Revisiting the zinc composition limit of cementation brass

Brian D Newbury, Michael R Notis and Dale E Newbury

ABSTRACT: It has been widely accepted that the zinc composition limit in historic cementation brasses is approximately 30wt%. However, reports have been published of the ability to produce cementation brasses in excess of this limit (Welter 2003, Zwicker et al *1992). This work reproduces both traditional cementation brass production methods and the high-zinc production technique reported by Zwicker* et al *to explore the true limit of zinc content and how this relates to historic brass compositions. Metallography and advanced scanning electron X-ray composition mapping showed that it is possible to produce brasses with over 40wt% zinc by cementation. However, to achieve these compositions the process must be performed in very small quantities and at very short furnace times, which is contrary to historical written accounts of the cementation brass production techniques. It is the opinion of the authors that while it is possible to produce a >40wt% brass via cementation, the commonly reported zinc content limit of ~30wt% is valid for historic artefacts.*

Introduction

Much has been written detailing the cementation process (also referred to as the calamine process) of historical brass manufacture (*eg* Tylecote 1976, 96; Craddock 1995, 292–302; Pollard and Heron 1996, 196–234). Before the technology to produce metallic zinc was developed, the cementation process was the only method of brass manufacture. Development of the process appears to have been in northwest Asia Minor in the regions of Phrygia and Bithynia (Craddock 1985, 12). The cementation process was first used on a large scale by the Romans to produce brass without requiring metallic zinc (Bayley 1984, 42). The process, first described in detail in Europe by Theophilus in the 11th century, was widely used around the world until the 19th century (Day 1998, 147). By heating a crucible containing metallic copper, zinc oxide (ZnO), and charcoal to a temperature of approximately 1000°C, it is possible to reduce the ZnO to zinc vapour and diffuse it into the copper to form brass.

Because the cementation process depends on the thermodynamic activity and diffusivity of zinc to form brass, it is reported that there is an upper limit to the amount of zinc that can be absorbed by the copper. This has been measured empirically to be approximately 28–32% depending on experimental conditions such as process temperature and crucible design (Tylecote 1976, 96; Craddock 1995, 292–302; Lambert 1997, 192–3). Haedecke, who reproduced the cementation process in a laboratory to definitively determine the maximum zinc content of the brass, has shown through thermodynamic calculation based on a specific reaction model, and by experimentation, that this limit is 32wt% Zn (Haedecke 1973, 229). As a result of this experiment and the zinc contents of historical samples, 32wt% Zn has been quoted widely as the limit for the cementation process; anything higher is presumed to have been manufactured by direct co-melting of copper and zinc metal.

However, a few papers have been published stating that the cementation process could produce brasses with compositions exceeding this 32wt% Zn limit – with compositions as high as 45wt% Zn being reported (Zwicker *et al* 1992; Ullwer 2001; Welter 2003). The work of Zwicker *et al* (1992) included micrographs illustrating the presence of α–phase grains at the centre of an ingot with a mixture of α– and β-phase grains on the edge. Figure 1 shows this corresponds with a zinc

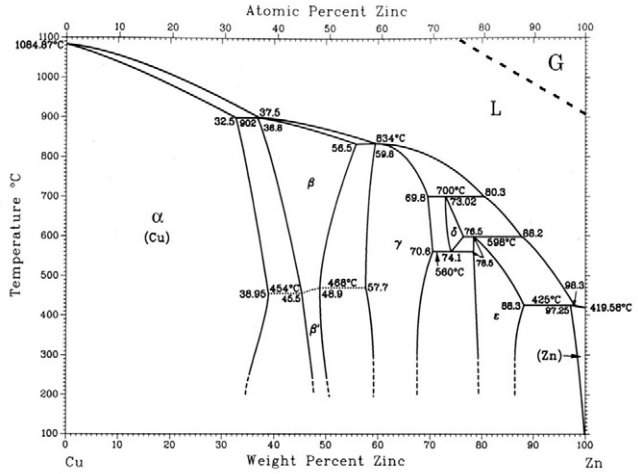

Figure 1: Cu-Zn phase diagram, modified from Baker (1992, 182).

composition of 40–50wt%.

