ARCHIVES
of
FOUNDRY ENGINEERING

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (1897-3310)
Volume 15
Special Issue
4/2015

29 – 34

6/4

The Metallographic Characterization of Metal Artifacts Based on Late Medieval Examples

A. Garbacz-Klempka[a]*, Z. Kwak[a], M. Perek-Nowak[b], M. Starski[c],
[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, Mickiewicza 30, 30-059 Kraków, Poland
[c] University of Warsaw. Institute of Archaeology, Krakowskie Przedmieście 26/28, 00-927 Warszawa, Poland
*Corresponding author. E-mail address: agarbacz@agh.edu.pl

Received 20.11.2013; accepted in revised form 29.12.2015

Abstract

This work presents the metallographical observations of the chosen copper objects from the Late Middle Ages. Part of these studies is the analysis of metal relics from the Puck area conducted at the Faculty of Foundry, AGH-UST, in collaboration with the University of Warsaw. Medieval European cities were centers of trade and production of metal artifacts. Also in the Puck area, the manufacturing activities can be confirmed based on the metal findings. The aim of this study was to identify and systematize copper alloys used in the Late Medieval Period, on the basis of historic artifacts from Puck. The chemical composition analysis and microstructure observation were carried out. The research is at the first stage of an experiment of reconstructing the medieval alloys in order to study deeper their properties.

Keywords: Non-Destructive Testing, Copper Alloys, Brasses, Casting, X-ray Fluorescence (XRF), SEM-EDS

1. Introduction

Both in history as well as today, non-ferrous alloys are commonly used with copper and its alloys earning their prominent place. It is worth mentioning here the main groups of copper alloys: bronzes, brasses, alloyed copper and copper-matrix alloys for special requirements. The physico-chemical and technological properties of casting copper alloys determine their quality and application. Also, these properties are strongly affected by metallurgical process connected with obtaining copper, alloying additions and the control of melting, refining and casting processes. One of the advantageous properties of copper alloys is their high resistance to corrosion, therefore the discovered artifacts are usually in good condition. Also, artistic value and availability of raw materials determine the use of copper alloys for casting utility and ornamental products. [1-5]

Historical research of copper alloys brings information about the old metallurgy and foundry technology, the quality of raw material and the ability to shape physico-chemical and technological properties of alloys through the influence of alloying elements [6-8]. Part of these studies is the analysis of metal relics from Puck conducted at the Faculty of Foundry at AGH- UST, in collaboration with the University of Warsaw.

The purpose of the project is to develop a multifaceted portrait of the material culture of late medieval Puck as a case study of small townships on Polish territory. This project shall be implemented through comprehensive and interdisciplinary analyses of archeological investigation results of the Puck settlement area and the rich and representative collection of movable relics collected in the course thereof, including metal collection of artifacts. The chronological range of the planned activities is defined by the location time of the township in mid 14th century, ending with the beginning of modern times; dating of the relics establishes a threshold arbitrarily assumed to be the mid-16th century. Characteristics of the existing handicrafts activities will be of equal importance. Reconstruction will involve analysis of written sources and the extensive set of metal collection of relics. The source collection of relics used to investigate the material culture consists of some 2 000 metal objects.

Medieval European cities were centers of trade and manufacturing of metal objects [9-11]. This was confirmed by research, mainly from Cracow and Olkusz [12]. Also, in the Puck area, the manufacturing activities can be confirmed based on the metal findings. The aim of this study was to identify and systematize copper alloys used in the Middle Ages, on the basis of historic artifacts from Puck. The chemical composition analysis and microstructure observation were carried out. The results of the laboratory analysis complements traditional archaeological characteristics of the product and determine the raw material and production techniques. This research is the first stage of preparation for an experiment of reconstruction of the medieval alloys in order to study comprehensively their character.

