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Brittle archaeological silver identification, restoration and conservation

R.J.H. Wanhill

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BRITTLE ARCHAEOLOGICAL SILVER. IDENTIFICATION, RESTORATION AND CONSERVATION

by

R.J.H. Wanhill

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BRITTLE ARCHAEOLOGICAL SILVER. IDENTIFICATION, RESTORATION AND CONSERVATION

R.J.H. Wanhill
National Aerospace Laboratory NLR, Anthony Fokkerweg 2,
1059 CM Amsterdam, The Netherlands

Archaeological silver can be brittle and may be found cracked or fragmented. The brittleness is a long term consequence of corrosion and microstructural changes, acting separately or together. This paper presents current knowledge of the embrittling mechanisms, factors contributing to the types and severity of embrittlement, and possibilities for restoration and conservation.

KEYWORDS: ARCHAEOLOGICAL SILVER, EMBRITTLEMENT, CORROSION, CRACKS, RESTORATION, CONSERVATION, METALLOGRAPHY, FRACTOGRAPHY, HEAT-TREATMENT, COATINGS, MICROSTRUCTURE, PRECIPITATION, SEGREGATION, GRAIN SIZE, COLD-WORK, HARDNESS.

INTRODUCTION

Silver is normally very ductile and easily fabricated. However, archaeological silver can be brittle and may be found cracked or fragmented (Thompson and Chatterjee 1954; Werner 1965; Ravich 1993; Wanhill *et al.* 1998). The brittleness is a long term consequence of corrosion and microstructural changes in the silver. In turn, the corrosion and microstructural changes depend on the chemical composition and manufactured condition of an artifact, and also on its subsequent history.

This paper presents current knowledge of the embrittling mechanisms, factors contributing to the types and severity of embrittlement, a survey of diagnostic techniques for determining embrittlement, and possibilities for restoration and conservation.

EMBRITTLEMENT OF ARCHAEOLOGICAL SILVER

The following general points are important:

(1) Corrosion-induced embrittlement and brittleness due to microstructural changes may be independent of each other but can also act synergistically (Wanhill *et al*. 1998).

(2) Chemical composition is significant because archaeological silver contains other elements (e.g. Gowland 1918; Gale and Stos-Gale 1981; Bennett 1994) and some of these elements may be implicated in either or both types of embrittlement.

(3) The manufactured condition of a silver artifact can strongly influence embrittlement (Wanhill *et al.* 1998). In the present context “manufactured condition” means whether the artifact is a casting or has been made by mechanical working (usually cold-work), whether decorations have been applied by chasing, engraving or stamping, and whether the final metallurgical state is as-cast, annealed or cold-worked.

Corrosion-induced embrittlement: description

Figure 1 shows the types of corrosion observed for archaeological silver. The examples are a Roman cup (Werner 1965), a late Roman plate (Bennett 1994), a Sican tumi (Scott 1996) and an Egyptian vase (Wanhill *et al*. 1995, 1998).