Most of these experiments were performed many years ago, yet the cementation process compositional limit is still reported as between 28–32wt% Zn. With seemingly contradictory evidence both for and against this limit, this work aims to explain whether this limit is true and to consider its implications for historic and archaeological brass artefacts.

Experimental procedures

Two experiments were performed in order to explore the upper zinc content limit for the cementation process. The first reproduced a traditional European cementation brass technique, while the second experiment reproduced Zwicker *et al*'s work in which cementation brasses of over 40wt% Zn were obtained (Zwicker *et al* 1992). The experiments were performed under 'ideal conditions', to determine the maximum zinc content for a given set of experimental parameters. To provide these ideal conditions, laboratory grade materials were used instead of more historically accurate mined zinc oxide ores and crude metallic copper produced by historical techniques. Not only did this make the experiment much simpler to perform, it eliminated the possible effect of the presence of minor elements in the various ores and other experimental unknowns on the product brass. Table 1 lists the ingredients used in these reproduction experiments, along with their historical counterparts.

Table 1: Ingredients used in cementation brass experiments.

This study	Historical process
carbon powder, activated, ash 4% max (Alfa Aesar stock # 33302)	charcoal, coal
copper powder, -40 +100 mesh (420µm) 99.5% pure (Alfa Aesar stock # 00908)	granulated copper
zinc oxide, 99.0% min assay (Alfa Aesar stock # 11558)	calamine, zinc ore

Fisher Scientific box furnaces (capable of 1200˚C) and lidded Al_2O_3 crucibles, 80mm wide by 100mm deep, were used for both experiments.

Traditional cementation experiments

The brass-making recipe of Lazarus Ercker (Sisco and Smith 1951, 254–258) was used for the traditional cementation experiment because it was the most explicit of the European historical accounts, and a temperature of 1000˚C was chosen based on Haedecke's results (Haedecke 1973). Table 2 summarizes the ingredients and amounts used in all cementation experiments. Ercker mentions that calamine (ZnO) should be added in the ratio of 3 parts calamine to 4 parts granulated copper (Sisco and Smith 1951, 254–258), so 75g ZnO and 100g Cu were chosen to produce a relatively large ingot (sample C1 in Table 2). The ZnO was mixed with carbon in a 1:1 volume ratio and placed in the bottom of the crucible. The copper was placed on top of this mixture, and then covered with excess carbon to fill the crucible (Fig 2). A loose Al_2O_3 crucible lid was placed on top of the crucible to limit zinc loss as much as possible. The cementation time and temperature were 15h at 1000˚C.

Table 2: Experimental conditions and quantities of ingredients for cementation brass production.

Sample ID	Quantities and conditions used				
	Temperature (°C)	weight Cu (g)	weight ZnO (g)	weight Carbon (g)	Time at temp (h)
Traditional cementation process					
C1	1000	100	75	50	15
C2	1000	100	20	50	15
C3	1000	100	25	50	15
Zwicker process					
ZC1	1100	0.255	5.021	5.020	1
ZC2	1100	0.252	5.016	5.006	0.25

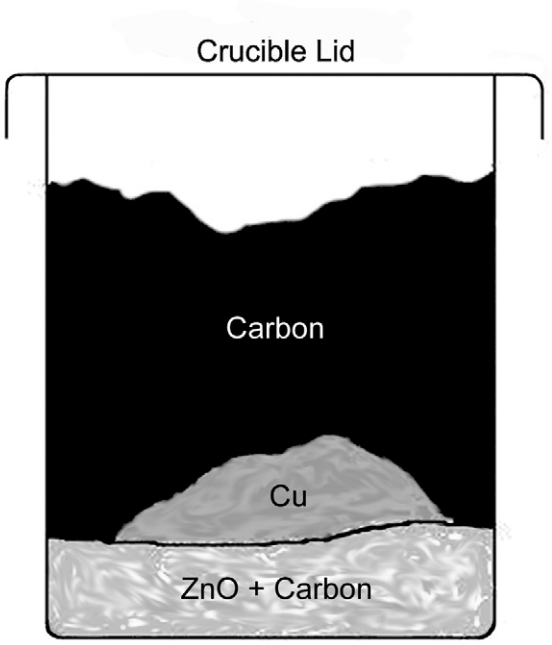

Figure 2: Arrangement of crucible charge for cementation experiments.

