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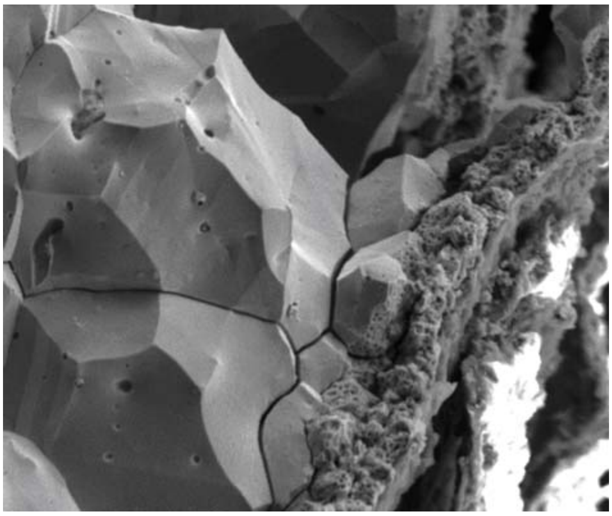
Executive summary

Corrosion-induced embrittlement of ancient silver



Problem area
Corrosion-induced embrittlement of ancient silver is a complex phenomenon that can cause severe cracking and fragmentation of valuable objects. This damage may require irreversible methods of restoration and conservation. Detailed case studies to characterize the embrittlement are important for selecting the optimum methods to ensure conservation with a minimum of intervention.

Description
This report has two parts. The first describes the types of corrosion-induced embrittlement in ancient silver, especially in the light of more recent evidence that some types may be due to stress corrosion cracking (SCC). The second part proposes and discusses ways to restore and conserve cracked and severely embrittled ancient silver objects.

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Corrosion-induced embrittlement of ancient silver

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Summary

Corrosion-induced embrittlement of ancient silver is a complex phenomenon that can cause severe cracking and fragmentation of valuable objects. This damage may require irreversible methods of restoration and conservation. Detailed case studies to characterize the embrittlement are important for selecting the optimum methods to ensure conservation with a minimum of intervention. This paper describes the types of corrosion-induced embrittlement observed in a wide variety of ancient silver artefacts and discusses the remedial measures that are or could be used.

Contents

CORROSION-INDUCED EMBRITTLEMENT OF ANCIENT SILVER

R.J.H. Wanhill[1] and J.P. Northover[2]

Abstract

Corrosion-induced embrittlement of ancient silver is a complex phenomenon that can cause severe cracking and fragmentation of valuable objects. This damage may require irreversible methods of restoration and conservation. Detailed case studies to characterize the embrittlement are important for selecting the optimum methods to ensure conservation with a minimum of intervention. This paper describes the types of corrosion-induced embrittlement observed in a wide variety of ancient silver artefacts and discusses the remedial measures that are or could be used.

Keywords: silver embrittlement, corrosion, stress corrosion, restoration, conservation

1 Introduction

Ancient silver artefacts and coins can be susceptible to microstructurally-induced and corrosion-induced embrittlement [1-14]. Microstructurally-induced embrittlement is much less common and is characterized solely by intergranular fracture with bodily displaced grains [1, 8-12]. In contrast, corrosion-induced embrittlement takes several forms [8-14].

This paper has two parts. The first part describes the types of corrosion-induced embrittlement, especially in the light of more recent evidence that some types may be due to stress corrosion cracking (SCC). Thorough characterization of embrittlement is important for determining the best ways to restore and conserve ancient silver objects. These aspects are discussed in the second part.

2 Types of corrosion-induced embrittlement

2.1 General corrosion: figure 1

In high silver content alloys general corrosion is slow conversion of the original metal surfaces or fracture surfaces to silver chloride [4, 13-16]. The silver chloride forms a brittle, finely granular layer, see figure 1, but does not affect the remaining metal's integrity. On the other hand, unfavourable environmental conditions and longevity of interment may result in an object being completely converted to silver chloride, sometimes retaining its shape, sometimes not [4, 15].