2. Materials and methodology

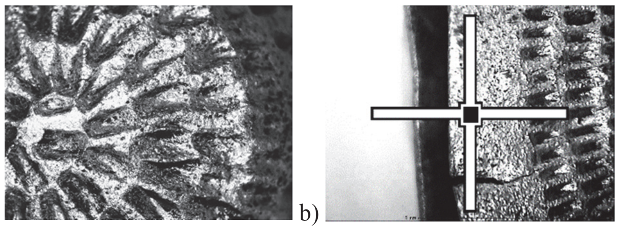
The artifacts were obtained during archaeological research at the Market Square in Puck. During the studies, the macroscopic observations of the metal objects were performed in order to evaluate their conservation status, production techniques and destination. Only the non-destructive methods were applied to characterize the samples: chemical composition was established by X-ray fluorescence spectroscopy (XRF), the microstructure was analysed using optical microscopy (OM) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS).

3. Results

The analysis of chemical composition showed that all copper alloys were used for production of non-ferrous metal products (Figs. 1-10, Tab. 1), with a few exceptions. At the same time, iron products were analyzed. In the copper alloys, intentional alloying additions such as Sn, Zn, Pb, and natural additions such as Fe, Sb, As, Ni, as well as others, difficult to remove by ancient metallurgists, which nowadays can be regarded as traces of their origin and the ancient technology, were identified.

For the detailed characteristics, three relics were selected from the extensive set of metal objects of different composition: a thimble (No. Pk.M.122.01E.46), fragment of ferrule (No. Pk.M.122.02C.11) and a weight (No. Pk.M.122.06.08). The thimble was made of a two-component Cu-Zn alloy with an average zinc content of 20.4%. The fragment of ferrule was casted of a multi-component Cu-Pb-Zn-Sn alloy, with a significant lead content (7.4%), but also zinc (4.66%), tin (3.55%) and iron (1.56%). The composition is completed by a small amount of antimony, arsenic, nickel and silver.

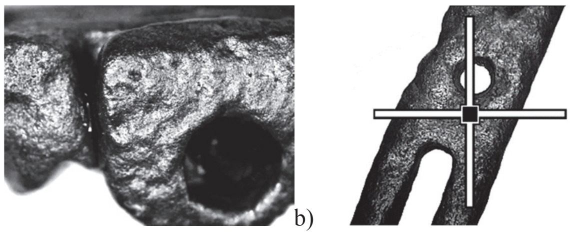
Fig. 1. Macrostructure of the thimble, No. Pk.M.122.01E.46



a) b)

Fig. 2.The thimble from Puck:
a) macrostructure b) one of the points of the chemical composition's results by means of XRF

Fig. 3. Macrostructure of the fragment of ferrule from Puck, No. Pk.M.122.02C.11



a) b)

Fig. 4. The fragment of ferrule from Puck:
a) macrostructure b) one of the points of the chemical composition's results by means of XRF

Tab. 1. Elemental Analysis of X-Ray Fluoresce (wt.%)

Element (wt.%)	Fe	Co	Ni	Cu	Zn	As	Ag	Sn	Sb	Au	Pb	Bi	Sum Conc.
Pk.M. 122.01E.46	0,10	0,05	0,36	**77,98**	**20,40**	0,01	0,04	< 0,051	0,02	< 0,020	0,75	0,30	100,00
Pk.M.122.02C.11	1,36	0,08	0,12	**82,07**	**4,66**	0,40	0,14	**3,55**	0,18	< 0,020	**7,40**	0,05	100,00
Pk.M.122.06.08	0,52	0,09	0,08	**45,79**	0,12	**3,84**	0,15	**9,53**	**4,56**	< 0,020	**35,10**	0,22	100,00
Pk.M.122.03.04	0,64	0,06	0,17	**78,48**	< 0,010	0,57	0,18	0,94	**8,88**	< 0,020	**10,00**	0,09	100,00
Pk.M.122.08.09I	0,44	0,07	0,09	**83,45**	**13,14**	0,07	0,10	1,61	0,29	< 0,020	0,73	0,01	100,00
Pk.M.122.08.09II	0,78	0,09	0,09	**79,95**	**16,90**	< 0,005	0,09	1,25	0,02	< 0,020	0,82	0,01	100,00
Pk.M.152.03.19A	1,59	0,10	0,02	4,85	0,22	< 0,005	0,02	**41,27**	0,04	0,03	**51,58**	0,28	100,00

The weight showed a heterogeneous structure already at the macro level, which was visible as roughness and pits on the surface (Figs. 5-6). Each of the macro areas were significantly different in their chemical composition, in particular the copper content (in the range of 31.77-59.16%) and the lead content (23.63-46.56%). The copper content was assessed to be at the level of 45.79%, lead at 35.10% and tin at 9.53% (Tab. 1). A significant percentage of antimony (4.56%), arsenic (3.84%), iron, bismuth, zinc and silver was identified in the alloy.