Two additional brass ingots were produced in an attempt to achieve zinc contents of 10wt% and 15wt% in the final ingot. The amount of ZnO required to produce these brasses was calculated and an additional 20–25% extra ZnO was added to account for zinc loss in the furnace. The quantities and experimental conditions for samples C2 (10wt% Zn) and C3 (15wt% Zn) are listed in Table 2.

High-zinc cementation experiments

To duplicate Zwicker's experimental conditions, granulated copper (0.25g) and powdered ZnO (5.0g) were placed in a closed crucible filled with charcoal. The experimental conditions are listed in Table 2. Two different times at temperature (1h and 15 min) were used to attempt to determine qualitatively the effect of diffusion kinetics on the final composition of the brass ingot. After these times the crucible was removed from the furnace and air cooled.

In Zwicker's original experiment, 0.2mm-thick copper sheet was used instead of granulated copper; this was not thought to be a significant difference because the ingredients were used in the same proportions. The zinc content is limited by gaseous diffusion into the solid copper until the copper melts at 1083°C, so the use of granulated copper will only help to improve the efficiency of the process due to the higher surface area over that of copper sheet.

All brass samples were then prepared for metallography and electron microscopy by standard grinding and polishing techniques down to a 0.03μm colloidal silica final polish. The samples were examined in the as-polished state for electron microscopy; a combined aqueous/alcohol ferric chloride etch (Table 3) was applied before the metallography.

Table 3: Aqueous/alcohol ferric chloride etchant.

Ingredient	Quantity
distilled water	60ml
ethanol	60ml
hydrochloric acid (HCl)	30ml
ferric chloride ($FeCl_3$)	10g

SEM/EDS microanalysis

Images showing the distribution of the elemental constituents were obtained using scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDS) and the X-ray spectrum imaging method. In X-ray spectrum imaging, the entire EDS spectrum is recorded at each location where the focused electron beam dwells, thus capturing all possible elemental information about that specimen location within the limitations of the spectrometer performance and the spectrum statistics. For this work, the image scan was 256 x 200 pixels with a pixel dwell of 500ms at an EDS output count rate of approximately 3000 cps. The resulting X-ray spectrum image data structure, referred to as a 'datacube', can be considered to consist of an array (256 x 200) of individual EDS spectra, or equivalently of a sequence of 2048 images of the specimen, each recorded at a different X-ray energy in 10eV increments from the lower threshold of 150eV to the beam energy of 20keV. Each datacube thus produced contained about 200 Mbyte and was analyzed using the LISPIX 'derived spectrum' software tools of Newbury and Bright (2005).

Results

Standard cementation

Standard cementation brasses were produced with compositions of 11.0 (Sample C2), 11.4 (Sample C3), and 30.0wt% Zn (Sample C1) as measured by spectroscopic analysis. All ingots were well-consolidated and did not contain porosity. The 30.0wt% brass represents the maximum zinc composition attained in this experiment following the traditional cementation method discussed by Lazarus Ercker, in which an excess of zinc oxide was provided in the crucible and time at temperature was 15h, consistent with the long times at temperature common in Europe (Sisco and Smith 1951, 256). This result supported

