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ORIGINATOR

National Aerospace Laboratory NLR, Amsterdam, The Netherlands

TITLE

Archaeological silver embrittlement

PREPARED FOR

Publication in the Journal Of Metals

AUTHORS	DATE	PP	REF
R.J.H. Wanhill	November 2003	14	17

DESCRIPTORS

ANCIENT SILVER	CORROSION	CRACKS
EMBRITTLEMENT	GRAIN BOUNDARIES	MICROSTRUCTURE

ABSTRACT

Archaeological silver may become brittle owing to long-term corrosion and microstructural changes. Recognition and determination of corrosion-induced and microstructurally-induced embrittlement, and also their synergy, are important for artefact conservation and possible restoration. This article considers the types of embrittlement, the diagnostic techniques and possible remedial measures.

Nationaal Lucht- en Ruimtevaartlaboratorium
National Aerospace Laboratory NLR

NLR-TP-2003-127

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This report was submitted for publication in the Journal Of Metals.

This report may be cited on condition that full credit is given to NLR and the author.

Customer:	National Aerospace Laboratory NLR
Working Plan number:	S.1.B.4
Owner:	National Aerospace Laboratory NLR
Division:	Structures and Materials
Distribution:	Unlimited
Classification title:	Unclassified
	November 2003

Approved by author:	Approved by project manager:	Approved by project managing department:
21/11/03	2/12	4/12

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(14 pages in total)

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Summary

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Introduction

Silver is normally ductile and easily fabricated. However, some archaeological silver artefacts and coins can be brittle, as a long-term consequence of corrosion and microstructural changes.[1-7] Corrosion-induced embrittlement results from selective corrosion that penetrates the metal and eventually fragments it. This occurs whether or not the object is acted on by external loads, though they may hasten the process, as will internal stresses and strains.[6] Microstructurally-induced embrittlement causes apparently pristine metal to crack and fracture under the action of external loads.

Corrosion-induced and microstructurally-induced embrittlement can act synergistically, with potentially devastating consequences for an object's integrity. Figure 1 shows an Egyptian silver vase that despite its reasonably intact appearance has been severely embrittled by corrosion and microstructural changes.[6]

This article describes the types of embrittlement and their probable mechanisms, based on current metallurgical knowledge. Attention is paid also to diagnostic techniques for determining embrittlement, and the possible remedial measures that could or should be taken during restoration and conservation.

Corrosion-induced embrittlement

Several kinds of corrosion can embrittle archaeological silver. General corrosion in high silver content alloys is slow conversion of the metal surface to silver chloride.[3,8,9] The silver chloride forms a brittle, finely granular layer but does not affect the remaining metal. However, unfavourable conditions may result in an object being completely converted to silver chloride.[3,8] Base silver containing much copper undergoes general corrosion whereby copper diffuses out of the alloy and becomes fixed on the surface as green copper carbonates.[3]

The other types of corrosion are intergranular; interdendritic (uncommon, since most ancient silver was repeatedly mechanically worked and annealed); along segregation bands that are the remains of coring and interdendritic segregation; and along slip lines and deformation twin boundaries in objects not annealed after final mechanical working. Examples of the latter are struck coins[1] and artefacts decorated by chasing and stamping.[6] Figure 2 illustrates all these types of corrosion.

Intergranular corrosion is attributed, at least partly, to low-temperature segregation of copper.[2,5] This segregation is a special type called discontinuous or cellular precipitation, and it appears to be sometimes associated with a meandering appearance of the grain boundaries, [10.11] see figure 3. Interdendritic and segregation band corrosion are also due to copper segregation, which in these cases occurred at high temperatures during metal solidification.

Corrosion along slip lines and deformation twin boundaries is due to locally high strains, and for archaeological silver the possibility of long-term segregation of solute or impurity elements to the highly strained regions.

