Metallographic investigation and experimental replication of an Etruscan bronze mirror

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ABSTRACT: The use of copper alloys is known from ancient times and they were appreciated for several reasons: they are easy to cast, have a wide range of mechanical properties and appearance, and good resistance to corrosion. Most of these properties are affected by composition, and the desired properties could be obtained by the right balance of alloying elements and thermo-mechanical treatment. In particular, to obtain complicated shapes by hammering it was necessary to have a full understanding, perhaps empirical, of how to handle annealing to promote recrystallisation, which depends on both the tin content and the previous deformation of the metal. This study determines the composition and manufacturing process of an Etruscan bronze mirror in order to produce a facsimile.

Introduction

An experimental approach is fundamental to increase knowledge concerning an object and the quality of conservation procedures. Every object presents evidence of the habits and aesthetic tastes of a culture, and also of the technological advances in material culture, *ie* the empirical knowledge needed to manufacture it (Tylecote 1976). Due to the lack of ancient documents describing cultural and technical details other approaches have to be used. The application of modern metallography is a powerful tool to 'read' the information present in the microstructural features of an ancient metallic object (Pinasco *et al* 2007). However, this is often not enough to solve problems relating to specific technical challenges overcome by ancient artisans. The way then to answer questions such as 'How was this alloy worked as it is so rich in tin?' is to formulate theories that can be tested by experiments. Reproducing an object is also an opportunity for modern museology where the 'hands-on' experience for visitors, through a replica accompanied by a detailed technical sheet, is added value. If one ignores the final shape of the object, a sample having the same alloy composition and microstructural features should behave in the same way and can thus be used as a 'sensor' in a specific environment (*eg* indoors or inside a showcase) preventing damage to the original object.

Materials and methods

The mirror was found during excavations in the 1990s by Vincent Jolivet (Jolivet 2004) of the Ecole Française de Rome in the small Etruscan village of Musarna (Viterbo, Italy). It has a typical shape for the 4th–3rd centuries BC (Pinasco *et al* 2007; Carpino 2003; Panseri *et al* 1957) and is made of a single piece of metal with no joints or welded areas (Fig 1). The reverse of the mirror has an engraved picture while the front side is highly polished and has raised edges. The object is incomplete and covered by a thick, compact green patina of oxidized copper compounds (carbonates, silicates and, rarely,

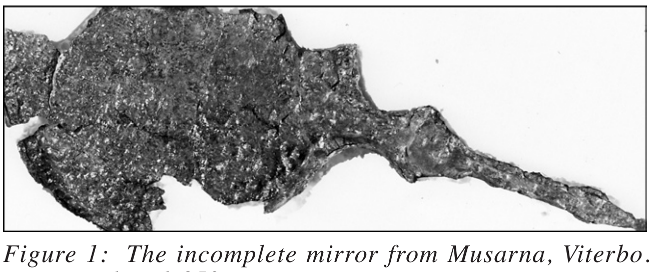

Figure 1: The incomplete mirror from Musarna, Viterbo. Maximum length 250mm.

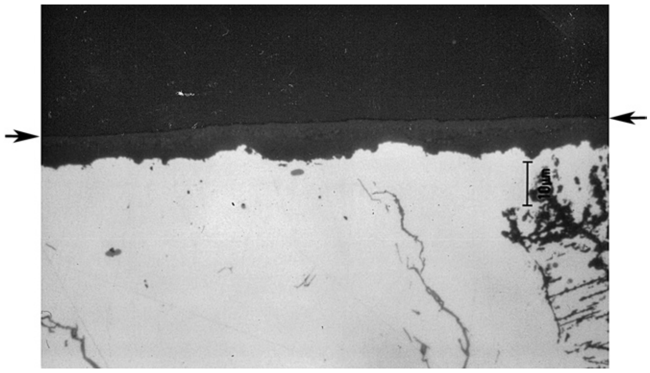

Figure 2: Unetched section of the mirror showing the thick surface patina. The arrows are at the surface. Scale bar: 10µm.

chlorides). The front is less corroded and has a smooth well-polished dark-green surface.

The study of the object had two aims, to know the nature of the metal and the processes by which it was manufactured. The methodologies used were those described by ASTM E 03-95, modified and adapted so they were appropriate for archaeomaterials (Pinasco *et al* 2007).