2.2 Intergranular or interdendritic corrosion: figures 2-6

Intergranular corrosion is the most common type since it occurs in mechanically worked and annealed ancient objects, which constitute the majority of recovered artefacts. This type of corrosion has been attributed partly to low-temperature segregation of copper [2, 3, 6, 13, 14], which is commonly present in ancient silver. In particular, so-called discontinuous precipitation of copper has been suggested to be very detrimental [2]. This precipitation sometimes causes the grain boundaries to appear meandering.

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However, intergranular corrosion need not occur along the meandering grain boundaries, while it does occur along boundaries with no evidence of discontinuous precipitation [12-14]. Another important factor is residual (retained) cold-work, which can increase the susceptibility to both intergranular and transgranular corrosion [8, 12]. Examples to illustrate all these points are given in figures 2-5.

Interdendritic corrosion can occur in castings, which are uncommon, especially in the Old World. An example from pre-Inca Peru is shown in figure 6.

2.3 Transgranular corrosion: figures 7 and 8

Corrosion along slip lines and deformation twin boundaries can occur in objects that have not been annealed after (final) mechanical working, which includes striking coins [1] and decorating by chasing and stamping [8, 12]. Inside the metal these types of corrosion can lead to additional corrosion along segregation bands. These are the much-modified remains of high-temperature solute element segregation (coring) and interdendritic segregation that occurred during solidification of an ingot or cupelled button. Examples to illustrate these types of corrosion are given in figures 7 and 8.

2.4 Evidence for transgranular SCC: figure 9

Stress-assisted corrosion-induced embrittlement of ancient silver was previously reported [8, 17], without explicitly implicating SCC. In both cases the embrittlement was attributed to residual cold-work, which resulted in transgranular cracking.

Figure 9 illustrates (a) slip line corrosion, (b) cracking, and (c) the resulting crystallographic fracture observed for an Egyptian silver vase [8, 9]. The vase was also microstructurally-embrittled, which enabled the observation of transgranular cracking superimposed on intergranular fracture, as in figures 9a and 9b.

Models linking slip line corrosion to transgranular SCC have been proposed for alloys with the same face centred cubic (fcc) crystal structure as silver [18-23]. These models consider two stages of cracking:

(1) Corrosion along slip lines and slip plane dissolution. Several classes of fcc alloys undergo corrosion along slip lines [21, 22, 24]. Corrosion begins as pitting attack of the highly strained crystal lattice at the cores of surface-connected dislocations. The pits develop into slots that can eventually merge to result in slip plane dissolution and cracking. Since the slip planes are {111} in fcc metals, these initial cracks are on {111} planes.

(2) Transgranular SCC. In this stage the cracking diversifies in the choice of average crystallographic fracture planes and the fracture topography. The average fracture planes are usually {110} in copper alloys [18-20] and {100} in austenitic stainless steels [21], although average {110} cracking also occurs in these steels [22]. In detail the fracture topographies reveal microfaceting. Copper alloy fracture surfaces show {110} microfacets [19], and the stainless steel fracture surfaces consist partly or even entirely of {111} microfacets [21, 22].

The models are "corrosion-assisted cleavage" [18-20]; its successor, "strain-enhanced dissolution" [23]; and "corrosion-enhanced plasticity" [21, 22]. A detailed discussion of the models and their applicability to ancient silver has been given previously [9]. Since the corrosion-assisted cleavage model was abandoned [23] and the corrosion-enhanced plasticity model requires hydrogen generation – which does not occur when silver corrodes [25] – only the strain-enhanced dissolution model remains to try and explain the features shown in figure 9.

A schematic of the strain-enhanced dissolution model is given in figure 10. The proposed (and here abbreviated) sequence of events is:

(a) Dislocation pile-up at an obstacle on a slip plane.

(b, c) Crack initiation and growth by slip plane dissolution, enhanced by the strain associated with the local normal stress, σ_{n1}. The slip plane dissolution continues as long as σ_{n1} exceeds the local normal stress, σ_{n2}, on alternative crystallographic planes.