Microstructurally-induced embrittlement

It has long been known that certain elements embrittle silver, notably lead, tin and antimony.[8,12] The first detailed investigation is due to Thompson and Chatterjee.[1] They analysed fifteen ancient brittle silver coins, finding only copper and lead above trace amounts, and they also mechanically tested age-hardened Ag-Pb, Ag-Cu and Ag-Pb-Cu alloys. They concluded that low-temperature precipitation of lead, primarily at grain boundaries, caused embrittlement.

Others have suggested that copper precipitation might cause embrittlement.[2.10] However, this is contra-indicated by mechanical testing of age-hardened Ag-Cu alloys,[13] modern metallurgical concepts of embrittlement,[14] and the composition of the vase shown in figure 1.[6] Lead remains the prime suspect, with bismuth, arsenic, thallium, antimony and tin increasingly less likely.[7]

Microstructurally-induced embrittlement is intergranular, for example figure 4. Features on the facets are due to slip lines from remanent cold-work and corrosion *after* intergranular fracture.[6] The intergranular cracks are characteristically narrow and sharp, except where grains become bodily displaced, which is itself a characteristic of severe embrittlement.

Synergistic embrittlement

Figure 5 gives examples of synergistic embrittlement. Corrosion along slip lines, deformation twin boundaries and segregation bands can result in cracks. These can then initiate fracture along microstructurally embrittled grain boundaries – which may fracture anyway, though less easily – under the action of external loads. In turn, grain boundary fractures expose more slip lines, deformation twin boundaries and segregation bands to the environment and increase the opportunities for corrosion.

Recognition of synergistic embrittlement is presently limited to the vase shown in figure 1. Another likely example is an Indian silver coin, figure 2 in Thompson and Chatterjee.[1] Synergistic embrittlement is nonetheless important, because it renders an object frangible or even friable.

Seriousness of the problem

Opinions differ on the extent of the problem of archaeological silver embrittlement. Some authors state that this problem is well-known,[1,2] or that ancient silver is often extremely brittle.[4,11] However, Peter Northover, a leading expert at Oxford University, has investigated some 300 silver vessels and over 2000 silver coins and found only a small proportion to be badly embrittled.

Diagnostic techniques

The techniques for determining the types of embrittlement can be well defined,[7] and are summarised in Table I.

Table I. Techniques and use for determining embrittlement[7] (summary)

Visual inspection;	:	artefact basic condition; colour of corrosion
X-ray radiography	:	“hidden” damage
Optical and SEM metallography, EDX or WDX, microhardness	:	manufactured condition; chemical analysis; internal damage; type(s) of embrittlement
SEM fractography	:	type(s) of embrittlement

Visual inspection and photography (colour!) are obvious. X-ray radiography can be a valuable adjunct: figure 6 shows the incompleteness and “hidden” cracking of the vase in figure 1. Metallography is generally the most important diagnostic technique, especially when combined with chemical analysis by using SEM + EDX or SEM + WDX.

Microhardness testing is also useful, since the indents help distinguish between corrosion and microstructurally-induced embrittlement. Figure 7 shows (a) an internally corroded area that underwent craze-cracking mainly *inside* an indent, and (b) a microstructurally embrittled area that cracked mainly *outside* the indent (the hardness was also much higher).
Fractography can aid in determining the types of embrittlement, particularly the broad distinction between microstructurally-induced embrittlement (intergranular facets) and corrosion. Detailed fractography requires considerable interpretive skill.

Remedial measures

Modern restorations and conservation take into account 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.[3,15] Bearing these points in mind, Table II summarises technically possible and potentially sanctionable remedies.

Table II: Potential remedial measures[7] (summary)

Nominally intact Artefacts and coins	:	undeformed	– corrosion protection
		deformed	– corrosion protection; heat treatment of coins to remove microstructural embrittlement, corrosion protection
Restored artefacts	:	old restoration	– corrosion protection; disassembly, reassembly, corrosion protection
		modern restoration	– corrosion protection
Fragmented artefacts And coins	:	heat treatment, assembly, corrosion protection; assembly and corrosion protection	

Nominally intact objects almost certainly would not be heat-treated, but coins are possible exceptions, owing to their small size and maybe being less rare. At the other extreme, if one is to restore severely embrittled and fragmented objects, then heat-treatment may be essential.[3,5] This should be done only after a meticulous diagnostic investigation, and if judged feasible by expert technicians.