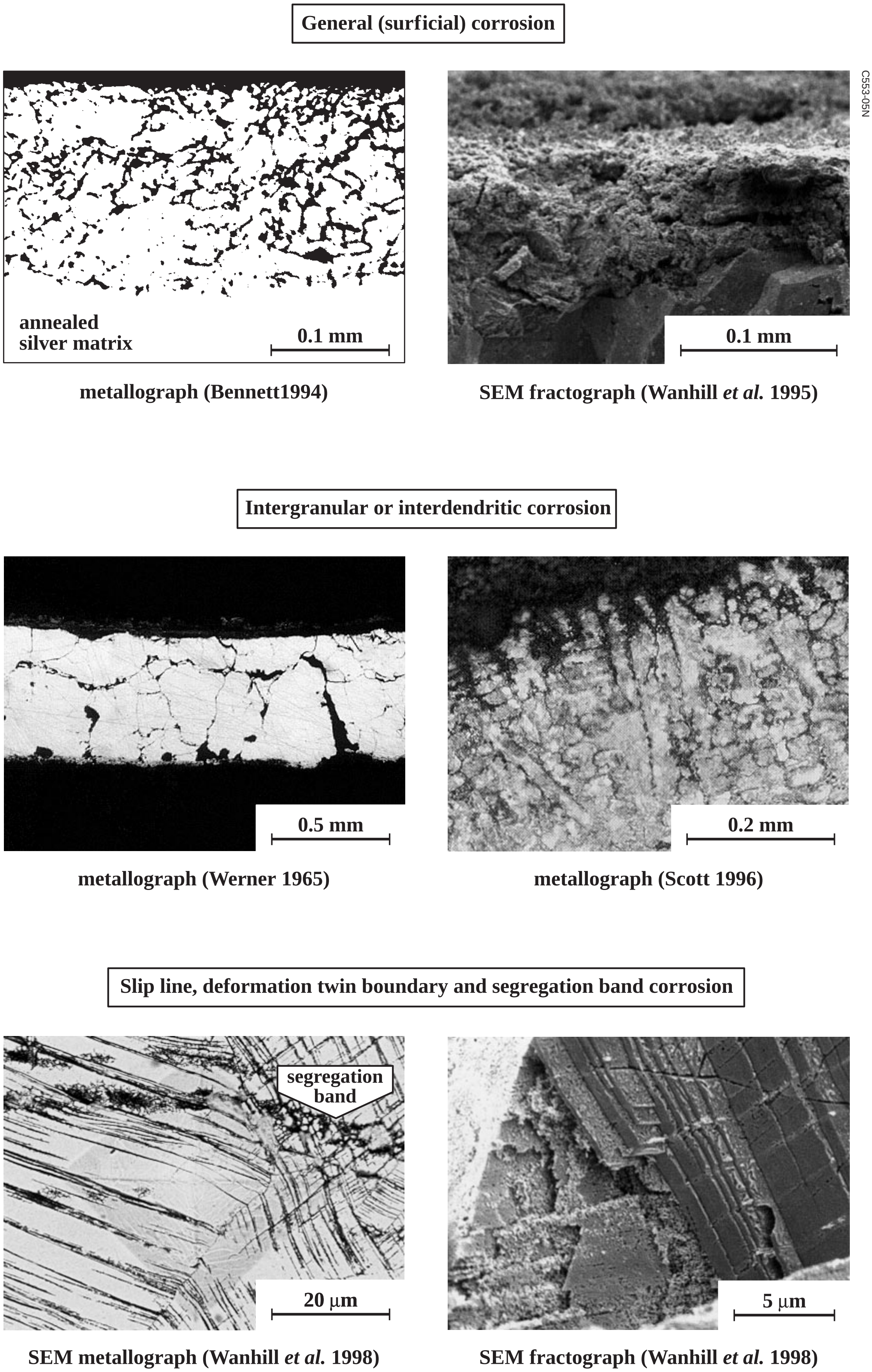

Fig. 1 Types of corrosion of archaeological silver: SEM = Scanning Electron Microscopy

General corrosion is slow conversion of the metal surfaces to silver chloride (Gowland 1918; Scott 1996). This forms a brittle, finely granular layer but does not affect the remaining metal's integrity. However, unfavourable conditions may result in an artifact being completely converted to silver chloride, sometimes retaining its shape, sometimes not (Gowland 1918).

The other types of corrosion penetrate the metal. Cracking along the corrosion paths reduces an artifact's resistance to fragmentation (Werner 1965; Ravich 1993; Wanhill *et al.* 1998). Intergranular corrosion can occur in mechanically worked and annealed artifacts. Interdendritic corrosion can occur in castings with essentially as-cast microstructures, i.e. little changed by any subsequent mechanical working or annealing, see Scott (1996). Corrosion along slip lines and deformation twin boundaries can occur in an artifact that has not been annealed after final mechanical working, which includes chased and stamped decorations (Wanhill *et al.* 1998). Inside the metal these types of attack can lead to additional corrosion along segregation bands. These bands are the remains, modified by mechanical working, of solute element segregation (coring) that occurred during solidification of an ingot or cupelled button.

Cracking along the corrosion paths in the metal usually results in irregular fracture surfaces with a finely granular appearance like that of the general corrosion in the upper fractograph of figure 1. However, highly localised corrosion along slip lines and deformation twin boundaries results in crystallographic fractures, for example the lower fractograph in figure 1.

Corrosion-induced embrittlement: mechanisms

Intergranular corrosion has been attributed, at least partly, to segregation of the solute element copper to grain boundaries (Werner 1965; Ravich 1993). This segregation is of a type called discontinuous or cellular precipitation. It occurs in the solid state at temperatures as low as 150°-200 °C (Scharfenberger *et al*. 1972; Gust *et al.* 1978; Schweizer and Meyers 1978) and could occur very slowly even at ambient temperatures (Schweizer and Meyers 1978). Besides temperature, the precipitation rate depends strongly on the solute element (copper) content of the metal and the amount of plastic deformation (cold-work) retained in the microstructure (Hornbogen 1972; Pawlowski 1979a, 1979b): lower solute contents reduce the precipitation rate, plastic deformation increases it.

The actual mechanism of intergranular corrosion is localised galvanic attack, whereby in the presence of a moisture-containing environment the more noble metal (in this case the copper-depleted silver matrix) acts as a cathode and the copper-enriched grain boundary region dissolves anodically.

The other two types of segregation-induced corrosion, interdendritic and along segregation bands that are the remains of coring, are also due to solute element (copper) segregation which, however, occurs at high temperatures during solidification of the metal. In both cases the corrosion mechanism is most likely the same as for intergranular corrosion, i.e. localised galvanic attack of the less noble copper-enriched regions.

It remains to discuss corrosion along slip lines and deformation twin boundaries, firstly in a general way. Slip, which occurs in bands, and deformation twinning involve locally high strains whereby some atoms are in non-equilibrium positions and have higher energies: in slip bands the atoms surrounding dislocation cores, and in deformation twins the atoms in noncoherent regions of the twin/matrix interfaces. When slip bands and deformation twin boundaries are surface-connected, as in the archaeological silver examples in figure 2, these higher energy regions are susceptible to preferential corrosion (e.g. Procter 1994, 1:37). Note that the annealing twin boundaries in figure 2 are uncorroded. Apparently the local environmental conditions were not severe enough to cause preferential corrosion at these twin/matrix interfaces, which by nature are coherent and without highly strained regions.