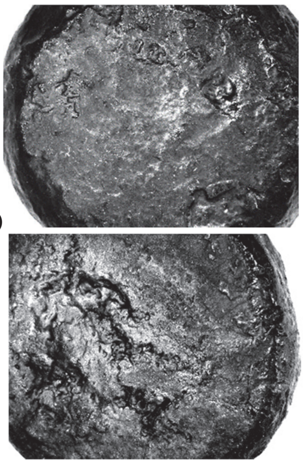
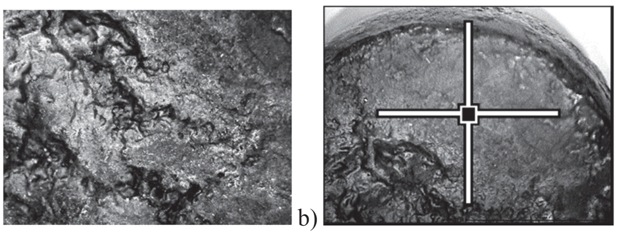
a)  b)

Fig. 5. Macrostructure of the weight, left (a) and right (b) site

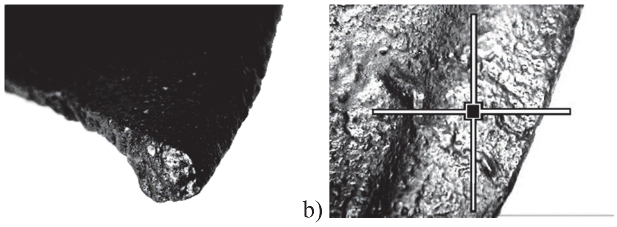


a) b)

Fig. 6. The weight: a) macrostructure b) one of the points of the chemical composition tests by means of XRF

In addition, three other artefacts were also analysed: a fragment of a bronze pot (grapen) (Fig. 7), applications (Figs. 8-9) and a ring (Fig.10) with the following numbers: Pk.M.122.03.04, Pk.M.122.08.09, Pk.M.152.03.19A, respectively. The results of the chemical composition of these products are summarized also in table (Tab. 1). Dishes were cast from leaded bronze containing 78,48% of copper, 10% of lead and a small amount of tin (0,94% Sn).

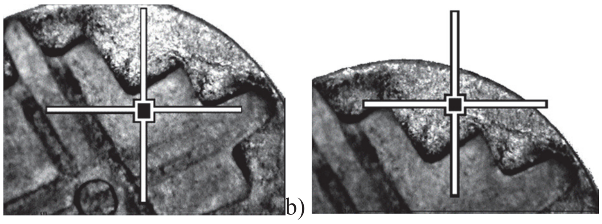
The application consists of two layers made of two-component-type of brass connected by a rivet. Both parts slightly differ in chemical composition: the first, top layer contains 83.45% of copper and 13,14% of zinc; the second, bottom layer contains 79,95% of cooper and 16,90% of zinc. Accompanied by a small amount of tin and lead.



a) b)

Fig. 7. a) Macrostructure of the bronze cooking pot No. Pk.M.122.03.04, b) one of the points of the chemical composition tests by means of XRF

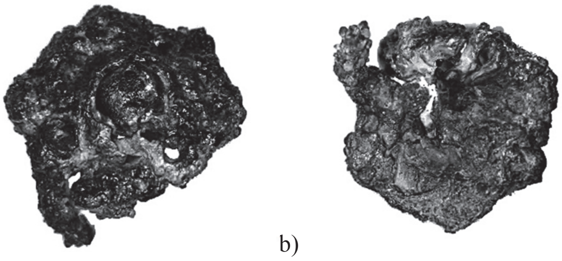
Fig. 8. Macrostructure of the application, No. Pk.M.122.08.09



a) b)