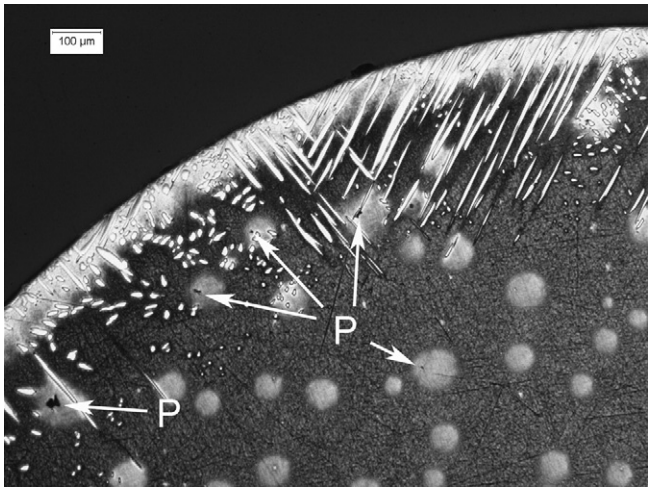

Figure 3: Optical micrograph of brass sample ZC1, showing bulk β-phase brass (dark grey) with zinc loss at the surface producing α-phase brass (white needle-shaped grains). The lighter grey circular regions are areas of lower zinc concentration. Note the residual pores marked 'P'.

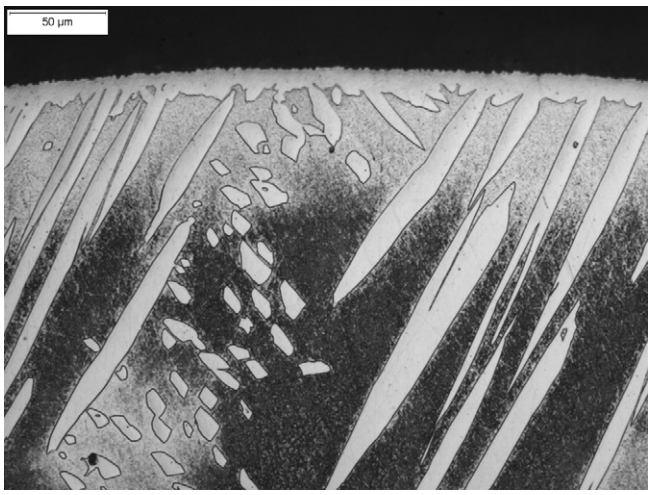

Figure 4: Optical micrograph of ZC1 showing the continuous surface layer of α-phase brass and penetrating α-phase brass needles.

the maximum zinc composition theory reported in the literature (Craddock 1995; Day 1998). The attempts to produce a 10wt% Zn and 15wt% Zn brass ingot by the traditional cementation process were only partially successful. By decreasing the amount of ZnO in the crucible we were able to decrease the zinc content of the ingot; however we were not able to 'fine tune' the composition since C2 and C3 had approximately the same zinc contents at 11.0wt% Zn (attempted 10wt% Zn ingot) and 11.4wt% Zn (attempted 15wt% Zn ingot) respectively.

High-zinc cementation

Figure 3 shows the microstructure of the one hour Zwicker reproduction experiment (ZC1). The micro-

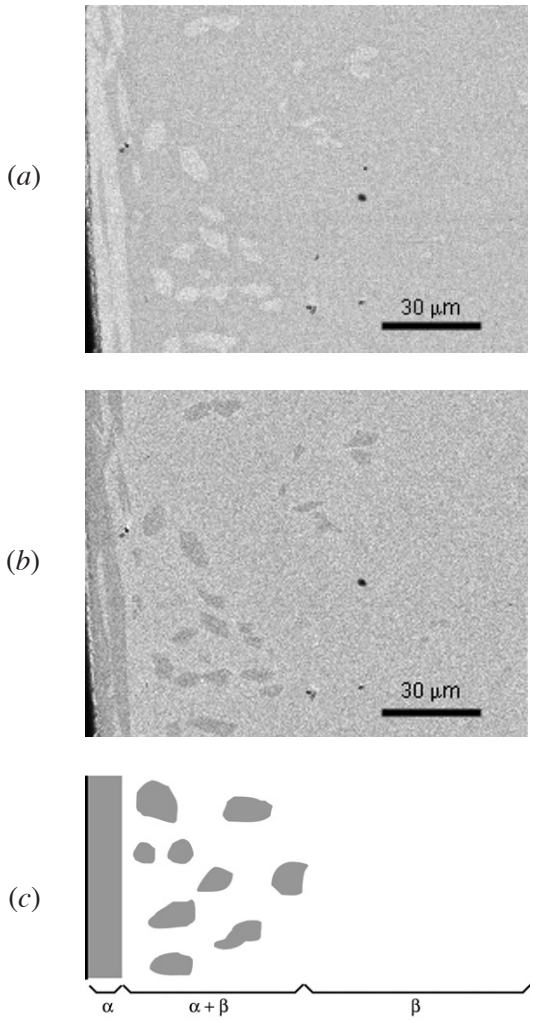

Figure 5: SEM/EDS analysis showing (a) Cu and (b) Zn LISPIX compositional maps of sample ZC1 with image brightness proportional to the element concentration. (c) is a diagrammatic microstructure showing three distinct microstructural regions in the sample. The sample surface is the left-hand side of the images.

