MATERIALS CHARACTERIZATION 90 (2014) 173–184

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# Microstructures of ancient and modern cast silver–copper alloys

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ARTICLE DATA

*Article history:*
Received 3 August 2013
Received in revised form
13 December 2013
Accepted 27 January 2014

*Keywords:*
Sterling silver
Castings
Precipitation
Twins
EBSD
TEM

ABSTRACT

The microstructures of modern cast Sterling silver and of cast silver objects about 2500 years old have been compared using optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray microanalysis (EDX) and electron backscatter diffraction (EBSD). Microstructures of both ancient and modern alloys were typified by silver-rich dendrites with a few pools of eutectic and occasional cuprite particles with an oxidised rim on the outer surface. EBSD showed the dendrites to have a complex internal structure, often involving extensive twinning. There was copious intragranular precipitation within the dendrites, in the form of very fine copper-rich rods which TEM, X-ray diffraction (XRD), SEM and STEM suggest to be of a metastable face-centred-cubic (FCC) phase with a cube–cube orientation relationship to the silver-rich matrix but a higher silver content than the copper-rich β in the eutectic. Samples from ancient objects displayed a wider range of microstructures including a fine scale interpenetration of the adjoining grains not seen in the modern material. Although this study found no unambiguous evidence that this resulted from microstructural change produced over archaeological time, the copper supersaturation remaining after intragranular precipitation suggests that such changes, previously proposed for wrought and annealed material, may indeed occur in ancient silver castings.



## 1. Introduction

Cast silver alloyed with copper has been used from at least the third millennium BC, for making both functional and decorative objects, but, in contrast to wrought silver alloys, their microstructures have been very little studied. It is important to our understanding of the history of these objects to know whether twin-like structures and surface oxidation layers, visible optically in some ancient cast silver objects, result from the manufacturing process, or from subsequent exposure to fire. More particularly, we need to know if they also show age-related microstructural changes. Almost all archaeological silver objects other than coins are hypoeutectic, and a significant proportion is close to the Sterling composition of 7.5% Cu by weight. This study aimed to clarify the morphology and nature of the phases present in cast silver–copper alloys close to the composition of Sterling silver, both soon after casting and after a very long-term exposure at ambient temperatures, and to determine if there are microstructural features of cast silver alloys that can unambiguously be attributed to age.

Objects made from silver alloyed with up to 10% Cu are well known to age-harden by the precipitation of copper, because of the difference in its solid solubility between the typical annealing temperatures of up to 700 °C (7%) and room temperature (<1%). This age-hardening has been well studied

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1044-5803/$ – see front matter 
http://dx.doi.org/10.1016/j.matchar.2014.01.028

in wrought, annealed and quenched pure binary Ag–Cu alloys [1–10]. Both continuous precipitation and discontinuous precipitation (DP) (classified on the basis of transformation mechanism not morphology) have been of interest and there have been many studies measuring DP growth rates at different temperatures mostly above 200 °C (e.g. [11]). The DP commonly takes the form of cellular 'colonies' growing away from grain boundaries [12–14], observed (by TEM) in homogenised and quenched Sterling silver aged at 200–500 °C [9] to consist of fine rods of Cu-rich β phase surrounded by Ag-rich α. At lower ageing temperatures the colonies often appeared finely mottled or structureless rather than lamellar [14].

Homogeneous precipitation occurs alongside DP and hardness measurements [15], differential scanning calorimetry [14,16], dilatometry [14], and resistivity measurements [10,16] have indicated the formation of two metastable precipitates, but no continuous β precipitation prior to DP. During ageing at low temperatures (<175 °C), homogeneous precipitation initiates by the formation of Cu-rich zones, which subsequently lose coherency to form intermediate precipitates as growth proceeds [8,9,17]. On the basis of changes in physical properties, it is generally reported, (e.g. [4]), that, at temperatures >175 °C, intermediate precipitates form directly. However, streaking in TEM diffraction patterns, interpretable as due to the presence of zones, has been reported [8] after very short ageing times at 300 °C.

Schweizer and Meyers [18] suggested using DP of copper at silver grain boundaries in wrought silver alloys as an indicator of historic age but it was later shown [19] that, with suitable heat treatments, it is possible to simulate some of these morphologies in modern wrought and annealed Britannia silver (Ag–4.16% Cu). More recently Wanhill and co-workers [20,21] have concluded that DP cannot be used to determine the age of silver objects but it may be evidence that age-related changes in microstructure can occur. The idea that DP can be related to historic age has, however, not previously been tested in cast silver alloys. One aim of this study was to find if there is any evidence of DP or of grain boundary migration in either ancient or modern cast silver alloys.

