Embrittlement of Ancient Silver

Introduction

Classical archaeology techniques can generally provide basic information about the identity, provenance and authenticity of ancient metallic artifacts. However, archaeometallurgy can provide answers to more detailed questions about such items.

This application note addresses the problem of the embrittlement of ancient silver. Electron Backscatter Diffraction (EBSD) and Energy Dispersive Spectroscopy (EDS) based analyses of three different embrittled silver artifacts are reviewed: (1) the Gundestrup Cauldron, (2) an Egyptian vase, and (3) a Byzantine paten (a plate used during celebration of the Eucharist) (Figure 1).

In addition to gaining relevant information about these particular objects, the knowledge gained from examination of such artifacts can be important in developing new methods of restoring and conserving embrittled silver objects in general.

Silver Embrittlement

Ancient silver can be embrittled by long-term corrosion and microstructural changes[1-10]. There are three basic types of embrittlement: corrosion-induced (which appears in several forms), microstructurally induced, and synergistic (a combination of the two).

Corrosion-Induced Embrittlement

Intergranular corrosion (Figure 2a) is the most common form of corrosion, since it occurs in mechanically worked and annealed objects, which constitute the majority of artifacts. Intergranular corrosion is partly attributed to low-temperature discontinuous segregation of copper[2,3,6] at grain boundaries.

Interdendritic corrosion (Figure 2b) occurs in castings. However, cast silver artifacts are uncommon, especially in the Old World. Interdendritic and segregation band corrosion are consequences of high-temperature segregation of copper during solidification.

Corrosion along slip lines or grain boundaries (Figure 2c) occurs in objects that have not been annealed after mechanical forming. Examples include struck coins[1] or decorating by chasing or stamping[7]. Corrosion along slip lines is due to locally high strained regions and possible long-term segregation of solute or impurity elements to those regions.

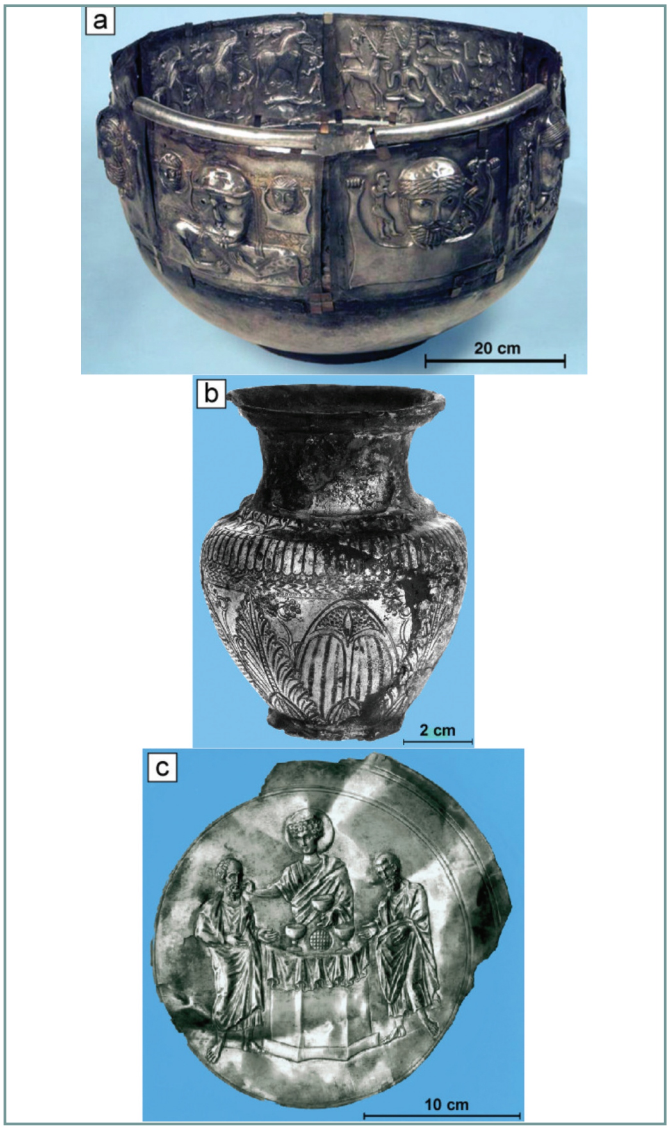

Figure 1. (a) The Gundestrup Cauldron, (b) Egyptian vase, and (c) Byzantine paten.