structure has two interesting features: needle-shaped α-brass grains penetrating from the surface toward the centre of the ingot, and circular light-coloured regions within the bulk of the ingot. The small α-phase grains interspersed among the needle-shaped α-phase grains are needles oriented perpendicular to the plane of the image. The α-phase grains appear untouched by the ferric chloride etch, while the β-phase grains with higher zinc concentration appear darker. If the magnification is increased (Fig 4), the continuous surface layer of α-phase brass from which the needles originate can be seen. At the lower left of the image, a dark pore can be seen at the centre of the circular light region. Because copper powder was used in the experiment, the ingot formed was very porous due to the relatively small amount of material used and short time at temperature. The 'Swiss cheese' appearance of Figure 3 is a result of this porosity – zinc diffuses from the brass surrounding these pores

(marked 'P' in the figure) creating the circular halos seen in the centre of the ingot. The composition of the centre of the sample was measured by electron probe microanalysis to be 44.1wt% Zn (std dev 0.9wt%), proving it to be a β-phase brass.

Figure 5 shows an EDS compositional map of sample ZC1. While this is not a quantitative map, it is possible to observe the regions of zinc loss at or near the surface. A continuous band of copper-rich α-phase brass is seen towards the surface (the left of Figure 5a), with separated 'islands' of copper rich α-phase brass decreasing in area fraction as one moves towards the centre of the sample (towards the right). This trend is mirrored in Figure 5b, with zinc-depleted regions on the surface of the sample. Figure 5c shows these three microstructural regions (α only, α + β, and β only) in diagrammatic form. These results support those found in the metallography (Figs 3 and 4).

Figure 6 shows the surface region of the 15min Zwicker reproduction brass (ZC2). The surface α-phase brass layer is similar to that of ZC1; however, there is no significant penetration of α-phase brass grains towards the centre of the sample. There is evidence for fast zinc diffusion along the β-phase grain boundaries after solidification as shown by the penetration of α-phase brass regions surrounding the β-phase grains in Figure 6.

One interesting feature that was absent in ZC1 but observed in ZC2 is the surface inclusions in the continuous α-phase brass layer (Figs 6 and 7). The compositional map of this region (Fig 8) illustrates the same trends seen in ZC1 (Fig 5) with the surface zinc-depleted α-phase brass layer, α-phase brass 'islands', and central β-phase brass region, however the surface inclusions can now be explained. From Figure 8b and 8c it is seen that these inclusions are entrapped ZnO from the initial raw materials.

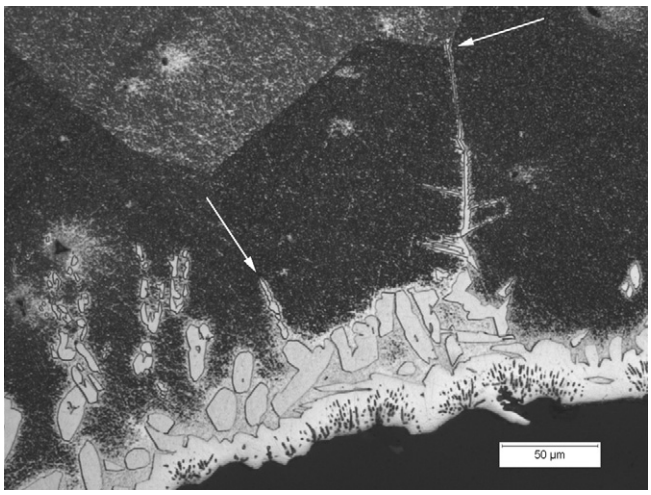

Figure 6: Optical micrograph showing surface region of sample ZC2 showing the continuous region of α-phase brass on the surface (the bottom of the image), and very limited penetration of α-phase brass 'islands' into the centre of the sample. Zinc diffusion along the grain boundaries is evidenced by the thin α-phase brass regions indicated by the white arrows.