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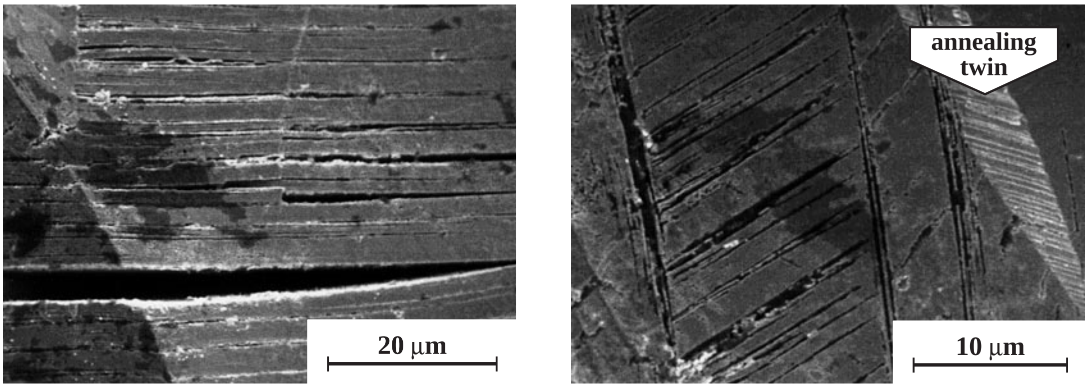
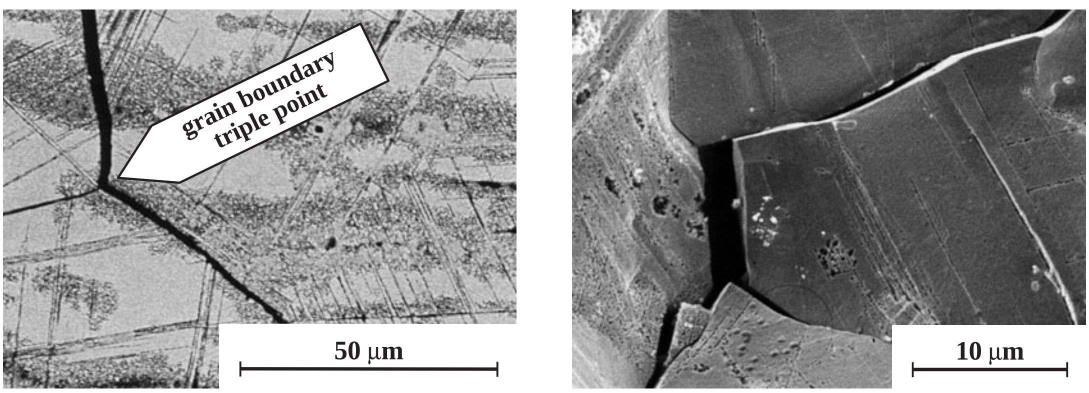


SEM fractograph

SEM fractograph

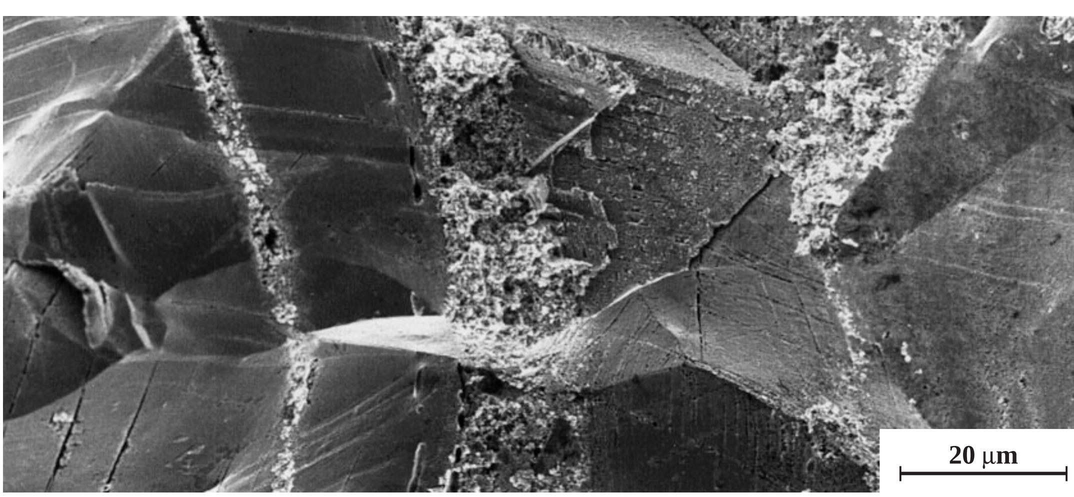
Fig. 2 Corrosion along slip lines, left, and deformation twin boundaries, right (Wanhill *et al.* 1998)



SEM metallograph

SEM fractograph

Fig. 3 Microstructurally-induced brittle intergranular fracture (Wanhill *et al.* 1998)



SEM fractograph

Fig. 4 Corrosion along segregation bands intersecting a brittle intergranular fracture surface (Wanhill *et al.* 1998)

More specifically, for silver there are additional factors that could promote corrosion along slip lines and deformation twin boundaries. These are silver's low stacking fault energy (Hertzberg 1983, 129) which results in planar slip and hence greater concentrations of dislocations in slip bands; the narrowness of the deformation twins, e.g. figure 2, which means higher local strains (Hertzberg 1983, 111); and for archaeological silver the possibility of long-term segregation of solute and impurity elements to the highly strained regions, thereby aiding preferential corrosion (Procter 1994, 1:39).