Samples from the mirror were studied by optical microscopy before and after etching, in order to characterize microstructural features, and by scanning electron microscopy coupled with EDX microanalyses to investigate inclusions, corrosion products and the chemical composition of the metallic matrix.

Characterization of the ancient alloy

The EDX analyses revealed that the alloy is a single phase α tin-bronze with 85wt% copper, 14wt% tin and less than 1wt% lead. Some copper sulphides (volume fraction well below 1%) with iron traces are homogeneously distributed in the metallic matrix. Optical metallography before chemical etching showed corrosion penetrating along the grain boundaries and, in some cases, being at the origin of cracks and fractures. The reflecting side, observed in cross-section, is covered by a thin and tough patina (Fig 2) with large areas unaffected by intergranular corrosion. The thickness of this surface layer is approximately 10µm and some lead enrichment has been found in it by EDX spectroscopy.

The microanalysis of the surface patina coupled with dark-field optical microscopy (Del Chiaro 1984) has allowed the identification of the corrosion products: red cuprous oxide and a mix of cuprous oxide and hydrated stannic oxide that appears yellow-to-brown depending on the Cu:Sn ratio (Piccardo 2000) are the main compounds at the reflecting surface, while at the edges and

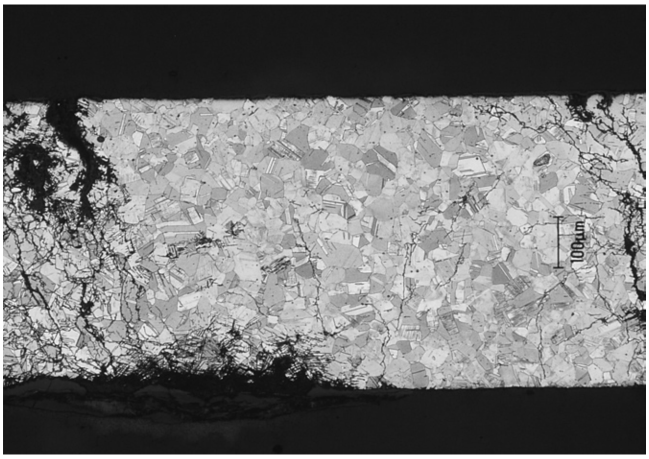

Figure 3: Etched cross section of the mirror showing homogeneous recrystallized structure with visible intergranular corrosion. Scale bar: 100µm.

on the engraved side there are carbonates (blue or green depending whether they are azurite or malachite) and, in some cracks, yellowish and transparent silicates.

After etching (with ethanol, HCl and $FeCl_3$), the microstructure appeared recrystallized with some localized cold-worked areas close to the surface (Fig 3). SEM images showed some rare and homogeneously-distributed (α+δ) eutectoid phases, lead inclusions and, as already mentioned, copper sulphide inclusions (Fig 4).

Sulphides as well as lead-rich inclusions (though the overall lead content was ≤1%) probably came from the ores smelted to provide the copper (Piccardo *et al* 2007; Heller 1996). The amount of lead found in the patina on the reflecting side seems to be due to some mechanical surface treatment (*eg* polishing or burnishing) to increase the brilliance and the reflectivity.

The metallurgical features described above are consistent

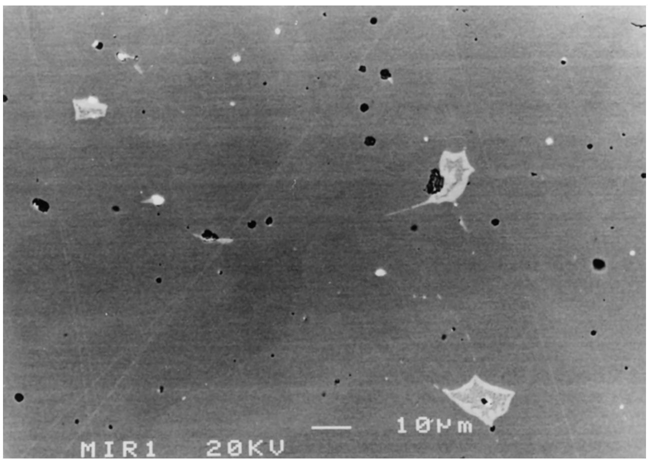

Figure 4: Backscattered SEM image showing sulphide inclusions (black), (α+δ) eutectoid second phase (pale grey) and small round lead-rich inclusions (white). Scale bar: 10µm.

