

## MIT Open Access Articles

### *Casting Simulations of Arsenical Copper: New Insights into Prehistoric Metal Production and Materials*

The MIT Faculty has made this article openly available. *Please share* how this access benefits you. Your story matters.

**As Published:** <https://doi.org/10.1007/s11837-020-04210-8>

**Publisher:** Springer US

**Persistent URL:** <https://hdl.handle.net/1721.1/131917>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

**Terms of Use:** Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.



## Casting Simulations of Arsenical Copper: New Insights into Pre-historic Metal Production and Materials

**Cite this article as:** Benjamin J. Sabatini, Andreas Cziegler and Marianne Mödinger, Casting Simulations of Arsenical Copper: New Insights into Prehistoric Metal Production and Materials, JOM <https://doi.org/10.1007/s11837-020-04210-8>

This Author Accepted Manuscript is a PDF file of an unedited peer-reviewed manuscript that has been accepted for publication but has not been copyedited or corrected. The official version of record that is published in the journal is kept up to date and so may therefore differ from this version.

Terms of use and reuse: academic research for non-commercial purposes, see here for full terms. <https://www.springer.com/aam-terms-v1>

Author accepted manuscript

# Casting Simulations of Arsenical Copper: New Insights into Prehistoric Metal Production and Materials

Benjamin J. Sabatini, Andreas Cziegler, Marianne Mödlinger

## **Benjamin J. Sabatini**

Ritsumeikan University Biwako-Kusatsu Campus (BKC)

Department of Mechanical Engineering, College of Science and Engineering

E62 1-1-1, Nojihigashi, Kusatsu, Shiga 525-8577, Japan

Department of Materials Science & Engineering, Massachusetts Institute of Technology, 13-5065,  
77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

## **Andreas Cziegler**

Lehrstuhl für Gießereikunde, Montanuniversität Leoben

Franz-Josef-Strasse 18, 8700 Leoben, Austria

## **Corresponding author: Marianne Mödlinger**

Dipartimento di Chimica e Chimica Industriale (DCCI)

Università degli Studi di Genova, Italy

email: [marianne.moedlinger@gmail.com](mailto:marianne.moedlinger@gmail.com)

Tel.: +39 340 1388 506 (Italy)

## Abstract

To improve our understanding of prehistoric casting methods and materials, simulations for copper arsenic (As-Cu) alloys with up to 15 wt.% As were calculated. Cooling curves and the secondary dendritic arm spacings (SDAS) for the alloy were plotted and calculated, respectively, under non-steady-state conditions with a time-stepping procedure for prehistoric mold materials (e.g., quartz sand, sandstone, terracotta, and steatite). The cooling and microstructure of the alloy was also simulated in iron molds for immediate comparison with as-cast microstructure. The microstructure and SDAS of the as-cast alloys were studied and measured in polished samples with a metallographic microscope. The purpose of this research was to improve our ability to retroactively evaluate the influence of mold materials on as-cast microstructures and determine their materials. This article focuses on As-Cu alloy microstructure and SDAS values, and also discusses the phenomenon of “inverse segregation” and its relation to cooling rate and As concentration.

## Keywords

Arsenic-Copper (As-Cu), arsenical bronze, secondary dendritic arm spacing (SDAS), cooling curve calculation, simulation casting

## Nomenclature

- $A$  = mold metal interface [in ( $\text{m}^2$ )]  
 $\alpha$  = overall heat transmission coefficient [in ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )]  
 $c$  = specific heat of the mold [in ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )]  
 $c_m$  = specific heat of the metal [in ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )]  
 $c_0$  = alloy concentration [in (wt.%)]  
 $c_l$  = concentration of the liquid phase [in (wt.%)]  
 $D$  = diffusion coefficient [in ( $\text{m}^2\text{ s}^{-1}$ )]  
 $h$  = heat transfer coefficient [in ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )]  
 $k$  = thermal conductivity of the mold [in ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )]  
 $k_0$  = partition coefficient  
 $f_s$  = mass fraction of solid phase  
 $m$  = slope of the liquidus line [in ( $\text{K}\cdot\text{wt.}\%^{-1}$ )]  
 $n$  = time-step sequence ( $10^{-3}$  seconds)  
 $t$  = time (in seconds)  
 $t_f$  = local solidification time (in seconds)  
 $T$  = temperature of the metal (in Kelvin)  
 $T_o$  = ambient temperature of the mold (in Kelvin)  
 $v$  = volume of casting [in ( $\text{m}^3$ )]  
 $\Delta T$  = solidification interval (in Kelvin)  
 $\Delta H_f$  = latent heat of fusion [in ( $\text{J}\cdot\text{mol}^{-1}$ )]  
 $\rho$  = density of the mold [in ( $\text{kg}\cdot\text{m}^{-3}$ )]  
 $\rho_m$  = density of the metal [in ( $\text{kg}\cdot\text{m}^{-3}$ )]  
 $\Gamma$  = Gibbs-Thomson coefficient [in ( $\text{K}\cdot\text{m}$ )]  
 $\lambda$  = secondary dendritic arm spacing [in ( $\mu\text{m}$ )]

## Introduction

Arsenic-copper alloys have limited application, having long since been replaced by safer and more capable alloys beginning in antiquity. Despite their early obsolescence, however, the alloys have great historical and archaeological importance, being the first produced by humankind on the Iranian plateau as early as the beginning of the fifth and, in Central Europe, in the fourth and early third millennia BC [1]. This paper contributes to ongoing archaeometallurgical discussions on the manufacture of this early alloy and the intentionality of its production through a combination of empirical evidence and simulation.

