

Copper Test Melts with Additions of Pb, Bi, As, Sb and Sn

Roland Haubner^{1,a*} and Susanne Strobl^{1,b}

¹Technische Universität Wien, Institute of Chemical Technologies and Analytics,
Getreidemarkt 9/164-03, A-1060 Vienna, Austria

^{a*}roland.haubner@tuwien.ac.at, ^bsusanne.strobl@tuwien.ac.at

Keywords: copper, test melts, bismuth, arsenic, antimony, tin.

Abstract. Archaeometallurgical copper-artefacts contain a wide variety of metal admixtures (e.g. Pb, Bi, As, Sb, Sn) which either originate from the ores or were intentionally added. When the melt solidifies, these elements can accumulate in different structural areas and form special phases. The different alloying elements also interact with each other. In order to be able to examine these interactions, model alloys with different elements (Pb, Bi, As, Sb, Sn) and concentrations (5 or 10 wt.% each) were produced. More simple alloys show a dendritic microstructure and the added elements accumulate in the interdendritic areas. This is clearly visible for Pb and Bi additions, as both metals are not soluble in copper. As and Sb form compounds with Cu which precipitate mainly in the interdendritic regions. Sn is soluble in Cu at lower concentrations and Cu-Sn phases are formed only at higher concentrations. The resulting microstructures become very complex if more elements are involved. Finally, they enable us to have a better understanding for microstructures of ancient copper alloys.

Introduction

The beginnings of copper metallurgy are essentially determined by the available copper ores and the methods used to extract the metallic copper [1]. Accompanying elements play an important role, because they remain in the copper to a greater or lesser extent (e.g. Fe, S, As, Sb, Pb) [2, 3]. During a subsequent production of bronze, the constituents of the two source ores are mixed and can react with each other (e.g. Sn, Pb) [4]. Further interactions can occur when ores are added intentionally or unintentionally (e.g. PbS, ZnS, Sb₃S₂) [5, 6].

This means that a prehistoric bronze can contain many elements that interact with each other [7]. The goal of producing test melts is to document and study such interactions and to get a better assessment for the measured results of historical bronzes.

Experimental Procedure

Melting of the samples.

The individual metal powders were weighed in appropriate ratios, transferred to a quartz crucible and slightly mixed. This mixture was then covered with carbon powder to prevent oxidation. It was then heated to approximately 1100 °C in a chamber furnace. When this temperature was reached, the mixture was left for approximately 15 minutes and subsequently air cooled.

Metallography.

After cutting the samples were cold mounted in epoxy resin. Metallographic preparation started with plane-grinding, followed by polishing with 9–1 µm diamond suspensions.

For etching Klemm 2 and (NH₄)₂CuCl₄ solutions were used.

It should be noted, that due to segregation, the composition of the alloys shown in the images, may not correspond to the initial concentrations.

A light optical microscope (LOM) and a scanning electron microscope (SEM) with backscattering electron (BSE) detector were used. X-ray analysis (EDX) was performed to measure the local elemental compositions.

Results and Discussion

The interactions between the different metals are based on thermodynamic data illustrated by phase diagrams. The binary phase diagrams of the investigated metals are all available [8], but not the ternary or quaternary ones. Therefore, attempts are made to explain the observed microstructures from the analytical results.

Alloy 10 % Bi, 10 % Pb, balance Cu.

Bi and Pb are insoluble in Cu [8]. Dendritic solidification of copper occurs from the melt and Bi-Pb are present in the interdendritic regions (Fig. 1a). The dendrites have a length of up to 1 mm. After etching different coloured dendritic cells are visible due to the diverse orientation of copper (Fig. 1b–d). Pb is insoluble in Bi, but in the binary system a Pb-Bi phase is formed. Finally, the Pb-Bi phase and Bi should be present. In the SEM-BSE images, the interdendritic regions of Pb and Bi are visible as a bright “network” (Fig. 1e, f).

Alloy 10 % Sb, 10 % Pb, balance Cu.