Microstructurally-induced embrittlement: description

Brittle fracture due to microstructural changes in archaeological silver appears to be entirely intergranular. Figure 3 shows this type of fracture is characterized by narrow cracks (cf. the intergranular corrosion in figure 1) and clean grain boundary facets - at least initially. However, in the presence of a moisture-containing environment the grain boundary facets can be locally corroded where slip lines, deformation twin boundaries and segregation bands intersect the fracture surfaces, for example figures 2 and 4.

Microstructurally-induced embrittlement: mechanisms

Thompson and Chatterjee (1954) proposed that microstructurally-induced embrittlement of archaeological silver is due to lead precipitating in the matrix and at grain boundaries. They based this proposal on low temperature ageing of several silver-lead alloys, metallographic examination and mechanical testing. Figure 5 summarises the metallographic results as part of the silver-lead phase diagram. Precipitation of a lead-rich phase (β) occurred even at very low lead contents, less than 0.1 weight %, and ambient temperatures. Thompson and Chatterjee (1954) also showed that the precipitation rate for a silver - 0.8 weight % lead alloy was much increased by retained cold-work.

However, lead-rich precipitates may not be necessary. Wanhill *et al.* (1998) found no evidence of grain boundary precipitates, e.g. figures 3 and 4, though there could be fine precipitates detectable only by Transmission Electron Microscopy (TEM). More fundamentally, Seah (1980) developed a theory of embrittlement due to solute or impurity atoms segregating to grain boundaries and reducing their cohesive strength. The theory has been supported independently, with minor modifications (Liang *et al*. 1994). Figure 6 shows the theory's predictions for silver vis-a-vis the most common solute and impurity elements in archaeological silver (e.g. Gale and Stos-Gale 1981; Bennett 1994). Now since Thompson and Chatterjee (1954) found only copper and lead in more than trace amounts in the brittle silver coins they examined, and Wanhill *et al*. (1998) found no trace of bismuth, one may conclude from figure 6 that lead is the most likely candidate for segregation-induced intergranular brittle fracture of silver.

Synergistic embrittlement

As stated earlier, corrosion-induced embrittlement and brittleness due to microstructural changes can act synergistically (Wanhill *et al.* 1998). Corrosion along slip lines, deformation twin boundaries and segregation bands can result in cracks under the action of external forces (e.g. crushing pressures during interment) and internal residual stresses due to retained cold-work. These cracks can then nucleate fracture along microstructurally-embrittled grain boundaries, which may fracture anyway - though less easily - under the action of external forces. In turn, grain boundary fractures expose more slip lines, deformation twins and segregation bands to the environment and therefore increase the opportunities for corrosion.