In this paper a brief discussion of the history and production of arsenical copper is presented, followed by a detailed explanation of our experimental protocol and methodology. We measured the secondary dendritic arm spacing (SDAS) in arsenical copper (As-Cu) samples at a cooling rate of 20 K/min using differential thermal analysis (DTA). The measured SDAS in the alloys were compared with calculated values for iron chill cast molds. In relation to the SDAS and characterized microstructures from our experiments, we also discuss segregation and provide simulated cooling rate calculations for several modern and prehistoric mold materials. The simulated curves were created to account for mold materials that were not empirically tested. These combined approaches provide insight into the relationship between As-Cu alloy cooling rates, segregation, and prehistoric manufacturing practices and preferences. By comparing the predicted cooling curves and a recent study of equilibrium in the binary system [2], this paper lays the groundwork for determining which

mold materials were used in antiquity and their relation to the manufacturing practices of past metal smiths.

## Background

Because of scant manufacturing material evidence and undocumented methodologies, the production of ancient arsenical copper alloys are not well understood. The means of producing the alloy also likely varied significantly between regions and across time periods. Because of this lack of knowledge, several possible manufacturing techniques have been proposed by metallurgists, archaeologists, and historians including: (1) the combining of native copper with copper-arsenide minerals [1]; (2) the smelting of copper ores rich in arsenic (e.g., Fahlore); (3) the reduction of roasted copper sulfarsenides such as tennantite and enargite [3]; (4) the co-smelting of oxidic and sulphidic ores such as malachite and arsenopyrite [4]; and (5) the melting together of speisses and copper [5]. From these five suggestions there is currently no evidence for the ancient production and use of pure arsenic for alloying, or the cementation of arsenic vapor to copper.

With the onset of the production of tin bronzes in antiquity, arsenical copper or, alternatively, arsenical bronze, became increasingly less common. The alloy was still produced for some time, but a general preference for tin bronze took hold. Arsenical copper eventually fell into disuse until millennia later when it briefly resurfaced at the end of the 19th century AD when As-Cu alloys were used in the manufacture of boilerplates for steam engines [6-7]. The alloy has a higher mechanical and chemical resistance than steel, and so was more suitable in high temperature and pressure locomotive fireboxes. Beyond this brief historic reprisal, and with few exceptions [8-9], a lack of practical use for arsenical copper throughout history and in modern society has resulted in few studies of the alloy outside of archaeological and historical contexts.

As-Cu alloys with more than 1 wt.% arsenic have been investigated almost exclusively in prehistoric contexts in recent years. Such studies are few and mainly focused on metallographic analyses of objects suspected to be made of arsenical copper [1, 10-11]. Several prominent studies of the alloy's characteristics include, but are not limited to, the works by H. Lechtman [3-4, 12], P. Budd [13-14], P. Northover [15], and J. R. Marechal [16]. Outside of archaeological interests, the As-Cu equilibrium phase diagram has most recently been summarily published by Subramanian-Laughlin [17] and calculated by Pei et al. [18].

Common to all archaeologically related research of As-Cu alloys, and misleading in studies focused on questions regarding an object's intended appearance and properties, especially, is the use of the system's equilibrium phase diagram, despite the certain absence of equilibrated conditions and outcomes during prehistoric metal production. It is certain that unintended local interfacial equilibrium conditions resulted due to varying cooling rates imparted by mold materials and their impurities and bulk, such that interpreting arsenical copper artifacts at equilibrium is inherently unsound. Because of the known variety of molds and suggestions of manufacturing techniques, it is therefore important that archaeometallurgists consider out-of-equilibrium phases when evaluating As-Cu as-cast alloys [19]. The overshadowing issue is that assumed equilibrated conditions do not accurately facilitate the interpretation of ancient manufacturing outcomes. These realizations are especially important in regard to the formation of inversely segregated arsenic-rich phases that can form on the alloy's surface, which frequently appear at compositions as low as 5 wt.% As and higher [1]. Also problematic, because of inverse segregation, is that surface analyses may indicate far greater concentrations of As than were intended during manufacturing [e.g., the ( $\alpha+\delta$ ) eutectic contains approximately 21 wt.% As], leading to misinterpretations of an alloy's function and its derived pyrotechnological culture. Because of these issues, and the overarching importance of placing metal

material culture in its correct historical context, we have simulated cooling curves in several mold materials.