Sb forms the intermetallic phase Cu_3Sb and Pb is insoluble in Cu [8]. This is already visible at the polished sample where Cu_3Sb appears light grey and Pb black (Fig. 2a, b). During solidification of the melt Cu dendrites are formed first and Sb as well as Pb concentrate in the remaining melt. The concentration gradients are clearly visible at the etched samples (Fig. 2c, d). The SEM images and the EDX element distribution obviously show that Cu_3Sb and Pb are separated (Fig. 2e–g).

Alloy 10 % As, 10 % Sn, balance Cu.

The interactions of As and Sn in copper are of striking interest for ancient bronzes [3, 9]. Again, a dendritic structure is formed, but no identification of the individual phases is possible from the etched samples. (Fig. 3a–d). Sn concentration in Cu increases with progressive solidification. Cu_3As forms in the interdendritic regions. The $\text{Cu}_{41}\text{Sn}_{11}$ phase is subsequently formed during a eutectoid transformation (Fig. 3e–g).

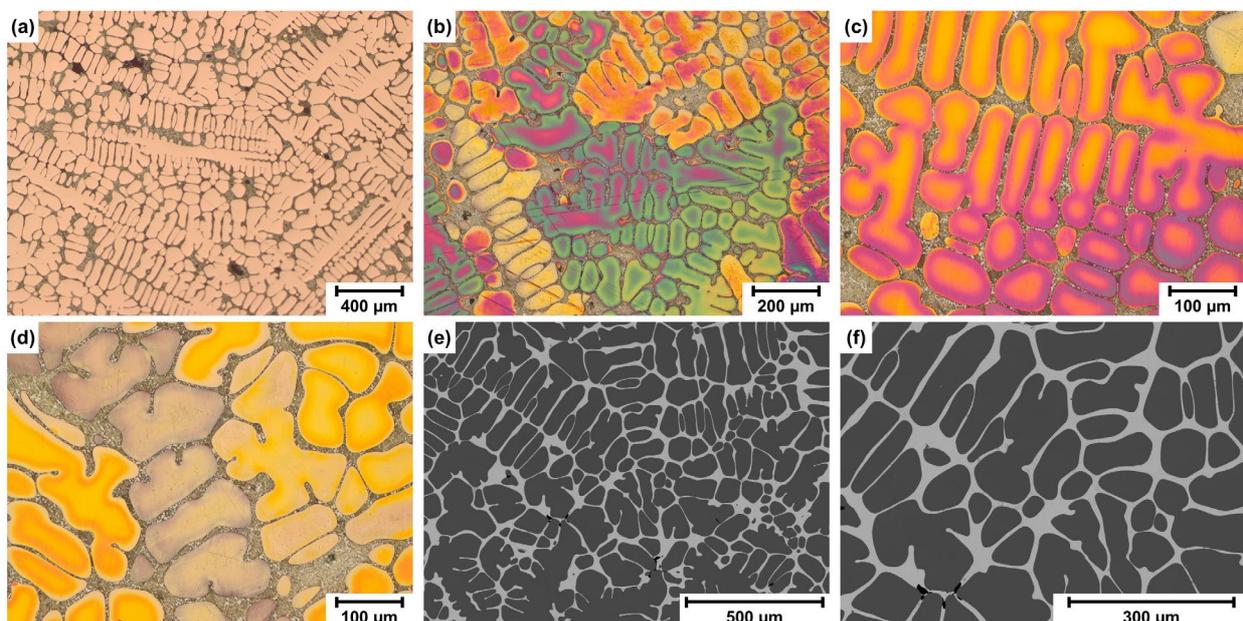


Fig. 1. Alloy 10 % Bi, 10 % Pb, balance Cu. (a) polished, (b–d) Klemm 2 etched, (e, f) SEM.

