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ABSTRACT

Ancient silver may become brittle and damaged owing to long-term corrosion and changes in the microstructure. Recognition and determination of corrosion-induced and microstructurally-induced embrittlement, and also their synergy, are important for restoration and conservation of ancient and historic silver. The types of embrittlement are described and illustrated, using examples of ancient and historic silver artefacts, including the famous Gundestrup Cauldron, a masterpiece of European Iron Age silverwork. In particular, the use of automated Electron BackScatter Diffraction (EBSD) enables improved analysis and assessment of corrosion-induced embrittlement. The knowledge obtained from detailed investigations is helpful not only in determining the best ways to restore and conserve embrittled silver objects, but also in defining the possible extent of the embrittlement problem. This is illustrated by a straightforward statistical analysis.

Nationaal Lucht- en Ruimtevaartlaboratorium
National Aerospace Laboratory NLR

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Ancient silver may become brittle and damaged owing to long-term corrosion and changes in the microstructure. Recognition and determination of corrosion-induced and microstructurally-induced embrittlement, and also their synergy, are important for restoration and conservation of ancient and historic silver. The types of embrittlement are described and illustrated, using examples of ancient and historic silver artefacts, including the famous Gundestrup Cauldron, a masterpiece of European Iron Age silverwork. In particular, the use of automated Electron BackScatter Diffraction (EBSD) enables improved analysis and assessment of corrosion-induced embrittlement. The knowledge obtained from detailed investigations is helpful not only in determining the best ways to restore and conserve embrittled silver objects, but also in defining the possible extent of the embrittlement problem. This is illustrated by a straightforward statistical analysis.

1 INTRODUCTION

Ancient metallic objects give rise to many questions. The basic questions of identity, provenance and authenticity are generally answered by Classical Archaeology, though uncertainties can remain. More detailed questions often require Archaeometallurgy, a discipline that has expanded greatly over the last decades. Table 1 lists many of the topics and questions that archaeometallurgists may be called upon to consider and answer.

The present paper considers a specific problem, the embrittlement of ancient silver. This might seem very restricted, but a comprehensive treatment of this problem involves all of the topics and most of the questions in table 1.

Ancient silver can be embrittled by long-term corrosion and microstructural changes[1-10]. There are two basic types of embrittlement, corrosion-induced and microstructurally-induced. These are able to act synergistically, resulting in a derivative third type.

The types of embrittlement have recently been discussed at length[8-10], and will be reviewed in section 2. This is followed by three case histories, widely separated in provenance: the famous Gundestrup Cauldron, a masterpiece of European Iron Age silverwork; an Egyptian silver vase from the Ptolemaic period; and a Byzantine paten circa 600 AD.

The knowledge gained from detailed examination of such ancient and historic artefacts can be important in determining the best ways to restore and conserve embrittled silver objects. The results of the case histories can also be combined with a straightforward statistical analysis of the chemical compositions of many ancient silver objects to enable some general statements about the extent of silver embrittlement.

2 TYPES OF EMBRITTLEMENT

2.1 Corrosion-induced embrittlement

Corrosion-induced embrittlement is due to several forms of selective corrosion. Intergranular corrosion is the most commonly reported. This can occur in mechanically worked and annealed objects, which constitute the majority. Interdendritic corrosion can occur in castings, which are uncommon, especially in the Old World.

Corrosion along slip lines and deformation twin boundaries can occur in objects that have not been annealed after (final) mechanical working, which includes striking a coin[1] and decorating by chasing and stamping[7]. Inside the metal these kinds of corrosion

Table 1 Archaeometallurgical topics and questions

• **Further identification and provenance**			
• metal / alloy compositions		• origins of metals and ores	
• **Manufacturing and craftsmanship**			
• fabrication methods		• choices of methods	
• **Damage assessment**			
• deformation	• corrosion	• embrittlement (cracks)	• previous restorations
• **Restoration and conservation**			
• methods			
• **Authenticity checks**			
• genuine	• modern fake	• ancient fake	

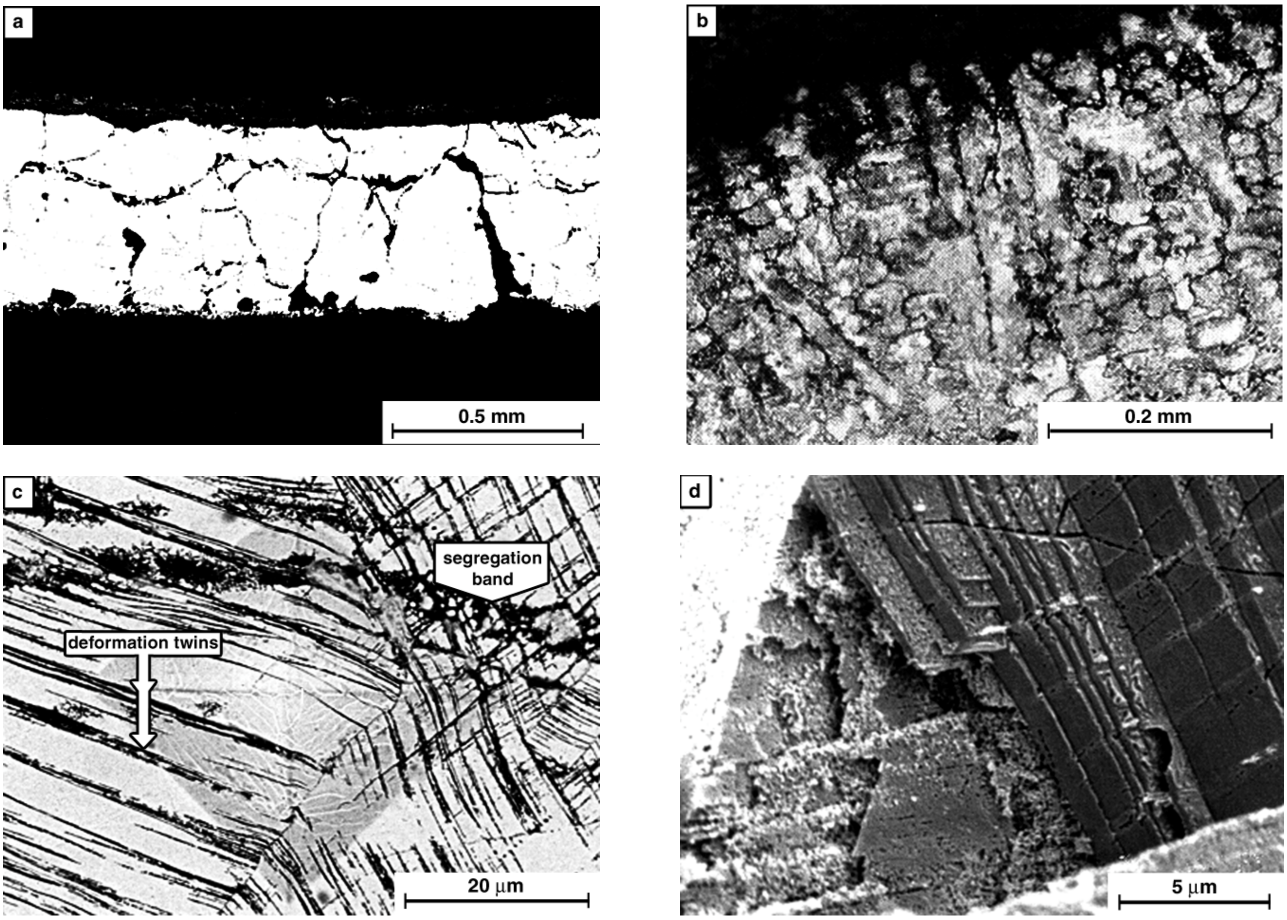


Fig. 1 Selective corrosion of high-silver-content ancient silver: (a) intergranular corrosion[3], (b) interdendritic corrosion[11], (c) corrosion along slip lines, deformation twin boundaries and segregation bands[7], and (d) crystallographic fracture due to corrosion along slip lines and deformation twins[7]

can lead to additional corrosion along segregation bands. These bands are the remains, modified by working and annealing, of solute element segregation (coring) and interdendritic segregation that occurred during solidification of an ingot or cupelled button.