In the following sections of this paper we illustrate the importance of studying microstructure and SDAS with an example for iron chill cast molds. We then plotted simulated cooling curves at 10 and 20 K/min in eight molds for concentrations of As at 1.2, 4.6, and 10.3 wt.%. These simulations illustrate the difference in cooling rate imparted by each prehistoric mold (quartz sand, terracotta, heated terracotta, tin-bronze, and steatite). Unfortunately, no data for sand mixed with natural oils were available for cooling curve calculations. It has been suggested that such molds were used in antiquity [1]. In brief, in the following sections, this paper illustrates how mold materials influence cooling rate and microstructural detail.

## Experimental Protocol and Methodology

Several ingots weighing 200 g each were prepared with electrolytic copper and arsenic lump (99.99% pure) with the following compositions, using the procedure below. The ingots were composed of slightly less than 1, 2, 3, 4, 5, 6, 7, 9, 10, and 14 wt.% As, and were chemically analyzed after being cast and before sampling [2].

1. Pure copper was placed into graphite crucibles, covered, and heated until molten in an electric furnace. Graphite was chosen in order to prevent losses of volatile arsenic oxides during preparation of the ingots.
2. When the furnace reached 1373 K (1100 °C), the arsenic lump was added to the molten copper through an aluminum pipe, and the crucible and furnace immediately covered and closed. The addition of the arsenic to the melt resulted in flames that burned for longer with increasing percentages of arsenic. The flames are caused by an exothermic reaction and the oxidation of hot arsenic vapors that come into contact with oxygen in the atmosphere.
3. The furnace temperature was then increased to 1378 K (1115 °C) and held for 30 min to homogenize the alloys before they were cast into cast-iron molds at 25 °C. Only iron molds were used in this study to retain consistency across our experiments.
4. Once cast, and upon cooling to room temperature, samples of approximately 0.5–1.0 g were cut for DTA (model: NETZSCH DSC 404C) from the top of the ingots. A horizontal cross-section of the ingot was sampled to account for segregation effects caused by the use of the iron molds.
5. The samples were then placed in tantalum crucibles that were welded shut in an argon atmosphere. The argon provides a non-reactive environment for the experiment.
6. Each sample was heated above its melting point within the tantalum enclosure, and cooled at a constant rate of 20 K/min.
7. Once DTA was complete, the samples were removed from the crucibles and embedded and mounted in hot epoxy resin. Sample cross sections were polished with diamond paste of up to 0.25  $\mu\text{m}$  for bulk and microstructural analysis.
8. The chemical composition of the alloys was then evaluated using SEM-EDXS (JEOL JSM-6460LV SEM with an Oxford Instruments SDD XMax 20), and by energy-dispersive X-ray (EDX) spectroscopy (PENTAFET<sup>®</sup> EDXS detector sensitive to light elements,  $Z > 5$ ) connected to a scanning electron microscope (SEM, Evo40 Zeiss). The observed results were compared to theoretical alloy compositions [2].
9. The microstructure of the samples was also studied using light microscopy under both bright and dark fields.
10. These newly produced data were then compared with our calculated cooling simulation curves for different mold materials (iron, 11 wt.% tin-bronze, terracotta, steatite, sandstone,

and quartz sand). These calculations identify which mold materials would have likely resulted in metastable phase formation during the casting of As-Cu alloys in antiquity.

## Secondary Dendritic Arm Spacing and Metallography

The degree of SDAS formation on primary dendrites depends on thermal conditions and composition during cooling. With slower cooling rates, some arms may freeze and re-melt again, resulting in wider distances between them and greater average SDAS values. During formation, secondary dendritic branching stops once a system's temperature is low enough to prevent re-melting and the arm's diffusion fields overlap; the arms then become thicker and the spacings wider. In a given alloy the SDAS is determined by linear intercept, i.e., by the length of a given dendrite measured from one arm to another, and divided by the number of arms it touches. Measurements of SDAS is important as it relates to mold type, since arm spacing distances correspond to cooling rates imparted by mold materials [20]. The study of prehistoric copper alloys, especially early finds from the Chalcolithic and Bronze Age, have been hindered by few surviving casting molds. However, with knowledge of the materials used in metal production it may be possible to infer casting mold types by comparing artifact and predicted microstructures. Being able to identify mold materials is particularly important to archaeologists as it can aid in explaining the spread and progression of pyrotechnology, and the interaction of prehistoric peoples and civilizations.

Since no SDAS data has been recorded for As-Cu alloys, we measured it in samples taken from DTA at a cooling rate of 20 K/min and iron chill cast molds (Figs. 1 and 2). The nominal and actual composition of each sample is given in Table 1. Unfortunately, cooling rates greater than 20 K/min were not possible using DTA, and lower rates are not archaeologically relevant for ancient mold materials. Note in Fig. 1 that increasing amounts of As in the DTA samples resulted in decreased SDAS averages; thus, the alloy had spent less time in a 'mushy' condition (freezing and re-melting) and formed increasingly more ( $\alpha+\gamma$ ) eutectic. In comparison, the SDAS averages for the iron chill cast ingots were not appreciably altered by As concentration because of the much higher cooling rate, which precluded the formation of wider spaced dendrites.