A more acceptable measure, for any embrittled object, is corrosion protection. This remedy involves cleaning, outgassing to dry crack surfaces and any entrapped corrosion products, and application of a coating. The choice of cleaning methods and coatings requires much forethought and care.[3.16] Recent developments suggest "Parylene" coatings would be ideal.[17] These coatings can be tailored to requirements, they are very thin and uniform, and can be applied by vapour condensation under greatly reduced atmospheric pressure. This means coating can be done directly after outgassing and drying.

Conclusions and suggestions

Current knowledge enables identifying the types of embrittlement of archaeological silver and specifying the diagnostic techniques. However, remedial measures are less certain. There is a need for more research, both to broaden the data base of embrittled objects and to better define the remedies, especially for microstructurally and synergistically embrittled silver.

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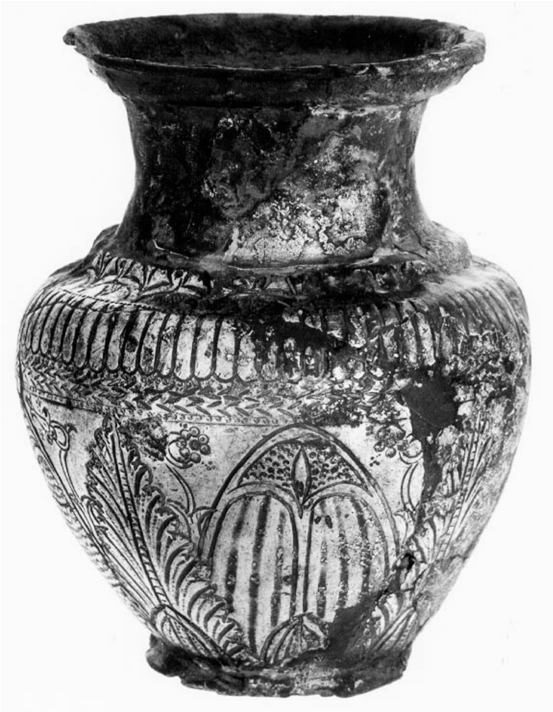
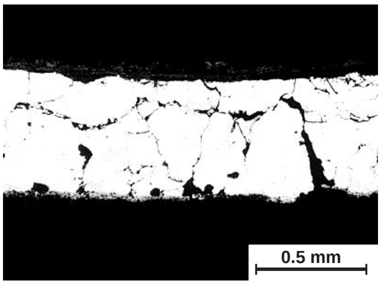
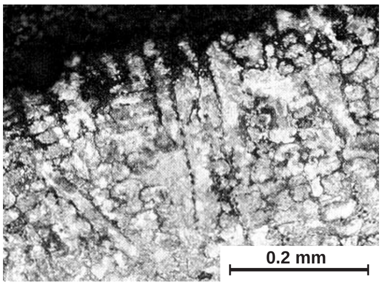


Fig. 1 Severely embrittled Egyptian silver vase (300-200 BC): Allard Pierson Museum, Amsterdam

Intergranular or interdendritic corrosion

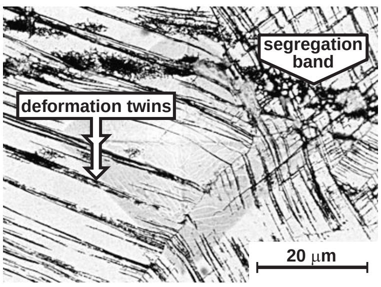


Intergranular: metallograph (Werner 1965)

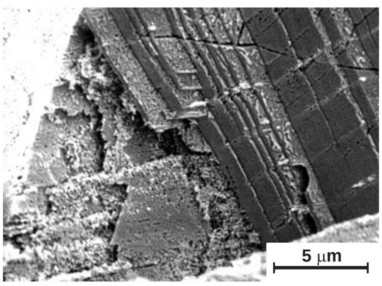


Interdendritic: metallograph (Scott 1996)