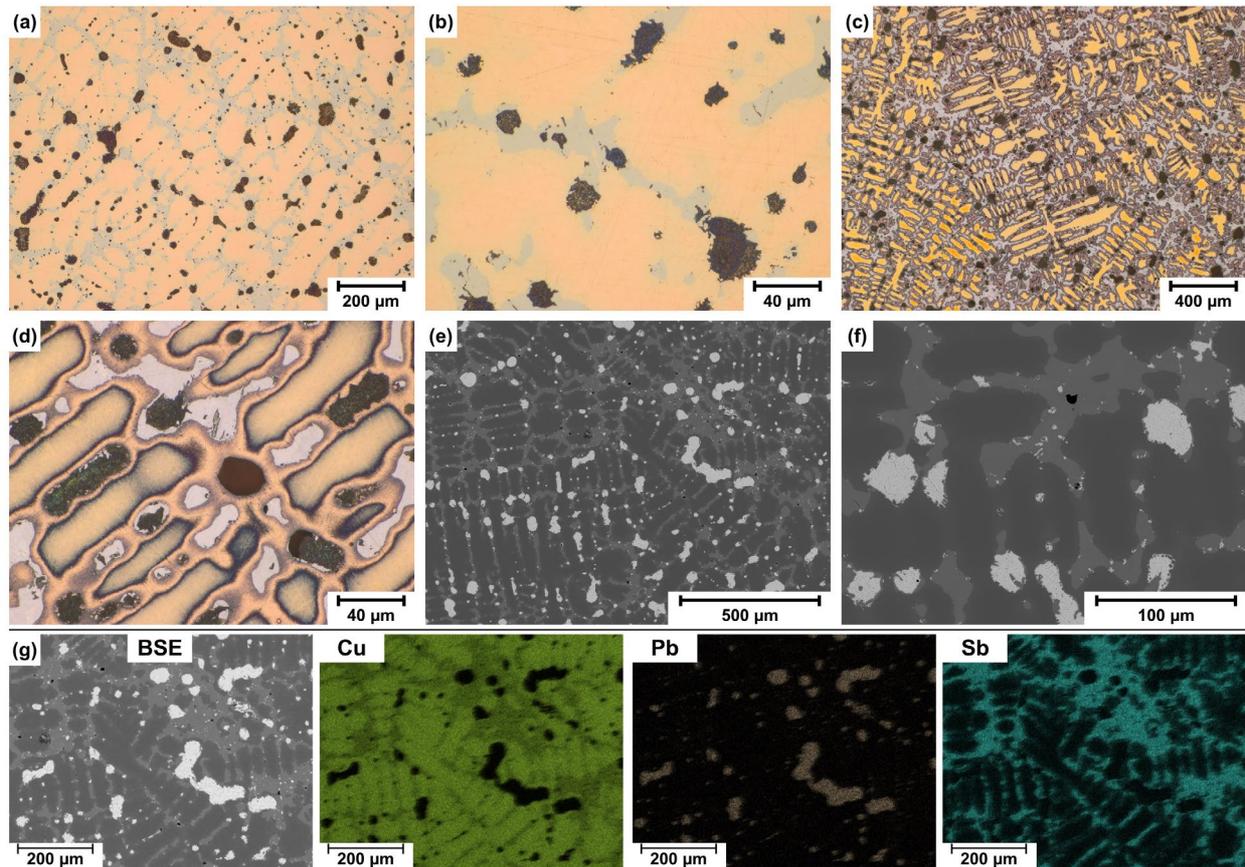


Fig. 2. Alloy 10 % Sb, 10 % Pb, balance Cu. (a, b) polished, (c, d) $(\text{NH}_4)_2\text{CuCl}_4$ etched, (e, f) SEM, (g) SEM-BSE element distribution.

