

Arsenic loss during metallurgical processing of arsenical bronze

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Abstract The chemical composition of ancient copper-based metal changes over time due to repetitive recycling and mixing of old metal. Prehistoric copper usually contains impurities from the copper ores themselves, and some have been used as evidence of anthropomorphically induced chemical change. Research into these changes has historically relied upon the assumption of element loss linearity, which is highly misleading and in fact varies with a multitude of factors. To illustrate the complexity of such losses for prehistoric alloys, we have selected arsenical bronze (Cu-As alloys) for study. The mass loss of several Cu-As-alloys under reducing atmosphere was measured by DTA/TGA. From our comparison of the experimental results to thermodynamic calculations and literature data, it was unclear whether weight losses were solely caused by the elemental loss of arsenic. However, a prolonged time temperature-cycling run demonstrated that mainly arsenic volatilizes; hence, the non-linear mass loss from the alloy can be directly attributed to arsenic.

Keywords DTA · TGA · Arsenical bronze · Prehistory · Recycling

Introduction

The task of interpreting archeological and scientific data is unquestionably as important as the collection of the data itself. The underlying meaning of metal artifact chemical analyses has been notoriously difficult to understand and interpret throughout the history of archeology. The issue is perhaps best evidenced by the results of the Stuttgart-based *Studien zu den Anfängen der Metallurgie* (SAM) and their use of tree diagrams to draw connections between copper-based alloys of similar composition (Junghans et al. 1968); the results of which were not immediately understood and criticized (Hodson 1969; Härke 1978). Chemical similarities between the tens of thousands of objects were, however, later confirmed (Krause 2003; Pernicka 1990). In recent years, attempts to reappraise the vast compiled data from the SAM project, and others (e.g. Chernykh 1972), have revived the idea that the chemical composition of ancient copper-based metal holds significant information indicative of recycling and “metal flow” (Bray and Pollard 2012; Pollard and Bray 2015; Bray et al. 2015; Pollard and Bray 2014; Pollard et al. 2014). In its revived form, the idea implicitly assumes that the recycling of alloys left a linear chemical change record that could be followed through time and space over vast swaths of territory incorporating peoples and civilizations. In comparison, this approach, which assumes the equal loss of particular elements through the successive recycling of an alloy, had been explored as early as 1964 to explain the loss of zinc from recast copper coinage in Roman Britain (Caley 1964). It is important to note that enough error existed in this earlier attempt to warrant its reappraisal. Subsequent recognition of its

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shortcomings was noted whereby a linear loss relationship was disproved for zinc in Roman coinage (Dungworth 1996; Redlich and Kister 1948). Outside of the sphere of archeological inquiry, non-linear element loss behaviors in molten alloys have long since been known (e.g. Pernicka 1999).

Nevertheless, several studies within the last few years have broadly addressed the issue of artifact compositional change with linear elemental loss models, and an assumed static element behavior to explain and identify chemical patterns in artifacts throughout Europe (Bray and Pollard 2012; Pollard and Bray 2015; Bray et al. 2015; Pollard and Bray 2014; Pollard et al. 2014). For example, it has been suggested that arsenic and other element losses are gradual and easily predictable by creating categories of “present” and “absent” elements. These categories require the use of predefined element cut-off percentages as constants (e.g., 1% arsenic and silver, or, as in (Bray et al. 2015), 0.1% after mathematical removal of any major alloying elements present and renormalization) in order to create a basis from which to work and draw conclusions. This approach does not consider the behaviorally influencing effects of both alloyed and trace elements, nor does it address primary and secondary processing, which can greatly influence the distribution of elements in a final product (e.g., segregation during solidification, interaction with a reducing or oxidizing atmosphere). Also, it does not consider the changes induced by recycling of metals with different chemical and isotopical composition, which excludes the possibility to reconstruct any “metal flow” (on the opposite, if metals from the same source were mixed, useful information can be gained). Inconsistent heat distribution and varying accompanying materials were also not considered (McKerrell and Tylecote 1972; Jochum-Zimmermann et al. 2005; Mödlinger and Sabatini 2016; Haubner et al. 2017).

A variety of factors can influence the loss of elements during the recycling, and reuse and working, of an alloy in order to best facilitate the decipherment of possible recycling patterns, and of “metal flow”. As discussed, we have measured the mass loss of arsenic from arsenical copper using thermogravimetric analyses (TGA). These data are in agreement with the loss behaviors described by past thermodynamic modeling in a controlled environment. This work supports past research into archeologically relevant alloy modeling (Mödlinger and Sabatini 2016; Sabatini 2015) and shows one aspect, of many possible influences, aimed towards understanding ancient recycled metal elemental change. Thermodynamics in metallurgy have long been used for chemical modeling and to understand the reactions during recycling of copper-based alloys (Yazawa and Nakazawa 1998; Plascencia and Utigard 2003; Voisin 2012).