Fig. 9. One of the points of chemical composition tests by means of XRF, application: a) first layer, b) second layer

In the group of metal artifacts there stands out the ring made from Pb-Sn alloy. This object is seriously damaged. The determination of its chemical composition posed problems due to the inability to prepare the surface for study. The result may be burdened with a considerable error due to the remaining layers of corrosion, pollution and protective coat. In this study, it was assumed that the ring is made of lead, however its factual composition was determined as follow: 51.58% Pb, 41,27% Sn and 4,85% Cu. The content of iron at 1.59% level could be attributed to the presence of impurities on the surface of the object.



a) b)

Fig. 10. Macrostructure of the ring from Puck, No. Pk.M.152.03.19A: front of the ring (a), back of the ring (b)

For the majority of the artefacts a detailed SEM-EDS analysis was carried out. In the thimble microstructure there is a grain of crystallites visible with a varied orientation (Fig. 11). Inside the individual grains there are dendrites visible of solid solution α. The nature of the microstructure shows the use of a casting technique and plastic processing. The chemical composition is uniform within the artifact volume (Fig. 12). The artifact with Pk.M.122.01E.46 number contains about 79% of Cu and 20% of Zn. It largely corresponds to the results obtained by XRF, which indicated, in addition to the main components, the presence of approx. 1% of impurities.

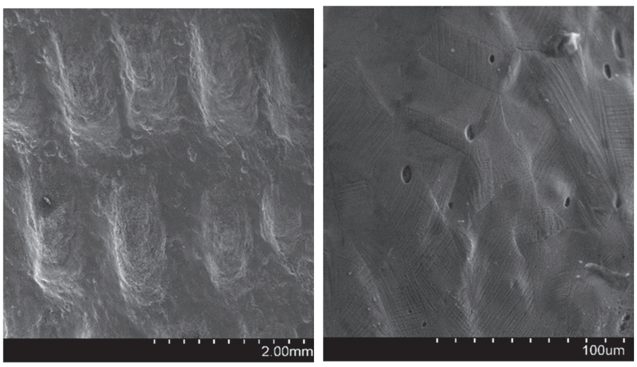
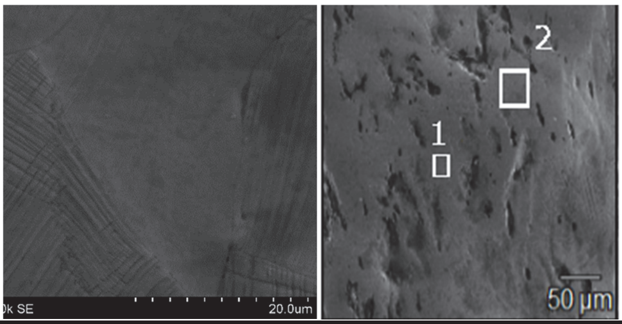


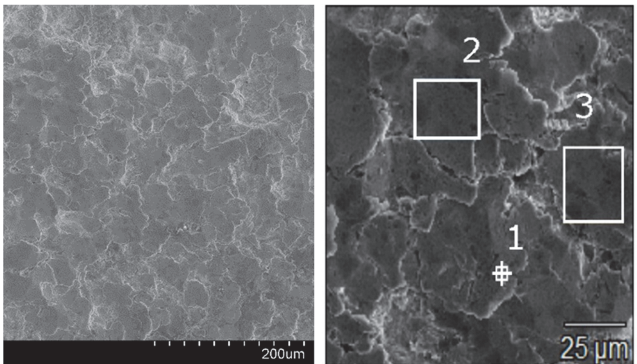
Fig. 11. Microstructure of the artifacts from Puck No. Pk.M.122.01E.46

Analysis of the microstructure of ferrule (Fig. 13) revealed the presence microsegregation, due to elevated levels of lead in the product (average 7.40% Pb). Particular areas show the share of the three major alloying elements: cooper (from 80,72 to 89,37% of Cu), zinc (from 3,49 to 5,93% of Zn) and tin from 3,29 to 4,06%. These areas contain also a small amounts of iron (1,42-2.29% of Fe). With a higher concentration of iron also nickel (0,75% Ni) was identified. The differences in the concentration of lead are significant; there are areas devoid of lead next to the areas containing 6.07% or 9.58% of lead.