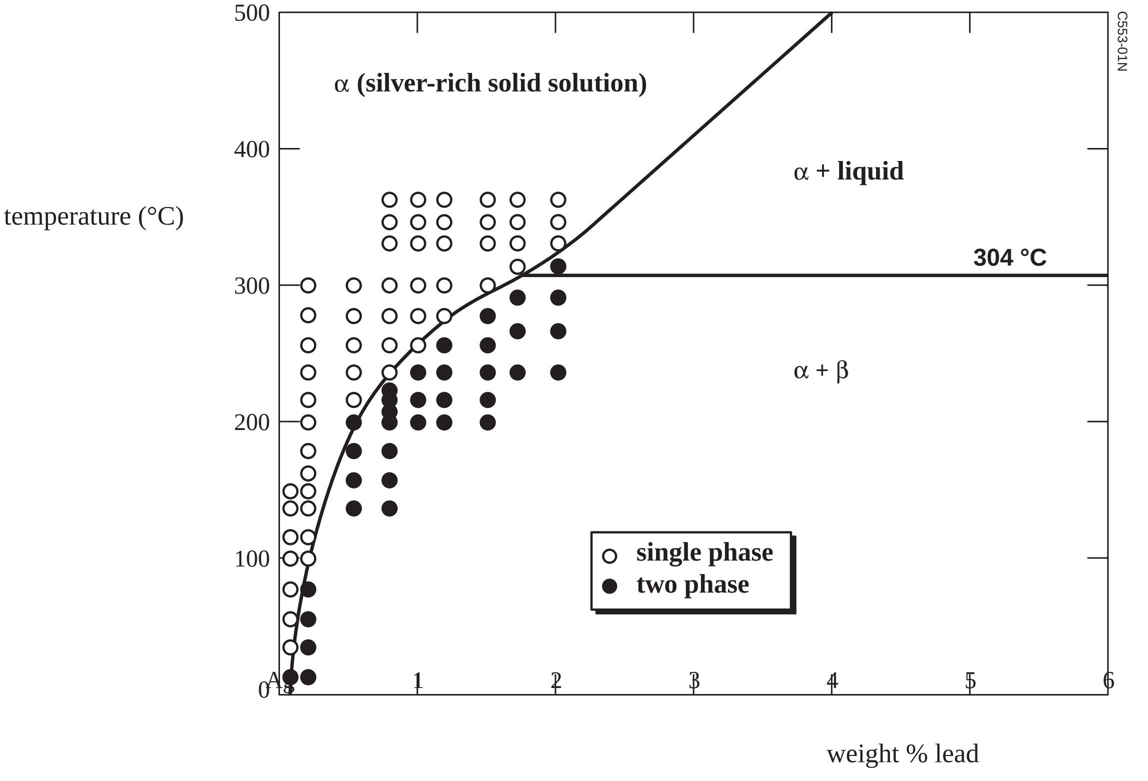


Fig. 5 Solid solubility of lead in silver (Thompson and Chatterjee 1954)

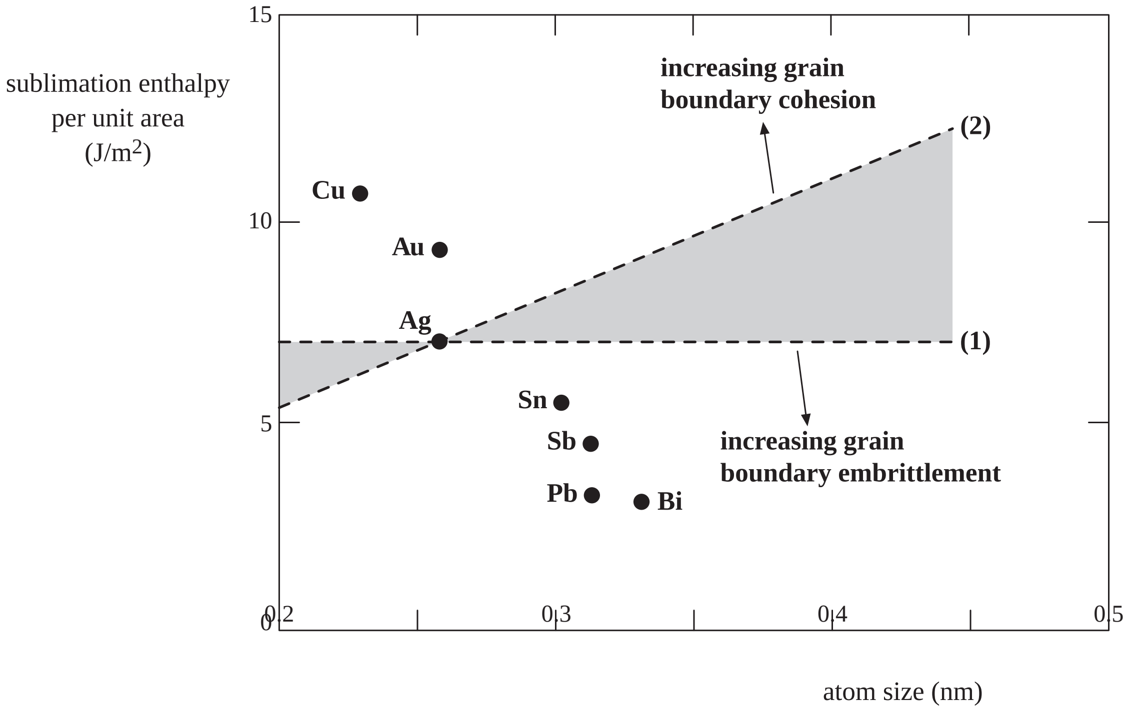


Fig. 6 Ideal solution remedial/embrittlement plot for matrix (Ag) and segregant elements. Line (1) divides those elements predicted to reduce the fracture energy of silver from those predicted to increase it. Line (2) is a similar division for the critical fracture stress. After Seah (1980)

Effects of grain size

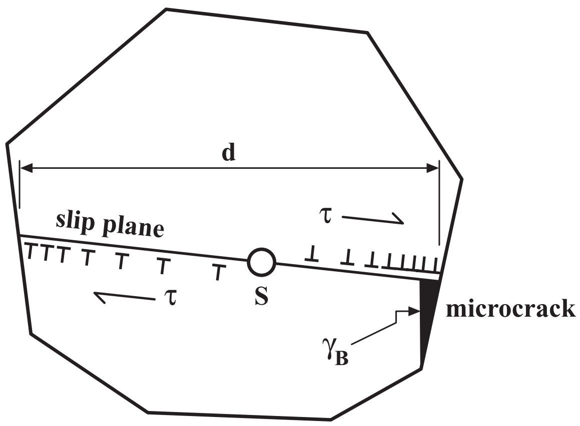
Archaeological silver artifacts may have large grain sizes owing to more or less uncontrolled annealing after mechanical working. Werner (1965) stated that large grain size is a primary cause of silver embrittlement. This is incorrect because large grain size silver is normally ductile (Wanhill *et al.* 1998). However, grain size is an important secondary factor for silver embrittlement.