It is important to note that we explore in our experiments elemental arsenic loss under reducing atmosphere (all

experiments were carried out under argon); hence, we do not assess arsenic loss under oxidizing conditions (such as the formation of arsenic oxides, or as it happens when sulfidic ores containing arsenic are roasted). Arsenic losses are much lower under reducing atmosphere, while higher losses appear under oxidizing atmosphere. But since the exact conditions during prehistoric recycling are unknown, and may well alternate from oxidizing to reducing atmosphere, we preferred to study the loss of arsenic under the “more difficult” reducing atmosphere in the following.

Experimental

Six Cu-As alloys each weighing 200 g each were prepared using electrolytic copper and powdered arsenic lump (99.99 wt.%, from Alfa Aesar). The alloys were prepared by adding 1, 3, 5, 9, 10, and 14 wt.% As directly to the molten copper at 1100 °C, which was melted in graphite crucibles under reducing conditions in an induction furnace. The arsenic was added to the copper through an aluminum pipe, stirred for approximately 10 s using a graphite rod, and then the crucible was covered with graphite and the furnace sealed. Flames that burned longer with increasing amounts of arsenic were noted. During this procedure, about 10% of the added arsenic volatilized, as was demonstrated by later SEM-EDXS analyses of the ingots. This resulted in final alloy compositions with slightly less arsenic.

The furnace temperature was then increased to 1115 °C, and held for 30 min to homogenize the alloys before they were cast into cast-iron molds, which were kept at room temperature. More details are described in (Mödlinger and Sabatini 2016). Once cast, and upon cooling to room temperature, samples of approximately 250 mg were cut or drilled out for the following analyses from the center of the ingots. Unfortunately, severe macro- and microsegregation made it impossible to accurately detect the final amount of arsenic before and after the TG/DTA analyses via EDXS since EDXS analyses of different cross-sections of the ingots showed variations in the amount of arsenic of up to ± 0.3 wt.%.

The differential thermal analyses (DTA) and the thermogravimetric analyses (TGA) were carried out simultaneously with a modular thermal analyzer (Netzsch STA 449 C) coupled with a quadrupole mass spectrometer (Netzsch Aeolos), which was adjoined by a fused silica capillary tube. Weight change and heat flow of each Cu-As sample were detected as a function of time and temperature. This setup allowed for weight change events to be coupled and compared directly to endo-/exothermic reactions in a single measurement run.

The samples were placed within Al₂O₃ crucibles and under argon for the DTA/TG measurements, which permits the

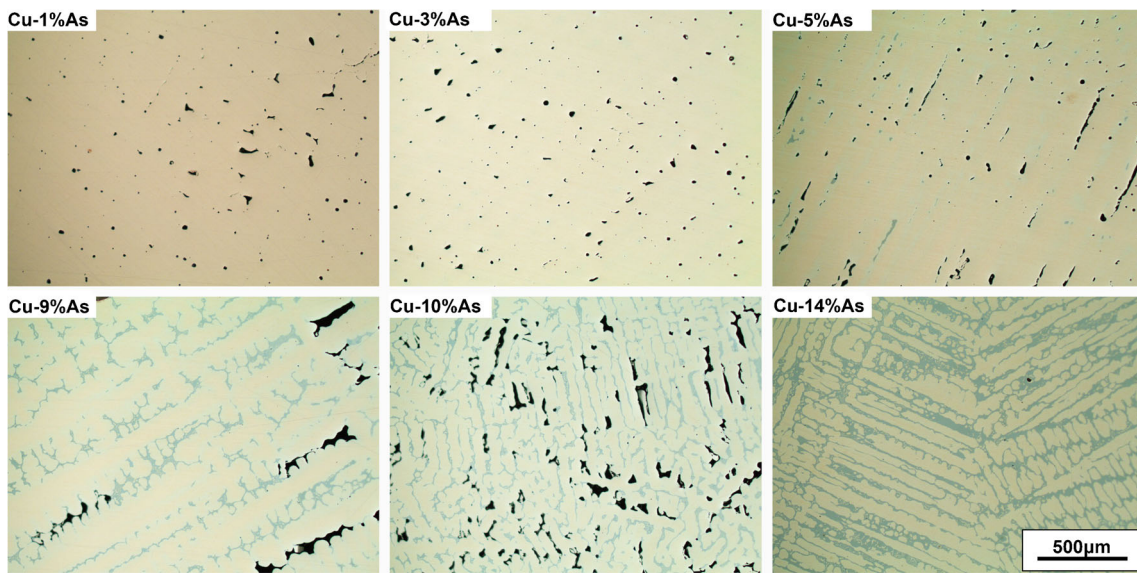


Fig. 1 Microstructures of the Cu-As samples after the DTA/TG measurements, unetched. Cu-1%As and Cu-3%As—the As is all in the α -solid solution. Cu-5%As—the formation of $\alpha + \gamma$ eutectic is observed; arsenic-rich and arsenic-poor zones of the α -solid solution are visible. Cu-9%As