**Extracted from an application note by R.J.H. Wanhill, National Aerospace Laboratory NLR, Amsterdam, The Netherlands and edited by Stuart Wright, EDAX Inc., Draper, Utah, USA*

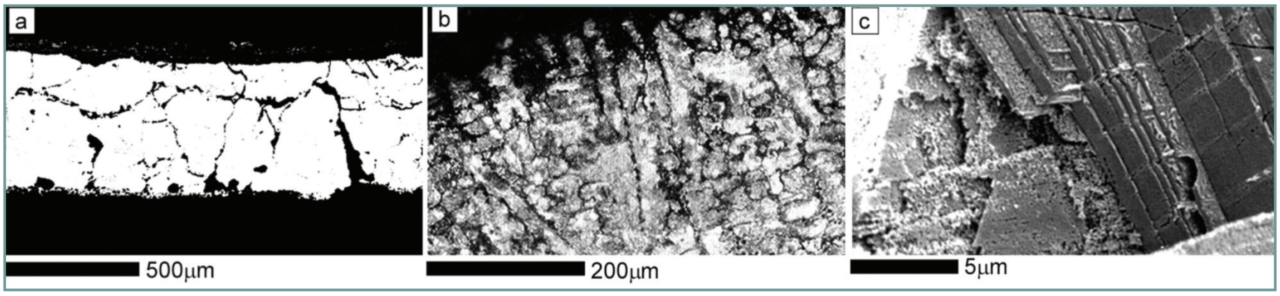

Figure 2. Examples of corrosion-induced embrittlement. (a) Corrosion along slip lines in a Roman cup[3]. (b) Interdendritic corrosion in a Sican (pre-Incan) tumi[11] (a sacrificial ceremonial knife). (c) Crystallographic fracture due to corrosion along slip lines in an Egyptian vase[7].

Microstructurally-Induced Embrittlement

Microstructurally-induced embrittlement is characterized by brittle intergranular fracture, with sharply defined cracks and grain boundary facets (Figure 3). The embrittlement is probably a consequence of long-term low-temperature aging, whereby an impurity element segregates to grain boundaries. Lead is the most likely perpetrator[1,8].

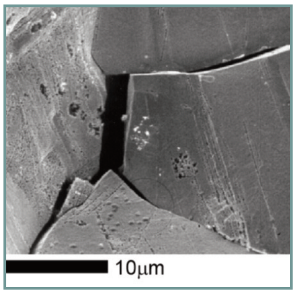

Figure 3. Microstructurally induced brittle intergranular fracture in an Egyptian vase[7].

Synergistic Embrittlement

An example of synergistic embrittlement is shown in Figure 4. Corrosion along slip lines, grain boundaries and segregation bands can result in cracks. These cracks can then initiate fracture along microstructurally embrittled grain boundaries under the action of external loads. In turn, the grain boundary fractures expose more slip lines, grain boundaries and segregation bands to the environment, increasing the opportunities for further corrosion.

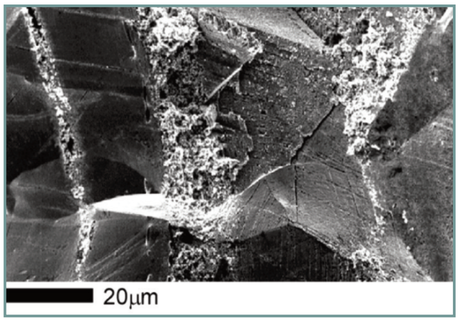

Figure 4. Synergistic embrittlement: corrosion along segregation bands intersecting grain boundary facets in an Egyptian vase[7].

Silver Embrittlement

The Gundestrup Cauldron shown reassembled in Figure 1a is the largest surviving silverwork from the European Iron Age, dating to the 2nd or 1st century BC. Its size, high quality workmanship and iconographic variety have made it the subject of many studies. Its origin remains controversial. The Cauldron consists of twelve plates and a bowl ranging in silver content from 95 to 98% with copper as the main alloying (or impurity) element. Four small samples from different parts of the cauldron were investigated using a Field Emission Gun Scanning Electron Microscope (FEG-SEM) combined with EBSD. The EBSD analysis results fall into two categories:

(1) One of the samples (Figure 5) exhibited an annealed microstructure (the majority of yellow boundaries are annealing twins) virtually free of corrosion. The most significant result was extensive evidence for discontinuous grain boundary precipitation of copper[11-13].