In the first instance, a large grain size facilitates deeper penetration of corrosion into an artifact. Secondly, embrittlement by impurity element precipitation or segregation is likely to be exacerbated. This is because there is less grain boundary area to embrittle by a given amount of impurity, and embrittlement increases with increasing local concentrations of impurity (Thompson and Knott 1993).

Thirdly, grain size influences microstructurally-induced and synergistic embrittlement in a similar way. Figure 7 shows nucleation of a grain boundary microcrack by a dislocation pile-up on a slip plane. The pile-up can also be regarded as a crack under an effective shear stress τ. Either way, elementary fracture mechanics gives the following condition for grain boundary microcrack nucleation:

$$\tau > (\pi \, \mu \, \gamma_B / d)^{1/2} \qquad (1)$$

where p is the well-known transcendental number, approximately 3.142, μ is the shear modulus, γ_B is the grain boundary fracture surface energy, and d is the grain diameter and pile-up or crack length.



γ_B : grain boundary fracture surface energy

d : grain diameter/dislocation pile-up length

S : dislocation source

τ : effective shear stress on the slip plane

: edge-type component of dislocation loop

Fig. 7 Nucleation of a microcrack by dislocation pile-up. Under the shear stress τ the source S generates dislocation loops which pile-up at barriers (the grain boundaries) in the slip plane. The resulting stress concentrations nucleate microcracks at one or both of the barriers. After Lawn (1993, 318) and Thompson and Knott (1993)

Equation (1) predicts that grain boundary microcrack nucleation is easier when d is larger and gB is smaller. Thus, in the context of archaeological silver, a larger grain diameter d means longer dislocation pile-ups on slip planes or longer corrosion-induced cracks along slip lines and deformation twin boundaries, and hence easier nucleation of cracks along microstructurally-embrittled grain boundaries (γ_B reduced by impurity element precipitation or segregation).

Effect of decorative mechanical working

Decorative mechanical working usually involves chasing, engraving or stamping. Chasing and stamping are indentation processes whereas engraving cuts metal away. Wanhill *et al.* (1998) observed a detrimental effect of chasing on synergistic embrittlement of an Egyptian silver vase, namely corrosion and intergranular fracture at and near the surface *opposite* the chased indentation.

An explanation can be given based on slip-line field theory (Johnson and Mellor 1962, 333-334). Figure 8 is a schematic of the chased indentation. This shows the compression and tension zones associated with the indentation (Wanhill *et al.* 1998) and also the hypothesized indenter and underlying support. Slip-line field theory predicts that when $t_i/w \approx 4.4$ a tension zone forms at the surface opposite the indenter, in addition to the compression zone directly under the indenter. The actual value of t_i/w is 4.2, close enough to support the theory. Be that as it may, the tension field, retained as cold-work in the finished vase, promoted corrosion and intergranular fracture at and near the internal surface of the vase.

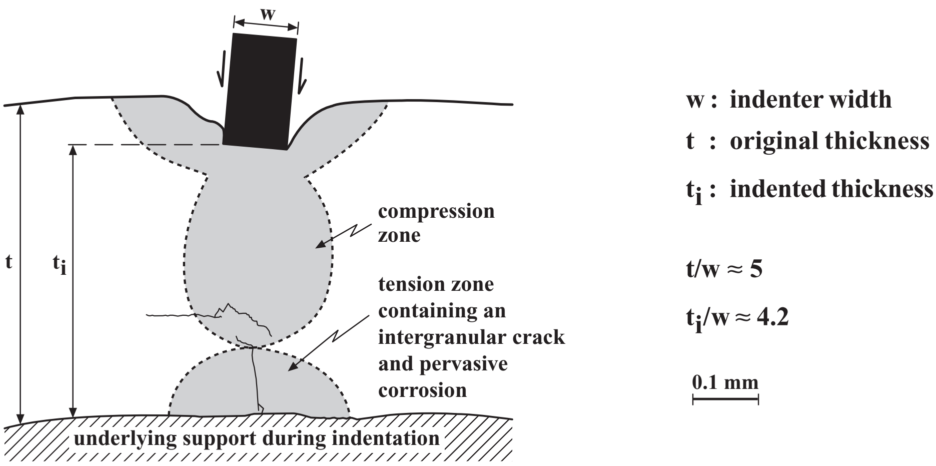


Fig. 8 Through-thickness schematic of a chased indentation in an Egyptian silver vase (Wanhill *et al.* 1998)

DIAGNOSTIC TECHNIQUES FOR DETERMINING EMBRITTLEMENT

Table 1 surveys the diagnostic techniques for determining embrittlement of archaeological silver. The survey is based on Wanhill *et al.* (1995, 1998) and the previous section of this paper. Metallography is the most important diagnostic technique, especially combined with chemical analysis by using SEM+EDX or SEM+WDX combinations: EDX is more widely available than WDX, which, however, is more accurate. Metallography is also an integral part of microhardness testing. For example, the lower metallograph in figure 1 shows a diamond-shaped microhardness indentation, whose size and hence HV value was measured with a specially-adapted optical microscope.