Element (wt.%)	**Cu**	**Zn**
Pk.M12201E46 pt1	**79.40**	20.60
Pk.M122.01E46 pt2	**79.56**	20.44

Fig. 12. Microstructure of the artifacts from Puck with measurement points and the corresponding chemical composition by means of SEM-EDS



Element (wt.%)	**Fe**	**Ni**	**Cu**	**Zn**	**Sn**	**Pb**
Pk.M.122.02C.11 **pt1**	1.42	-	**89.37**	5.93	3.29	-
Pk.M.122.02C.11 **pt2**	2.29	0.75	**82.22**	5.07	3.61	6.07
Pk.M.122.02C.11 **pt3**	2.15	-	**80.72**	3.49	4.06	9.58

Fig. 13. Microstructures of the artifacts from Puck with measurement points and the corresponding chemical composition by means of SEM-EDS

The microsegregation is visible to a larger extent in the microstructure of weight (Figs. 14-15). It contains an average amount of lead 35.10 % (Tab.1). In a heterogeneous structure, the bright areas which are associated with higher content of lead equal to 92.21% Pb are extensive. In others darker areas, next to the lead, copper, tin and zinc are also found. Single, fine inclusions contain iron (1.39% of Fe). Additionally, in the microstructure of the weight numerous cracks are visible.

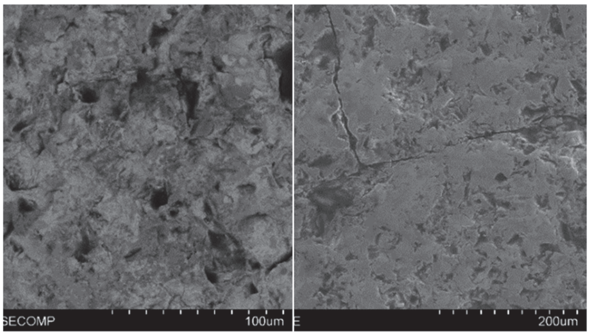
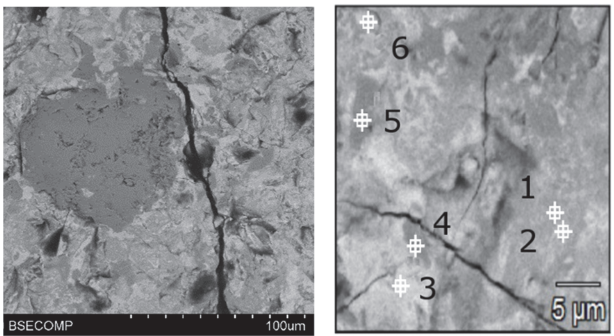


Fig. 14. Microstructures of the artifacts No. Pk.M.122.06.08 from Puck



Element (wt.%)	**Fe**	**Cu**	**Zn**	**Sn**	**Pb**
Pk.M.122.06.08 **pt1**	-	25.22	8.36	20.36	**46.06**
Pk.M.122.06.08 **pt2**	-	18.44	4.23	13.88	**63.45**
Pk.M.122.06.08 **pt3**	-	7.79	-	-	**92.21**
Pk.M.122.06.08 **pt4**	-	14.18	3.27	-	**82.55**
Pk.M.122.06.08 **pt5**	-	22.82	6.35	15.93	**54.90**
Pk.M.122.06.08 **pt6**	1.39	17.12	4.41	24.80	**52.28**

Fig. 15. Microstructures with measurement points and the corresponding chemical composition by means of SEM-EDS

A tendency for segregation also characterises a leaded bronze, which was used to cast the cooking pot, (Figs. 16-17). In the microstructure there were phases identified with the content of 91.94% Cu and the 8.06% Sb, as well as the areas of pure copper. Next to them were the bright areas, which mostly consisted of lead (53.00-57.35%) and antimony (27.30-31.31% of Sb).

