Embrittled Ancient Silver and Iron Objects and Their Conservation

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Introduction

Embrittlement of ancient metals is often complex. The details of embrittlement should be investigated in order to select the best remedial measures for restoration and conservation. This article surveys the techniques used for investigating several ancient embrittled silver artifacts and an iron pile-shoe from a Roman bridge. The possibilities for preserving such objects are also discussed.

Silver Embrittlement

The investigated artifacts were an Egyptian vase, the Gundestrup Cauldron, and a Byzantine paten (a plate used during celebration of the Eucharist). Table 1 lists the techniques and their purposes: SEM = Scanning Electron Microscope; SE, BSE = Secondary and BackScattered Electron imaging; EBSD = Electron BackScatter Diffraction; EDX = Energy Dispersive analysis of X-rays. The choice of techniques depended on the accessibility and condition of samples from the artifacts. For example, the vase samples were initially unembedded fragments that could be examined fractographically. The other samples had already been prepared for metallography.

There are three types of embrittlement likely in these objects: corrosion-induced, microstructurally induced, and synergistic.

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 and decorating by chasing and stamping. Inside the metal these kinds of corrosion 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.

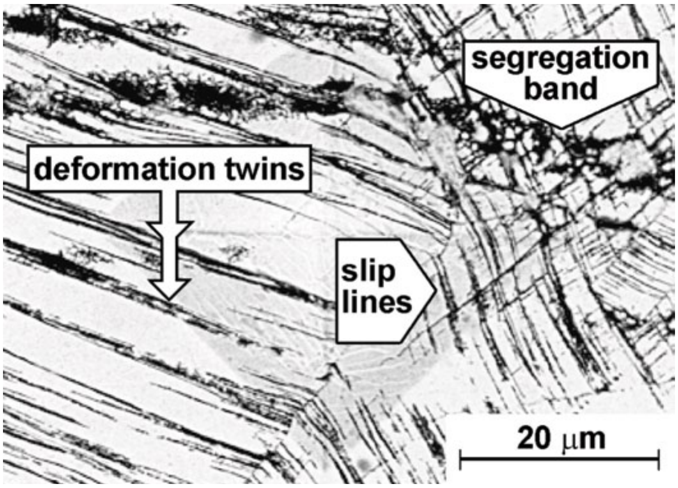

Figure 1: Corrosion-induced embrittlement along deformation twins, slip lines, and copper-rich segregation bands in the Egyptian vase [1].

Microstructurally induced embrittlement is characterized by brittle intergranular fracture, with sharply defined cracks and grain boundary facets. The embrittlement is most probably a consequence of long-term low-temperature aging, whereby an impurity element, or elements, segregates to grain boundaries. The available evidence indicates lead to be the most likely perpetrator [2, 3], though this has yet to be verified directly. Other impurity elements might be involved, notably bismuth [3].

Table 1: Diagnostic techniques for ancient silver embrittlement [1].

Purposes	Techniques	Egyptian Vase	Gudestrup Cauldron	Byzantine Paten
Determine basic condition and "hidden" damage	Visual inspection	●		●
	X-ray radiography	●		
Final manufactured condition; grain size; chemical composition; internal damage and cracking; types of embrittlement	Light optical metallography			
	SEM metallography and analysis			
	-SE andf BSE images	●		●
	-EBSD		●	
	-EDX	●		●
	Microhardness	●		
Types of embrittlement	SEM fractography	●		