With respect to chemical composition, fully quantitative EDX or WDX analyses using elemental standards should provide two kinds of information. Firstly, the analyses should distinguish whether the silver was obtained from lead cupellation, native silver or aurian silver. However, determination of provenance is more difficult: see, for example, Gale and Stos-Gale (1981).

Table 1 Diagnostic techniques for embrittlement of archaeological silver

VISUAL INSPECTION (×1-×10) (UNAIDED EYE AND HAND LENS)	X-RAY RADIOGRAPHY (×1) (LIMITED ENLARGEMENT)	OPTICAL (×10-×1000) AND SEM (×10-×30,000) METALLOGRAPHY, EDX OR WDX, AND MICROHARDNESS TESTING (HV)	SEM FRACTOGRAPHY (×10-×30,000)

Purpose: Artifact Basic Condition
 	
• nominally intact
 	
• restored
  • macrocrack patterns
  • missing pieces
 	
• fragmented
  • macrocrack patterns
  • missing pieces
	Purpose: “Hidden” Damage
	
	• nominally intact, restored, or fragmented
	  • hairline cracks
	  • macrocracks
	  • cracks following indented decorations
	
	• restored
	  • missing pieces
		Purpose: Manufactured Condition, Chemical Analysis, Internal Damage and Embrittlement
		
		• manufactured condition
		  • mechanically worked
		  • mechanically worked and annealed } grain size, segregation bands, slip lines, deformation and annealing twins
		
		  • as-cast (dendritic)
		  • cast and annealed (cellular) } coring, eutectic distribution
		
		• chemical analysis (SEM + EDX or WDX)
		  • source: lead cupellation, native silver or aurian silver
		  • copper content
		    - high purity may be linked to retained cold-work
		    - intentional additions of copper for strength
		    - long-term cellular precipitation along grain boundaries
		  • lead content: linked to microstructural embrittlement
		
		• corrosion-induced embrittlement
		  • surficial
		  • wide intergranular cracks: linked to cellular precipitation of copper
		  • interdendritic
		  • corrosion along segregation bands, slip lines, deformation twin boundaries and in slip-line fields below indented decorations: severe corrosion leads to cracks
		
		• microstructurally-induced embrittlement
		  • narrow intergranular cracks: linked to lead content
		
		• microhardness testing (HV)
		  • annealed
		  • retained cold-work } HV values also depend on chemistry, especially copper content
		
		  • corrosion
		  • microstructural embrittlement } HV values and possible nucleation of new cracks
			Purpose: Embrittlement Types
			
			• corrosion-induced embrittlement
			  • surficial corrosion
			  • corroded fracture surfaces with fine granular appearance like surficial corrosion
			  • transgranular fracture (crystallographic) along slip bands and deformation twin boundaries
			
			• microstructural embrittlement
			  • mainly clean grain boundary facets: can show local corrosion where slip lines, deformation twins and segregation bands intersect the fracture surfaces
			
			C553-tab.pm6

SEM = Scanning Electron Microscopy; EDX = Energy Dispersive X-ray fluorescence; WDX = Wavelength Dispersive X-ray fluorescence

Secondly, the copper and lead contents are potentially important for diagnosing the types of silver embrittlement, as follows:

(1) At present it is uncertain what the lowest bulk content of copper is that could enable long-term cellular precipitation and corrosion-induced intergranular embrittlement. The lower limit is probably between 1-3 weight % copper (Schweizer and Meyers 1978; Wanhill *et al.* 1998). However, corrosion induced by high temperature copper segregation (interdendritic and along segregation bands that are the remains of coring) and possible long-term low temperature copper segregation along slip bands and deformation twin boundaries could cause embrittlement at even lower copper contents: the Egyptian silver vase investigated by Wanhill *et al*. (1998) contained 0.9 weight % copper.

(2) Lead seems the most likely cause of microstructurally-induced embrittlement (Thompson and Chatterjee 1954; and figures 5 and 6). Long-term precipitation or segregation of lead at grain boundaries could result in brittle fracture even at very low bulk contents of lead, less than 0.1 weight %.

Note, however, that the foregoing remarks on copper and lead contents need putting in perspective. Archaeological silver often contains more than 1-3 weight % copper and 0.1 weight % lead (Gale and Stos-Gale 1981; Bennett 1994). Embrittlement is therefore due to an adverse combination of factors besides the copper and lead contents. These factors include the artifact's manufactured condition and burial time, the average temperature and moisture content of the burial environment and its chemical composition, especially the salt, nitrate and nitrite contents (Gowland 1918).

