O).
- aluminium (Al), can be explained by the former age usage of furnace lining consisted of sedimentary rock clay. Its main components were obtained by weathering of feldspar, mainly aluminosilicates, calcium, potassium, and sodium [16–18].

- There is a lack of literature data about the presence of potassium (K) and fluorine (F) in such artefacts, but they could be useful to identify the type of ore, production technique or pre-dating [19–21].

4. Conclusions

The implementation of the DSC technique for determination and description of the archaeological metallic artefacts, helps to extend the knowledge about early Age Cu alloys, e.g. due to new findings concerning the diversity of the intermetallic phases, the morphology of the microstructure and impurities or defects.

Particularly it was found that:

1. The excavated kettlebell is made of copper with additions like arsenic, lead, antimony, iron or aluminium, containing cast defects like voids and wholes.
2. The DSC method allowed to obtain valuable results not possible to achieve by other techniques, especially as a complementary method to determine characteristic temperatures of the alloy components and its purity. Contamination was confirmed with oxides and impurities in form of residues after the cast process - mainly carbon and silicon.
3. The highest HV hardness was measured for the lowest part of the kettlebell, probably its higher chemical purity or Sn addition, for alloy strengthening.
4. High impurity level is a possible indicator confirming the production of the artefact from early Age metal scrap (recycling) or a preparation in a new foundry.

References

[1] Haubner, R., Ertl, F. & Strobl, S. (2017). Examinations of a Bronze Ingot Made of Fahlore (Untersuchungen an einem aus Fahlerz gewonnenem Bronzegusskuchen). *Praktische Metallographie/Practical Metallography*. 54(2), 107-117. DOI: 10.3139/147.110446.

[2] Konieczny, J. et al. (2017). Microstructure of archaeological 17th century cast copper alloys, *Archives of Foundry Engineering*. 17(2), 190-196. DOI: 10.1515/afe-2017-0073

[3] Navasaitis, J. & Selskienė, A. (2007). Metallographic Examination of Cast Iron Lump Produced in the Bloomery *Iron Making Process, Materials Science*. 13(2), 167-173.

[4] Garbacz-Klempka A. et al. (2017). Bronze Jewellery from the Early Iron Age urn-field in Mała Kępa. An approach to casting technology. *Archives of Foundry Engineering*. 17(3), 175-183. DOI: 10.1515/afe-017-0112.

[5] Merkel, S. (2016). Carolingian and Ottonian Brass Production in Westphalia. Evidence from the Crucibles and Slag of Dortmund and Soest. *Metalla*. 22(1), 21-3.

[6] Ertl, F., Strobl, S. & Haubner, R. (2017). An ancient Bronze ingot smelted from Fahlore. *Materials Science Forum*. 891, 613-617. DOI:10.4028/www.scientific.net/MSF.891.613.

[7] Stamelou, E. et al. (2018). The sanctuary of Hercules in Sesklo Region, Volos, Greece: an archaeometric approach of the archaicbronze objects. *STAR: Science & Technology of Archaeological Research*. 1-10. DOI: 10.1080/20548923.2018.1424301.

[8] Buchanan, M. E. et al. (2017). Mistaken identity? A reassessment of the angel mounds state historic site's historic cemetery using X-Ray fluorescence. *Indiana Archaeology*. 12(2), 59-77.

[9] Sutherland, P. D., Thompson, P. H. & Hunt, P. A. (2014). Evidence of Early Metalworking in Arctic Canada. *Geoarchaeology: An International Journal*. 30(1), 74-78. DOI: 10.1002/gea.21497.

[10] Herrero, J.M. & Vendrell, M. (2012). Archaeometry and Cultural Heritage: the Contribution of Mineralogy. In Seminarios de la Sociedad Española de Mineralogía. 9. 27 Juni 2012 (pp. 112), Madrid, Spain: Sociedad Española de Mineralogía.

[11] Balasubramaniam, G. R. (2003). Alloy design of ductile phosphoric iron: Ideas from archaeometallurgy. *Bulletin of Materials Science*. 26(5), 483-491.

[12] Steffen, K. et al. (2011). Archaeometallurgical studies on the slags of the Middle Bronze Age copper smelting site S1. In Proceedings of the 3rd International Conference Archaeometallurgy in Europe. 3. 29 June - 1 July 2011 (pp. 301-308), Styria, Austria: Deutsches Bergbau-Museum Bochum.

[13] Garbacz-Klempka, A. et al. (2017). Metallurgical Slags as Traces of a 15th century Copper Smelter. *Archives of Foundry Engineering*. 17(2), 25-30.

[14] Rudzinska, M. et al. (2013). Non-destructive examination of the medieval mace. *Archives of Foundry Engineering*. 13(3), 139-142.

[15] Garbacz-Klempka, A., Wardas-Lason, M. & Rzadkosz, S. (2014). Foundry waste from the area of Złoty Stok. *Archives of Foundry Engineering*. 14(2), 23-28.

[16] Ashkenazi, D. & Fantalkin, A. (2017). Archaeometallurgical and archaeological investigation of Hellenistic metal objects from Ashdod-Yam (Israel). *Archaeological and Anthropological Sciences*. 1-23. DOI:10.1007/s12520-017-0579-1

[17] Garbacz-Klempka, A., Wardas-Lason, M. & Rzadkosz, S. (2012). Copper and lead - historical pollution on the Main Market Square in Krakow. *Archives of Foundry Engineering*. 12(1), 33-38.

[18] Rzadkosz, S. & Garbacz-Klempka, A. (2006). Metal archaeological monuments witness the history of Krakow. *Archives of Foundry*. 143(18), 365-372.

[19] Ozgowicz, W. & Labisz, K. (2011). Analysis of the state of the fine-dispersive precipitations in the structure of high strength steel Weldox 1300 by means of electron diffraction. *Journal of Iron and Steel Research International*. 18(1), 135-142.

[20] Labisz, K. et al. (2017). Thermo-derivative analysis of Al-Si-Cu alloy used for surface treatment. *Journal of Thermal Analysis and Calorimetry*. 129(2), 895-903. DOI: 10.1007/s10973-017-6204-9.

[21] Killick, D. & Fenn, T. (2012). Archeometallurgy: The Study of Preindustrial Mining and Metallurgy. *Annual Review of Anthropology*. 41, 559-575. DOI: 10.1146/annurev-anthro-092611-145719