



Reconstructing bronze production technology from ancient crucible slag: experimental perspectives on tin oxide identification



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1. Introduction

Bronze production has been marked as one of the major technological transitions in the archaeological record worldwide. From the onset of archaeological materials analysis, copper alloys have been a favoured subject (Pollard, 2013), and they remain so to this day. While major diachronic trends in the use of different copper alloys such as arsenical, tin and leaded bronze have been mapped for various archaeological cultures, the basic production technology of these alloys has not enjoyed anywhere near as much attention (Pigott et al., 2003; Rovira, 2007). However, these production techniques may vary significantly, and their identification provides insights into shifting technological choices within particular contexts, as well as the spread of metallurgical technology in a broader perspective. Furthermore, these considerations inform debates on the interpretation of metal provenance as well.

Essential evidence towards understanding the technological choices underlying bronze production is reflected in crucible remains, in addition to casting and shaping techniques attested in moulds and final objects. This paper focuses on the analysis of crucible slag as a tool to distinguish between different tin bronze (henceforth: bronze) production processes. To this end, controlled laboratory experiments are employed to highlight important tin oxide (SnO₂ unless otherwise noted) phases embedded in crucible slag and their diagnostic value for recognising different production techniques.

This research is prompted by the authors' previous research on ancient bronze production evidence, whereby the distinction between bronze recycling and alloying was elaborated based on archaeological remains from ancient Egypt, Phrygia and Spain (Farci et al., 2017, Rademakers, 2015, Rademakers et al., 2017a, 2017b, 2018¹), and an increasing attention for this subject witnessed in recent publications

(discussed below). The main ancient techniques for bronze production are:

- Alloying of copper and tin metal
- Alloying (*cementation*) of copper with mineral cassiterite (SnO₂)
- Co-smelting of copper and tin ores
- Recycling of existing bronze, with the possible addition of copper/tin metal/ore

Bronze melting and alloying crucibles have previously been analysed by other researchers in varying degrees of detail. Of particular interest here are attempts to distinguish between bronze production modes by recognising particular phases in crucible slag: tin oxide is most often cited in this context (see, for example, Adriaens, 1996, Bandama et al., 2015, Benvenuti et al., 2000, 2003, Chirikure et al., 2010, Cooke and Nielsen, 1978, Denbow and Miller, 2007, Dungworth, 2000, 2001, Eliyahu-Behar et al., 2012, Erb-Satullo et al., 2015, Figueiredo et al., 2010, 2017, Garbacz-Klempka et al., 2017, Mahé-Le Carlier et al., 2001, Merideth, 1998, Murillo-Barroso et al., 2010, Nezafati et al., 2009, Papadimitriou, 1992, Renzi et al., 2009, Renzi and Rovira, 2016, Rostoker et al., 1983, Rovira, 2007, Rovira et al., 2009, Rovira, 2011, 2011–2012, Rovira et al., 2009, Yener and Vandiver, 1993, Valério et al., 2013, Wang et al., 2016). While tin oxide is noted upon in a multitude of publications, the diagnostic significance of its variable occurrence (particularly morphology) is only explicitly discussed in more detail by few.

Dungworth (2000) highlights the appearance of “highly euhedral [tin oxide] inclusions”, “present as rhomboids or as needles” in experimentally cast bronze. They are interpreted as resulting from oxidation during casting, rather than the use of cassiterite for alloying. An important

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¹ Rademakers et al. (2018) was formerly cited in other publications as Rademakers et al. (2018) while still in press, but the final revised version of this paper has recently appeared in print.

feature here “is the presence of copper-based prills within the tin oxide inclusions”. Dungworth thus suggests such tin oxide crystal shapes do not distinguish between production techniques, but are rather indicative of an oxidising atmosphere during melting, alloying or casting. Dungworth further refers to work by [Cooke and Nielsen \(1978\)](#), who note the presence of “cassiterite rhombs and skeletal crystals” in bronze but equally metallurgical slags. Here too, tin oxide phases often enclose copper-based prills in their crystal cores. Being more prone to oxidation than copper ([Ellingham, 1944](#)), tin will “burn off” under oxidising crucible conditions and is often incorporated in the crucible slag.

While the presence of clusters of nodular tin oxide inclusions is considered indicative of the use of cassiterite ore mineral by [Rovira \(2007\)](#), tin oxide crystals of various morphology are observed along with relics of mineral cassiterite in the co-smelting experiments performed by [Renzi et al. \(2009\)](#). Indeed, once tin oxide is newly crystallised, which may occur in slag of crucibles used for various bronze making techniques, the original shape of tin (metal or ore) becomes undistinguishable according to [Figueiredo et al. \(2010\)](#). [Figueiredo et al. \(2017\)](#) similarly present the results of three cassiterite smelting field experiments, but do not discuss observed tin oxide phases in detail.

In a small Etruscan bronze scrap, [Benvenuti et al. \(2003\)](#) likewise observed tin oxide with various crystal habits ranging from rhombohedral and rectangular, to needle (acicular) and anhedral shapes, while some crystals show partial resorption by the matrix. They tentatively interpret this as evidence for a cementation process, based on the resemblance of elongated habits observed in natural “needle cassiterite”. However, these observations could equally be interpreted as the oxidation of bronze (following reasoning outlined above), while Benvenuti et al. consider these crystals as partially unreacted cassiterite crystals due to insufficiently reducing furnace or crucible conditions. However, they nuance their interpretation, noting – to their credit – that insufficient comparative evidence was available to make final judgments on bronze production techniques. Apart from crystal shapes, [Benvenuti et al. \(2003\)](#) report on the chemistry (microprobe data) of SnO₂ phases in bronze scrap and those in mineral cassiterite. This approach, recently reported by [Renzi and Rovira \(2016\)](#) as well, may provide another possible means to discern tin oxide types.