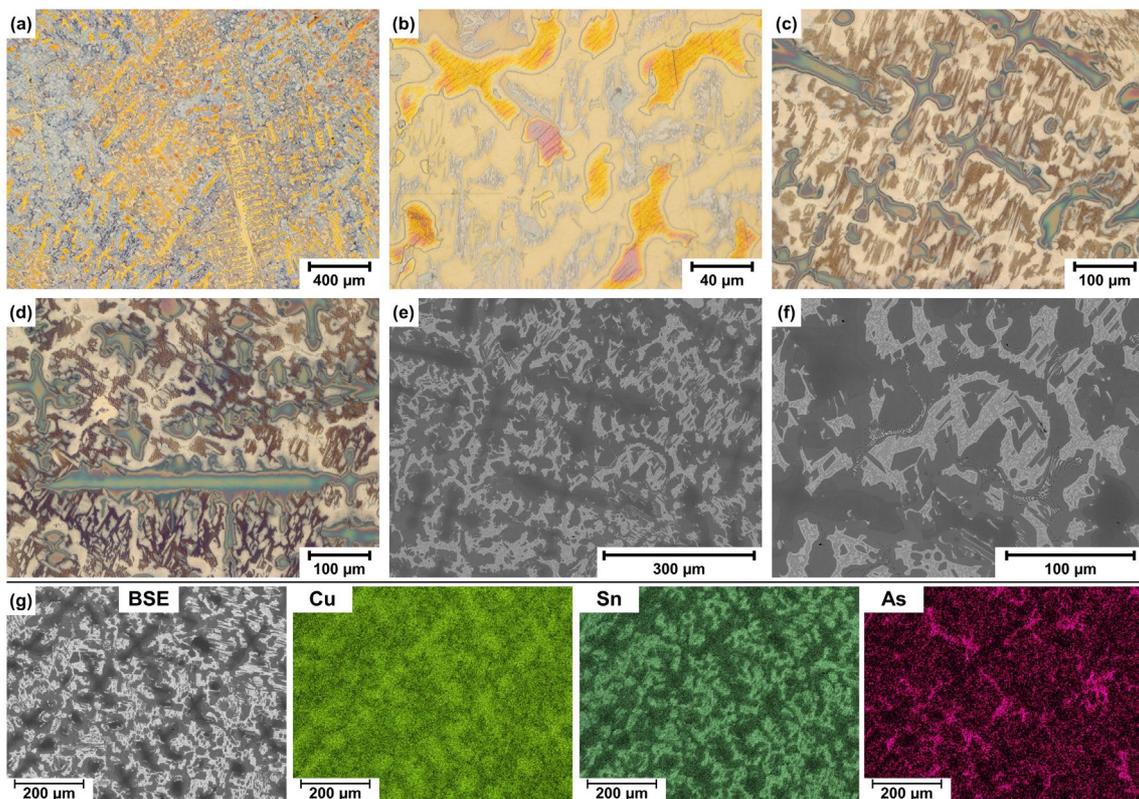


Fig. 3. Alloy 10 % As, 10 % Sn, balance Cu. (a, b) Klemm etched, (c, d) $(\text{NH}_4)_2\text{CuCl}_4$ etched, (e, f) SEM, (g) SEM-EDX element distribution.

Alloy 10 % Sb, 10 % Sn, balance Cu.

All binary phase diagrams between Cu, Sb and Sn are very complex, and many intermetallic phases are possible [8, 10]. Cu forms the dendritic structure and the alloying elements are enriched in the interdendritic regions (Fig. 4a–d). In the SEM-BSE images, the interdendritic areas appear homogeneous (Fig. 4e, f). According to the EDX element distribution, the elements Sb and Sn are present side by side in the interdendritic regions and are not separated (Fig. 4g). It is assumed that the phases Cu_3Sb and $\text{Cu}_{41}\text{Sn}_{11}$ are present. It cannot be determined whether or not an Sb-Sn phase had been formed.

Alloy 5 % Sb, 5 % As, 5 % Pb, balance Cu.

In this alloy, four elements already interact, making the system considerably more complex. Looking at the individual elements, Cu_3As and Cu_3Sb are formed. Pb and As form an eutectic at 2.6 wt.% As, Pb and Sb form one at 11.1 wt.% Sb [8].