Figure 1 illustrates the kinds of selective corrosion. The examples are eclectic: a Roman cup[3], a Sican tumi[11], and an Egyptian vase[7]. Intergranular corrosion is attributed partly to low-temperature segregation of copper[2,3,6]. This segregation, called discontinuous or cellular precipitation, sometimes causes the grain boundaries to appear meandering, as will be shown in section 3. Interdendritic and segregation band corrosion are consequences of high-temperature segregation of copper during metal solidification. Corrosion along slip lines and deformation twin boundaries is due to locally high strains and possible long-term segregation of solute or impurity elements to the highly strained regions.

2.2 Microstructurally-induced embrittlement

Microstructurally-induced embrittlement is seen to be characterized by brittle intergranular fracture, with sharply defined cracks and grain boundary facets, as shown in figure 2. Note the bodily displaced grain: this is a characteristic of severe embrittlement.

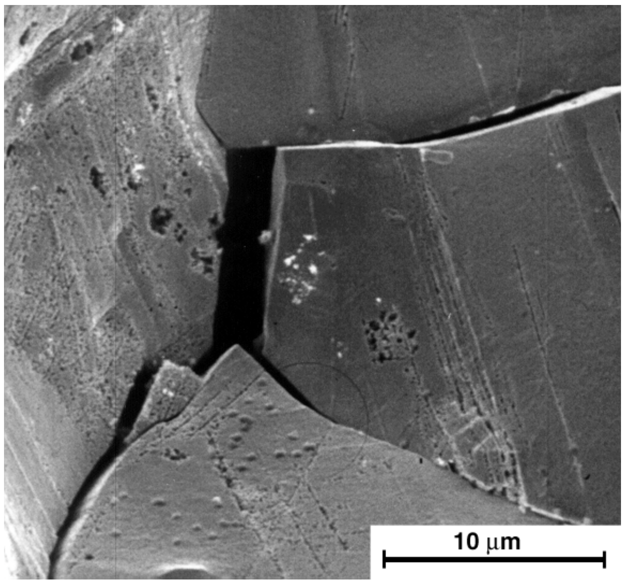


Fig. 2 Brittle intergranular fracture (microstructurally-induced embrittlement) in an Egyptian vase[7]

The embrittlement is most probably a consequence of long-term low-temperature ageing, whereby an impurity element, or elements, segregates to grain boundaries. The available evidence indicates lead to be the most likely perpetrator[1,8], though this has yet to be verified directly. Other impurity elements might be involved, notably bismuth[8].

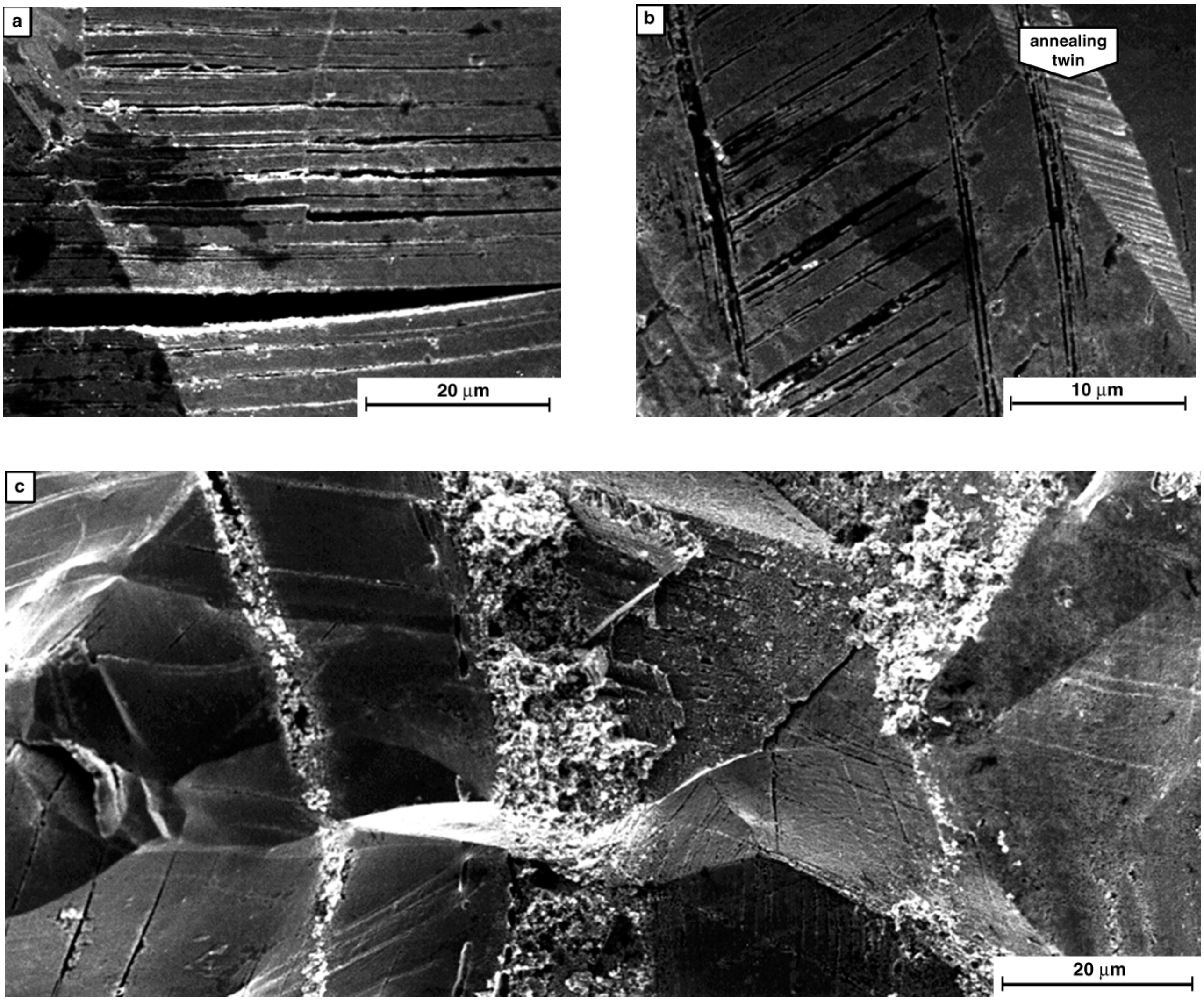


Fig. 3 Examples of synergistic embrittlement: (a) corrosion (causing fracture) along slip lines intersecting grain boundary facets, (b) corrosion along deformation twin boundaries intersecting a grain boundary, and (c) corrosion along segregation bands intersecting grain boundary facets[7]

2.3 Synergistic embrittlement

Figure 3 gives examples of synergistic embrittlement. Corrosion along slip lines, deformation twin boundaries and segregation bands can result in cracks. These cracks can then initiate fracture along microstructurally embrittled grain boundaries – which may fracture anyway, though less easily – under the action of external loads. In turn, the grain boundary fractures expose more slip lines, deformation twins and segregation bands to the environment and increase the opportunities for corrosion.