(d) Crack growth by strain-enhanced directed dissolution on an alternative plane whose local normal stress, σ_{n2}, exceeds σ_{n1} but is not high enough to blunt the crack tip by dislocation emission.

By proposing that the fracture planes do not always have to be the slip planes (as found for copper alloys and austenitic stainless steels [18-22]), this model also provides an explanation for the transgranular fracture features in figures 9b and 9c. Figure 9b shows a 90º "dog-leg" crack which cannot be on a {111} plane, but must be on either a {110} or {112} plane. Figure 9c shows similar "dog-legs" that result in high-angle steps on slip plane fracture surfaces. There is no evidence of microfaceting similar to that observed for copper alloys [19] and stainless steels [21, 22], but this was variable anyway, see (2) above.

The strain-enhanced dissolution model also has a more general implication. It reduces the distinction between corrosion along slip lines, slip plane dissolution and transgranular SCC. In other words, these phenomena are seen to have a common cause, namely the enhancement of corrosion by local strains in the crystal structure.

2.5 Evidence for intergranular SCC: figures 2 and 11

Intergranular SCC is a widespread phenomenon in metals and alloys [24, 26], though generally confined to high strength materials. Several mechanisms have been proposed, but there is no overall consensus, even for a particular class of alloys. However, a common feature of intergranular SCC is the relatively clean-looking grain boundary facets. Here this feature is used by analogy to suggest that intergranular SCC can occur in ancient silver.

Figures 2 and 11 give examples of corrosion-induced intergranular fracture. Figure 11a is a detail of figure 2b, and figure 11b is a fractograph of intergranular corrosion and SCC in an aluminium-lithium alloy [27].

Figure 11a shows a transition caused by general corrosion destroying the corrosion-induced intergranular fracture in a silver kaptorga [13]. The intergranular fracture is very clean-looking, with only isolated pits. Figure 11b shows a transition from intergranular corrosion with corroded (pitted) facets to intergranular SCC with facets hardly attacked by pitting [27]. Other fractographs showed more pitting attack, which mainly affected the intergranular corrosion areas [27].

Although the fracture surfaces and transitions in figures 11a and 11b are not identical in appearance, the overall similarity suggests that the corrosion-induced intergranular fracture in figure 11a could be SCC. However, in this case the source of the necessary stresses and strains would be external forces due to interment rather than residual cold-work, since the kaptorga had a recrystallized microstructure with large annealed grains [13].

3 Restoration and conservation

Modern restoration and conservation must consider both technical and ethical aspects. This means that preference is given to *reversible* remedial measures that respect an object's integrity. However, reversibility is not always practicable [4, 6, 7]. This is especially the case for severely embrittled and fragmented ancient silver objects, for which non-reversible consolidation is essential [4, 28].

The remedial measures for corrosion-embrittled ancient silver objects depend on their condition [9, 12, 29]:

(1) In general, nominally intact (but cracked) or previously restored objects may be cleaned, outgassed to dry crack surfaces and any entrapped corrosion products, and given a *removable* transparent organic coating. Even so, the choice of cleaning methods and coatings requires careful consideration [4, 30].
Traditional cleaning methods restore the surface finish by *light* polishing, cleaning and rinsing in demineralised water and alcohol, and allowing the object to dry, preferably in a low-humidity environment, e.g. in a desiccator.
A recently developed cleaning method is hydrogen plasma reduction [31]. This requires no more than an hour, at temperatures of 40-100 ºC, which minimises or avoids significant alterations to an object's microstructure. The hydrogen plasma reduces *surface* corrosion products to metallic silver, but it is not suitable for thick corrosion layers [28, 31].

(2) If the embrittlement is severe it may be necessary to consolidate the object, especially if it is fragmented. Customarily this is done using impregnation or soaking in lacquers or resins [28] and joining cleaned fragments with adhesives and adhesive-impregnated backing cloths [7]. These treatments are irreversible.
An additional dimension is added if the fragments are covered in corrosion products and/or deformed, in which case it may be necessary to heat-treat them before consolidation [6, 7, 29]. Again, this is irreversible, and not without risk of further damage.