with casting a shape close to the final one followed by several cycles of cold-deformation and annealing until the final shape is achieved. The high tin content, very close to the solubility limit of tin in copper (15.8wt% in the range 520–586°C (Saunders and Miodownik 1994)) and normally considered beyond the limits of workability, represents a clear sign of the developed skills of the craftsman, able to set up a manufacturing technique to shape and homogenise this alloy. This is the hardest alloy in α tin-bronze family, which is a positive point for an object thought to be a mirror and hence highly polished. The high tin content, however, forced the craftsman to keep the annealing temperature under 590°C, and the cooling treatment that followed had to be controlled to avoid any formation of a second phase. In fact, a bronze with 14wt% of tin annealed over 590°C is entering in the dual phase region where α and β phases are in equilibrium, while a too slow cooling rate under 300°C will produce the precipitation of δ-phase at the α grain boundaries and, in some cases, in the metallic matrix itself. In both cases the workability would be dramatically affected increasing the difficulties in metal forming. The cooling rate is an especially important parameter due to the fact that micro (or nano) precipitates of δ-phase will result in the increase of fragility of the whole alloy.

In early engineering handbooks (Altamayer and Guillet 1925) tin bronzes are treated as alloys having ‘inverse’ or ‘softening’ quenching, by which is meant ‘solubility quenching’, *ie* freezing a more malleable phase or a single-phase solid solution (Saunders and Miodownik 1994). The equilibrium diagram clearly shows that quenching from an annealing temperature between 500–600°C retains the metastable (at room temperature) α solid solution with highest tin content without the formation of hard and brittle phases such as δ and ε. It is worth remembering that α–bronzes are face-centred cubic crystals and therefore highly deformable while β-bronzes are body-centred cubic crystals, by their nature less deformable but still showing a certain hot workability, while δ and ε have more complex lattices (respectively $Cu_{41}Sn_{11}$ belonging to the space group F-43m, and Cu_3Sn belonging to the space group Cmcm (Shim *et al* 1996)).

Production of a facsimile

The experiment to produce a facsimile object is important in understanding the ancient manufacturing technology and the peculiarities due to the use of a borderline single-phase alloy (an α tin-bronze) at the highest tin content. The production of the facsimile followed these steps:

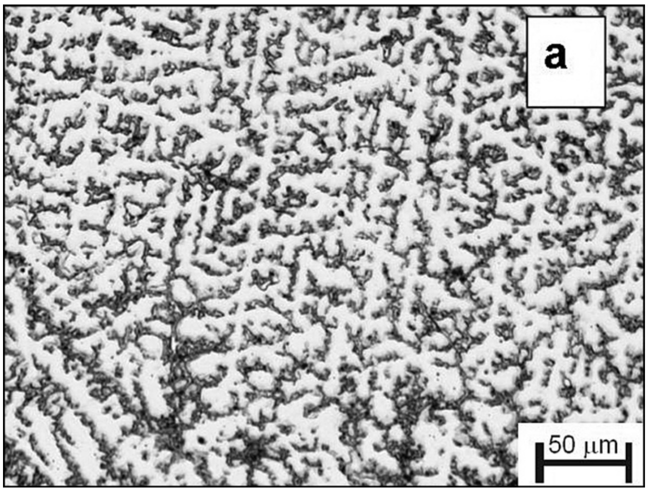

Figure 5: Etched cross section of as-cast facsimile.

- preparation of the alloy by casting in a refractory, terracotta-like mould
- several cycles of cold plastic deformation (by hammering) followed by annealing in an open charcoal fire
- quenching in water after every thermo-mechanical cycle.