3 CASE HISTORIES

3.1 The Gundestrup Cauldron

Figure 4 shows the reassembled Cauldron, which is the largest surviving silverwork from the European Iron Age, dating to the 2nd or 1st century BCE. Owing to its size, high quality workmanship and iconographic variety, the Cauldron has been the subject of many studies, particularly its origin, which is still controversial.

Fig. 4 The Gundestrup Cauldron

The Cauldron consists of twelve plates and a bowl, all of 95-98 % silver. Chemical analyses show copper as the main alloying (or impurity) element.

3.1.1 Analysis technique: EBSD

Four small metallographic samples from different parts of the Gundestrup Cauldron were lent to the NLR by Peter Northover, Oxford University. The samples were examined using a Field Emission Gun Scanning Electron Microscope (FEG-SEM) combined with automated Electron BackScatter Diffraction (EBSD) equipment.

EBSD is a powerful technique for microstructural analysis, providing many options. For the Gundestrup Cauldron samples the following options were found to be of most use[12]:

- Inverse pole figure (IPF) colour-coded maps.
- Boundary rotation angle maps.
- Coincidence site lattice (CSL) maps.

Figures 5-9 illustrate the EBSD analysis results, which fall into two categories:

(1) *Sample 366*. This sample was essentially annealed and virtually free of corrosion. The most significant results were a random microtexture, figure 5a, and extensive grain boundary precipitation of copper, giving the grain boundaries a meandering appearance, as in figure 5b. The details in figure 6 prove it to be discontinuous precipitation[13-15]. The precipitate was finely mottled and had widths up to 7 μm. These characteristics are important, as will be discussed in section 5.

(2) *Samples 361, 363, 365*. These samples contained increasing amounts of remanent cold-deformation and corrosion damage. In figures 7-9 the remanent cold-deformation is visible as red regions (slip) and irregular yellow boundaries (deformation twins). The corrosion damage is visible as black regions, representing mainly intergranular cracks but also transcrystalline cracks (best seen in figure 9a). However, there was no evidence of discontinuous precipitation.

3.1.2 Discussion of EBSD results

The differences between sample 366 and samples 361, 363 and 365, with respect to remanent cold-deformation, corrosion and discontinuous precipitation, are remarkable for two reasons:

(1) Although the link between remanent cold-deformation and corrosion damage was noted previously[7], the present results indicate that cold-deformation was primarily responsible for corrosion, while extensive discontinuous precipitation was innocuous. This is notable because the eminent metallurgist Cyril Stanley Smith took the view that grain boundaries along which discontinuous precipitation had occurred seem to be highly susceptible to corrosion[2]. On the other hand, the present results are consistent with the experience of Peter Northover[16], who observed intergranular corrosion and cracking in ancient Bactrian silver despite copper contents less than 1 %, which is almost certainly too low for discontinuous precipitation to occur[8].

(2) There is a possible, or probable, link between remanent cold-deformation and the occurrence of discontinuous precipitation. Experiments have shown that cold-deformation can reduce the early growth rate of discontinuous precipitation in silver-copper alloys at elevated temperatures, and this could be due to deformation-induced continuous precipitation within the grains[17]. A similar effect may have occurred in samples 361, 363 and 365, even to the extent that discontinuous precipitation was prevented. However, verification of this will require transmission electron microscopy (TEM).

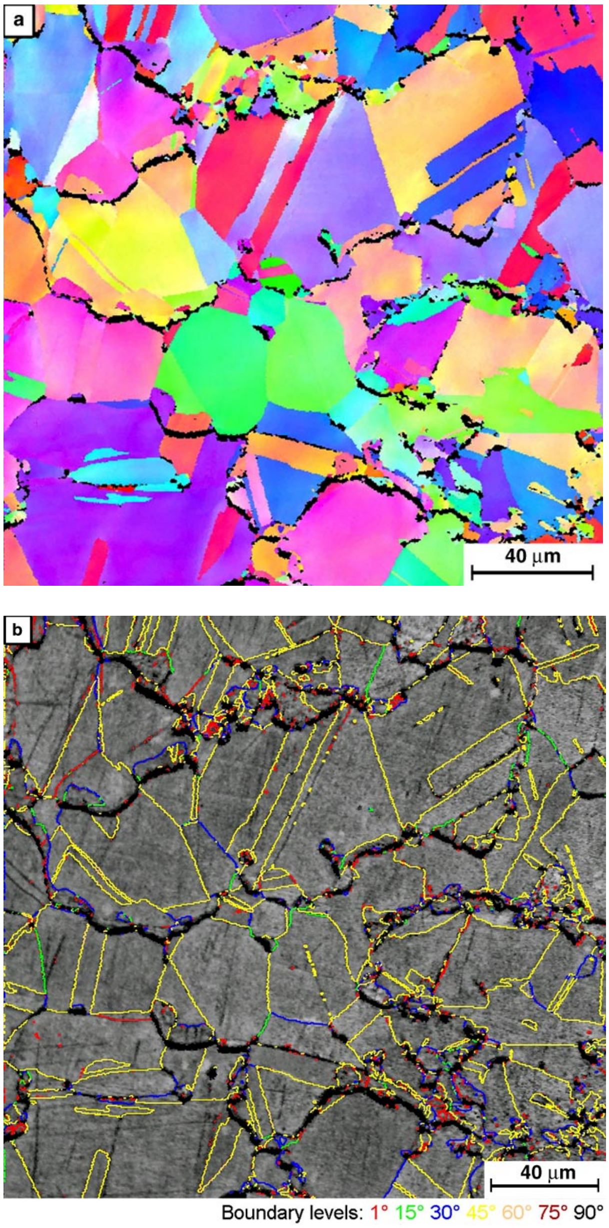
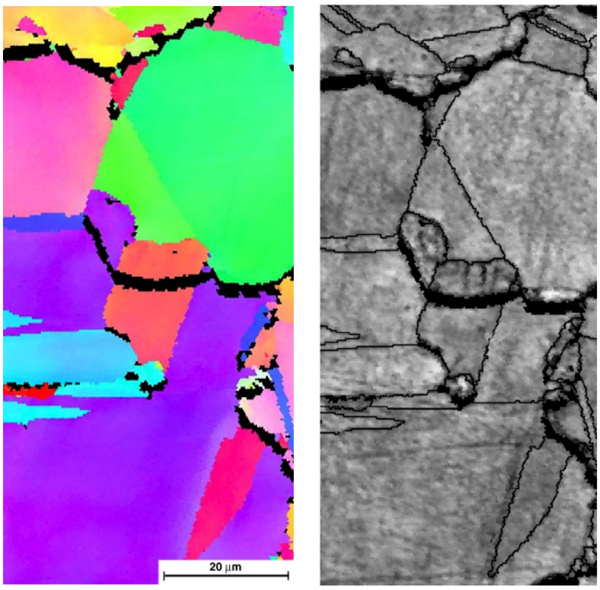
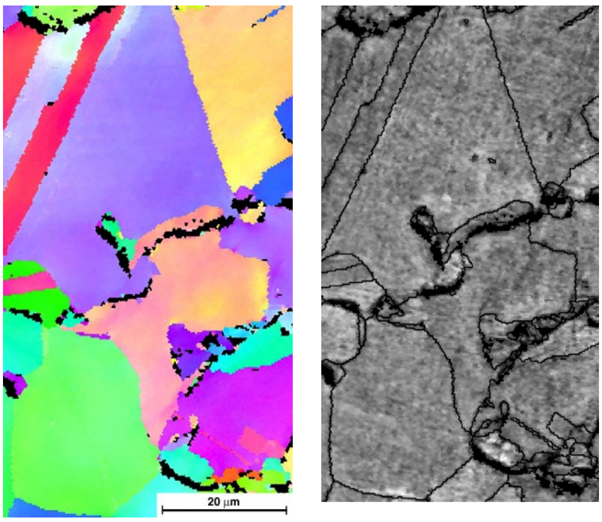