A possible alternative to consolidation using lacquer or resins is cleaning followed by the use of Parylene coatings. For example, an object could be cleaned in hydrogen plasma, which would penetrate surface-connected cracks as well as clean the surface. In this respect, the relatively clean-looking intergranular fracture exemplified by the kaptorga, figure 11a, suggests that many intergranular cracks would be clean after a short time. Following cleaning, the object could undergo a Parylene coating procedure.

Parylene coatings have special properties and advantages, since they are applied in the vapour phase in a reduced-pressure environment [32]. They have controllable thickness, high crevice or crack penetration, and are pinhole-free. Also, most moisture would be removed by the reduced-pressure environment (13.3 Pa, 0.1 Torr) in the coating chamber. Another potential advantage is the possibility of "tailoring" the coating thickness to fill cracks, thereby providing adhesion between the fracture surfaces and improving the consolidation.

Disadvantages of using Parylene coatings are that they are not removable below 150-175 ºC, i.e. they would be effectively irreversible treatments for ancient silver, and they require special equipment. However, this equipment need not be purchased and can be employed for small coating runs.

In view of the fact that the Canadian Conservation Institute in Ottawa is already conserving brittle and fragile objects by using Parylene coatings, it seems very worthwhile to investigate their use for the conservation of severely embrittled ancient silver.

4 Concluding remarks

Ancient silver can be susceptible to several types of corrosion-induced embrittlement. Examples have been given for several artefacts with widely different provenance: an Egyptian vase, a kaptorga from the Czech Republic, a Byzantine paten, a Sassanian repoussé head, the Gundestrup Cauldron, and a Sican tumi. There is evidence that some of this embrittlement could be due to stress corrosion cracking.

The damage can be so severe that irreversible restoration and conservation methods must be used. The technical and ethical aspects of these methods must be carefully considered, aiming for a minimum of intervention. In this respect detailed case studies [1, 5, 8, 12-14] to characterize embrittlement are most useful.

5 Acknowledgements

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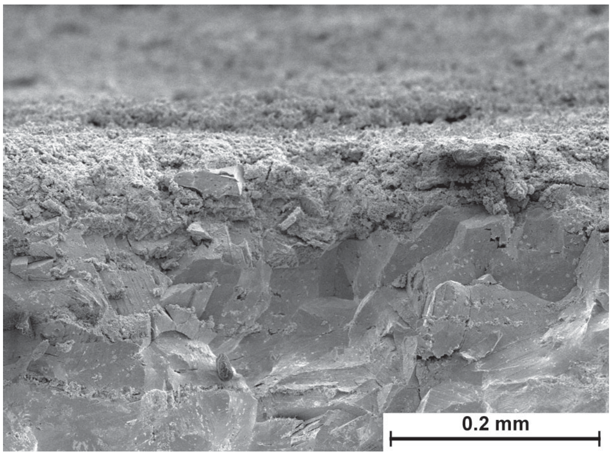
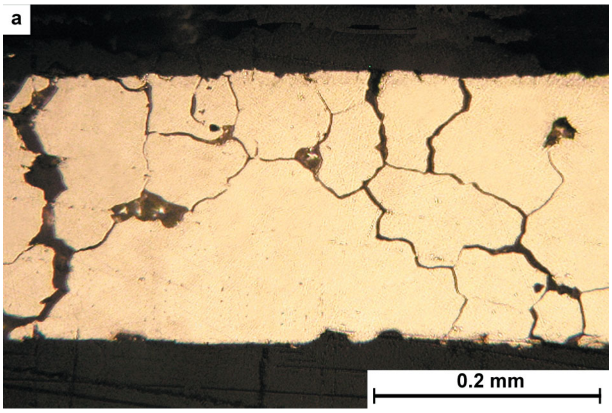