Discussion

The discrepancy between the traditional cementation process and the Zwicker process can be explained qualitatively by examining the relationship of the reaction thermodynamics and kinetics. The reaction thermodynamics predict only the final equilibrium state but say nothing about the time required to achieve that state. A reaction's kinetics determines the rate at which it occurs; at different times the reaction components will be present in different proportions before equilibrium conditions are reached. For the traditional cementation experiments, it can be assumed that the longer time at temperature allows the metal to reach equilibrium conditions (with a maximum of approximately 30wt% Zn, depending on the temperature). The shorter time-at-temperature Zwicker-process brasses have yet to reach these equilibrium conditions. The microstructures in Figures 3, 4 and 5 support this: the higher-zinc β-phase in the centre surrounded by α + β dual phase with a continuous α-phase region towards the sample's edge illustrate zinc diffusion out of the sample.

Figures 3, 4 and 5 show it is possible to produce brass in excess of 32wt% Zn by cementation. However, the steady-state maximum zinc content is 32wt%, as reported by Haedecke (1973). The question then becomes how does one reconcile the current findings and Haedecke's reported maximum zinc content? In Haedecke's work,

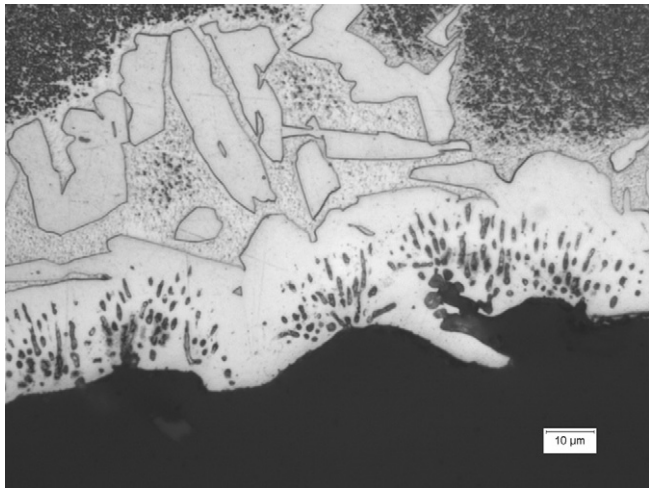

Figure 7: Optical micrograph showing inclusions in the α-phase brass layer along the edge of sample ZC2.