Fig. 5 IPF colour-coded map and boundary rotation angle map for Gundestrup Cauldron sample 366. The yellow-coded boundaries are mainly annealing twins



Precipitate behaviour
- nucleation at original "green" grain boundary
- growth into "green" grain, changing its lattice orientation to that of the contiguous grain having the "purple" matrix and "reddish-brown" annealing twin



Precipitate behaviour
- separate nucleations at original grain boundary between "purple" and "pink" grains
- growth in opposing senses: one nucleation into the "pink" grain, changing its lattice orientation to that of the contiguous "purple" grain; one nucleation into the "purple" grain, changing its lattice orientation to that of the contiguous "pink" grain

Fig. 6 Details of precipitate nucleation and growth in Gundestrup Cauldron sample 366

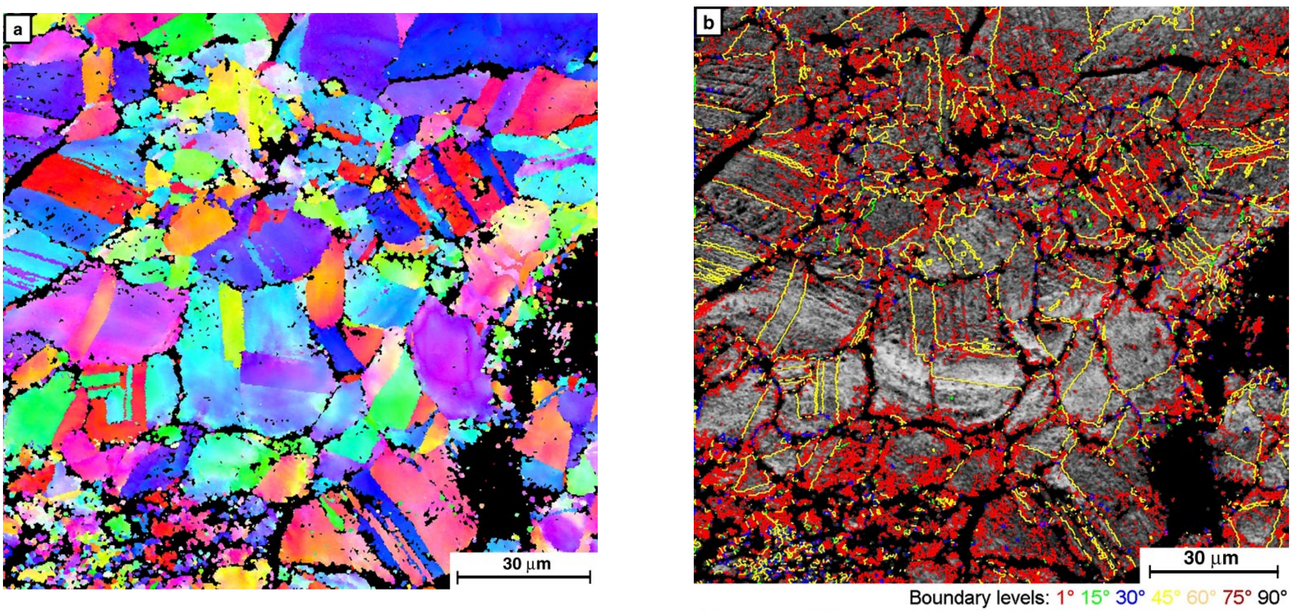


Fig. 7 IPF colour-coded map and boundary rotation angle map for Gundestrup Cauldron sample 361

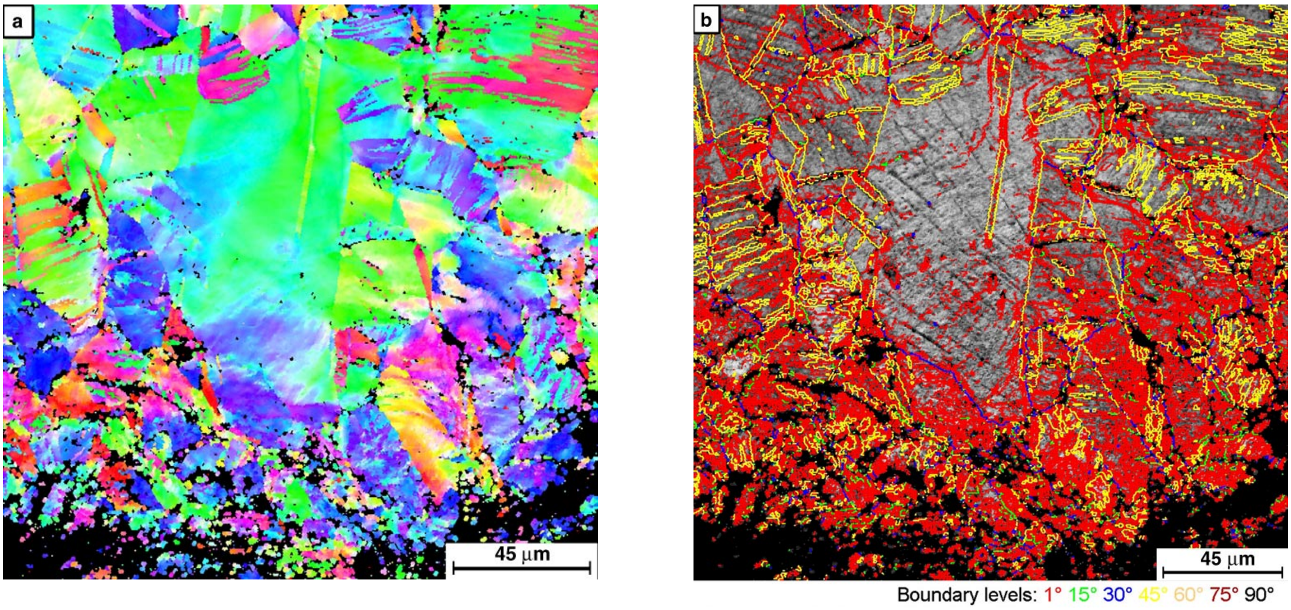


Fig. 8 IPF colour-coded map and boundary rotation angle map for Gundestrup Cauldron sample 363