Slip line, deformation twin boundary and segregation band corrosion



Corrosion along slip lines, deformation twins and segregation bands: SEM metallograph (Wanhill *et al.* 1998)



Crystallographic fracture owing to corrosion along slip lines and deformation twins: SEM fractograph (Wanhill *et al.* 1998)

Fig. 2 Types of corrosion of high silver content archaeological silver

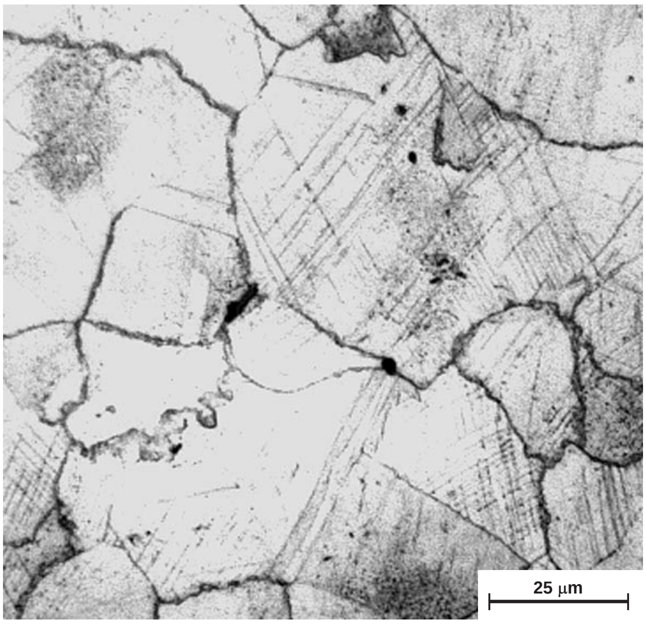


Fig. 3 Grain boundary precipitation and associated meandering:
Gundestrup cauldron (100 BC), courtesy of J.P. Northover, Oxford University, Oxford, U.K.
Remanent cold-work visible as slip lines.
Optical metallograph

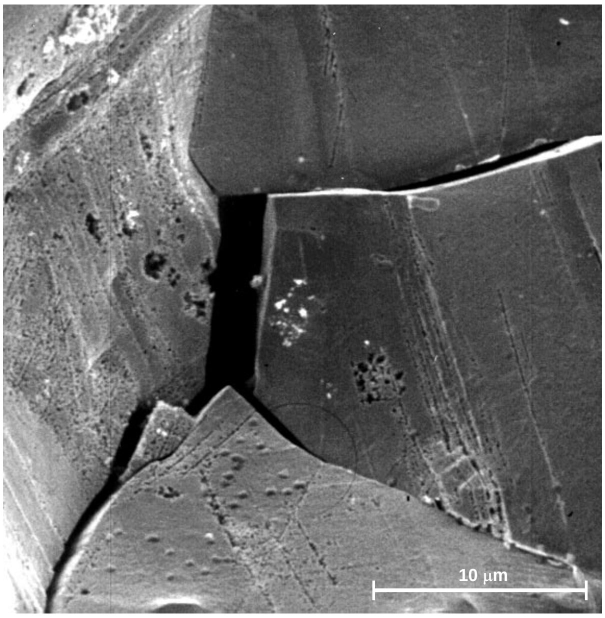
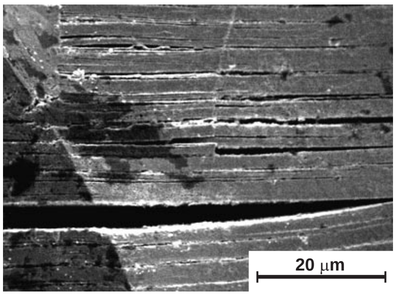
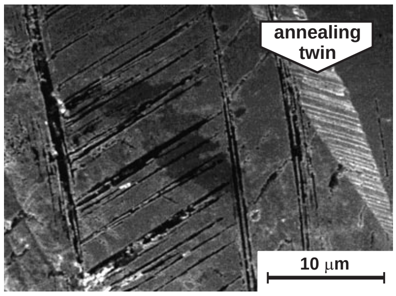


