ARCHAEOMETALLURGY OF COPPER AND SILVER ALLOYS IN THE OLD WORLD

The production and processing of advanced materials, namely metals and alloys, began in the Old World about 8000 years ago and developed over many millennia, providing a lasting legacy for modern civilizations.

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Metals and alloys constitute an essential part of the development of societies from Neolithic times, and the earliest process metallurgy, melting and consolidation of native metals, may be traced back to about 6000 B.C. The importance of metals technology in ancient societies is shown by referring to the main periods of post-Neolithic prehistory as the Copper, Bronze, and Iron Ages[1]. Approximate dates for the beginnings of these technologies in the Near East areas are: copper (6000 B.C.), bronzes (3500 B.C.), and iron (1500 B.C.). However, recent data suggest that complex tin bronzes were smelted much earlier in the Balkans, around 4500 B.C.[2], but this technology was effectively lost after 4000 B.C.

Understanding process metallurgy in the ancient world is a major remit of archaeometallurgy. Over the last 50 to 60 years there have been international efforts to establish and promote scientific studies of (i) metallurgical processes and artifacts, from raw materials to final production, and (ii) by-products, tools, and equipment, e.g., slags, crucibles, and furnaces (Fig. 1).

These studies use a wide range of modern scientific methods and laboratory instruments to better understand the complex processes involved, and also the artifacts themselves and their eventual deterioration (especially corrosion) over the millennia. This latter aspect is directly linked to conservation and restoration techniques.

The difficulties that had to be overcome are well demonstrated by experimental archaeometallurgy, i.e., pyrometallurgical experiments to smelt metals from ores in ancient-style crucibles and furnaces. Even with modern scientific knowledge these experiments may be only partially successful and sometimes fail completely. Such experiments enable a veritable appreciation of the empirically derived skills of ancient metalworkers.

This article gives a brief overview of the production and processing of ancient bronzes and silver in the Old World, and also mentions post-processing problems including corrosion and embrittlement, owing to long-term burial before archaeological recovery.

ANCIENT COPPER ALLOYS

The first evidence of using native copper to make small and decorative objects comes from the Near East and Caucasus and is dated to about 8000 B.C.[1]. Processing native copper by melting and casting began around 6000 B.C., and reduction of copper ores (smelting) to derive copper began around 4000 B.C. It is important to note that the ores were mined from copper sulfide deposits, where the weathered upper layers consisted mostly of copper carbonates and oxide. These could be simply added to smelting crucibles and furnaces. However, continued mining reached the sulfide deposits, and these had to be oxidized (roasted) before smelting.

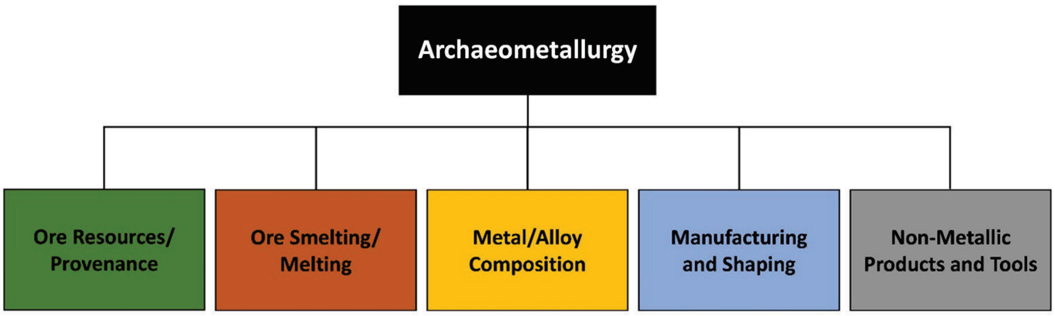

Fig. 1 — Schematic of the main aspects of archaeometallurgical studies. Adapted from Bayley et al.[3].

Early processing was done using crucibles containing crushed ores and charcoal, with forced airflow provided by bellows-powered blowpipes. Later on, crucible and hearth furnaces using forced air via tuyères provided more controlled conditions. Figure 2 is a schematic of a smelting furnace from the Near East Late Bronze Age (LBA: 1550–1200 B.C). Besides initial metal production, such a furnace could be used to remelt additions of other copper metal before tapping into clay or stone molds to cast ingots or artifacts, for example, vessels, tools, and ornaments.

Large "oxhide-shaped" copper ingots were widely used in Eurasia as trade items in the LBA[4], and these could be remelted with additions of tin or tin oxide (cassiterite), and possibly other alloying metals, to produce bronze ingots or cast artifacts including vessels, tools, weapons, and ornaments.