Fig. 1 SEM fractograph of general (surface) corrosion overlying intergranular fracture in an Egyptian vase [8]: see figure 2b also



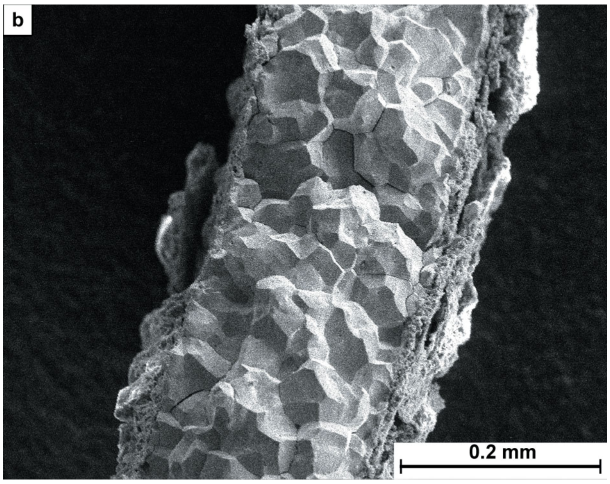


Fig. 2 Optical metallograph (a) and SEM fractograph (b) of corrosion-induced intergranular fracture in a kaptorga (container for relicts or amulets) [13]. There was no discontinuous precipitation at grain boundaries. Note the general (surface) corrosion in the fractograph, cf. figure 1

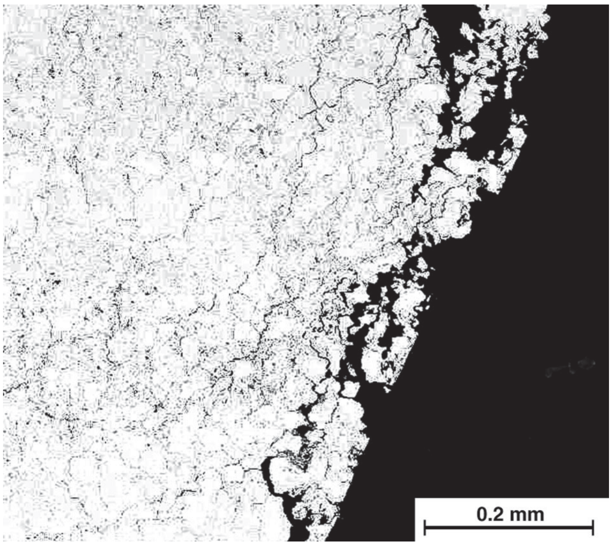


Fig. 3 SEM metallograph of corrosion-induced intergranular fracture in a Byzantine paten (altar plate) [12]. There was extensive discontinuous precipitation of copper at grain boundaries, not visible at this magnification

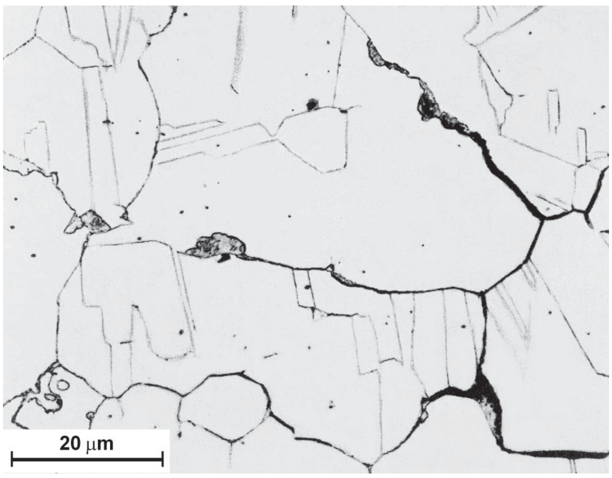


Fig. 4 Optical metallograph of corrosion-induced intergranular fracture in a Sassanian repoussé head [2]. Note the association of cracking with discontinuous precipitation of copper at some grain boundaries