and Cu-10%As—significant amounts of $\alpha + \gamma$ eutectic is observed, as is increasing porosity. Cu-14%As—significant amounts of $\alpha + \gamma$ eutectic is observed, but less porosity

measurements of potential elemental evaporation only, and no volatilization of arsenic oxides. Each sample was heated to 1100 °C and cooled at a rate of 10 °C/min. With this setup, no reactions between Cu and the crucibles take place. For the short-time DTA/TG measurements, reference runs were executed to take buoyancy and other operative effects into account. The measured results were directly compensated by the reference runs by the Netzsch software. For the long-time DTA/TG run, no reference run was carried out. The exothermic reactions and transformations that occurred during the solidification process were recorded and plotted. These raw data provided the liquidus, solidus, and eutectic transformations and reactions in each system.

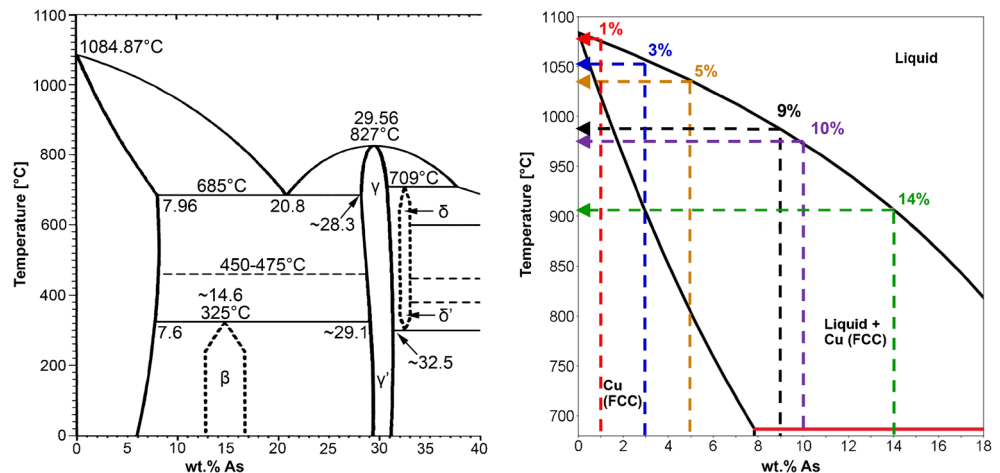
For the study of the microstructure, samples were taken from the alloys analyzed by DTA/TG. The samples were

mounted in cold epoxy resin and polished for metallographic analysis using diminishing SiC paper (500 to 1000 grit), and then finely polished with diamond suspension paste of up to 0.25- μ m grain size. The samples were etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ (according to the ASTM E407 no. 44 recipe) for metallographic examination. The microstructures were characterized by optical microscopy in bright field (BF) (Fig. 1).

For the description of the samples, the nominal starting concentrations of arsenic in the alloys are used (e.g., Cu-1%As for copper with 1 wt.% added As).

Thermodynamic calculations were performed to explain the DTA/TG data used. The software Thermocalc® is configured on the calculations of alloys and phase diagrams. There is no information about the vapor pressures of each species.

Fig. 2 The Cu-As phase diagram. Left—the Cu-As phase diagram after (Subramanian and Laughlin 1988). Right—enlarged part of the phase diagram, as calculated with the Thermocalc® software