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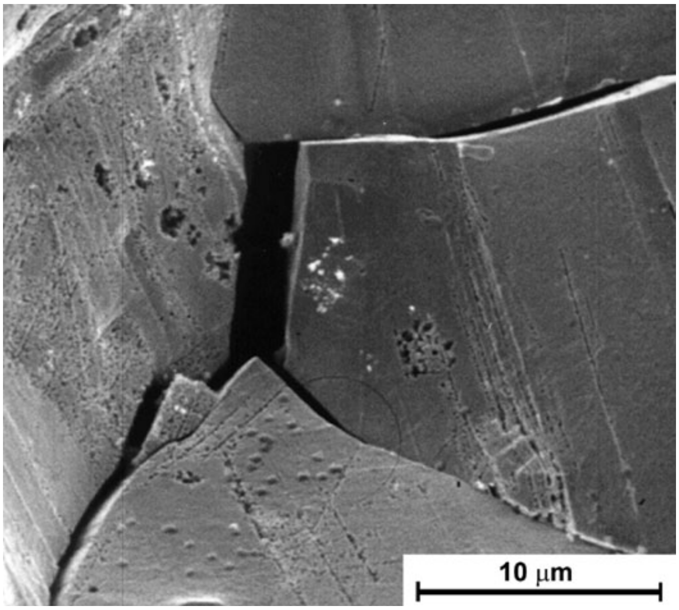

Figure 2: Microstructurally induced brittle intergranular fracture in the Egyptian vase [2].

Synergistic embrittlement combines corrosion-induced and microstructurally induced embrittlement. For example, 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.

SEM metallographic and fractographic examples of all three types of embrittlement are given in Figures 1-3. Retained cold-work is generally responsible for corrosion-induced embrittlement. This can be seen from the EBSD Inverse Pole figure (IPF) color-coded maps in Figure 4, which show annealed and cold-worked samples from the Gundestrup Cauldron. The annealed sample is uncorroded even though there is extensive discontinuous precipitation of copper along the grain boundaries. This is notable because the eminent metallurgist Cyril Stanley Smith took the view that grain boundaries along which discontinuous precipitation had occurred seemed to be highly susceptible to corrosion [4]. Also, limited evidence for the Byzantine paten [2, 3] suggested that corrosion occurred along grain boundaries with discontinuous precipitation. On the other hand, the Gundestrup Cauldron results are consistent with the experience of Peter Northover [5] who observed intergranular corrosion and cracking in ancient Bactrian silver despite copper contents less than 1 percent, which is almost certainly too low for discontinuous precipitation to occur [6].

Iron Embrittlement

A recent brittle fracture in a Roman pile-shoe recovered from the Maas riverbed in 1992 was investigated in collaboration with three other institutes in the Netherlands. See Table 2.

Figure 5 shows a detail of the fracture, which was caused by the pile-shoe falling onto a concrete floor during storage. This obviously intergranular fracture was attributed to local decarburisation during manufacture (a local carbon content of only 33 ppm) and subsequent embrittlement by high-temperature phosphorus segregation to the ferrite grain boundaries. The decarburisation would have occurred owing to locally oxidizing conditions in the smithing hearth, and the virtual absence of carbon would then permit phosphorus segregation to the ferrite grain boundaries [7]. It was also found that the pile-shoe was covered by a surface corrosion layer of akaganeite (an iron oxide) which would have formed after the pile-shoe was recovered [8].

Remedial measures for restoration and conservation

Modern restorations and conservation are 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 not always practicable.

Remedial measures for silver. Table 3 summarizes how the basic condition and type of embrittlement of ancient silver

Table 2: Diagnostic techniques for embrittlement of an iron pile-shoe [1, 7].

Techniques	Specific Aspects	Organization
Macrofractography	Brittle fracture, corrosion	Het Valkhof
SEM/FEG-SEM fractography	Intergranular + cleavage fracture	PR-MA/NLR
Optical metallography	Microstructure, hardness	CORUS, NLR
Chemical analysis		
Bulk		
X-Ray Diffraction (XRD)	Iron and surface corrosion layer	PR-MA
X-Ray Fluorescence (XRF) spectroscopy	Iron composition	CORUS
Combustion + InfraRed (IR) detection	Carbon and sulphur content of iron	CORUS
Metallographic surfaces		
SEM+EDX, Electron Probe MicroAnalysis	Iron and inclusion compositions	
(EPMA)+WDX	Phosphorus and oxygen line scans	CORUS/PR-MA
Fracture surfaces		
X-ray Photoelectron Spectroscopy (XPS)	Grain boundary segregation	PR-MA

Het Valkhof = Museum Het Valkhof, Nijmegen; PR-MA = Philips Research-Materials Analysis, Eindhoven; CORUS = Corus Research, Development and Technology, IJmuiden

Table 3: Potential remedial measures for restoration and conservation of ancient silver [2, 3].