Again, in this alloy Cu dendrites are formed first and the alloying elements accumulate in the melt to solidify in the interdendritic areas (Fig. 5a–d). The intermetallic phases Cu_3Sb , Cu_3As and Pb are expected (Fig. 5e, f). Based on the EDX element mappings one can see that As is associated with both Pb and Sb (Fig. 5g). Since Pb is insoluble in Cu, it is separated.

Alloy 5 % As, 5 % Sb, 5 % Sn, balance Cu.

This Cu alloy contains As, Sb and Sn, each 5 wt.%, but no typical solidification structure was obtained. This quaternary system probably has multiple eutectics and other phase transitions unknown to us.

The typical dendritic solidification structure of Cu is not observed, but Cu forms elongated bars instead of dendrites (Fig. 6a–f). Similar to the ternary Sb-Sn-Cu system, the Sb and Sn phases are co-localized (Fig. 6g).

Complete different is the behaviour of the As compounds: they solidify from a residual melt.

Thus, various microstructures are present, which can be explained by eutectic solidification or eutectoid transformations. These microstructures overlap, but it was not possible to identify the individual phases by EDX.

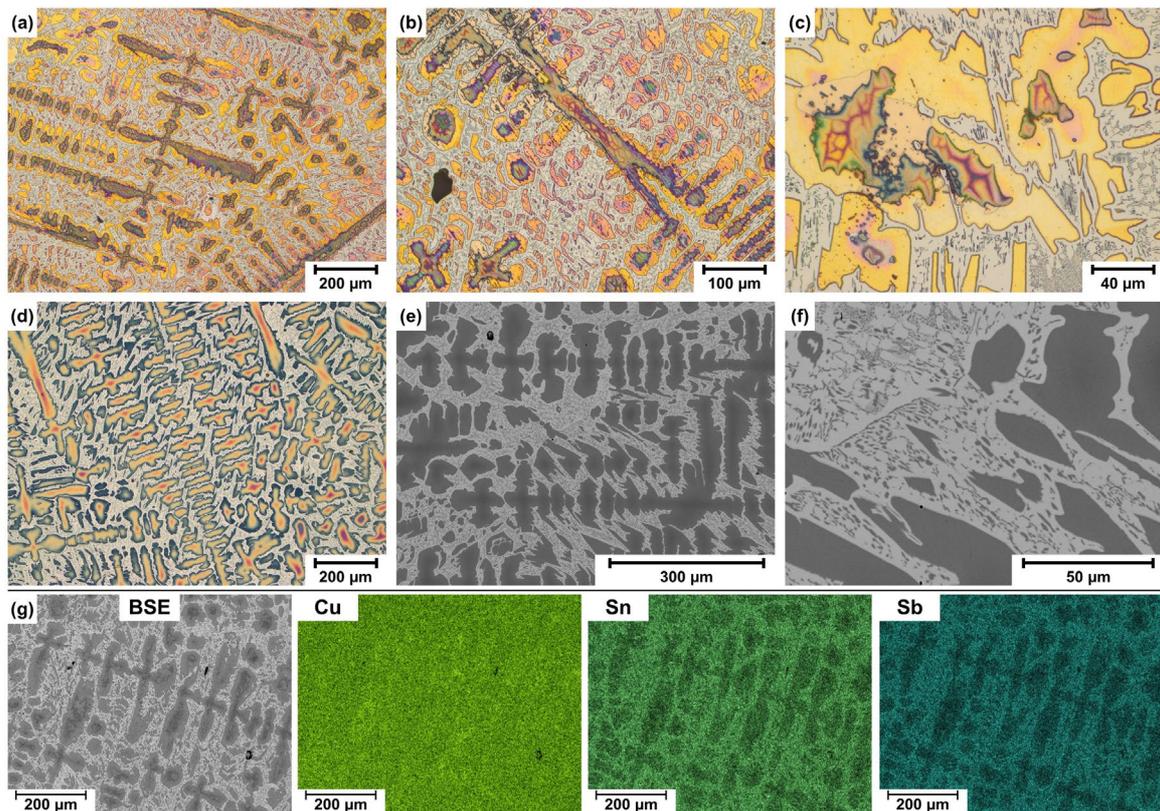


Fig. 4. Alloy 10 % Sb, 10 % Sn, balance Cu. (a, b) Klemm etched, (c, d) $(\text{NH}_4)_2\text{CuCl}_4$ etched, (e, f) SEM, (g) SEM-EDX element distribution.