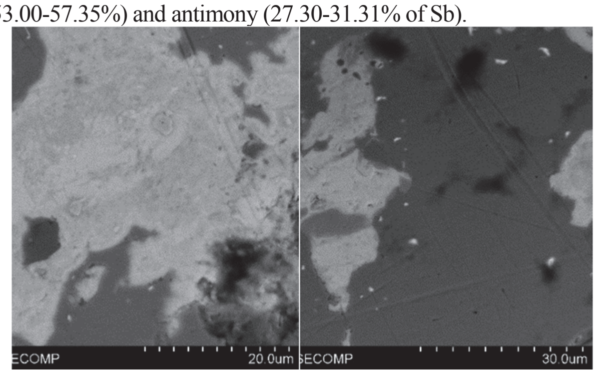
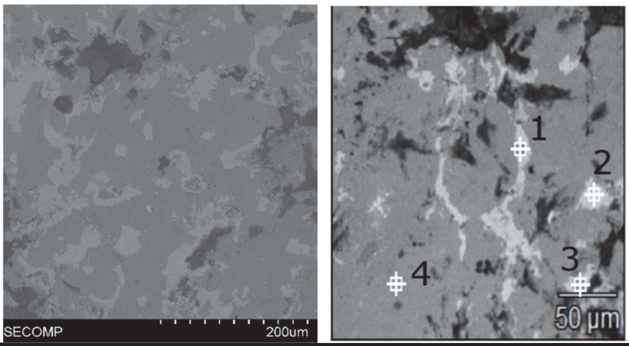


Fig. 16. Microstructures of the artifacts No. Pk.M.122.03.04 from Puck



Element (wt.%)	**Cu**	**As**	**Sb**	**Pb**
Pk.M.122.03.04 **pt1**	11.07	4.62	31.31	**53.00**
Pk.M.122.03.04 **pt2**	15.34	-	27.30	**57.35**
Pk.M.122.03.04 **pt3**	**100.00**	-	-	-
Pk.M.122.03.04 **pt4**	**91.94**	-	8.06	-

Fig. 17. Microstructures with measurement points and corresponding chemical composition by means of SEM-EDS

In the application's microstructure (Figs. 18-19) a dendritic structure was identified, what is an evidence for the use of the casting to obtain this item. The arrangement of grains indicates the plastic forming.

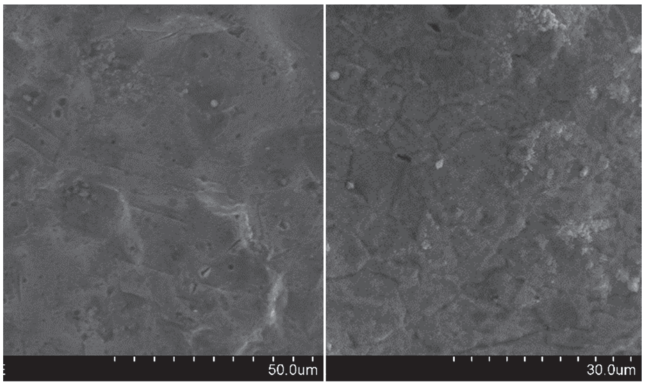
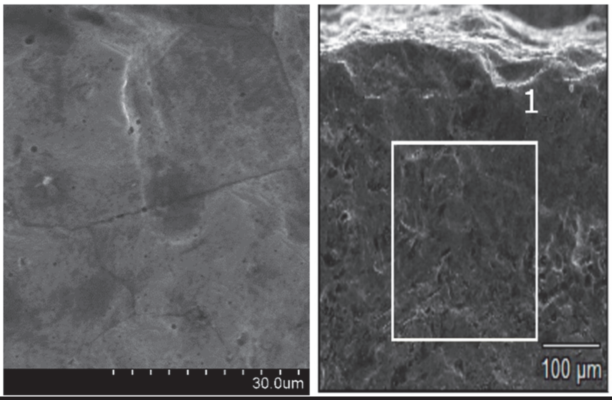


Fig. 18. Microstructures of the application from Puck:
a) second layer, b) rivet

The content of the application material (layer I) is homogenous, it consists mainly of copper and zinc, that is why it belongs to brasses. Also, a less significant contribution of lead, tin and iron was documented here. The composition of the layer II is similar, including the rivet that joins them.