Near East Early Bronze Age (EBA: 3300–2100 B.C.) ingots were probably forged by cold-working rather than hot-working[5], and with intermittent annealing, depending on the metalsmith's experience with the materials and the required artifacts. This practice continued well into the Iron Age, beyond 1500 B.C. Hot-working would have gradually developed as an alternative, except for high-tin bronzes, because "hot shortness" (brittle cracking at high temperatures) would become increasingly likely with tin contents above 8 wt%[6].

ANCIENT BRONZES

The history of ancient bronzes is complex, spanning a "classic" period of more than 2000 years in Eurasia (3300–1200 B.C.). Many issues are still unresolved, despite extensive studies since the early 20th century. Perhaps the most important question is whether the presence of alloying elements in copper was always accidental or became intentional. Considering the three main types of bronzes, antimony bronze, arsenical bronze, and tin bronze, the evidence of intentional alloying for tin bronzes is incontrovertible. However, deliberate alloying with antimony and arsenic can be questioned[5,7], since these elements were often present in copper-bearing ores. On the other hand, analysis of Early Bronze Age slags from Iran shows that speiss, an iron-arsenic alloy, was probably added to copper ore or during remelting to obtain arsenical bronzes[8,9]. Also, although digressing here from the Old World, there is convincing evidence that the Andes region arsenical bronzes containing 0.5–2 wt% arsenic were intentionally produced from about 850 A.D. for cold-hammering into culturally desirable small implements and thin sheet materials[10].

Returning to Eurasia, two more important questions arise. Why did tin bronzes become the main type, largely replacing arsenical bronzes after 2500 B.C., and why did antimony bronzes almost disappear after 2000 B.C.[7]? Possible answers have been given, but there is no consensus. Firstly, antimony bronzes may have been supplanted because their lesser hardness, and hence lesser strength, made them unsuitable for tools or weapons. This could have resulted in a lack of demand and trade in favor of tin bronzes, though this is not (yet) known[7].

The more intriguing question is the predominance of tin bronzes over arsenical bronzes, beginning in the later EBA. There are three basic hypotheses: (i) tin bronzes were intentional alloys but arsenical bronzes were not; (ii) tin bronzes had superior mechanical properties; (iii) smelting arsenic-containing ores resulted in poisonous fumes that became recognized as a health hazard. The first hypothesis has been discussed already: intentional alloying to obtain Eurasian arsenical bronzes is a distinct possibility[8], and the Andean region study reinforces this[10]. The second hypothesis is disfavored by an extensive study and comparison of the mechanical properties of arsenical and tin bronzes[10]. There remains the possibility that smelting arsenical ores was abandoned in Eurasia owing to health concerns. However, arsenical bronzes were still being produced in the LBA (Fig. 3), *1000 years* after tin bronzes became predominant.

The majority of Near East tin bronzes have tin contents less than about 12 wt%, typically ranging from 5–10 wt% from about 3000 B.C.[4]. The earliest EBA alloys have lower tin contents, 1–3 wt%; and there are occasional exceptions, the high-tin alloys already mentioned. Hence most of the materials and artifacts would have had homogeneous single-phase microstructures after working and annealing, very different from the inhomogeneous as-cast structures (Fig. 4).

ANCIENT SILVER ALLOYS

Owing to native silver's scarcity, there is limited evidence of its direct use for artifacts, a few of which have been dated to 4300–4000 B.C.[11]. Silver was more abundant as a minor component in the ores of other metals, especially lead[12]. Beginning before 3000 B.C., lead obtained from smelting argentiferous lead ores was further processed by cupellation to extract the silver. This process became the primary source of ancient silver and silver artifacts, although some artifacts were obtained from direct smelting of silver ores[12].

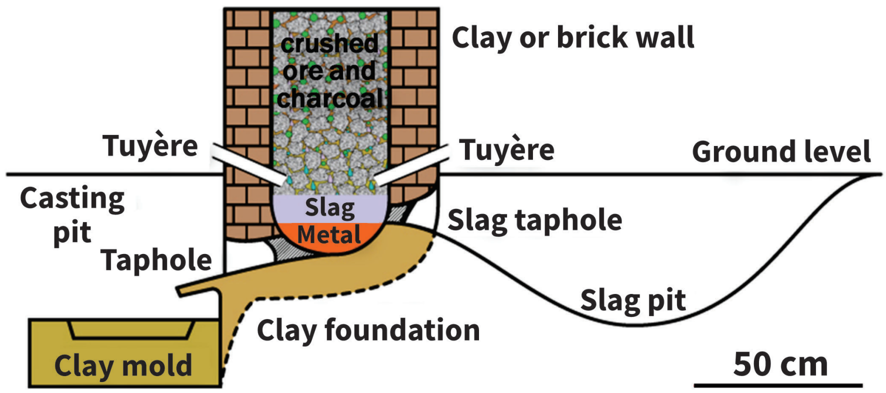

Fig. 2 — Schematic copper smelting furnace, Crete, Late Bronze Age. Adapted from Tylecote[4].