Nominally intact artifacts and coins
- undeformed: corrosion protection
- deformed: corrosion protection; heat treatment of coins to remove microstructural embrittlement, followed by corrosion protection

Restored artifacts
- old restoration: corrosion protection; disassembly, reassembly, corrosion protection
- modern restoration: corrosion protection

Fragmented artifacts and coins
- assembly and corrosion protection
- heat treatment, assembly, and corrosion protection

point to potentially appropriate remedies. Corrosion protection can be a generally applicable measure, but heat treatments are not. Heat treatments obviously are irreversible and should be allowed only if preceded by thorough diagnostic investigations and if judged essential by expert technical staff.

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 [3, 9]. An innovative cleaning method is hydrogen plasma reduction. This requires no more than an hour at temperatures of 40-100°C, which minimizes or avoids significant alterations of an artifact'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 alternative to heat treatment of artifacts that are penetrated and severely embrittled by corrosion. Such heat treatments require temperatures of 700°C, or more, to remove the corrosion and are generally unacceptable because of a high risk of damaging the artifacts. Hence further investigation of the hydrogen plasma reduction method for corrosion-embrittled artifacts is warranted.

Remedial measures for iron pile-shoes. Many more pile-shoes were recovered besides the accidentally fractured one. Investigation of this pile-shoe indicated two aspects for conserving the others. Firstly, these must be expected to have surface corrosion layers containing akaganeite. Because akaganeite is hygroscopic, corrosion will continue unless actively prevented by drying out the corrosion layers and either storing the pile-shoes in a low-humidity environment [8] or applying a protective (organic) coating. Secondly, some of these pile-shoes could also have local carbon contents that are extremely low. Thus if any are to be removed from storage, and whether or not they are still attached to piles, they should be handled and transported with care to avoid breakages. MT

References

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Figure 3: Synergistic embrittlement example: Microstructurally induced intergranular fracture and corrosion-induced damage and cracking along segregation bands in the Egyptian vase [1].