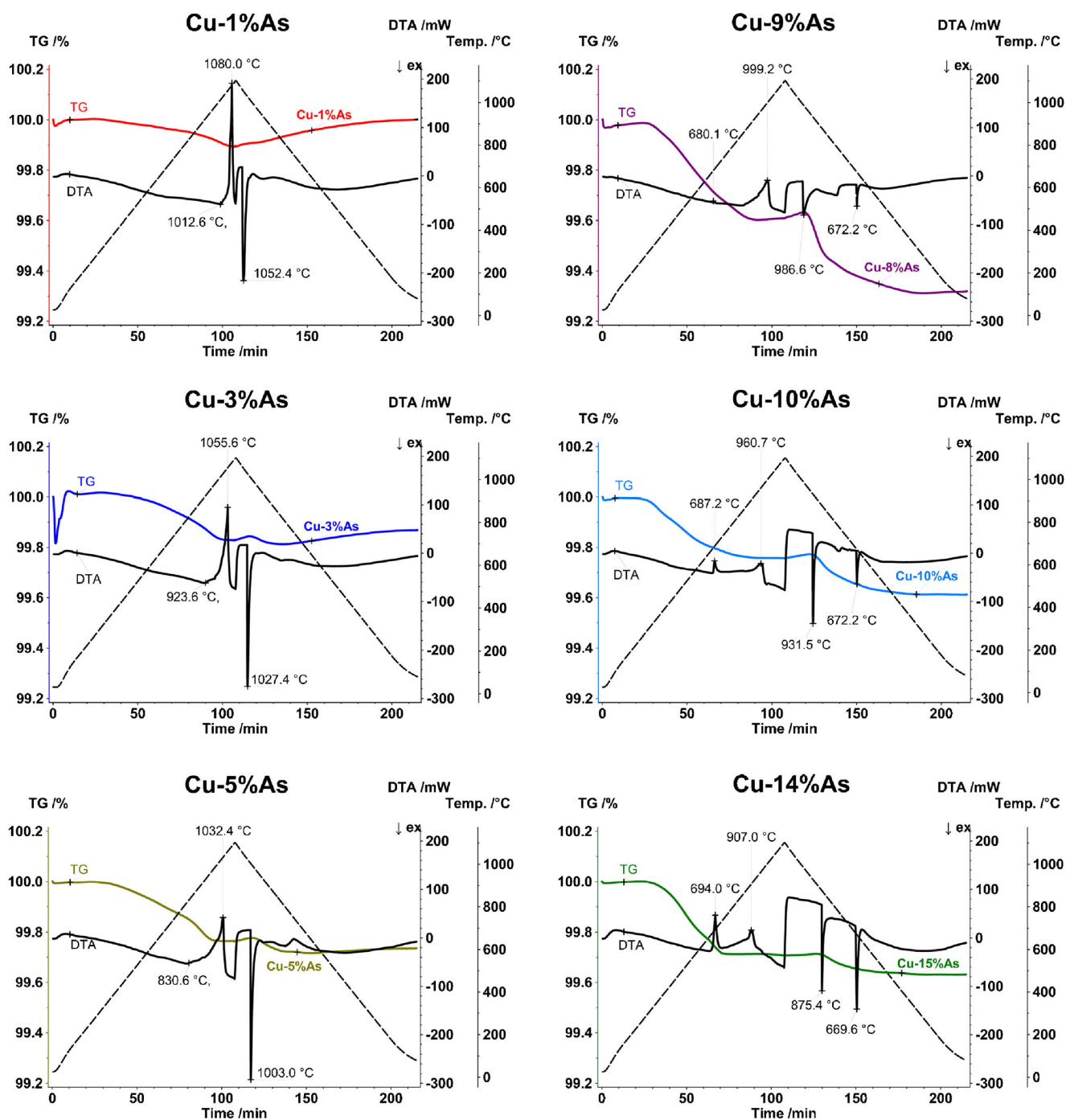


Fig. 3 DTA/TG results for the investigated Cu-As alloys

Results and discussion

Thermodynamic calculations were performed on a set of different Cu-As alloys in order to allow the interpretation of the DTA/TG measurements. To achieve further information on the weight decrease during heating and cooling processes, DTA/TG measurements with holding periods at constant temperatures were performed. The final experiment was a long-

time DTA/TG run with cycling the temperature around the melting point of the alloys.

Thermodynamic calculation of the Cu-As phase diagram

As showed in Fig. 2 (left), melting temperatures increased with decreasing As content. The most important point is the eutectic at 22.2 wt.% As and 686.8 °C. Below this point, Cu-