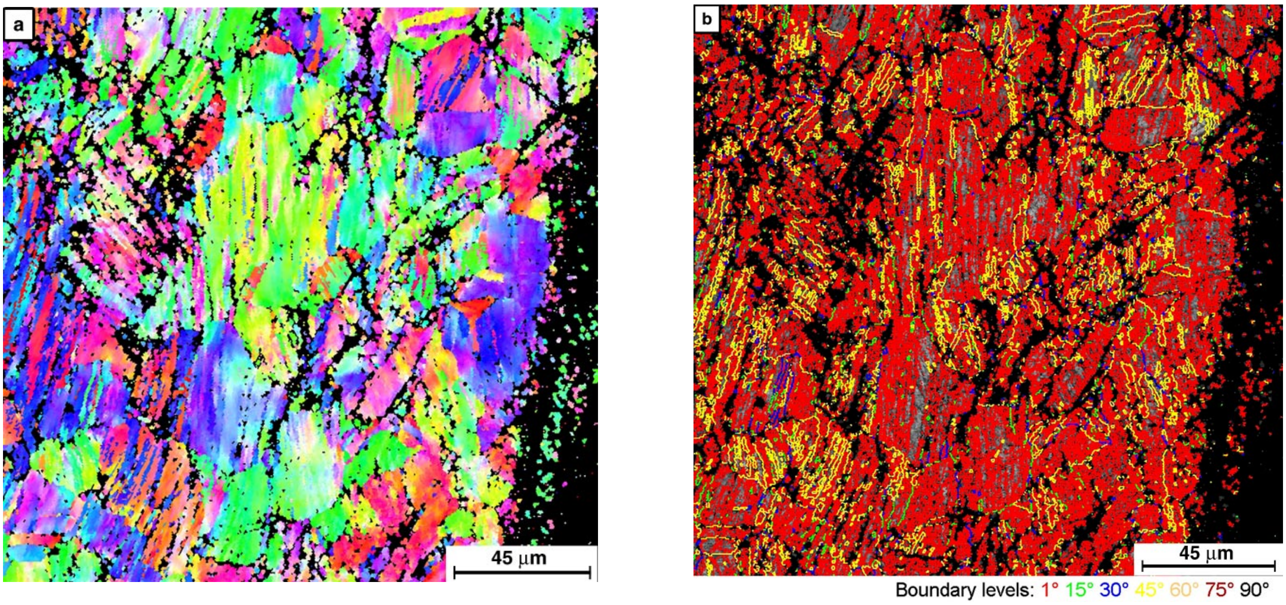


Fig. 9 IPF colour-coded map and boundary rotation angle map for Gundestrup Cauldron sample 365

3.2 The Egyptian vase

Figure 10 shows the restored vase, which is a rare survivor from the Ptolemaic period, being dated to between 300 and 200 BCE. The chased and stamped decorations represent flowers and lotus and acanthus leaves. The designs and form blend different cultural traditions, including Egyptian and Persian.

3.2.1 Analysis techniques: SEM, EDX

The vase was investigated by SEM metallography and fractography in 1995, taking two small samples from the lip and one from the lower wall[7]. EDX analyses gave the following average chemical composition, in wt.%: Ag 97.1. Au 0.8; Cu 0.9; Pb 0.7; Bi 0; Sn 0.2; Sb 0.3.

Figures 1c, 1d, 2, 3 and 11 illustrate the SEM results. The vase has proven to be archetypal for:

(1) Corrosion along slip lines, deformation twin boundaries and segregation bands.
(2) Microstructurally-induced embrittlement, whereby the vase's chemical composition (0.7 % Pb, no Bi) indicates lead to be the most likely perpetrator.
(3) Synergistic embrittlement.
(4) The link between remanent cold-deformation and corrosion damage.

Figure 11 illustrates the link between cold-deformation and corrosion in an especially significant way. The SEM metallograph used backscattered electron imaging, which revealed a local deformation pattern. The adjacent schematic interprets the deformation pattern from the slip-line field theory of indentation[18].

This theory predicts that when t_i /w = 4.4, a tension zone forms at the surface opposite the indented (chased) groove, as well as the always-present compression zone directly under the groove. The actual value of t_i /w is 4.2, which is close enough to justify the interpretation. The tension zone promoted corrosion and intergranular fracture at and near the *internal surface* of the vase, i.e. it caused "hidden" damage.

3.2.2 Discussion of the results

As mentioned in subsection 3.2.1, investigation of the Egyptian vase provided archetypal information on several aspects of ancient silver embrittlement. Two points particularly relevant to restoration and conservation are mentioned here:

(1) Though microstructurally-induced embrittlement is probably much less common than corrosion-induced embrittlement (see section 6), the combination synergy is very detrimental, rendering an object not only frangible but friable. Special care should be taken to conserve such objects[7].

(2) The interpretation of figure 11 leads to a conclusion of general significance: all thin-walled artefacts with chased decorations should be examined for damage at and near the corresponding *internal* or *rear surface* locations. This conclusion is reinforced by the Byzantine paten case history, discussed next.