The artifacts from Puck are characterized by a large variety of chemical composition. This points to the advanced level of the technology and the artifacts manufactured at the local workshops, as well as trade links with the other towns. In addition to the basic elements, such as Cu, Zn, Sn and Pb, the artifacts also contain Sb, As and Fe.

The characteristics of the altogether 17 artifacts, examined from many angles, show that the most commonly used alloys are Cu-Pb, Cu-Zn, Cu-Zn-Sn and Cu-Sn-Pb (Fig.20). Among the most common alloys documented during the research, also the artifacts made from copper, brasses, tin brasses and lead bronzes should be noticed.



Element (wt.%)	**Fe**	**Cu**	**Zn**	**Sn**	**Pb**
Pk.M.122.08.09 I pt1	1.04	**83.39**	11.34	1.48	2.74

Fig. 19. Microstructures with measurement points and the corresponding chemical composition by means of SEM-EDS

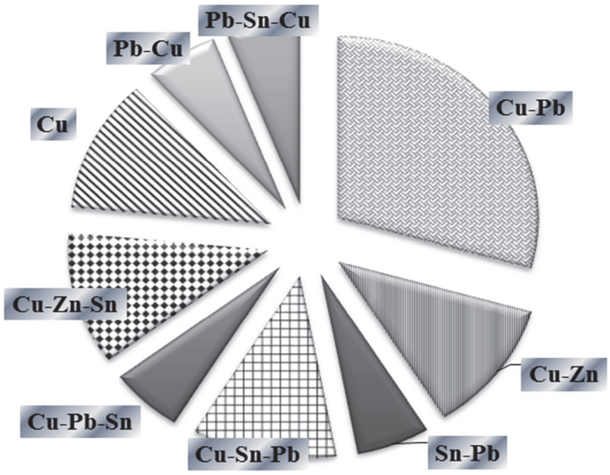


Fig. 20. Content variety of the artifacts examined, including the four major elements: Cu, Zn, Sn, Pb

4. Conclusions

The results of the special analyzes of the late medieval artifacts from Puck market allow to sum up and draw conclusions. Macro and microscopic studies confirmed the opinions of widespread use of casting decorative elements in the late medieval period. This technology makes it possible to obtain ornamental objects of complicated shapes.

Besides, half-products were cast, which were subsequently shaped by hammering. During the Middle Ages ornaments were cast into clay moulds, which were then destroyed, or into two-part stone moulds, destined for reusing.

On the basis of chemical composition of the studied artifacts, the presence of various metals and alloys was identified, including copper, binary alloys: Cu-Sn, Cu-Zn, Cu-Pd and multi-component alloys: Cu-Zn-Sn, Cu-Sn-Pb, Cu-Pb-Sb, Cu-Pb-Zn-Fe, Pb-Cu-Sn-Sb, Pb-Sn-Cu-As, Cu-Zn-Sn-Sb-Pb and Pb-Cu-Sb-Sn-As.

Among the alloys a prominent place is taken by brasses, which are characterized by good castability. Also, the aesthetic aspects, like colour and shine, which made the brasses similar to precious metals alloys. In the utility objects, where the appearance is secondary (cooking, pots, weights), a significant lead content was identified, which probably resulted from economy.

Both for the copper alloys as well as the ornamental pieces, there are analogies with the research of the historical artifacts from the Main Square in Krakow.

The test results will allow to compare the chemical composition of the alloys from Puck with other research results and create the basis for analysis of historical alloys.

Apart from testing the chemical content and microstructure also the corrosion damage was identified, which has an impact on the preparation of conservation program.

Acknowledgements

The financial support of a cooperation with Warsaw University under the grant numbers nr 1.1.170.526 (Gr-4601 2013/09/D/HS3/04468). The researches support of the State Committee for Scientific Research of Poland under the grant numbers 11.11.170.318–11 is acknowledged.

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