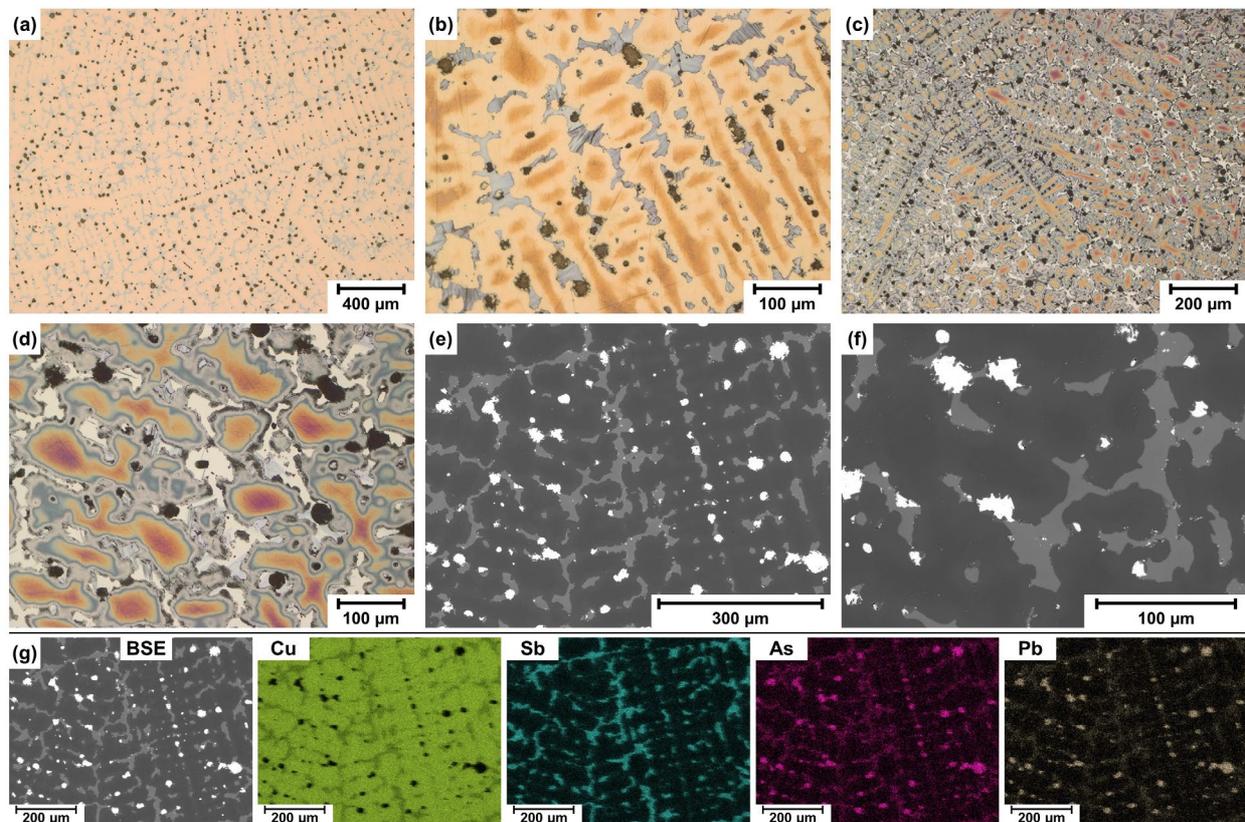


Fig. 5. Alloy 5 % Sb, 5 % As, 5 % Pb, balance Cu. (a) polished, (b) Klemm etched, (c, d) $(\text{NH}_4)_2\text{CuCl}_4$ etched, (e, f) SEM, (g) SEM-EDX element distribution.