**Table 1.** Nominal and actual arsenic content in each respective sample

Sample	Arsenic nominal content	Arsenic actual content
AsCu-1	1	1.2
AsCu-2	2	1.6
AsCu-3	3	2.4
AsCu-4	4	3.7
AsCu-5	5	4.6
AsCu-6	6	5.9
AsCu-7	7	6.6
AsCu-8	8	7.5
AsCu-10	10	10.3
AsCu-11	11	9
AsCu-15	15	13.3

After DTA each alloy was removed from its tantalum crucible, sampled, and characterized using optical light microscopy with only the AsCu-1 sample being etched with  $\text{FeCl}_3$  aqueous solution (5%). The  $\gamma$ -phase was observed in small but increasing amounts with increasing As in all samples

except AsCu-1. The phase was mainly present on the surface or close to regions with shrinkage porosity. For samples AsCu-6 through AsCu-15, the  $\gamma$ -phase was concentrated on the metal's surface forming a thin and almost continuous layer; however, for AsCu-3, it appeared frayed and discontinuous. The thickness of the layer in each sample also increased with increasing amounts of As, as did the appearance of  $(\alpha+\gamma)$  eutectic. Beginning with AsCu-2 (with 1.56 wt.% As), and predictably continuing to sample AsCu-15, a  $(\alpha+\gamma)$  eutectic appeared, too, and in increasing amounts with increasing As. The formation of the eutectic is archaeologically important as it has been shown to occur during the inverse segregation of As in cast As-Cu alloys, even at concentrations less than 2 wt.% [1].

## Local Solidification Time

The chemical and physical properties of a given mold material influence both the surface quality and microstructure of a casting. In order to simulate the ancient foundry process in several mold materials, a time-stepping analysis was performed assuming insulative resistance in the mold at the mold/metal interface for metal molds after the procedure described by Stefanescu [19]. The procedure was originally designed for alloys below their maximum solubilities, but was modified for hypoeutectic compositions. The following mold materials were chosen for modeling: quartz sand, sandstone, steatite, terracotta, iron, and copper; the last two materials were certainly not used in antiquity, but were included for reference. Of note for these mold materials, it has been shown that the inverse segregation of As can occur in steatite despite its low thermal conductivity, even in instances where the mold was preheated to 300 °C and with 6 and 9 wt.% As [21] (see Table 2 and Fig. 3).

The equations and results of our calculations are given below. It is important to note that the modeling method is accurate for both alloys that form a eutectic and those cast in metal molds. The procedure given by Stefanescu [19] calculates the cooling of a casting where volume  $v$  is equated to the heat flow rate into the mold at the mold/metal interface  $A$  where:  $k$ ,  $\rho$  and  $c$  are the thermal conductivity, density, and heat capacity of the mold material, respectively;  $\rho_m$  and  $c_m$  the density and heat capacity of the metal;  $\Delta H_f$  and  $f_s$  the latent heat of fusion and the fraction solid; and  $T_o$  the ambient temperature of the mold [Eq. (1)].

$$\sqrt{\frac{k\rho c}{\pi t}}(T - T_o)A = -\rho_m c_m v \frac{dT}{dt} + \rho_m v \Delta H_f \frac{df_s}{dt} \quad (1)$$

Rearranging and modifying Eq. (1) to account for time-stepping gives Eq. (2) where  $T^n$  and  $T^{n+1}$  are the temperatures of the casting at time step intervals  $n$  and  $n+1$ , respectively; it assumes no gradient in the casting and a linear evolution of the fraction solid over the solidification interval.

$$T^{n+1} = T^n - \sqrt{\frac{k\rho c}{\pi t^{n+1}}}(T - T_o) \frac{A}{v\rho_m c_m} \Delta t + \frac{\Delta H_f}{c_m} \Delta f_s \quad (2)$$

This equation was used to simulate the local solidification time in As-Cu alloys below the maximum solubility (7.96 wt.%) in insulating molds. For hypoeutectic alloys, the procedure was slightly modified to compute temperature vs time. The fraction solid of the primary phase  $f_{s,primary}$  for various As-Cu alloys is evaluated from the binary equilibrium phase diagram [17-18] using the lever rule (eutectic concentration = 20.6 wt.%; max. solubility = 7.96 wt.%). To compute the time for eutectic transformation, Eq. (2) was rearranged leading to Eq. (3) where eutectic transformations take place at  $T^n$  and  $T^{n+1}$  intervals equal to the eutectic temperature  $T_{eutectic}$ .



$$\Delta f_{s,eutectic} = \sqrt{\frac{k\rho c}{\pi t^{n+1}}} (T_{eutectic} - T_o) \frac{A}{v\rho_m\Delta H_f} \Delta t \quad (3)$$