During cooling of a Ag–Cu alloy casting, cored Ag-rich α dendrites form from the melt, and at 779.4 °C eutectic solidifies in between. Quenching produces both many more excess vacancies and a higher supersaturation of Cu, so precipitation in cast Ag alloys might be expected to differ significantly from that reported in experiments on wrought Ag alloys. Studies of the cast alloys are hindered by the very fine scale of the precipitation which forms within the grains over a broad range of cooling rates. This challenges the resolving power of optical methods, while the use of either X-ray methods or TEM poses significant experimental difficulties because of the small samples of ancient material available for examination. The work presented here used a combination of SEM, EBSD, EDX, TEM, STEM and OM to explore the range of microstructures represented in cast silver from archaeological contexts, and compare them with those observed in modern cast Ag alloys, with the aim of both improving our understanding of precipitation in these alloys, and of finding out if this can provide information on the age of the artefact.

## 2. Materials and Methods

### 2.1. Modern Sterling Silver

Modern Sterling silver was studied in the form of runners and sprue from lost wax castings, made at a sculpture foundry, into plaster moulds (so that the cooling rates were similar to those of ancient objects cast into clay). Both vacuum cast and traditionally cast material were examined, and samples were taken from the cup end, intermediately, and from the casting end, of runners and sprues of different sizes. Both longitudinal and transverse sections were examined.

### 2.2. Ancient Silver

Samples were taken from a range of cast silver artefacts from the eastern provinces of the Achaemenid Empire (Eastern Iran and Western Afghanistan) dating from 6th–4th century BC. Their compositions, as determined by electron probe microanalysis, are shown in Table 1. Images of the ancient objects are available as Supplementary material in the online version of this article.

### 2.3. Methods

Samples were given a conventional metallographic preparation to a 1 μm polish, then etched with ammoniacal hydrogen peroxide (17 ml $NH_4OH$, 3 ml 30% $H_2O_2$, 10 ml $H_2O$). Specimens for SEM and EBSD examinations were more lightly etched than those for OM, and were subsequently given a light C coating, before examining in a Zeiss Supra™ 55VP FEGSEM with an EDAX Genesis 4000 Energy Dispersive X-ray (EDX) spectrometry system and an Oxford Instruments NordlysF EBSD camera. The EBSD data acquisition and post-processing were carried out using HKL fast acquisition 5.11 and Channel-5

**Table 1 – Analyses of archaeological cast silver objects studied (all concentrations in wt.%).**

| Sample | Fe | Co | Ni | Cu | Zn | As | Sb | Sn | Ag | Bi | Pb | Au | S | Al | Si | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R2339/mean | 0 | 0 | 0.01 | 8.49 | 1.19 | 0 | 0 | 0 | 90.07 | 0.02 | 0.05 | 0.04 | 0.06 | 0.03 | 0.03 | 0.01 |
| R2970/mean | 0.01 | 0.01 | 0.02 | 8.26 | 0.01 | 0.01 | 0 | 0 | 91.55 | 0.01 | 0.09 | 0.03 | 0.01 | 0 | 0 | 0 |
| R2967/mean | 0.01 | 0 | 0.01 | 21.86 | 0.02 | 0.01 | 0 | 0 | 78 | 0.01 | 0.05 | 0.03 | 0 | 0 | 0 | 0 |
| R2968/mean | 0.01 | 0 | 0 | 12.48 | 0.02 | 0.01 | 0 | 0 | 87.35 | 0.02 | 0.07 | 0.02 | 0.01 | 0 | 0 | 0 |
| R2969/mean | 0.01 | 0.01 | 0.01 | 10.08 | 0.02 | 0 | 0 | 0 | 89.73 | 0.01 | 0.1 | 0.01 | 0 | 0.01 | 0 | 0 |
| R2971/mean | 0.01 | 0.01 | 0.01 | 7.25 | 0.02 | 0.01 | 0 | 0 | 92.62 | 0.01 | 0.04 | 0.01 | 0 | 0.01 | 0 | 0 |
| R2972/mean | 0.01 | 0 | 0.01 | 10.35 | 0.01 | 0.01 | 0 | 0 | 89.47 | 0.01 | 0.11 | 0.01 | 0 | 0 | 0 | 0 |
| R2978/mean | 0 | 0.01 | 0 | 12.79 | 0.01 | 0.01 | 0 | 0 | 86.97 | 0 | 0.03 | 0.17 | 0 | 0 | 0 | 0 |