Fig. 10 The Egyptian vase

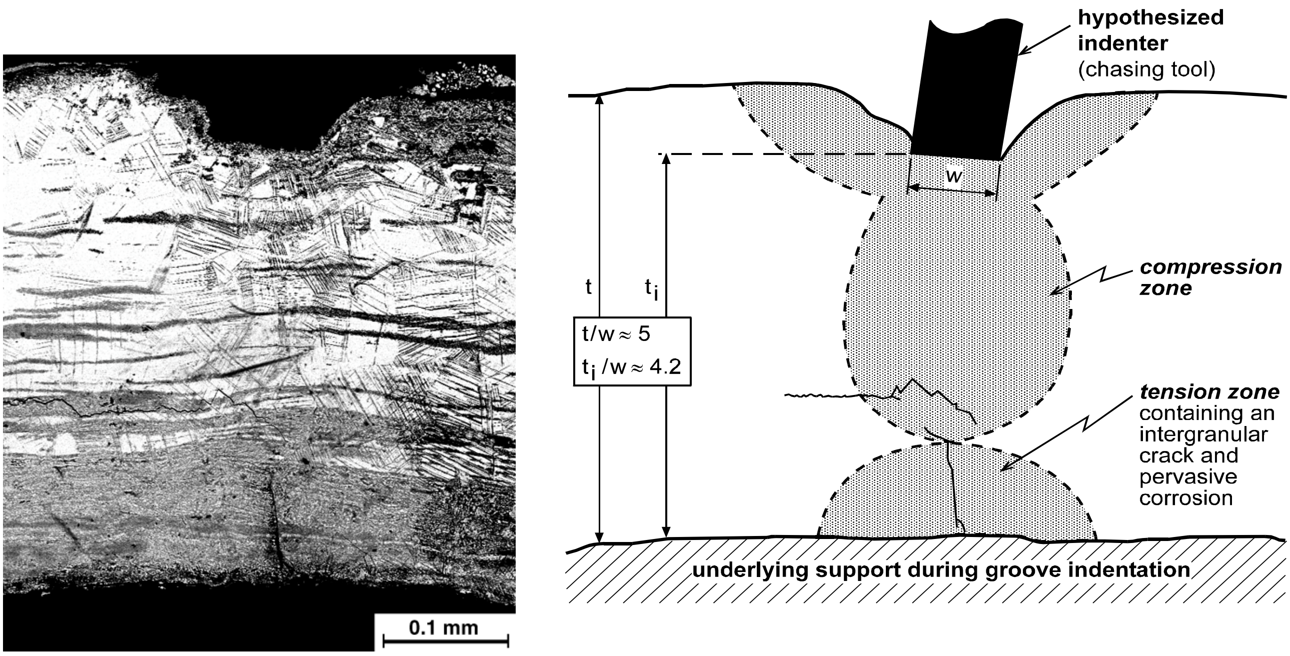


Fig. 11 Through-thickness backscattered electron SEM metallograph and schematic of an external chased decorating groove in the Egyptian vase shown in figure 10[7,8]. The sample is from the vase lower wall

3.3 The Byzantine paten

Figure 12 shows the Byzantine paten, which has been dated to circa 600 AD. The paten is a rare and high-quality liturgical altar object. The important central tableau is well preserved. However, there has been extensive breakage along annular decorating grooves.

3.3.1 Analysis techniques: SEM, EDX, EBSD

A sample from the paten has been examined by SEM metallography and EDX in a preliminary investigation at the Netherlands Institute for Cultural Heritage (ICN) in Amsterdam. It is intended to continue this investigation using FEG-SEM + EBSD equipment at The Open University in the UK.

Figure 13 illustrates the SEM + EDX results. The sample showed surficial intergranular corrosion, figure 13a, and at higher magnifications abundant evidence of discontinuous precipitation of copper at the grain boundaries, figure 13b. This precipitation gave the grain boundaries a meandering appearance, as in figure 5b.

3.3.2 Discussion

The preliminary status of this investigation allows concluding only that the paten has undergone limited intergranular corrosion, and that discontinuous precipitation of copper has occurred. However, by analogy with the Egyptian vase, see subsections 3.2.1 and 3.2.2, the damage pattern seen in figure 12 strongly suggests that breakage was due to preferential corrosion along the annular decorating grooves, and that the corrosion was due to remanent cold-deformation under the grooves. In turn, this suggests that the grooves on the intact part of the paten should be assessed for damage and use of a possible remedial measure, such as applying a protective coating to the rear side.

Fig. 12 The Byzantine paten: photograph courtesy of The Menil Collection, Houston

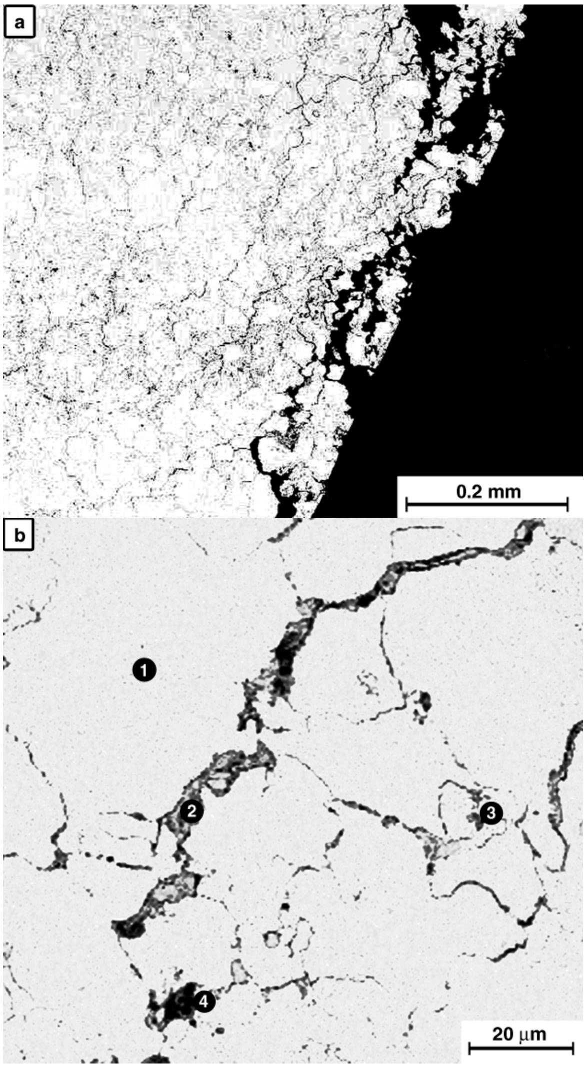


Fig. 13 Examples of (a) intergranular corrosion and (b) discontinuous precipitation of copper at grain boundaries in the Byzantine paten. EDX analyses showed primarily silver at location 1, and silver and copper at locations 2-4. SEM metallographs and analyses courtesy of Ineke Joosten, ICN.

4 REMEDIAL MEASURES

4.1 Introduction

Modern restorations and conservation are concerned (or should be concerned) with both technical and ethical aspects. Essentially, this means respecting an object's integrity and using *reversible* remedial measures. However, reversibility is a controversial topic and is not always practicable[4,19].

4.2 Potential remedial measures

Bearing the remarks in subsection 4.1 in mind, table 2 summarises how the basic condition and type of embrittlement of ancient silver point to potentially sanctionable remedies. This table shows that corrosion protection can be a generally applicable measure, but heat treatment is not.

4.2.1 Corrosion protection

The most likely and feasible corrosion protection measure is cleaning, outgassing to dry crack surfaces and any entrapped corrosion products, and application of a protective coating.

The choice of cleaning methods and protective coatings requires much forethought and care[4,20]. An innovative cleaning method is hydrogen plasma reduction[21]. This requires no more than an hour, at temperatures of 40-100 °C, which minimises or avoids significant alterations of an object's microstructure, especially at the lower end of the temperature range.The hydrogen plasma reduces surface corrosion products to metallic silver, and offers a possible

Table 2 Potential remedial measures for restoration and conservation of ancient silver

- **Nominally intact artefacts and coins**
  - undeformed : corrosion protection
  - deformed : corrosion protection; heat treatment of *coins* to remove microstructural embrittlement, followed by corrosion protection
- **Restored artefacts**
  - old restoration : corrosion protection; disassembly, reassembly and corrosion protection
  - modern restoration : corrosion protection
- **Fragmented artefacts and coins**
  - assembly and corrosion protection
  - heat treatment, assembly and corrosion protection

alternative to heat treatment of objects severely embrittled by corrosion. Such heat treatments require temperatures of 700 °C or more[6].