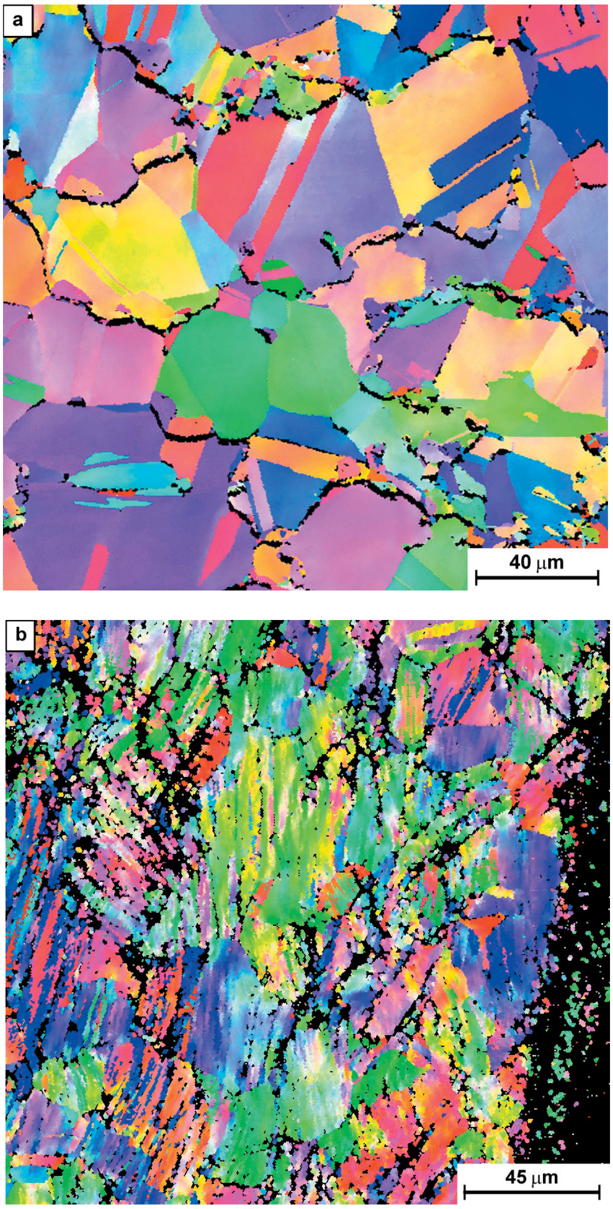


Fig. 5 Electron Backscatter Diffraction IPF (Inverse Pole Figure) colour-coded maps of (a) annealed and (b) heavily cold-worked samples from the Gundestrup cauldron [12]. The annealed sample was uncorroded despite extensive discontinuous precipitation of copper (delineated by the black dots) at grain boundaries. The cold-worked sample had no discontinuous precipitation of copper at grain boundaries but there was extensive corrosion-induced intergranular and transgranular fracture (the internal black-dotted areas)

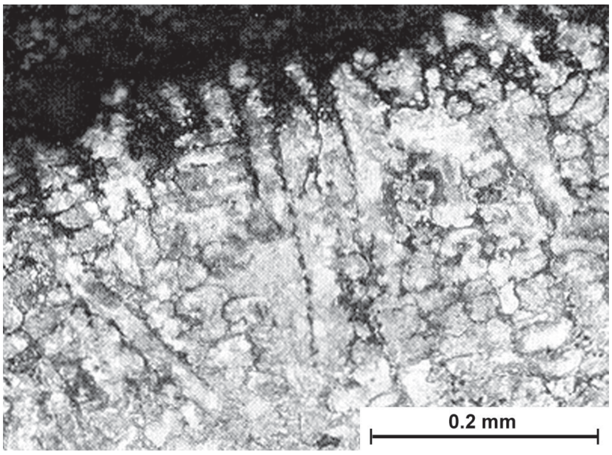


Fig. 6 SEM metallograph of interdendritic corrosion penetrating into a virtually as-cast sample from a Sican tumi (ceremonial knife) [16]