Cupellation was a multistage process employing three separate hearths. Figure 5 is a schematic of a first stage hearth for enriching smelted lead bullion. This was remelted to a high temperature using wood fuel. Bellows-powered tuyères oxidized the lead to litharge (PbO), which melts at 880°C, hence the need for a high temperature. The litharge drained via a surface groove and was discarded. More bullion was added until sufficient silver-enriched lead was obtained for the second stage. Then the enriched lead was transferred to a second hearth and again oxidized, but here the litharge was removed by dipping iron rods into it (before 1000 B.C., wooden poles) to form layered litharge cones on the rods. These rods were repeatedly removed, the litharge cones discarded, and the rods re-dipped. Eventually this second stage left a silver globule on the hearth. In the third stage, a number of globules were melted and further refined in another hearth to obtain ingots, the remaining PbO being absorbed by pores in the cupel wall.

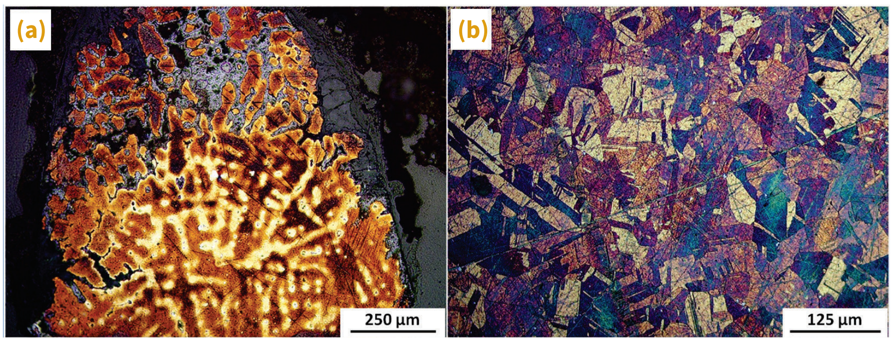

Fig. 3 — Metallographs of two binary Cu-As alloy artifacts from Iran. (a) An EBA as-cast axe head, 2.17 wt% As. (b) An LBA worked and annealed bowl, 2.10 wt% As.

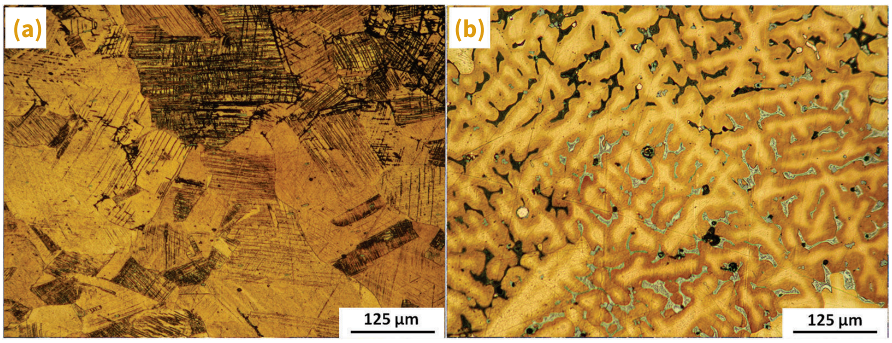

Fig. 4 — Metallographs of two binary Cu-Sn alloy artifacts from Iran. (a) An EBA worked and annealed vessel, 8.67 wt% Sn. (b) An Iron Age I as-cast tool, 10.83 wt% Sn. Note that (a) shows some retained cold-work, and (b) shows interdendritic (α + δ) eutectoid, shrinkage porosity and coring.

