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COPPER AND ARSENICAL COPPER FROM ENEOLITHIC IN METALLOGRAPHIC AND MECHANICAL STUDIES

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1. Introduction

Arsenical copper has been used since early fourth millennium BC, later exchanged by application of Cu-Sn alloys in metallurgy [1-3]. Arsenic was an element naturally introduced to alloys with no control in concentration as it was incorporated in mineral arsenides of copper: Cu_3AsS_4 (enargite), $Cu_{12}As_4S_{13}$ (tennantite), Cu_3As (domeykite) or $Cu_{5.2\text{-}8}As$ (algodonite) [4,5]. Today, an attempt is made towards reproduction of those earliest Cu-As alloys.

This work presents the results of metallographic and mechanical properties studies performed on two flat axes connected with local Eneolithic societies (4000-3500 BC). The axes are one of the oldest metal artifacts from Polish land. Due to a fact that they are of none archaeological context and its academic value is therefore strongly reduced, the aim of this work was to improve and verify current state of knowledge about the axes.

2. Experimental

The flat axes were obtained from Leon Wyczółkowski Bydgoszcz District Museum. They were of considerable size, up to 35 mm wide and 95 and 140mm long. 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 in lab reproduced. In

order to achieve the characteristic of the alloys, its mechanical properties including ultimate tensile strenght (UTS), hardness (HB), ductility (A_5) were examined. The solidification process was studied by means of thermal analysis.

3. Results and discussion

Analysis of chemical composition showed that both copper and arsenical copper were applied in production of flat axes (Tab.1). The studied artifacts contained max. 0.67% As. Other analyses showed higher concentration of arsenic in the copper artifacts, 2-3% or even above 7% [3-4]. Microstructure of the studied By2 sample is presented in Figure 1, what suggests application of plastic deformation after casting.

Tabela 1. Wyniki badania składu chemicznego odlewanych siekier z okresu eneolitu (wt.%).

Elements (wt. %)	Fe	Co	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	another	Sum Conc.
By_1	0,08	0,05	0,07	98,71	0,12	0,67	0,01	< 0,051	< 0,051	< 0,020	0,01	0,05	100,00
By_2	0,01	0,05	0,07	99,47	0,13	0,01	0,10	< 0,051	0,04	< 0,020	0,01	0,12	100,00

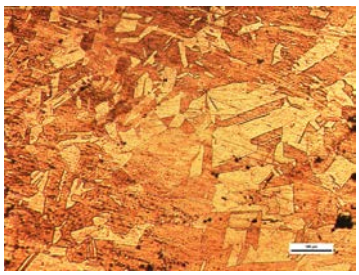

Fig. 1. Microstructure of prehistoric flat axe casted and plastically deformed (forged) By2

4. Conclusions

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

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

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