RESTORATION AND CONSERVATION OF EMBRITTLED ARCHAEOLOGICAL SILVER

Modern restoration and conservation are concerned with both technical and ethical considerations. Any treatments should be reversible. If not, they must be well justified from an art-historical viewpoint. Bearing these points in mind, table 2 shows how the basic condition and type of embrittlement of archaeological silver result in technically possible and potentially sanctionable remedies. For example, nominally intact objects almost certainly would not be heat-treated: coins are possible exceptions. At the other extreme, heat-treatments may be necessary for restoring severely embrittled and fragmented objects (Ravich 1993).

The main objection to heat-treatments is they change the microstructure (Werner 1965; Ravich 1993). Thus information about an artifact's manufactured condition and subsequent history can be partially or completely lost. Heat-treatments also entail a risk of further damage. These considerations mean heat-treatments should be allowed only if preceded by thorough diagnostic investigations, see table 1, and if judged feasible and done by experienced technical staff.

Table 2 also includes a more acceptable measure, outgassing to dry crack surfaces and entrapped corrosion products and then applying a protective coating, to stop further corrosion and embrittlement (Wanhill *et al.* 1995, 1998). Some conservators may regard a protective coating, specifically to prevent tarnishing, as undesirable (Born 1986). However, even though corrosion-induced and synergistic embrittlement must be very slow processes, they will likely continue if atmospheric moisture has access to the cracks and corrosion damage. Thus in this context a protective coating is necessary after drying.

The need to remove 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. In fact, this is a good procedure, if feasible, whether or not the silver is embrittled by corrosion, since it ensures that not only cracks and entrapped corrosion products are dried, but also any externally-connected crevices between the metal and adhesives and fillers.

Table 2 Possible remedial measures for embrittled archaeological silver

ARTIFACT BASIC CONDITION		TYPE OF EMBRITTLEMENT	TECHNICALLY POSSIBLE REMEDIES	POTENTIALLY SANCTIONABLE REMEDIES
Nominally Intact	undeformed	• corrosion-induced; synergistic • microstructurally-induced	• A • B	• A • none
	deformed	• corrosion-induced; synergistic • microstructurally-induced	• A • C • B	• A • C : coins • B : coins
Restored	old restoration	• corrosion-induced • microstructurally-induced • synergistic	• A • disassembly + reassembly + A • disassembly + C + reassembly • disassembly + B + reassembly • A	• A • disassembly + reassembly + A • none • A
	modern restoration	• corrosion-induced; synergistic • microstructurally-induced	• A • disassembly + B + reassembly	• A • none
Fragmented		• corrosion-induced; synergistic • microstructurally-induced	• C + assembly • assembly + A • B + assembly	• C + assembly • assembly + A • B + assembly

NOTES

A Restore original surface finish, if necessary. Clean and rinse successively in demineralised water and ethanol. Outgas *in vacuo* ($< 10^{-4}$ Pa) and place in desiccator to await coating. Apply a colourless transparent organic coating, e.g. an acrylic resin or aliphatic polyurethane. After Wanhill *et al*. (1995, 1998).

B Heat in an inert environment (e.g. argon or nitrogen) for 0.5-1 hour at 500 °C, cool in a forced air draught. This is based on data and suggestions of Thompson and Chatterjee (1954) for silver containing copper as well as lead. The heat treatment's efficacy may be checked by microhardness testing (no new cracks).

C Heat in an inert environment or under charcoal for 5-10 minutes at 700 °C, cool in a forced air draught. This is based on Ravich (1993). Prior heating in flowing hydrogen for 0.5 hour at 300-400 °C could be beneficial (Werner 1965), presumably because some of the intergranular corrosion products - notably silver chloride - are converted back to metal.
The heat-treatment temperature of 700 °C is probably close to the minimum, see Ravich (1993). Higher temperatures may have to be considered. This is very problematical, although successful experiments have been done at temperatures up to 900 °C (Werner 1965; Ravich 1993).

Coins : These are relatively small and easier to heat-treat, even by hand.

Old restorations : Disassembly and reassembly may be feasible and required. Reassemble with modern non-hygroscopic adhesives and fillers (Niemeyer 1997).

Composite objects : B and C assume artifacts do not have soldered joints or niello inlay or gilding. Soft solders (lead-tin) begin melting above 183 °C (Bailey 1961, 513) and will also dissolve the silver if overheated (Niemeyer 1997). Hard solders (silver-copper) begin melting above 779 °C (Smithells 1967, 379). Roman silver sulphide niello should not be heated much above 600 °C, and later silver-copper and silver-copper-lead sulphide niellos melt at about 680 °C and 440 °C respectively (La Niece 1983, Bennett 1994). Gilding is easily ruined by (over)heating: gold layers are so thin, ~10 µm, they soon diffuse into the silver substrate.

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Finally, I must emphasize that although table 2 is quite detailed it is only a guide, based on current knowledge, for dealing with embrittled archaeological silver. Each case has to be considered on its own merits.

SUMMARY

Archaeological silver can be brittle. Embrittlement is a long term consequence of corrosion and microstructural changes, which depend on an artifact's chemical composition, manufactured condition and subsequent history. Current knowledge enables identifying and explaining the types of embrittlement and specifying diagnostic techniques for determining them. However, remedial measures to be taken during restoration and conservation are less certain. Suggested remedies are intended to be used as a guide.

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