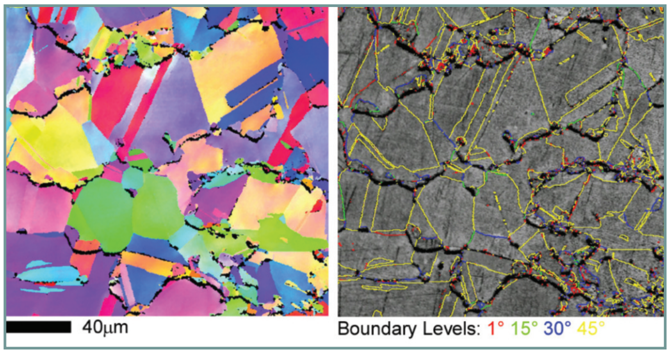

Figure 5. Orientation map and IQ map overlaid with boundaries colored according to misorientation for a sample from the Gundestrup Cauldron.

(2) The microstructures observed in the other three samples contained residual cold deformation and corrosion damage. Figure 6 is representative of the range of microstructures observed in all three samples. The deformation manifests itself as color variations within grains in the orientation maps and red regions in the boundary maps. The black regions are due to

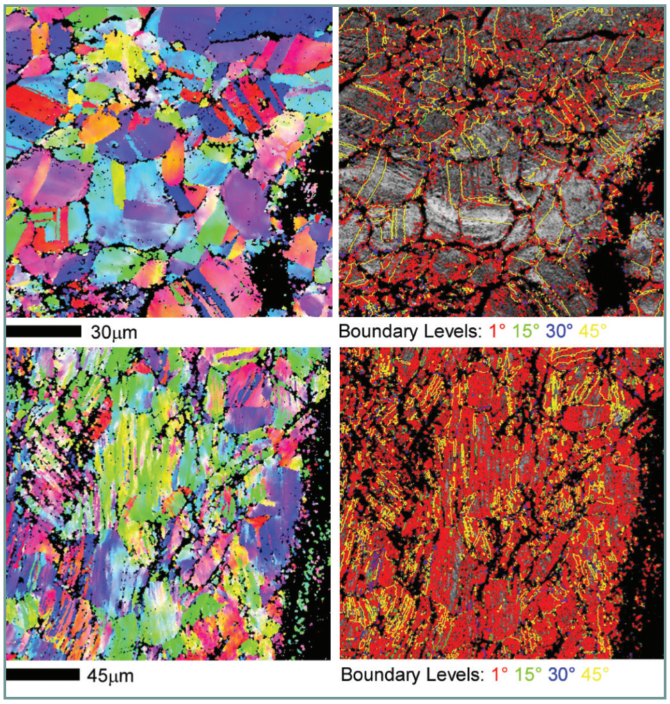

Figure 6. Orientation map and IQ map overlaid with boundaries colored according to misorientation for two samples from the Gundestrup Cauldron.

cracks, primarily intergranular but some transgranular as well. No evidence for discontinuous precipitation was observed.

The differences between these samples with respect to remnant cold-deformation, corrosion and discontinuous precipitation, are remarkable for two reasons:

(1) The results indicate that cold-deformation was primarily responsible for corrosion as opposed to discontinuous precipitation. This is in contrast to the eminent metallurgist Cyril Stanley Smith, who maintained that grain boundaries along which discontinuous precipitation had occurred were highly susceptible to corrosion[2]. Nonetheless, these results are consistent with observations of intergranular corrosion and cracking in ancient Bactrian silver[14] despite copper contents less than 1%, which is too low for discontinuous precipitation[8].

(2) There is a probable link between remnant cold-deformation and discontinuous precipitation. Experiments have shown that cold-deformation can reduce the early growth rate of discontinuous precipitation at grain boundaries in silver-copper alloys at elevated temperatures. The reduction could be due to deformation-induced continuous precipitation within the grains[15].

Egyptian Vase

The Egyptian vase shown in Figure 1b is from the Ptolemaic period, dating to between 300 and 200 BC. The designs and form are a blend of different cultural traditions, notably Egyptian and Persian. The vase is decorated with flowers and leaves formed by stamping and chasing.

The chemical composition measured by EDS[7] was found to be, in wt.%, Ag 97.1; Au 0.8; Cu 0.9; Pb 0.7; Bi 0; Sn 0.2; Sb 0.3. Scanning Electron Microscope (SEM) results obtained from the vase (see Figures 2-4) show all three forms of embrittlement: (1) corrosion along slip lines, deformed grain boundaries and segregation bands; (2) microstructurally-induced embrittlement; and (3) synergistic embrittlement.

A link between the remnant cold-deformation and corrosion damage can be surmised from backscattered electron imaging results, which reveal a deformation pattern. The pattern suggests that the tooling used to chase the decorations on the outer surface of the vase created a tension zone on the inner surface. The tension zone promoted corrosion and intergranular fracture at and near the internal surface of the vase (Figure 7).