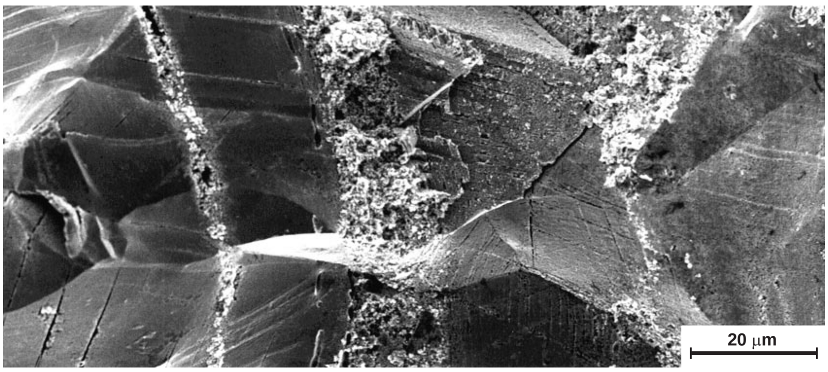
Fig. 4 Brittle grain boundary fracture in a sample from the vase in figure 1. SEM fractograph



Corrosion along slip lines intersecting grain boundary facets: SEM fractograph



Corrosion along deformation twin boundaries intersecting a grain boundary facet: SEM fractograph



Corrosion along segregation bands intersecting grain boundary facets: SEM fractograph

Fig. 5 Examples of synergistic embrittlement [6]

*Fig. 6 X-ray image of the vase shown in figure 1.
Note the hairline cracks and their brittle “eggshell” pattern. The cracks indicated by A follow external chased decorating grooves*

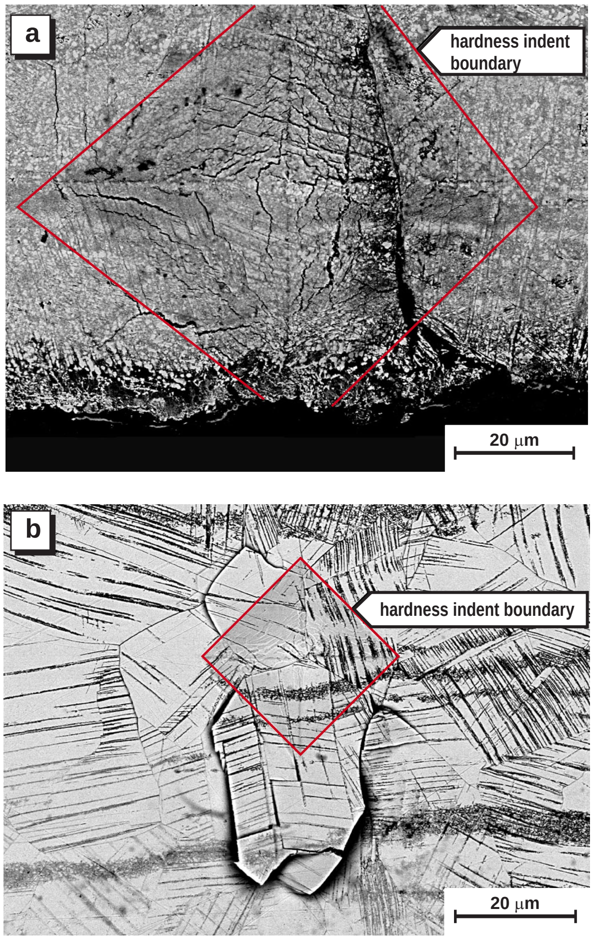


Fig. 7 Vickers microhardness indents on a sample from the vase in figure 1. The hardness values were (a) less than 20 HV, and (b) 43 HV. SEM metallographs