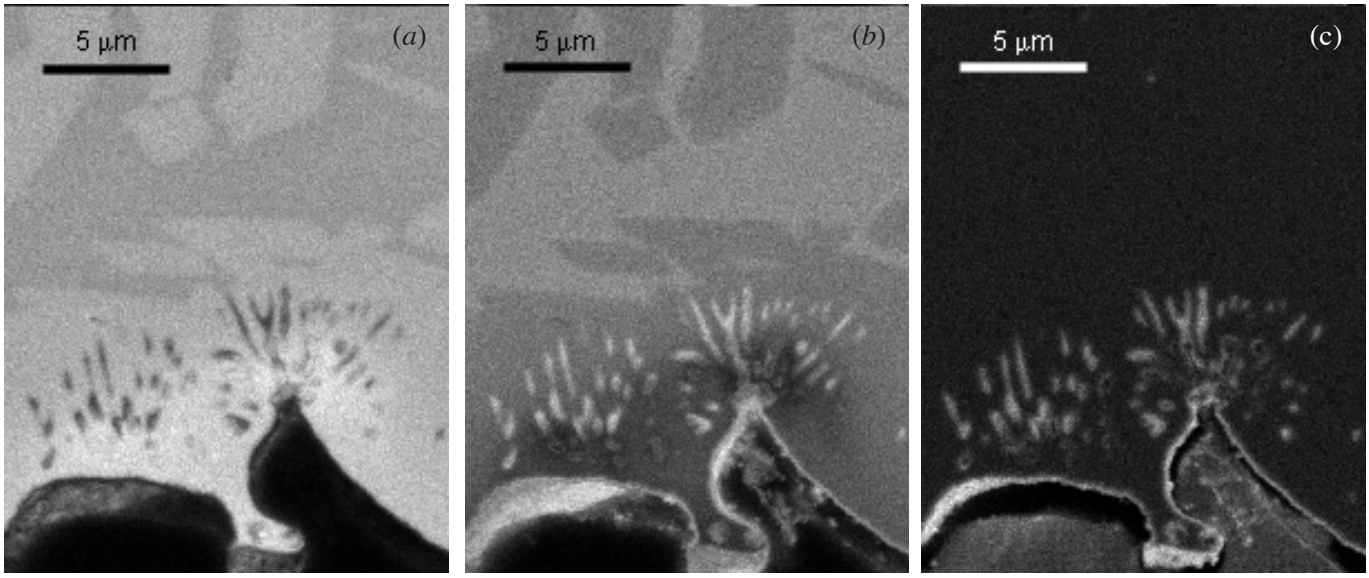

Figure 8: (a) Cu, (b) Zn and (c) O LISPIX compositional maps of the edge inclusions of sample ZC2 with image brightness proportional to element concentration.

the maximum zinc contents were calculated by thermodynamics and backed up with experimentation. It is important to remember that thermodynamics assume an equilibrium state, and this is the key to explaining the present results. In Zwicker's original experiments, and this reproduction of his procedure, the crucial step in producing zinc contents in excess of 30wt% is the short time at temperature.

In the current Zwicker reproduction experiment, enough zinc oxide is present around the copper metal in the crucible to provide a surplus of zinc vapour. When the crucible reaches the furnace temperature, this excess zinc vapour diffuses into copper forming a high-zinc brass. However, according to Haedecke, the thermodynamics of the crucible conditions predicts a brass composition of 32wt% based on the balance of zinc-gas diffusion into the copper and the volatilization of zinc gas out of the brass. Thus, the high-zinc brass produced is not in an equilibrium state, permitting zinc to diffuse out of the sample to reach the equilibrium composition of ~32wt%. The microstructure of sample ZC2 (Fig 6) shows that this outward zinc diffusion has progressed significantly after only 15 minutes. Both ZC1 and ZC2 samples produced in this experiment (Figs 3, 4 and 6) are in this intermediate state – the centre is still all β-phase while the surface consists of a skin of α-phase brass. As zinc diffuses out of the surface, α-phase brass grains grow in towards the centre. Historical accounts of cementation brass production indicate a significant period of time at temperature, during which equilibrium conditions would have been met so that the maximum zinc composition reported in the literature would hold true.

In addition, it is important to acknowledge the scale of the experiments. The high-zinc brass ingots produced in this work were on the order of 3–4mm in diameter (and under 1g in weight), while historical accounts suggest that during the Middle Ages brass foundries were producing approximately 5kg (11 lb) of brass per crucible (Sisco and Smith 1951, 256–7). Many historical recipes specify that 'broken copper' should be used (Zacharias 1989, 37), however it is doubtful that the copper would have been as fine as the approximately 420μm copper powder used in this experiment. As the copper powder decreases in size, the surface area per unit weight increases which allows for more efficient zinc diffusion. It is generally accepted that surface diffusivity is greater than grain boundary diffusivity which in turn is greater than lattice diffusivity (Porter and Easterling 1992, 98–103). To produce large quantities of a high-Zn brass via the Zwicker technique would be very demanding given that the process is dependent on diffusing a large amount of zinc into the copper in a very short time to prevent zinc loss. Reproducing this on an industrial scale would be nearly impossible with the crucible size of medieval brass makers. It is believed that given the historical documents, which state times upwards of 15h at temperature (Sisco and Smith 1951, 256), it would be highly improbable that high-zinc brass was produced via cementation in historical times. Therefore, in practice, the upper limit of 32wt% Zn remains a good guideline to follow for artefact dating, with only some exceptions as documented by Welter (2003).