The thermo-mechanical step could be successful only if accompanied by a ‘precise’ empirical evaluation of the main production parameters which were the annealing temperature and the amount of deformation produced by cold working. During the experiments it was possible to check the annealing temperature simply by observing the colour of the metal. To do this it was necessary to work in a dark place as every slight change in the shade of red means a temperature change. The empirical skill that associates colours with temperature can be rapidly acquired and it is still in use in some craft workshops. The degree of cold deformation is easily estimated by the well-trained craftsman’s ear, as the sound of hammering becomes sharper and more ringing the harder the metal becomes. Solubility quenching should be applied to the initial casting as soon as it is solid (Altamayer and Guillet 1925) to make it ready for the first cycle of mechanical deformation. Figure 5 shows the as-cast material quenched from around 600°C with some β-phase present. The β-phase has a cubic lattice (Saunders and Miodownik 1994) and so is able to deform in a similar way to the α solid solution. Its presence, as shown in previous studies (Piccardo *et al* 2004), is thus less critical than other secondary phases in the first stage of shaping.

After a first cycle of hammering and annealing at 550°C followed by quenching, the microstructure still contains some residual β-phase dispersed in the α-phase matrix and not transformed (Fig 6). From the second

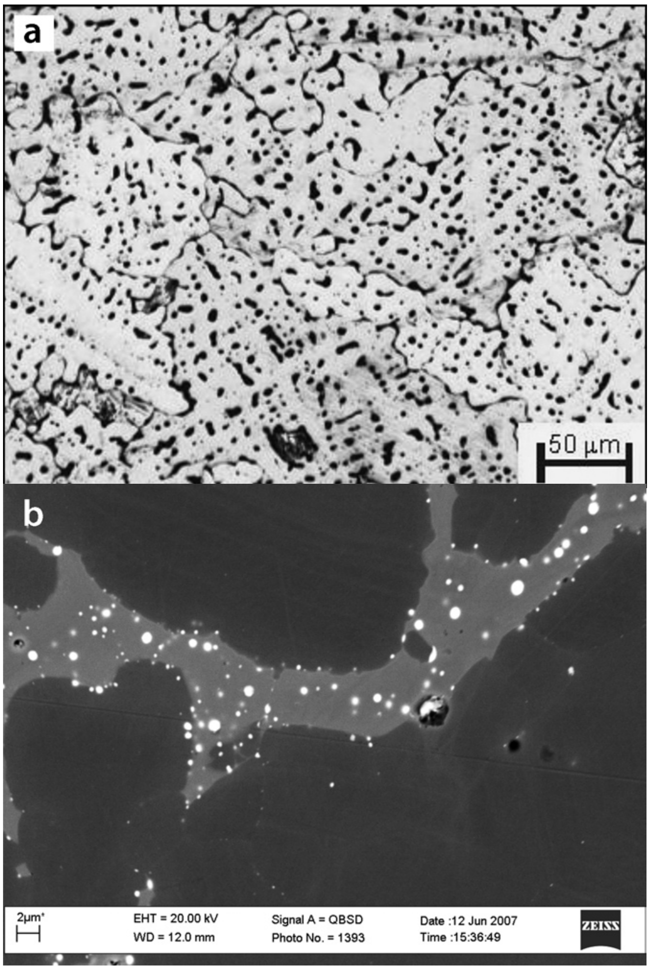

Figure 6: a) Optical image of etched cross section of facsimile after the first cycle of hammering and annealing at 550°C followed by quenching, showing large grains still recalling the primary structure and with a dark second phase; b) Backscattered SEM image showing the second phase (pale grey), confirmed by EDX analyses and XRD as Cu-Sn β-phase. The white spots are lead-rich inclusions.

cycle the alloy is rapidly evolving into a nearly homogeneous solid solution with a reduced volume fraction of β-phase (Fig 7). Figure 8 shows that after the last cycle of deformation and annealing, the metallic matrix is homogeneous and recrystallized with a few traces of (α+δ) phase. To obtain a harder and easier-to-polish material, the last annealing step should be followed by slow cooling which transforms any β-phase into the (α+δ) eutectoid.

Conclusions

It has been possible to characterise an Etruscan mirror and to suggest a production methodology consistent with its structure. The following details have been identified:

- The β-phase is confirmed as being more readily deformable than the (α+δ) eutectoid: however, the original casting must be water quenched.