The change in the mass fraction of the solid phase  $\Delta f_{s,eutectic}$ , where  $f_s$  is calculated from  $f_{s,primary}$  to 1, was used to compute the cooling curve. In order to simulate the solidification time of As-Cu alloys poured into iron and copper molds, resistance at the mold/metal interface was assumed [19]. To account for the different thermal conductivities of copper and iron, the overall heat transmission coefficient  $\alpha$  can be calculated using Eq. (4) where  $h$  is the heat transfer coefficient and  $R$  the resistance of the mold. Resistance is given by Eq. (5) [19] and the heat transfer coefficient for these calculations was assumed to be constant.

$$\frac{1}{\alpha} = \frac{1}{h} + R \quad (4)$$

$$R = \sqrt{\pi t / k\rho c} \quad (5)$$

The above set of equations were used to perform the simulations and create plots in Matlab<sup>®</sup> with a time-step of 0.001 s for each mold. The values used for the calculation are shown in Table 2. In our simulations we calculated the local solidification time  $t_f$  for alloys cast at 1373 K (1100 °C) in molds at 298 K (25 °C), as well as for one terracotta mold at 873 K (600 °C) (Fig. 3). The alloys contained 1, 5, and 10 wt.% As. For these calculations the geometry of the calculated casts were fixed at 11 × 4 × 0.5 cm, which are the same dimensions used for the casting experiments with As-Cu in iron chill molds. Interestingly, our results are similar in trend, but not temperature, to those recorded by Jochum Zimmermann et al. [23] at 1373 K (1100 °C) for 10 wt.% tin-bronze cast in molds of sand, steatite, sandstone, and tin-bronze (Fig. 4); the one exception to the trend being the cooling rate of tin and arsenical copper in their corresponding bronze molds.

**Table 2.** Values used in the solidification simulation calculations for each mold material. For the latent heat of fusion, thermal conductivity, and alloy specific heat, the values for pure copper were used. \* Values in brackets derive from the phase diagram (after [17])

		1 wt.% As	5 wt.% As	10 wt.% As
Alloy	Density	8.87	8.68	8.45
	Solidification range	54	225	275
	Solidus K (°C) *	1297 (1024)	1083 (810)	958 (685)
	Liquidus K (°C) *	1351 (1078)	1308 (1035)	1233 (960)
	Latent heat of fusion	207 [kJ/mol] [19]		
	Alloy specific heat	384 [J/kg K] [22]		
	Heat transfer coefficient	Approx. 1700 [W/m <sup>2</sup> K] (ductile iron in iron mold, after [19])		
	Approx. average heat transfer coefficient for Al in Cu mold	2125 W/m <sup>2</sup> K (after [19])		

Mold		Iron	11 wt.% Sn-bronze	Terracotta	Steatite	Sandstone	Quartz sand
	Thermal conductivity	46	40	0.383	3	2	0.3
	Specific heat	377	580	850	785	750	700

	Density	8.77	7.75	1.30	2.90	2.50	2.30
--	---------	------	------	------	------	------	------

## SDAS of the Casting Simulations

To calculate the SDAS ( $\lambda$ ) values corresponding to cooling, the local solidification time  $t_f$  from Fig. 3 was inserted into Eq. (6) after Kurz-Fischer [24]. The slope of the liquidus line  $m$  (-12.76) and the partition coefficient  $k_0$  (0.15) [25] are assumed constants that derive from equilibrium binary alloy phase diagrams [19]. As there are currently no data for the diffusion coefficient of As in liquid Cu, that of Fe [26] was used in our calculations.

$$\lambda = 5.5 \cdot (M \cdot t_f)^{1/3} \quad (6)$$

$M$ , from Eq. (6), is calculated using Eq. (7) where  $D$  is the diffusion coefficient,  $\Gamma$  is the Gibbs-Thomson coefficient,  $c_0$  the alloy concentration, and  $c_l$  the concentration of the liquid phase. The calculated solidification times and SDAS values are given in Table 3. One can see that the calculated and measured SDAS averages for iron molds are similarly low in trend, which is due to the rapid cooling of the ingots and assumed cooling rate in the calculations (Fig. 1).

$$M = \frac{\Gamma \cdot D \cdot \ln\left(\frac{c_l}{c_0}\right)}{m \cdot (1-k) \cdot (c_0 - c_l)} \quad (7)$$

**Table 3.** Top, solidification time (in seconds) and bottom, SDAS (in  $\mu\text{m}$ ) for the as-cast simulations in different mold materials

Sample	Iron	Tin-bronze	Terracotta	Terracotta 600 °C	Steatite	Sandstone	Quartz
AsCu-1	3.26	2.55	44.02	208.00	6.50	8.91	39.37
AsCu-5	4.20	3.92	92.91	692.91	11.76	16.84	82.64
AsCu-10	4.57	4.24	114.02	1611.61	13.67	19.86	101.23

  

Sample	Iron	Tin-bronze	Terracotta	Terracotta 600 °C	Steatite	Sandstone	Quartz
AsCu-1	12.55	11.55	29.87	50.12	15.79	17.54	28.78
AsCu-5	13.65	13.34	38.32	74.86	19.24	21.68	36.85
AsCu-10	14.04	13.69	41.02	99.18	20.23	22.91	39.43