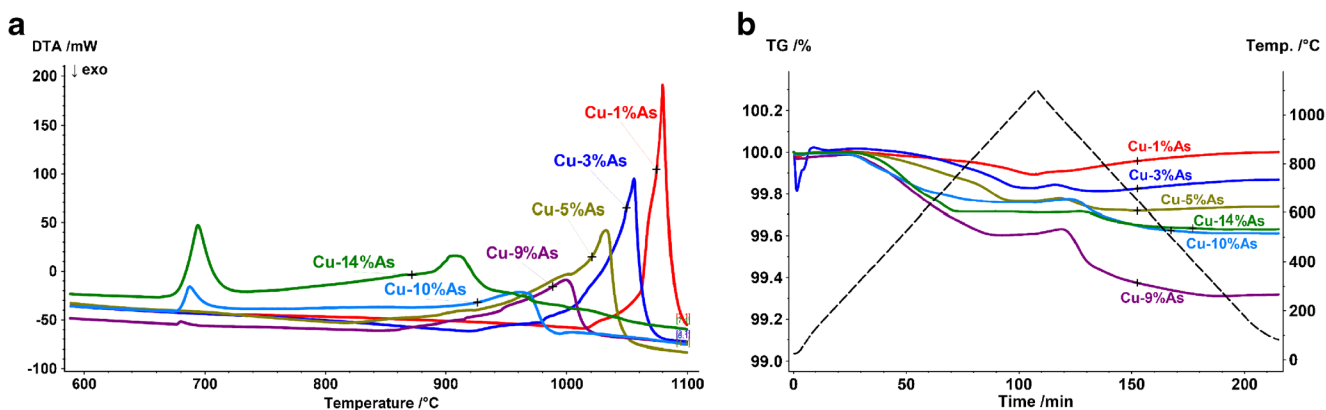


Fig. 4 **a** Summary DTA heating curves for the investigated Cu-As alloys shown in Fig. 3. **b** Summary of the TG curves shown in Fig. 3

As solid solution (with up to 7.8 wt.% As) and the intermetallic phase Cu_3As are formed. The area above the eutectic temperature is shown enlarged in Fig. 2 (right), and the arsenic percentages investigated (1, 3, 5, 9, 10, and 14 wt.% As in Cu). The alloys containing 1, 3, and 5 wt.% As are located in the area of the Cu-As solid solution but the alloys containing 9, 10, and 14 wt.% As will form a eutectic mixture under equilibrium conditions. However, since the cooling rate was rapid at 10 °C/min, eutectic formed in the Cu-5%As alloy (Fig. 1) and beyond.

Unfortunately, Thermocalc® does not provide the possibility to calculate the vapor pressure of As and Cu above the melting temperature. However, thermodynamic calculations of (Sabatini 2015) showed that at 1100 °C, the activity of As in the gas phase is lower than that of Cu.

DTA/TGA measurements

For the DTA/TG experiments, about 250 mg of alloy were used and a heating/cooling rate of 10 °C/min defined. The DTA/TG results for all alloys and the whole temperature cycle are summarized in Fig. 3. The DTA results show precise data of phase transformation in the heating section, while the peak for solidification and other phase transformations may be shifted to lower temperatures in the cooling

section. Since undercooling certainly is present during solidification (hence also the solidus is measured not in equilibrium), measurements during cooling were not taken into account with the DTA, but for the TGA only.

The diagrams are rather different with increasing concentration of arsenic in the alloy (Figs. 3 and 4a). Alloys with 1–5 wt.% As show larger peaks at higher temperatures (1080–1032 °C) (Table 1) than one might expect from the phase diagram. Alloys with over 9 wt.% As instead show both the peak of the eutectic (about 690 °C) and the melting peak of the Cu-As solid solution (1000–900 °C); both peaks are smaller and broader than those of the alloys with less arsenic. However, the Cu-9%As sample shows a different appearance: the peak for eutectic is missing, and the TG values are higher than those of the other samples. The measurements were repeated but showed similar results again. Concerning the loss of arsenic during heating/cooling, the Cu-9%As sample is of special interest, since it showed with 0.7% a significantly higher mass loss than the other samples with 0–0.4% (Fig. 4b and Table 1). We do not consider these results as anomalous since similar, yet unpublished measurements carried out under same conditions at the University of Leoben showed the same results. One explanation might be the close vicinity of the alloy composition to the maximum solubility of As in Cu.

The fluctuation of the mass during the run can be caused by several phenomena. At the beginning, desorption of surface impurities can take place. During the run phase, transformations including changes in density can cause a change in the TG curve.

No or very little change in the TG curve after the melting point takes place after the TG drop during heating. Instead, an increased TG drop is observed during cooling, once the solidus line of Cu-As system is reached.