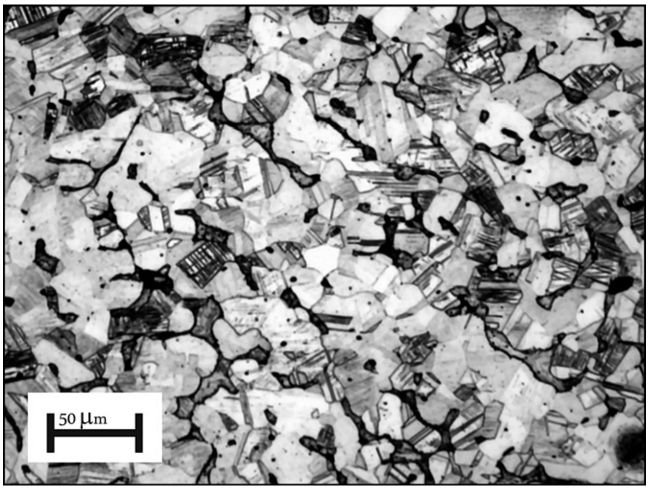

Figure 7: Etched cross section of facsimile after several cycles of hammering and annealing followed by quenching.

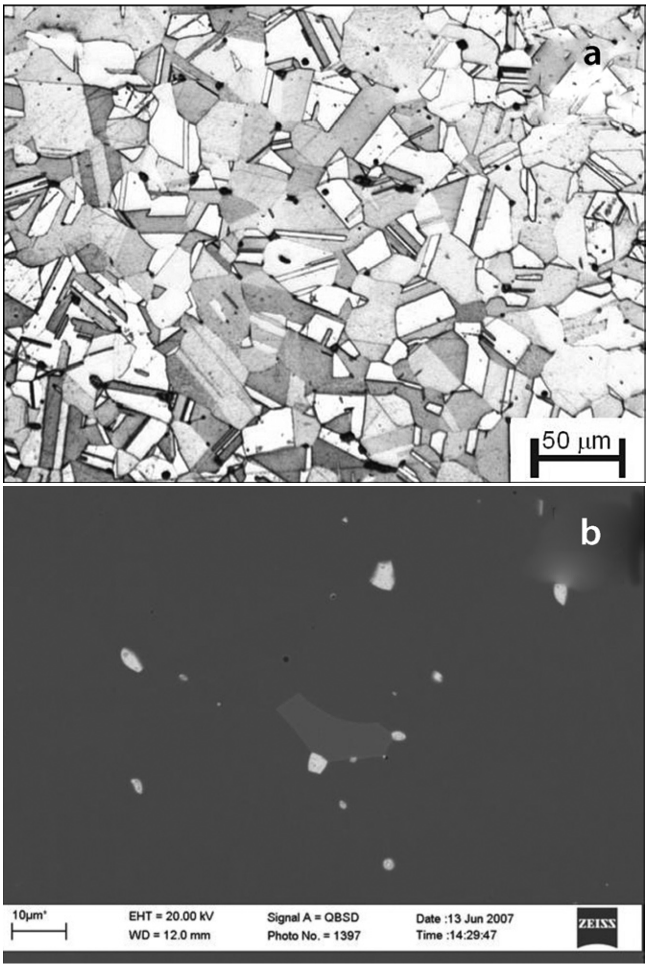

Figure 8: a) Optical image of etched cross section of facsimile after the final cycle of hammering and annealing, showing polygonal well-recrystallized α grains with black lead-rich inclusions; b) Backscattered SEM image showing lead-rich inclusions (white) and residual β-phase (grey) that would transform into (α+δ) eutectoid if the cooling rate was low.

- A single phase, or close to single phase, α-bronze with tin content up to 15wt% is suitable for shaping by cold working.

- The control of temperature is very important and must be in the range 500–600°C, in order to avoid second phase formation.
- The ideal temperature would be 550°C±10°C. Higher temperatures risk producing new β-phase instead of increasing tin solubility in the α-phase. Lower temperatures result in slowing down those annealing phenomena driven by diffusion rate (*eg* recrystallization, homogenization) and then require an increase in the treatment time with other negative consequences (*eg* excessive grain growth)
- Water quenching should follow every annealing treatment; this solubility quenching will stop the precipitation of brittle (α+δ) eutectoid.

Once all of those parameters are taken into account the craftsman's skill is what makes the difference but it is clear that all compositions in the range of α tin-bronzes can be shaped by cold deformation.

Further studies are being carried out in order to understand the influence of alloying elements such as lead on the kinetics of formation of second phases and thus on the manufacturing techniques needed to obtain the desired object.

Acknowledgments

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