Recent coating developments suggest that Parylene-type coatings would be ideal for final protection. These coatings can be tailored to requirements, they are very thin and uniform, and they can be applied by vapour condensation under greatly reduced atmospheric pressure[22]. This latter feature means their application can be *directly* preceded by considerable outgassing and drying of cracks and entrapped corrosion products in the objects.

The need to remove or exclude moisture is also why it may be sanctionable to disassemble old restorations and reassemble with modern non-hygroscopic adhesives and fillers, followed by outgassing and a protective coating.

4.2.2 Heat treatment

Nominally intact artefacts almost certainly would not be heat treated. Coins are possible exceptions if microstructurally embrittled, see table 2, since they are small, which makes it easier to heat treat them. Coins are also often less rare, so that heat treatments may be perceived as less risky.

At the other extreme, if it is decided to restore severely embrittled and fragmented objects, then heat treatment may be essential[4,6]. As mentioned in subsection 4.2.1, heat treatment to remove severe corrosion-induced embrittlement requires a temperature of at least 700 °C. The objects need to be in an inert environment or under charcoal. Time at temperature can be short, 5-10 minutes, but the temperature is so high that it excludes artefacts with soldered joints, niello inlay and gilding. There is also a risk of incipient melting in silver containing several weight percent of copper and other alloying elements.

Heat treatment to remove microstructurally-induced embrittlement can be done at lower temperatures. However, the available data suggest temperatures of at least 200 °C, and possibly as high as 500 °C[1].

Heat treatments are obviously irreversible remedial measures, and information about an object's manufactured condition and subsequent history is or can be lost. There is also the possibility that future investigators could be misled by the changed microstructure. These considerations, together with the risk of further damage, show that heat treatments should be allowed only if preceded by thorough diagnostic investigations and if judged feasible by expert technical staff. A classic example is the restoration of the Hockwold Treasure[19].

5 AUTHENTICITY

Some twenty-five years ago Schweizer and Meyers made the interesting proposal that the widths and detailed morphology of discontinuous precipitation of copper in silver could enable authentication of ancient silver objects[23,24]. This proposal has been reconsidered, taking into account the Gundestrup Cauldron results presented in subsection 3.1.1[25]. A summary is given in the next two subsections.

5.1 Discontinuous precipitate widths

Discontinuous precipitate growth rates in binary silver-copper alloys have been determined in the temperature range 200-375 °C[17,26,27]. Lower temperatures are unfeasible[17], requiring impracticably long heat treatment times.

Assuming Arrhenius-type reaction kinetics, extrapolation of the data indicates a *maximum* growth rate of 10^{-3} µm/year at ambient temperatures[8,25]. For the Gundestrup Cauldron this would mean a maximum precipitate width of 2.1 – 2.2 µm. However, sample 366 had precipitate widths up to 7 µm, see figures 5b and 6a. This is so far beyond the predicted maximum as to discount using precipitate widths for authentication.

5.2 Discontinuous precipitate morphology

By analogy with other alloy systems, for example pearlite in iron-carbon alloys, Schweizer and Meyers suggested that discontinuous precipitation of copper in silver might be characterized by regular lamellae, whose spacing would depend on the ageing temperature such that one could distinguish between genuine long-term precipitation at ambient temperatures and short-term precipitation at elevated temperatures.

However, all the evidence[25], exemplified by figure 6 and higher SEM magnifications, shows that the precipitate is finely mottled, not lamellar. As before, one must conclude that the precipitate cannot aid authentication.

6 EXTENT OF THE EMBRITTLEMENT PROBLEM

6.1 Background

Opinions differ on the seriousness of ancient silver embrittlement. Schweizer and Meyers[24] and Kallfass *et al.*[5] aver that silver is often extremely brittle. However, Peter Northover has examined hundreds of silver artefacts and coins, finding only a small proportion to be badly embrittled[16]. On neutral ground, Thompson and Chatterjee[1] and Werner[3] state that it is well known that certain silver objects have become very brittle.

In view of the evidence, see sections 2 and 3 of the present paper, there appear to be three primary factors in the embrittlement of ancient silver. These are the copper and lead contents and remanent cold-deformation. By considering these factors it is possible to make some general statements on the extent of the embrittlement problem, but first it is necessary to discuss the chemical compositions of ancient silver and statistically analyse the data for many objects of high silver content.

6.2 Compositions of ancient silver

6.2.1 General remarks

Native silver alloys may or may not have been used for Old World ancient objects[28-30]. However, the scarcity of native silver compared to silver-containing minerals, mostly lead ores, and the early development of lead cupellation, resulted in pyrometallurgy becoming the main source of silver[29,31-34].

Cupellation is very effective in producing silver above 95 wt.% purity[33,35], though it usually contains minor-to-trace amounts of gold, copper, lead and bismuth, and traces of antimony, arsenic, tellurium, zinc and nickel[29,34,35]. Gold, copper, lead and bismuth contents are generally below 1 wt.% for each element.

Cupellation experiments by McKerrell and Stevenson[35] showed that copper was reduced to 0.3-0.5 wt.%, with lead and bismuth remaining between 0.5-1 wt.%. From these results it appears that copper contents above 0.5-1 wt.% indicate deliberate additions to increase the strength, and also the wear resistance of coins. Remarkably, this practice seems to have been followed from as far back as 3000 BCE[29].

6.2.2 Statistics of copper and lead in objects of high silver content

A compilation was made of the copper and lead percentages for many Old World artefacts and coins containing at least 95 wt.% silver[8,36]. Figure 14 presents the median ranked data on probability plots. Figure 14a indicates that the cumulative occurrence of copper percentages fits a normal distribution, apart from the "tails". The χ^2 test for goodness of fit confirmed that the distribution was normal, including the tails, at a significance level of 5 %. Figure 14b shows that the cumulative occurrence of lead percentages appears to follow a log-normal distribution. The χ^2 test for goodness of fit rejected this, since there were too many data in the range 0.4-0.7 wt.% lead.

Of course, there is no intrinsic reason why any set of data should be perfectly described by simple mathematical distributions. However, when *adequate* descriptions are obtained, the statistical results can be most useful. From this admittedly subjective viewpoint, figure 14 leads to the following three conclusions:

(1) The data show a high degree of homogeneity, even though taken from a wide variety of sources[8,36]. This is most probably because cupellation was the source of the silver.
(2) Since the copper percentages are normally distributed, this implies that any additions of copper to improve the strength and wear resistance were unsystematic.
(3) Although the lead percentages did not satisfy the χ^2 test for goodness of fit to a log-normal distribution, the straight line fit in figure 14b is adequate. The practical significance of this is that a log-normal or approximately log-normal distribution pertains to the concentrations of chemical process residues[37]. In other words, the adequate correlation in figure 14b suggests that the lead percentages represent the residual lead contents after cupellation.