## Discussion

Comparison of the measured and calculated SDAS 20-K/min cooling and that in iron molds (Fig. 1), the microstructures of each the sample (Fig. 2), and a recent assessment of the As-Cu binary system [2], summarily indicate that local interfacial equilibrium conditions determine microstructural characteristics. As demonstrated by the theoretical work here, and supported by experimental casts of As-Cu alloys in iron chill cast molds by some of the authors elsewhere [1], the mold material and its temperature, and the amount of As, influence the formation of inverse segregation. Given this information, one must consider that prehistoric molds, even those that did not cool alloys as rapidly as

iron, enabled the formation of inversely segregated As, characteristic surface phases, and SDAS averages. In comparison to iron, the mold materials used in prehistory, such as steatite, sandstone, and ceramic, were more insulating and capable of slowing the cooling of cast alloys; however, extant examples of inversely segregated artifacts implies that the phenomenon nevertheless occurred, even in mold materials with far lower thermal conductivities (e.g., Table 3 in reference [1]). Of particular note, the fastest possible cooling rate of 20 K/min using DTA showed that the  $\gamma$ -phase can form with as little as 2 wt.% As and at temperatures below the equilibrium eutectic [2]. Further, in a previous study of the As-Cu system, it has been shown that as-cast objects, even at low As concentrations, can result in arsenic-rich silvery surfaces. Depending on composition, the surface of an as-cast As-Cu alloy may appear silvery due to the presence of  $\alpha$  solid solution with up to ca. 8 wt.% As or ( $\alpha+\gamma$ ) eutectic [1]. Because the  $\gamma$ -phase and ( $\alpha+\gamma$ ) eutectic are commonly noted on the surfaces of prehistoric arsenical copper, it is thus important to also consider SDAS, since inverse segregation may have been a byproduct of the mold material rather than produced intentionally. Specific mold materials may have been purposely sought to induce inverse segregation, but most evidence for this practice is circumstantial and few objects definitively show this intention [27]; nevertheless, in either case, with enough data it should be possible to use SDAS measurements as a means to retroactively determine mold materials. In our experiments and calculations, the SDAS averages of As-Cu alloys cast in iron chill molds were reasonably comparable to calculated values for the same material (Fig. 1 and Table 3). In this example, the chill cast alloy SDAS value, too, at approximately 9 wt.% As, was similar to that derived from the DTA sample. At higher concentrations, where As reached saturation in the alloy at the eutectic upon cooling, the calculated and average experimental SDAS values were in better agreement. Also, the trend of decreasing SDAS averages with increasing As suggests that the calculations for SDAS at the eutectic are trustworthy. Of note, sample AsCu-8, with an actual concentration of 7.5 wt.% As (Table 1), is just shy of the eutectic at ca. 8 wt.%, and therefore did not adhere to the calculated lower SDAS trend. As for the far lower calculated SDAS values at concentrations of 8 wt.% As and lower, compared to the samples taken from our DTA experiment, the difference lies in the far greater cooling rate in the calculations; the rate for iron molds far exceeded what is possible in DTA, which is designed to produce equilibrated results. In real-world casting in iron, then, as it would be in prehistory in the available mold materials (Fig. 3), the cooling rate would be much faster than DTA, leading to far lower SDAS averages and a trend more similar to our calculated values. In each calculated cooling curve, an anticipated lower average and trend for SDAS is supported by the initial rapid cooling from the liquidus that levels off at the eutectic.

Inverse segregation and ( $\alpha+\gamma$ ) eutectic increase with increasing As as the SDAS average decreases (see Figs. 1 and 2). For AsCu-1 through AsCu-15, the SDAS averages decreased as more As was present in the system; however, this effect was more intense between AsCu-1 and AsCu-3, and less intense between AsCu-8 and AsCu-15. In the first instance, the decrease in SDAS is likely due to the increase in As, which is associated with growth restriction effects that promote the formation of a constitutional undercooled zone and increases the tendency of perturbation formation and finer dendrites [26-28]. In the second, the drop in SDAS from 8 to 10 wt.% As is likely associated with a decrease in the solidification range and therefore with a decrease in the local solidification time. The increased SDAS from 3 to 5 wt.% As, found in the iron mold-solidified samples, is assumed to be associated with an increase in the solidification range, which superimposed the effects of increasing As concentration. Concomitant to this phenomenon is a significant drop in the SDAS averages, indicating faster cooling of the arsenic-rich eutectic when present on the surface. It is likely that cooling rates faster than 20 K/min would result in ( $\alpha+\gamma$ ) eutectic surface segregation, even at lower wt.% As, which is often seen in metallographically characterized prehistoric arsenical copper [1]. These results suggest that the formation of surface segregated As would not be difficult to achieve given our calculated cooling curves for castings made in prehistoric mold materials (Fig. 3). These

results are particularly important as they provide a framework from which one can identify the mold materials likely used to produce ancient arsenical copper objects. If sampled for metallographic examination, the microstructures of ancient As-Cu objects could be compared with the results of this study to infer the mold materials and the likely means of their production.