This work has attempted to explain existing inconsistencies in the reported maximum zinc content of historical brasses. It has been shown that the cementation process

can produce brasses with upwards of 44wt% Zn given proper, but very restrictive, experimental parameters:

- furnace temperature of 1000–1100˚C to promote diffusion of zinc vapour into solid or liquid copper
- a surplus of ZnO to ensure sufficient zinc vapour present to produce a high-zinc β-brass ingot
- copper of very thin sheet or powdered form to provide a high surface area to volume ratio in the solid state
- short time (≤1h) at temperature to prevent attainment of equilibrium conditions

However, given documented accounts of the cementation process, it is improbable that these experimental parameters were ever used in historical brass foundries. The lack of a sealed, tight-fitting lid to prevent zinc vapour loss and the very long times at temperature used in the historical processes make it very unlikely to find cementation brasses with over 32wt% Zn.

Acknowledgements

Brian Newbury was supported by the Department of Energy Office of Science, Office of Basic Energy Sciences, under contract # W-31-109-Eng-38.

References

Baker H (ed) 1992, *ASM Handbook Volume 3 Alloy Phase Diagrams* (Materials Park, OH) Section 2, 182.

Bayley J 1984, 'Roman brass-making in Britain' *Historical Metallurgy* 18(1), 42–43.

Craddock P 1985, 'A history of the distillation of metals' *Bulletin of the Metals Museum* 10, 3–25.

Craddock P 1995, *Early Metal Mining and Production* (Edinburgh), 292–302.

Day J 1998, 'Brass and zinc in Europe from the Middle Ages until the mid-Nineteenth century' in P Craddock (ed), *2000 Years of Zinc and Brass,* revised edition (London: British Museum Occasional Paper 50), 133–158.

Haedecke K 1973, 'Equilibria in the production of brass by the calamine process', *Erzmetall* 26(5), 229–233.

Lambert J 1997, *Traces of the Past: Unraveling the Secrets of Archaeology Through Chemistry* (Reading, Massachusetts), 192–193.

Newbury D and D Bright 2005, 'Derived Spectra software tools for detecting spatial and spectral features in spectrum images', *SCANNING* 27, 15–22.

Pollard A and C Heron 1996, *Archaeological Chemistry* (Cambridge), 196–238.

Porter D and K Easterling 1992, *Phase Transformations in Metals and Alloys* (London), 98–103.

Sisco A and C Smith 1951, *Lazarus Ercker's Treatise on Ores and Assaying* (Chicago), 254–272.

Tylecote R 1976, *A History of Metallurgy* (London), 90–98.

Ullwer H 2001, 'Messingherstellung nach dem alten Galmeiverfahren', *Erzmetall* 54(6), 319–326.

Welter J-M 2003, 'The zinc content of brass: a chronological indicator?', *Techne* 18, 27–36.

Zacharias S 1989, 'Brass making in medieval western Europe', in M Wayman (ed), *All That Glitters: Readings in Historical Metallurgy* (Montreal), 35–40.

Zwicker U, H Greiner, K-H Hoffmann, and M Reithinger 1992, 'Smelting, refining, and alloying of copper and copper alloys in crucible furnaces during prehistoric up to Roman times', in P Craddock and M Hughes (eds), *Furnaces and Smelting Technology in Antiquity* (London: British Museum Occasional Paper 48), 103–115.

The Authors

Brian Newbury recently completed his doctorate in Materials Science and Engineering at Lehigh University studying brass metallurgy and construction techniques used in medieval astrolabe manufacture.
Address: Archaeometallurgy Laboratory, Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015
email:bdn2@lehigh.edu

Michael Notis is a Professor Emeritus of the Materials Science and Engineering Department of Lehigh University and current Director of the Archaeometallurgy Laboratory at Lehigh.
Address: Archaeometallurgy Laboratory, Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015
email: mrn1@lehigh.edu

Dale Newbury is a Fellow of the National Institute of Standards and Technology where he researches novel X-ray microanalysis.
Address: Surface and Microanalysis Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD, 20899-8370
email: dale.newbury@nist.gov