Measurements by the mass spectrometer showed no arsenic but copper. This can be explained by the fact that arsenic can form clusters in the gas phase and their masses are too

Table 1 DTA/TG values read from the graphs shown in Fig. 3

| Sample | DTA | | TG [%] |
|----------|-------------------------|-----------------------|-----------|
| | T_{start} [°C] | T_{max} [°C] | |
| Cu-1%As | 1012 | 1080 | 0 |
| Cu-3%As | 923 | 1056 | 0.12 |
| Cu-5%As | 831 | 1032 | 0.27 |
| Cu-9%As | 680 | 999 | 0.69 |
| Cu-10%As | 687 | 961 | 0.37 |
| Cu-14%As | 694 | 907 | 0.38 |

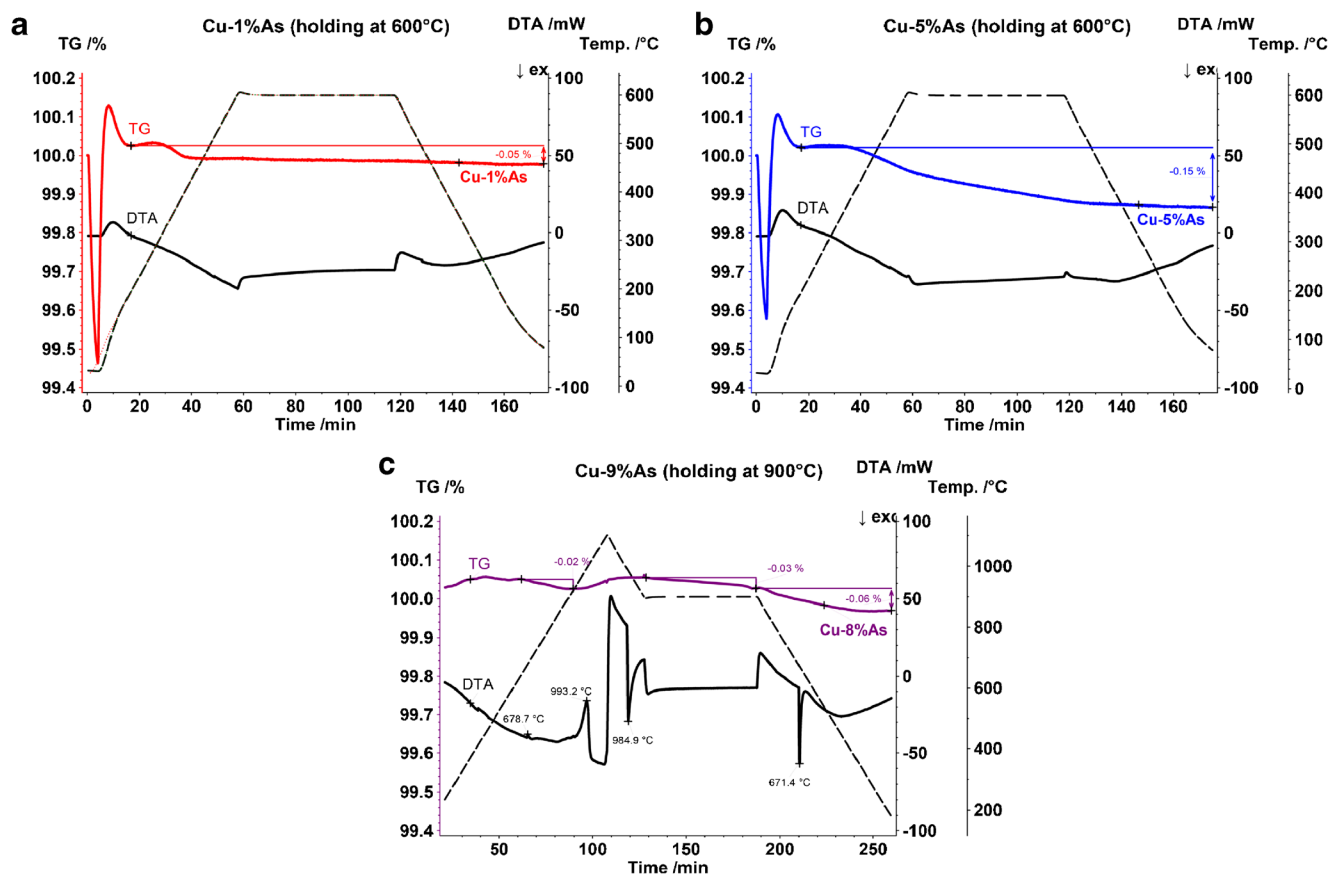


Fig. 5 DTA/TG runs with different holding times at varying temperatures. **a** Cu-1%As at 600 °C. **b** Cu-5%As at 600 °C. **c** Cu-9%As at 900 °C

high to be detected by the mass spectrometer model used in the experiment. For better understanding of these results, further experiments with holding times were performed.