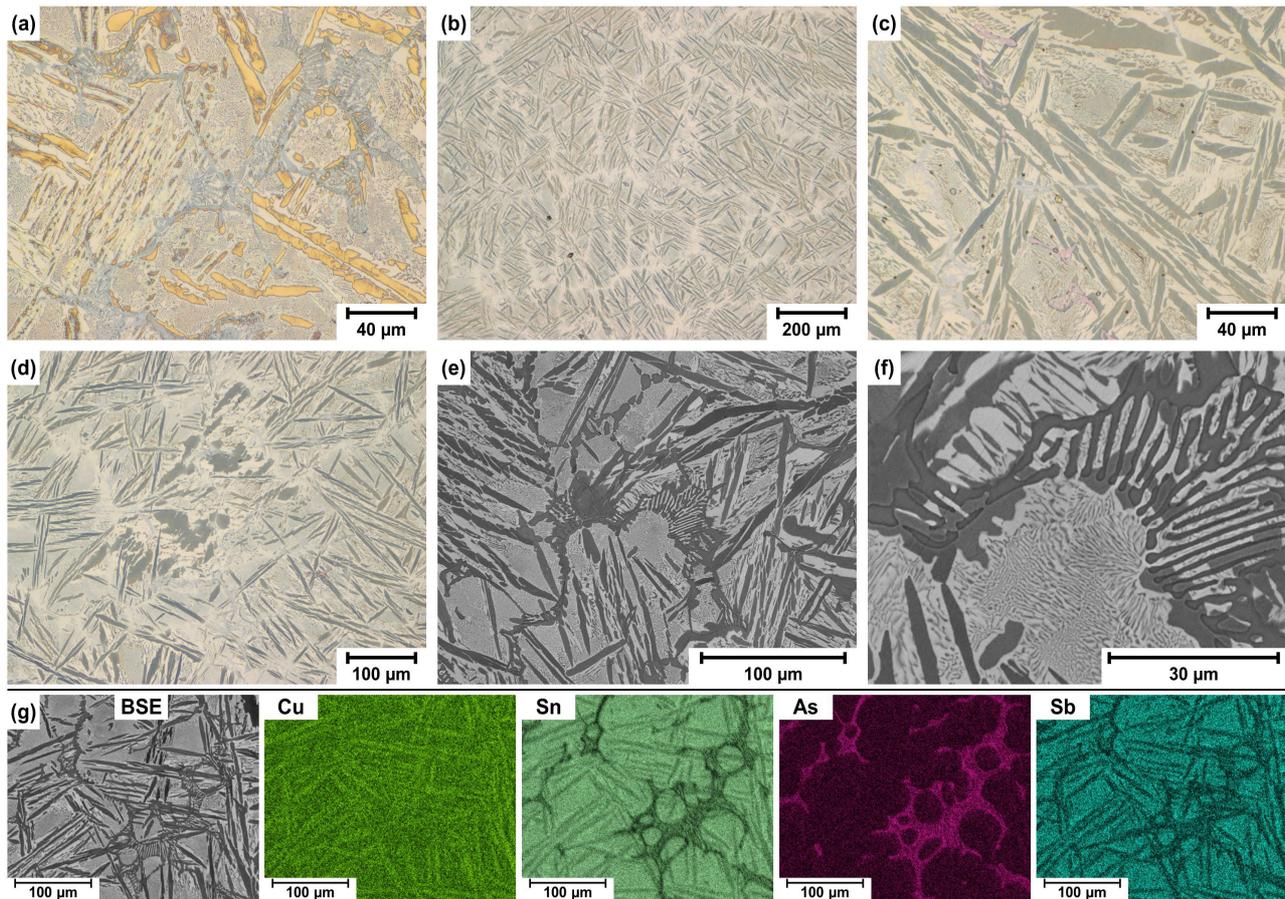


Fig. 6. Alloy 5 % As, 5 % Sb, 5 % Sn, balance Cu. (a) Klemm etched, (b–d) $(\text{NH}_4)_2\text{CuCl}_4$ etched, (e, f) SEM, (g) SEM-EDX element distribution.