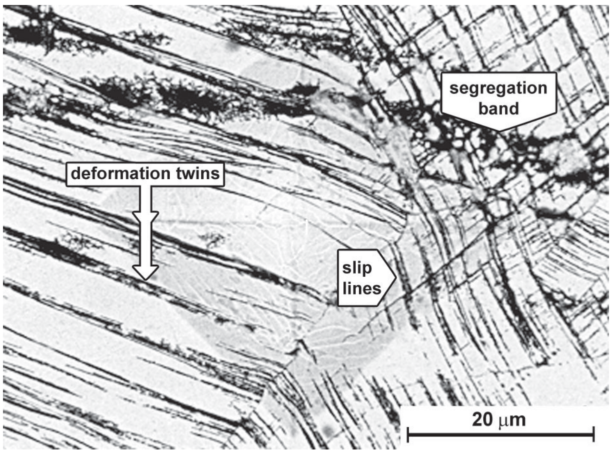


Fig. 7 SEM metallograph of corrosion along slip lines, deformation twins and segregation bands in an Egyptian vase [8, 12]. The diamond-shaped shadow is due to a microhardness indentation that rendered the corrosion more visible

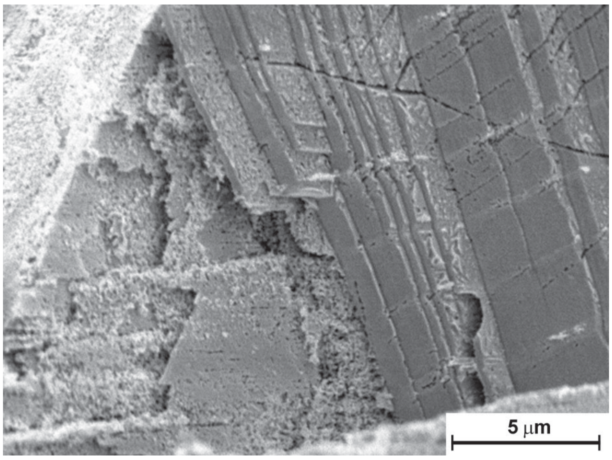


Fig. 8 SEM fractograph of corrosion along slip planes and deformation twins in an Egyptian vase [8, 12]. General corrosion has attacked and partly destroyed the left-hand fracture surface