## Conclusion

With recent DTA results for the As-Cu system [2], the presence of metastable phases were identified, which can be used to predict the initial casting outcomes for as-cast As-Cu ingots. Due to the wide solidification range and assumed low diffusivity of As, similar to the Cu-Al system [28-29], the As-Cu system is subjected to strong segregation phenomena, even at low cooling rates. The formation of  $\gamma$ -phase is therefore possible and almost certainly regularly occurred in prehistoric arsenical copper with more than 2 wt.% As. At faster cooling rates, the DTA results suggest that the casting of As-Cu alloys in any of the discussed mold materials at ambient temperature would result in inverse segregation and surface enrichment of As. Extreme segregation and surface silvering would have almost certainly been easily achieved by prehistoric metal smiths, whether it was intentional or not. Some good recent examples of this phenomenon are several Caucasian daggers from the Late Bronze Age, which have As-Cu hilts with inverse segregation [27].

By knowing the solidification time of As-Cu alloys in simple casting forms, and by utilizing time-stepping analysis, it was possible to calculate the chilling effects imparted by several mold materials. For each simulated mold material, the geometry of the castings remained constant, allowing for straightforward calculations of cooling curves for each mold. Not surprisingly, the metal molds had the most substantial chilling effect, followed by steatite, sandstone, quartz sand, and terracotta. Since no similar As-Cu alloy casting experiments existed prior to this paper, the simulated cooling rates were compared to published data for 10 wt.% cast tin-bronze. The cooling curves of the different mold materials correspond well with the calculations in trend. Of note for these materials, it has been shown that the inverse segregation of As can occur in steatite molds despite its low thermal conductivity, even in instances where the mold was preheated and tested with 6 and 9 wt.% As [21] (see Table 2 and Fig. 3). In regard to SDAS, one should expect to find decreased distances between arms in As-Cu alloys that were rapidly cooled. A comparison of arm spacing in each of the discussed mold materials would be necessary to demonstrate the degree of variation, but it is expected that unheated molds would contain far smaller SDAS than heated ones. In the case of metal molds, and those with high thermal conductivities, SDAS averages decrease with an increase in the solidification range for alloys containing more As.

These findings, along with the newly assessed and modified equilibrium diagram for the As-Cu binary system [2], are important to archaeologists as they demonstrate how the cooling rate and different mold materials, in combination with the volume of the casting, can be used to predict phase formation and SDAS averages. These findings and data are especially important when one considers that casting molds are rarely preserved. However, despite the significance of the experiments and analytical data collected in this paper, additional data is required to understand the As-Cu system and casting microstructural results. It is hoped that both modern and ancient studies of the As-Cu system will utilize and build upon the methods presented by this research, and that the modified equilibrium phase diagram will be used more frequently as a reference by both archaeologists and metallurgists. In future research, experimental archaeologists in particular should consider the information and results presented in this work. While it is possible to roughly mimic prehistoric metal production using intuition, past archaeological studies, and local foundry experience, there are underlying and interwoven physicochemical interactions that are calculable and must also be considered. Metallurgy as a discipline is continually advancing using techniques including, but certainly not limited to, those

presented in this paper, in order to better understand external influences during metal production. Future experiments investigating prehistoric alloys should ideally, then, also rely on these advancements to better interpret ancient metallurgy.

## Acknowledgements

Dr. Benjamin J. Sabatini is an International Research Fellow of the Japan Society for the Promotion of Science (JSPS) no. PE17781. This work was also supported by the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Actions grant no. 656244.