DTA/TGA measurements with holding times

The samples Cu-1%As and Cu-5%As were held at 600 °C for 1 h (Fig. 5a, b). At 600 °C, the Cu-As alloys are already solid and consist of Cu-As solid solution and Cu₃As intermetallic phase (α and γ phase). The DTA curves show only small fluctuation caused by the heating process. The TG curves instead show for both samples a strong fluctuation at the beginning caused by the instrument. During further heating, the weight keeps constant until c. 450 °C. At higher temperatures and during the holding time, a weight decrease was measured. The total weight decrease was 0.05 wt.% for the sample Cu-1%As and 0.16 wt.% for the sample Cu-5%As (Fig. 5a, b). This weight loss is very low and it was not possible to measure arsenic species by the mass spectrometer. Consequently, it was not possible to specify if the mass loss under argon atmosphere was caused by arsenic or copper evaporation.

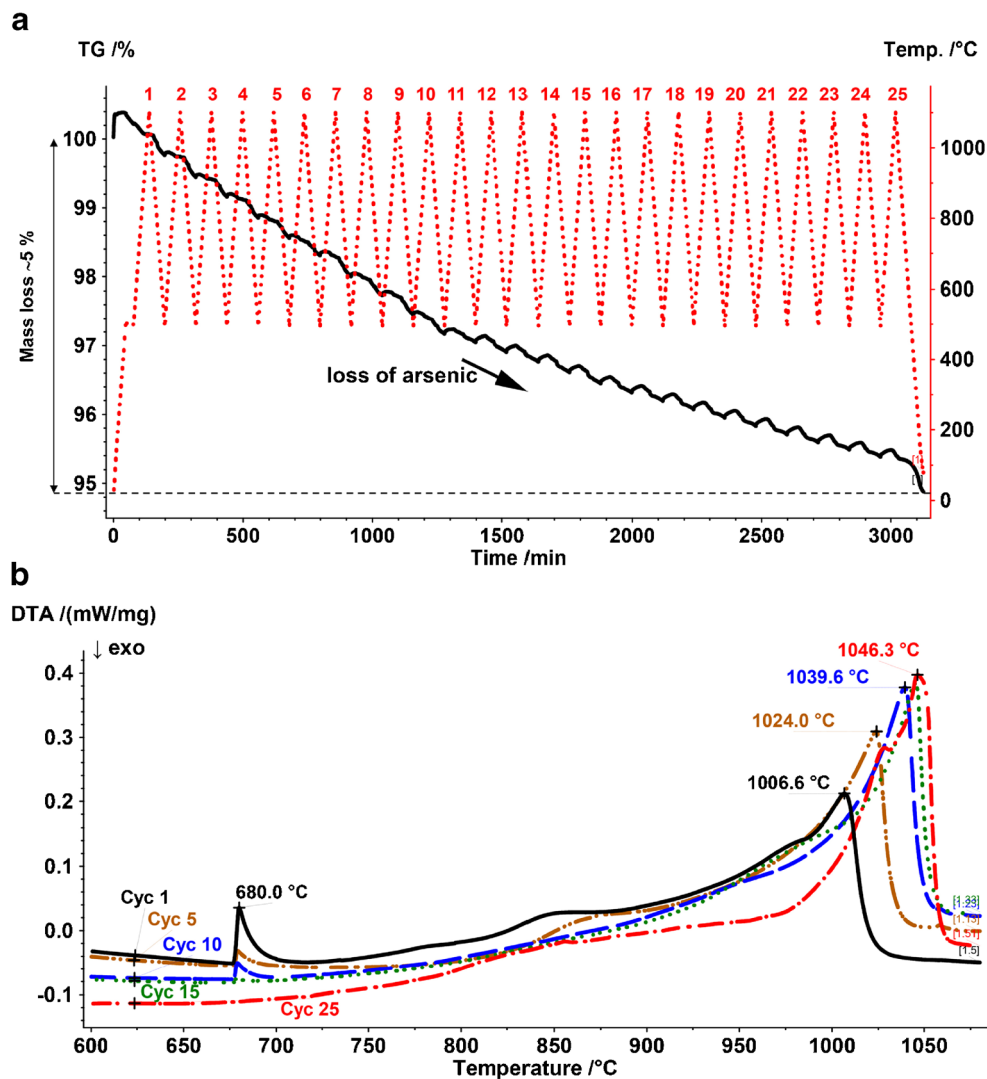
Another holding experiment was performed with sample Cu-9%As for 1 h at 900 °C (Fig. 5c). To simulate the conditions of the first experiments (Fig. 3), the sample was heated up to 1100 °C and the holding time at 900 °C during cooling.

The DTA curve shows the data for melting and solidification (Fig. 5c). According to the phase diagram (Fig. 2), the alloy should contain at 900 °C Cu-As solid solution (3 wt.% As) and melt (14.5 wt.% As). The TG curve shows some fluctuation at the beginning. After reaching 900 °C, the weight decrease during the holding time was 0.03 wt.%. Further cooling increased the weight decrease to 0.06% (Fig. 5c). This total weight loss is small, but it is surprising that there is an increased evaporation during cooling. To study this effect in more detail, a long-time cycling experiment was carried out.