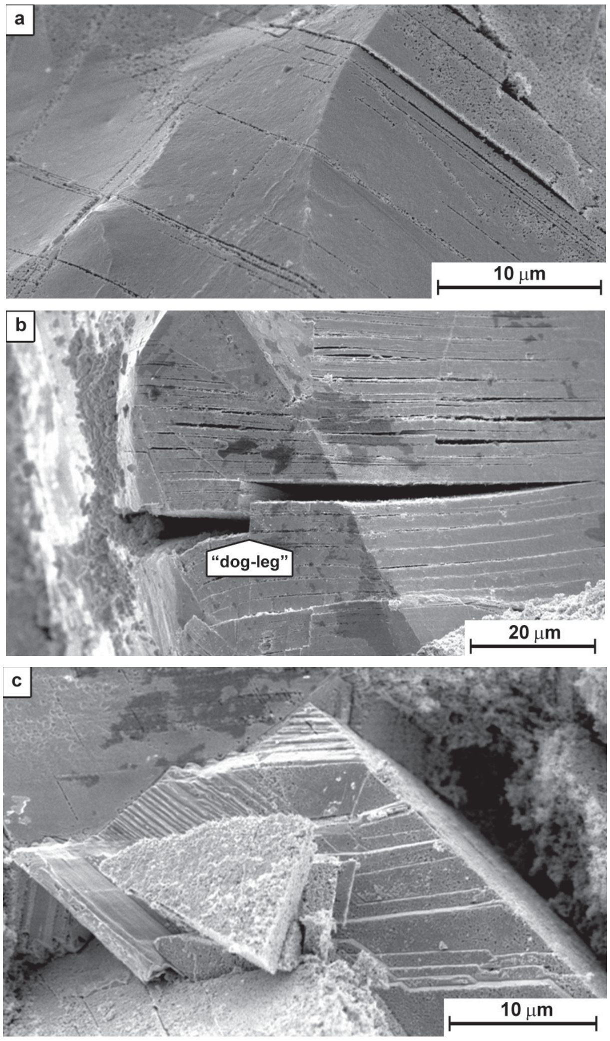


Fig. 9 SEM fractographs of (a) slip line corrosion, (b) slip plane dissolution and cracking and (c) crystallographic fracture topography in an Egyptian vase [9]

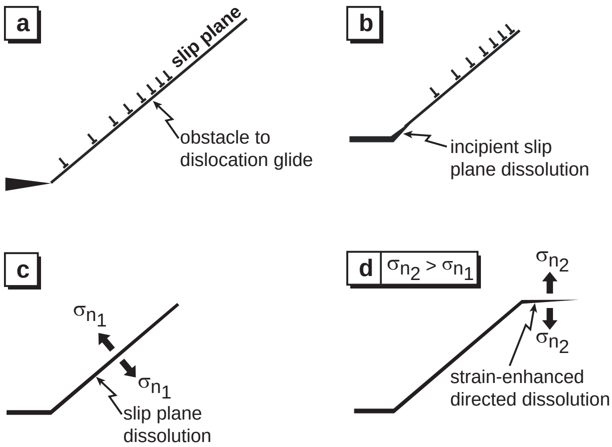


Fig. 10 The “strain-enhanced dissolution” model of transgranular SCC [23]

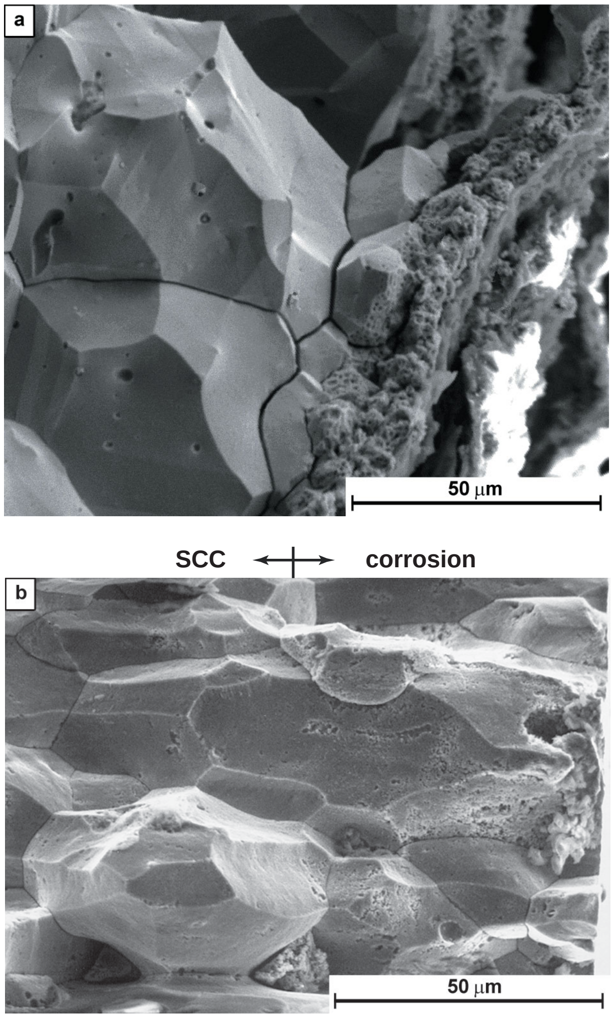


Fig. 11 SEM fractographs of (a) corrosion-induced intergranular fracture and general corrosion in a silver kaptorga (detail of figure 2) and (b) the boundary between SCC and intergranular corrosion in an aluminium-lithium alloy [27]