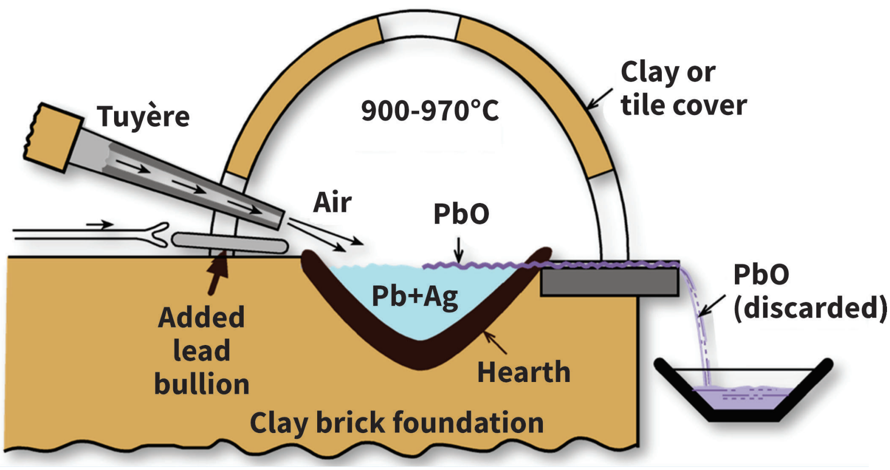

Fig. 5 — Schematic of Stage I cupellation about 500 B.C., Laurion, Greece. Adapted from Conophagos[13].

Cupellation is very effective in producing silver above 95% purity. It usually contains minor-to-trace amounts of copper, gold, bismuth, and lead (generally below 1 wt% for each), and traces of antimony, arsenic, tellurium, zinc, and nickel. Several studies have shown that copper contents above 0.5–1 wt% indicate deliberate additions, most probably to increase the strength and wear resistance in high-silver alloys, and also in larger amounts to make lower-quality artifacts and coins. Copper additions appear to have been done since about 3000 B.C.[14]. The artifacts themselves were commonly made from ingots by cold working with intermittent annealing, although cast silver objects were also produced. Many artifacts were high-quality thin-walled vessels with exquisite craftsmanship.

POST-PROCESSING PROBLEMS: CORROSION AND EMBRITTLEMENT

Unfortunately, many ancient bronze and silver artifacts have suffered corrosion and embrittlement damage owing to millennia of burial before recovery. An example from the famous high-silver Gundestrup Cauldron, dated to the 1st or 2nd century B.C., is given in Fig. 6. There are numerous publications on the burial damage, and they usually concentrate on conservation and restoration techniques but not on details of the damage. Basically, both ancient bronzes and silver may undergo both general corrosion and stress corrosion cracking (SCC), which is promoted by retained cold work and also external forces on thin-walled hollow artifacts (e.g., vessels and cups) during burial. The SCC damage is both intergranular and transgranular (along slip planes). Also, some silver artifacts show evidence of intergranular microstructural embrittlement, most probably due

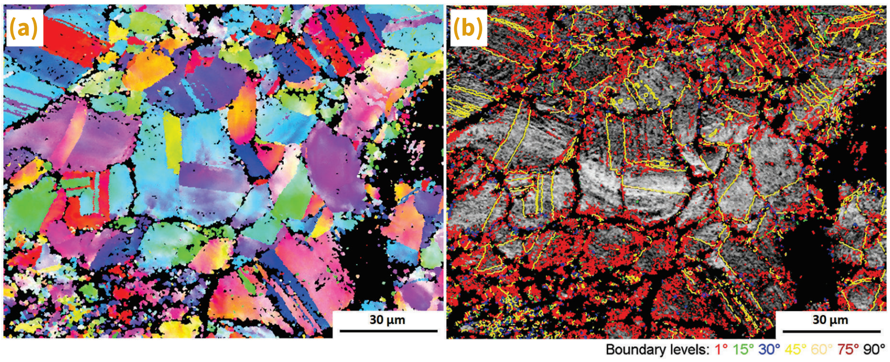

Fig. 6 — Electron back-scatter diffraction metallographs of corrosion damage in a sample from the Gundestrup Cauldron[15]. (a) Inverse pole figure color-coded map, showing equiaxed grains and annealing twins. (b) Boundary rotation angle map showing retained cold-work as dislocations (red) and deformation twins (narrowly spaced irregular yellow boundaries). The corrosion is preferentially associated with retained cold work and has been identified as stress corrosion cracking (SCC)[16].

to long-term segregation of lead, originally retained in solid solution after cupellation and working and annealing. **~AM&P**

Note: The authors recently prepared an article for a new (2022) edition of *ASM Handbook,* Volume 12, *Fractography,* which discusses the types of damage in ancient metals, including tin bronze and high-silver artifacts[17]. The implications of all these types of damage for conservation and restoration are discussed in the article.

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