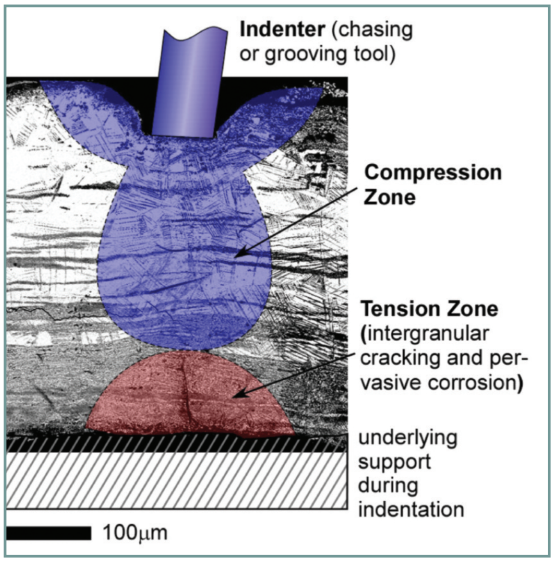

Figure 7. Through-thickness backscattered electron image below a decorating groove in the Egyptian vase[7,8] overlaid with a schematic of the deformation pattern.

This raises two points particularly relevant to restoration and conservation:

(1) The combined synergy of corrosion- and microstructurally-induced embrittlement is extremely detrimental, rendering the vase fragile and brittle. Special care must be taken to conserve such objects[7].

(2) Thin-walled artifacts with chased decorations should be examined for damage at and near the corresponding opposite surface locations.

Byzantine Paten

Figure 1c shows a Byzantine paten from approximately 600 AD. While the central tableau of this rare liturgical altar artifact is well preserved, much of the outer rim has broken off along the annular decorating grooves. SEM and EDS results obtained from a small sample of the paten are shown in Figure 8. Intergranular corrosion at the surface is evident and abundant evidence of discontinuous grain boundary precipitation of copper was observed at higher magnification.

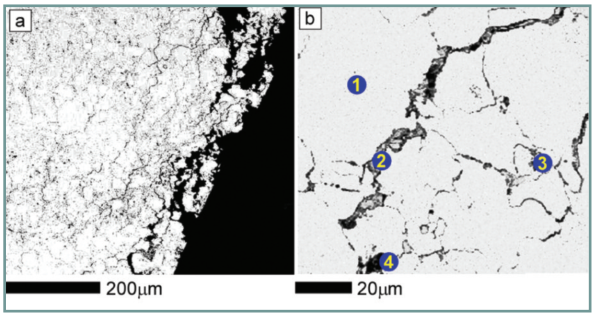

Figure 8. Examples of (a) intergranular corrosion and (b) discontinuous precipitation of copper at grain boundaries in the Byzantine paten. EDS analysis showed primarily silver at location 1, and silver and copper at locations 2-4. SEM metallographs and analyses courtesy of Ineke Joosten.

Similarily to the Egyptian vase, the observed damage strongly suggests that breakage was due to preferential corrosion along the annular decorating grooves, and that the corrosion was due to a tension zone 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.

Authentication

The widths and detailed morphology of discontinuous precipitation of copper in silver have been proposed as indicators for authenticating ancient silver objects[16,17]. In light of the results obtained from the Gundestrup Cauldron, this proposal is reconsidered.

Discontinuous precipitate growth rates in silver-copper alloys have been determined in the temperature range of 200-375°C[15,19,20]. An extrapolation of the rate data gives a maximum growth rate of 10^{-3} µm/year at ambient temperatures[8,18] resulting in a maximum precipitate width of ~2.2 µm for the Cauldron. However, precipitate widths up to 7 µm were measured. This is well beyond the predicted maximum, thus discounting the use of the precipitate widths for authentication.

By analogy with other alloy systems which produce regular lamellae, due to discontinuous precipitation, a second approach suggested that lamellar spacing could be used to differentiate genuine long-term precipitation at ambient temperatures from short-term precipitation at elevated temperatures, since the spacing would depend on the aging temperature[17]. Unfortunately, the discontinuous precipitation of copper in silver is finely mottled, not lamellar[18]. Thus, precipitate morphology cannot be used as an authentication tool.

Conclusions

Using the SEM in conjunction with EDS and EBSD enables the identification and understanding of the possible origins for the different types of embrittlement found in ancient silver artifacts. This information can also be used to determine the best ways to restore and conserve embrittled silver objects.

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For more details on this work see:

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