6.2.3 Embrittlement – composition relationships

Figure 14 includes data for the Gundestrup Cauldron samples and the Egyptian vase. These data and the case histories in section 3 enable the following remarks on corrosion-induced, microstructurally-induced and synergistic embrittlement:

(1) *Corrosion-induced embrittlement: see figure 14a.* The Gundestrup Cauldron samples 363 and 365 and the Egyptian vase contained remanent cold-deformation and had undergone extensive corrosion-induced embrittlement. In contrast, the Gundestrup Cauldron sample 366, with much higher copper content, was essentially annealed and free of corrosion. These results demonstrate that remanent cold-deformation is more important for corrosion-induced embrittlement than copper content. Also, figure 14a shows that half the objects had copper contents less than 2 wt.%. Like the Egyptian vase, many of these objects would contain remanent cold-deformation to provide sufficient strength for everyday use. In other words, corrosion-induced embrittlement could be a widespread problem in high-purity ancient silver. Of course, there are additional factors, including an object's burial time and the average temperature, moisture content, pH and chemical composition of the burial environment, especially the salt, nitrate and nitrite contents[31]. However, the foregoing hypothesis is consistent with Peter Northover's observations about Bactrian silver[16], mentioned in subsection 3.1.2.

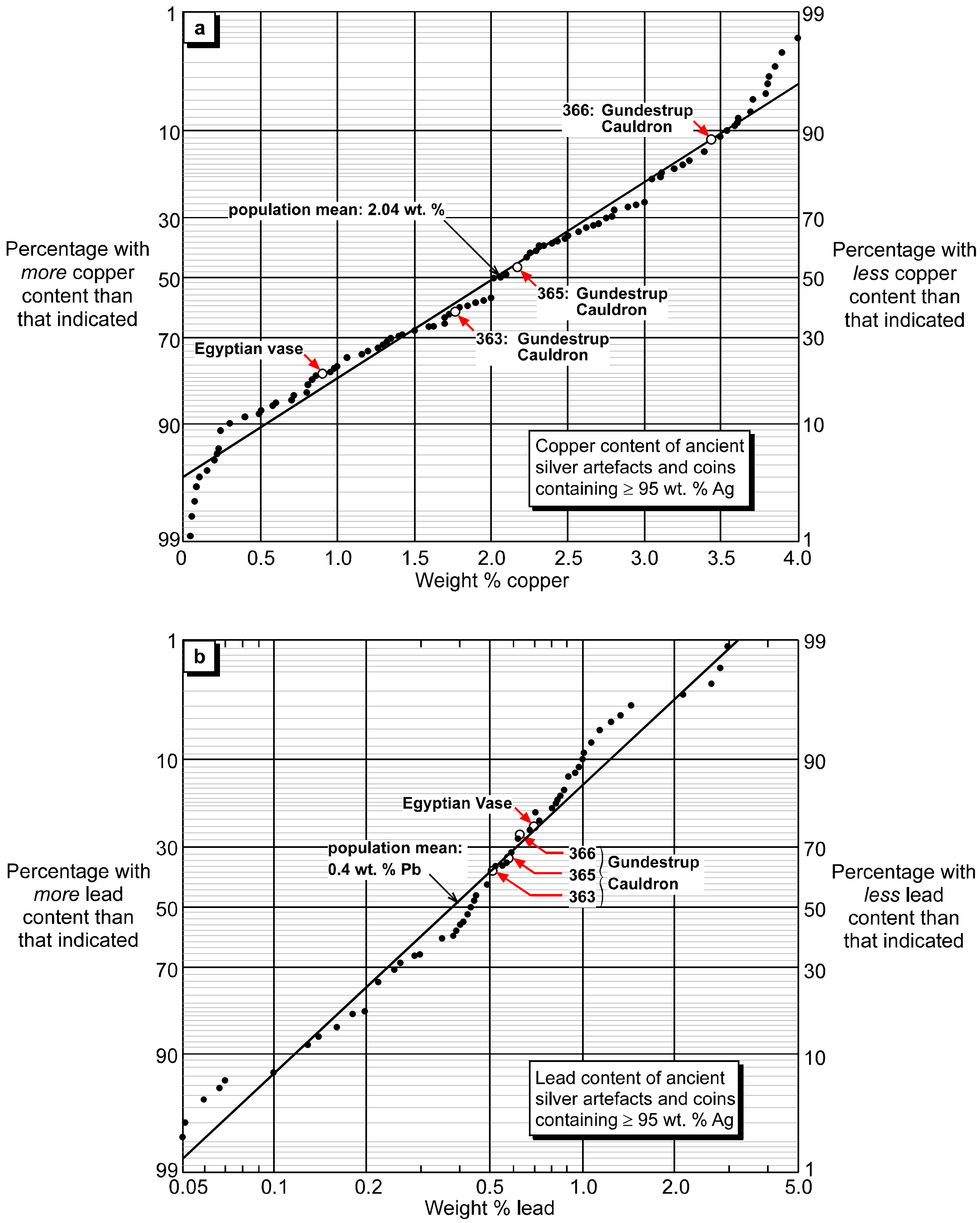


Fig. 14 Probability plots of copper and lead contents in ancient artefacts and coins containing at least 95 wt.% silver

(2) *Microstructurally-induced embrittlement: see figure 14b.* Mechanical testing of age-hardened silver-lead and silver-lead-copper alloys[1] and observations about the Egyptian vase indicate that 0.7 – 0.8 wt.% lead is sufficient to embrittlement silver. The published evidence for microstructurally-induced embrittlement of ancient silver is very limited at present[1,7], but figure 14b shows that about a quarter of the objects had lead contents more than 0.7 wt.%. This is a significant fraction, and so detailed examination of other embrittled objects should reveal further instances of microstructurally-induced embrittlement: however, see point (3) immediately following.

(3) *Synergistic embrittlement.* Since corrosion-induced embrittlement is more in evidence than microstructurally-induced embrittlement, it seems more likely that synergistic embrittlement would occur rather than microstructurally-induced embrittlement on its own. As mentioned in

subsection 3.2.2, synergistic embrittlement is very detrimental. It is important to recognise synergistically embrittled objects because their conservation requires special care[7].

7 CONCLUDING REMARKS

Current knowledge enables identifying and providing explanations of the types of embrittlement of ancient silver, namely corrosion-induced, microstructurally-induced and synergistic embrittlement. Two case histories, the Gundestrup Cauldron and an Egyptian vase, have given important and archetypal information. Automated Electron BackScatter Diffraction (EBSD) has improved the analysis and assessment of corrosion-induced embrittlement by demonstrating the primary detrimental effect of remanent cold-deformation in an object. This is also attested to by a third case history, a Byzantine paten.

The information from detailed case histories is important for determining the best ways to restore and conserve embrittled silver objects. The remedial measures fall into two main categories: corrosion protection and heat treatment. Corrosion protection is a generally applicable measure, though the choice of method requires much prior consideration. Heat treatments are difficult to justify, but may be essential for some severely embrittled and fragmented objects.

Case histories can also contribute to assessing the extent of ancient silver embrittlement. This was shown by combining results for the Gundestrup Cauldron and the Egyptian vase with a straightforward statistical treatment of the copper and lead contents of many ancient objects containing at least 95 wt.% silver. The indications are that corrosion-induced embrittlement could be a widespread problem in high-purity ancient silver, and that detailed examination of other embrittled objects is likely to reveal further examples of synergistic embrittlement. It is also possible, but less likely, that microstructurally-induced embrittlement will be found on its own.

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