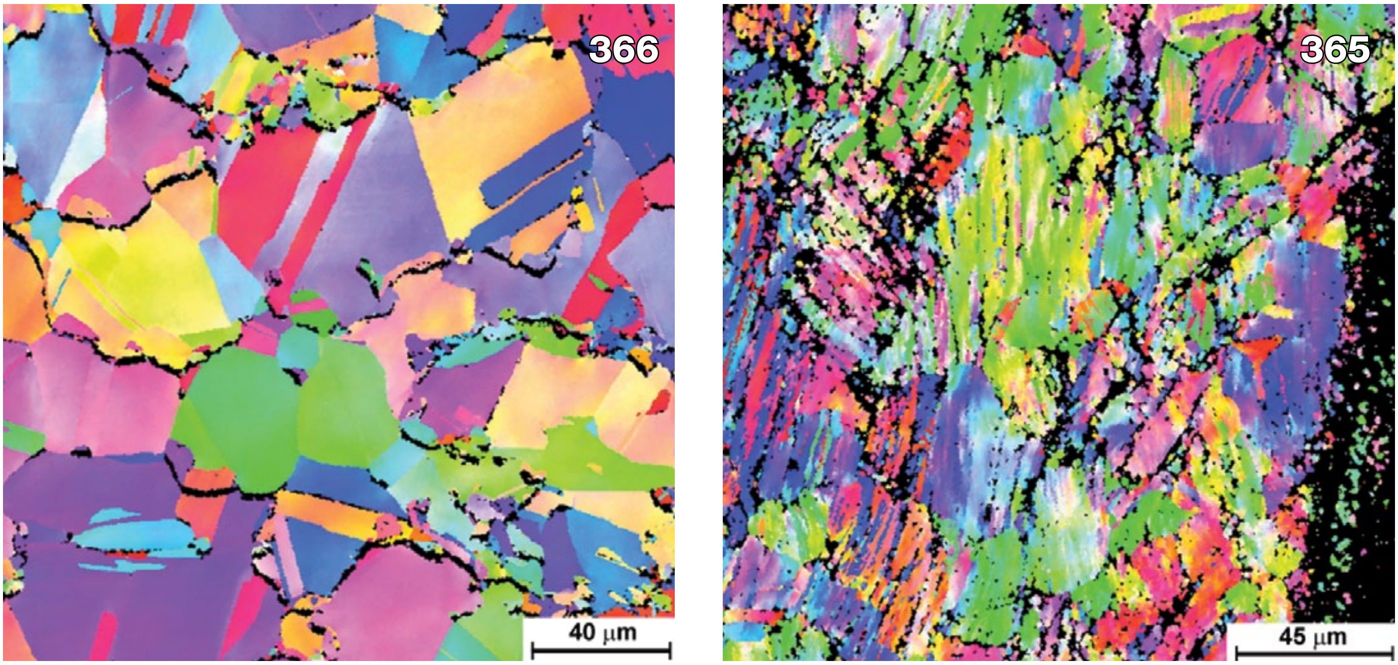

Figure 4: EBSD IPF color-coded maps for Gundestrup Cauldron sample 366 (annealed) and sample 365 (cold-worked). The sample 366 image shows extensive discontinuous precipitation of copper along the grain boundaries. Black regions in the sample 365 image are due to corrosion damage and cracking [1].

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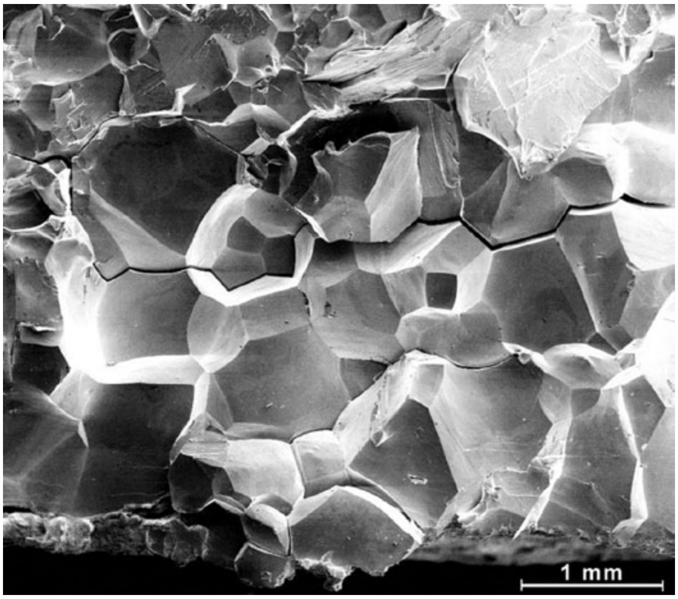
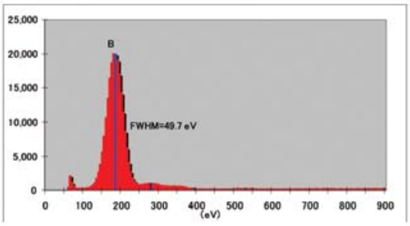
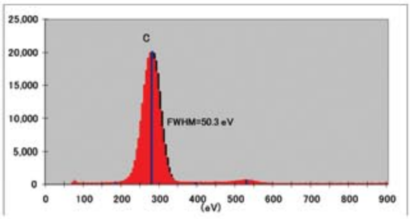


Figure 5: Brittle intergranular fracture of an iron pile-shoe from a Roman bridge [1].



Boron



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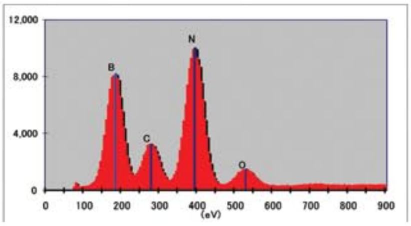

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