Long-time cycling experiments

Starting with the Cu-9%As sample, still under argon atmosphere, the temperature was cycled between 1100 and 500 °C for 25 times (Fig. 6a). This resulted in a total mass loss during the cycling experiment of about 5% (about 0.2% per cycle). Also, it was also noted that the weight decrease per cycle is higher during the first cycles compared with the later one. Out of the corresponding DTA curves, 5 cycles were selected (cycles 1, 5, 10, 15, and 20) (Fig. 6b) in order to know if either arsenic or copper, or both, are evaporating. Due to the fact that the no As species were detected by the mass spectrometer during the previous DTA/TG experiments, and due to the length of the experiment, the mass spectrometer was not

Fig. 6 TGA and DTA curves of the cycling experiment with sample Cu-9%As (25 cycles of heating/cooling, max. temperature at 1100 °C, heating/cooling rates 10 °C/min). **a** TGA curves. **b** DTA heating curves for selected cycles



used. The total of 60 h for 25 heating/cooling cycles correlates with c. 2.4 h per cycle, and a heating/cooling speed of 10 °C/min.

The concentration of arsenic in the alloy can be calculated by plotting the solidus temperature of the selected cycles measured via DTA in the phase diagram (Fig. 7). We can note a clear drop from roughly 7.5 to 4 wt.% of arsenic from cycle 1 to 25. With decreasing concentration of arsenic in the alloy, the loss of arsenic decreases also relatively. A strong argument for an actual loss of arsenic is the decreasing peak for the eutectic at about 680 °C (Fig. 6b).

Discussion and conclusions

Adding pure arsenic to molten copper results in about 10% loss of arsenic in the alloy. Thermodynamic calculations of (Mödlinger and Sabatini 2016) suggest that arsenic evaporation from a Cu-As melt is low mainly because of the good bonding of arsenic to copper. Our results confirm this

hypothesis under argon atmosphere, since no relevant weight decrease was observed from the melt. Losses under oxidizing conditions would have been much higher but were not carried out due to safety issues. Instead, weight decrease was observed during holding experiments at 600 and 900 °C; however, it was not possible to specify the ratio of the evaporation of copper and arsenic. The long-time cycling experiment under argon atmosphere instead showed a clear loss in arsenic during cooling. The graphs suggest that the arsenic-rich melt (such as eutectic melt at 20.8 wt.% As) during crystallization allows a higher evaporation of arsenic compared with a homogenous melt with lower amounts of arsenic. This would signify that arsenic evaporates preferably during solidification, and less during melting and manipulation with the melt.

The loss of arsenic is not linear and seems to be higher at the end of solidification. In order to evaluate the loss of arsenic during prehistoric recycling activities, one has to consider also other factors which significantly influence the loss of arsenic in arsenical bronzes, such as: the chemical composition of the metal; the composition of the metals melting together during

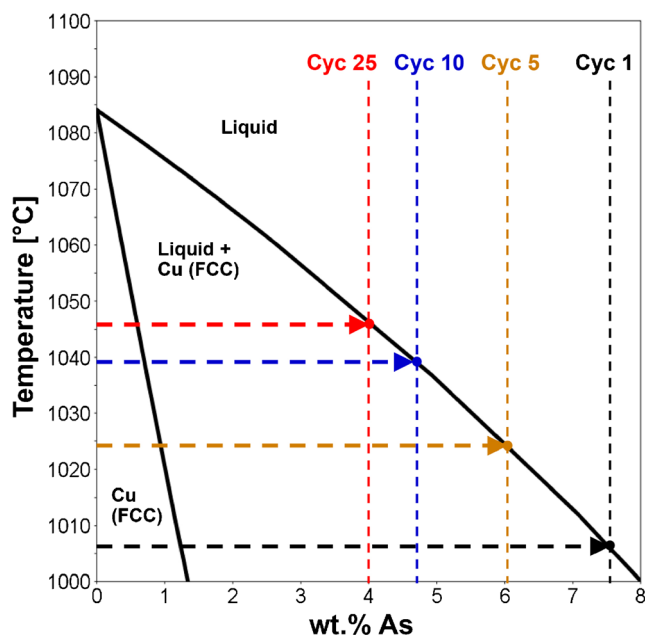


Fig. 7 Cu-As phase diagram—solidus temperatures from the DTA results shown in (Fig. 6)

recycling activities; melting and casting conditions (temperature, atmosphere, time); and, finally, the geometry of recycled metal objects, crucible, and mold.

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