Summary

For a better understanding of historical copper alloys, various model alloys with Pb, Bi, As, Sb and Sn additives were molten and investigated by metallography.

Typically, Cu solidifies first, forming dendrites, while the alloying elements are concentrated in the interdendritic areas. The microstructure of the alloy depends on the amount of Cu, which is involved in the formation of intermetallic phases. Since Pb and Bi do not form phases with Cu, and the metals are not soluble in Cu, the interdendritic regions are small. But As, Sb and Sn form corresponding cupreous phases (Cu_3As , Cu_3Sb and $\text{Cu}_{41}\text{Sn}_{11}$) and so the proportion of Cu dendrites is reduced and the interdendritic regions increase.

In ternary copper alloys, with a ratio of 10:10:80, a dendritic microstructure is observed, and the alloying elements accumulate in the interdendritic regions.

This phenomenon is further amplified in quaternary systems with a ratio of 5:5:5:75.

In the system As-Sb-Sn-Cu no dendritic growth is observed due to the formation of different Cu-containing intermetallic phases.

Acknowledgement

The authors would like to thank the TU Wien Library for the financial support through its Open Access Funding Program.

References

- [1] R. Haubner, Die prähistorische Kupfermetallurgie - allgemeine Betrachtungen, BHM Berg- und Hüttenmännische Monatshefte, 166 (2021) 343-351, doi: 10.1007/s00501-020-01056-0.
- [2] R. Haubner, S. Strobl, Considerations on Copper Smelting from Fahlores and the Metallurgy of Cu-As Bronzes, BHM Berg- und Hüttenmännische Monatshefte, 168 (2023) 434-444, doi: 10.1007/s00501-022-01230-6.
- [3] F. Ertl, S. Strobl, R. Haubner, An ancient bronze ingot smelted from fahlore, Materials Science Forum, 891 (2017) 613-617, doi:10.4028/www.scientific.net/MSF.891.613.
- [4] R. Haubner, S. Strobl, Direct Production of Tin Bronzes from Copper and Cassiterite, Materials Science Forum, 1081 (2023) 137-142, doi:10.4028/p-s4jt77.
- [5] R. Haubner, S. Strobl, Microstructure of an extraordinary Bronze Age copper ingot with a high antimony content, Pract. Metallogr., 59 (2022) 732-748, doi: 10.1515/pm-2022-1004.
- [6] R. Haubner, S. Strobl, M. Thurner, H. Herdits, Ein Kupfergusskuchen mit hohem Antimongehalt aus Velem/Westungarn, BHM Berg- und Hüttenmännische Monatshefte, 165 (2020) 453-460, doi: 10.1007/s00501-020-01017-7.
- [7] R. Haubner, S. Strobl, Investigations on Copper Cast Cakes, Sickle Fragments and a Spout Axe of the Hoard Find from Drassburg/Burgenland, Metallography, Microstructure, and Analysis, 12 (2023) 187-201, doi: 10.1007/s13632-023-00936-4.
- [8] T.B. Massalski, Binary Alloy Phase Diagrams. ASM International, Metals Park OH (1990).
- [9] R. Haubner, S. Strobl, The Copper-Arsenic eutecticum and the Cu₃As phase, Defect and Diffusion Forum, 405 (2020) 19-25, doi: 10.4028/www.scientific.net/DDF.405.19.
- [10] R. Haubner, S. Strobl, Microstructural Examinations of Copper Antimony Alloys, Pract. Metallogr., 58 (2021) 620-629, doi: 10.1515/pm-2021-0054.