## References

- [1] M. Mödlinger and B. Sabatini: *J. Archaeol. Sci.*, 2016, vol. 74, pp. 60–74, DOI 10.1016/j.jas.2016.08.005.
- [2] M. Mödlinger, D. Macció, A. Cziegler, H. Schnideritsch and B. Sabatini: *Metall Mater Trans B*, 2018, vol. 49/5, 2505–2513. DOI: 10.1007/s11663-018-1322-8
- [3] H. Lechtman: *J. Field Archaeol.*, 1996, vol.23/4, pp. 477–514. DOI: 10.2307/530550
- [4] H. Lechtman and S. Klein: *J. Archaeol. Sci.*, 1999, vol. 26, pp. 497–526.
- [5] T. Rehren, L. Boscher and E. Pernicka: *J. Archaeol. Sci.*, 2012, vol. 39/6, pp. 1717–27.
- [6] E. C. Rollason: *Metallurgy for engineers*. Edward Arnold & Co, London, 1949.
- [7] E.G. Garrison: *A history of engineering and technology. Artful methods*. 2nd ed., CRC Press, Boca Raton, 1998.
- [8] J. Günter, K.J.A. Kundig, J.A. Konrad: *Copper: its trade, manufacture, use, and environmental status*. Materials Park, Ohio, 1999.
- [9] A. Nayar: *The metals databook*. McGraw-Hill Companies, New York, 1997.
- [10] A. Giumla-Mair: *Surf Eng*, 2008, vol. 24/2, pp.110-117.
- [11] F. Pereira, R.J.C. Silva, A. Soares, M. Araújo and J. Cardoso: *Mater Manuf Process*, 2016, vol. 21/6, pp. 1-11.
- [12] H. Lechtman: *Historical metallurgy*, 1985, 19/1, p. 141.
- [13] P.D. Budd: *A metallographic investigation of Eneolithic arsenical copper* (University of Bradford 1991).
- [14] P.D. Budd: *Historical metallurgy*, 1991, vol.25, p. 99.
- [15] P. J. Northover: In: A. Hauptmann, E. Pernicka and G. A. Wagner, G. A. (eds). *Old work archaeometallurgy* (Bochum 1989), pp. 111–118.
- [16] J. R. Marechal: *Métaux, Corrosion, Industries*, 1958, vol. 33, p. 377.
- [17] B. R. Subramanian and D. E. Laughlin: *Bull. Alloy Phase Diagrams*, 1988, vol. 9/5, p. 605.
- [18] B. Pei, B. Björkman, B. Jansson and B. Sundman: *Z Metallk*, 1994, vol. 85/3, pp. 178–184.
- [19] D.M. Stefanescu: *Science and engineering of casting solidification*. Springer, New York, 2015.
- [20] R. N. Grugel: *J. Mater. Sci.*, 1993, vol. 8/3, p. 677. doi:10.1007/BF01151244
- [21] N.V. Ryndina and L.V. Kon'kova: *Sovetskaya Archeologia*, 1982, vol. 2, pp. 30–42.
- [22] ASM handbook: properties and selection: nonferrous alloys and special-purpose materials (Asm Handbook) Vol. 2
- [23] E. Jochum-Zimmermann, N. Künzler-Wagner, and U. Kunnert: *Experimentelle Archäologie in Europa*, 2005, vol. 1, p. 285.
- [24] W. Kurz and D. J. Fisher, *Fundamentals of solidification*. Trans Tech Publications, Switzerland-Germany-UK-USA, 1986.
- [25] A. Cziegler: Aspects of grain refinement in copper alloys, Master Thesis, Montanuniversität Leoben, 2015.

- [26] T. Ejima and M. Kameda: *Journal of the Japan Institute of Metals and Materials*, 1969, No. 1, pp. 96-103.
- [27] M. Mödlinger and B. Sabatini, *J. Archaeol. Sci.: Reports* 2017, vol. 16, pp. 248-257. DOI: 10.1016/j.jasrep.2017.10.018
- [28] M. Easton, C. Davidson, D. St John: *Metall Mater Trans A*, 2010, vol. 41, pp. 1528–1538. doi: 10.1007/s11661-010-0183-9
- [29] M.B. Djurdjevic and M.A. Grzincic: *Archives of foundry engineering*, 2012, vol. 12/1, pp. 19-24.

## Figure captions

(Figures in the pdf/online version are in color, otherwise they are in black and white)

- Fig. 1.** Measured SDAS values at a cooling rate of 20 K/min and in iron chill cast molds (ingot center, longitudinal section). The amount of As is indicated in wt.% in the diagram
- Fig. 2.** Microstructure of As-Cu alloys for samples cooled at 20 K/min using DTA (reprinted from [2]). Note the increasing amounts of  $\gamma$ -phase and  $(\alpha+\gamma)$  eutectic with increasing amount of As. Only the AsCu-1 sample required etching with  $\text{FeCl}_3$ . The *black* areas in the centers of the samples are mainly interdendritic porosity. In samples AsCu-1 to AsCu-3, the As is mainly in  $\alpha$ -solid solution. AsCu-4 and AsCu-5 showed increasing  $\gamma$ -phase and  $\alpha+\gamma$  eutectic. Arsenic-rich and arsenic-poor zones of the  $\alpha$ -solid solution are visible even without etching. AsCu-7 to AsCu-15 showed significant amounts of  $\gamma$ -phase and  $\alpha+\gamma$  eutectic with increasing porosity. AsCu-11 and AsCu-15 clearly show the inverse segregation of As as  $\alpha+\gamma$  eutectic on the surface of the samples (see reference [1])
- Fig. 3.** Temperature vs time simulated cooling curves in different mold materials for AsCu-1, AsCu-5, and AsCu-10 (As-Cu with 1.2 wt.% As, 4.6 wt.% As, and 10.3 wt.% As, respectively). The *sharp bends* indicate the liquidus and solidus, and the *horizontal lines* the eutectic temperature
- Fig. 4.** Cooling rate temperature vs time in different mold materials for 10 wt.% Sn (adapted from [23])
- Table 1.** Nominal and actual arsenic content in each respective sample
- Table 2.** Values used in the solidification simulation calculations for each mold material. For the latent heat of fusion, thermal conductivity, and alloy specific heat, the values for pure copper were used. \* Values in brackets derive from the phase diagram after [17]
- Table 3.** Top, solidification time (in seconds) and bottom, SDAS (in  $\mu\text{m}$ ) for the as-cast simulations in different mold materials