[Chirikure et al. \(2010\)](#) discuss tin oxide within tin smelting slags, distinguishing between incompletely dissolved grains of cassiterite and secondary cassiterite crystallised from the melt as skeletal laths or blocky crystals (and in one case dendrites and “spaghetti-like curved strands of cassiterite”). They further noticed the appearance of SnO₂ in tuyère slag (not treated in this paper), which they suggest entered there by re-oxidation of SnO vapour formed in the furnace. Both [Chirikure et al. \(2010\)](#) and [Mahé-Le Carlier et al. \(2001\)](#) provide comparative data on tin ore and smelting slag, with particular elements (e.g., Nb₂O₃ and Ta₂O₅) being of similar importance to those noted in the context of bronze making. Further references on tin smelting slag (similarly under-studied in comparison to ancient copper and iron smelting slag) are provided by these authors.

Beyond these examples, several publications cited earlier rely on comparable arguments for the interpretation of tin oxide crystals, though usually less explicitly. We therefore limit this literature review to these few examples, which illustrate the existing divergence on the interpretation of tin oxide crystals. The main issue here is that most publications rely on earlier interpretations of similar archaeological materials, while there is a lack of systematic experimental data (though some exists: e.g., [Dungworth, 2000](#), [Rovira, 2011–2012](#), [Rovira et al., 2009](#)) as a reference to interpret the highly varied archaeological evidence. Therefore, the experiments presented in this paper were conceived to provide, for the first time, a more systematic (though inevitably incomplete) overview of the range of tin oxide phases that may occur under different bronze production modes, as a more impartial guide towards their interpretation in archaeological case studies.

2. Material and methods

Experiments are developed to alloy bronze from a variety of starting products, under varying redox-conditions. Similarly, bronze, tin and cassiterite are heated under varying redox-conditions. To this end, the different starting products, summarised in [Table 1](#), are placed inside clay-lined graphite crucibles, and heated in a Lenton chamber furnace (Lenton T - Controller Type 3216). The raw products employed in these experiments are bronze coils, copper beads,² metallic tin³ and mineral cassiterite⁴; their composition is summarised in [Table 2](#) (all percentages are wt%, unless otherwise noted). Though the furnace does not allow for a fully controlled atmosphere, the redox-conditions within the crucibles are varied by the amount of charcoal used to cover the raw materials (where “min”, “med”, and “max” stand for a non-covering, thinly covering and thickly covering charcoal layer respectively).

The followed experimental procedure is illustrated in [Fig. 1](#):

- Graphite crucibles are lined with clay and heated for several hours at 100 °C to dry. This crucible lining (ca. 0.5 cm thick) eliminates possible interaction between the graphite crucibles and the charge, and is newly applied for each experiment.
- The weighed starting products are placed inside the crucibles and covered with charcoal (for “max” covered charges, charcoal is first stirred through and then added until the charge is fully covered). The crucibles are then placed inside the furnace and heated (in ca. 1.5 h) to 1150 °C. Once this temperature is reached, the furnace is turned off and crucibles are left to cool inside overnight (no casting was performed, which may constitute useful complementary future experiments).
- After removal from the furnace, the fired crucible lining easily detaches from the graphite crucibles, which can thus be reused for the next experiments.
- The crucible lining is then embedded in resin to maintain the original *in situ* structure of (sometimes fragile) bronze production remains within. After hardening, a cross-section of the crucible lining and its contents is made, and again embedded in a standard resin block.
- After hardening, the resin blocks are ground using increasingly fine abrasive paper and polished with diamond paste to 0.25 μm.
- The mounted sections are analysed by optical microscopy (Leica DM4500 P LED polarisation microscope) and, after carbon coating to ensure surface conductivity, scanning electron microscopy (SEM), with energy dispersive spectrometry (EDS). A JEOL 8600 Superprobe is used, operating at 20 kV, at a working distance of 10 mm, and with a live time of 50s. SEM-EDS (Oxford Instruments EDS attachment and INCA software) analysis is performed to obtain quantitative chemical compositions of particular phases (point-microanalysis) and larger areas.

The use of a clay lining⁵ allows the reuse of (expensive) graphite crucibles, but furthermore facilitates the sampling process outlined above. It additionally makes the experiments more comparable to their

² Both bronze coils and copper beads obtained from www.reactivemetals.com. Their composition, given in [Table 2](#), was verified by SEM-EDS: 4.2–4.6% Sn for the bronze coils (advertised as 4.5% Sn) and pure copper.

³ Both 99.96% pure granulated tin (AnalaR, BDH Chemicals Ltd., prod. No. 10281, composition verified by SEM-EDS omitted here) and tin previously smelted by the first author from Cornish cassiterite (“Sn (exp)”, procedure outlined by [Timberlake, 1994](#)) were used. Results using the latter “Butser tin” were omitted from the discussion, as their purity was found to be too variable (e.g., copper contamination, unreacted fragments).

⁴ This Cornish cassiterite was kindly provided by Dr. Simon Timberlake. Its composition was determined by SEM-EDS. A Si peak was noted in one of the bulk analyses, but could not be quantified: 0–0.4 wt% Si is below the detection limit (see Online Supplementary Materials for further details).

⁵ The clay is composed of ca. 20% alumina, 65% silica, 2.5% potash, 1% lime, 1.5% titania and 6% iron oxide (non-certified values, measured by SEM-EDS).

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