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KRTOST ANTIČKOG SREBRA IZAZVANA KOROZIJOM

CORROSION-INDUCED EMBRITTLEMENT OF ANCIENT SILVER

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Ključne reči

- srebro
- korozija
- naponska korozija
- obnavljanje (restauracija)
- konzervacija

Izvod

Krtost antičkog srebra izazvana korozijom je složena pojava koja može da izazove izražene prsline i raspadanje dragocenih predmeta. Ovakvo oštećenje može da zahteva ireverzibilne postupke obnavljanja i konzervacije. Detaljna analiza oštećenja koja karakteriše krtost je neophodna za izbor optimalnog postupka radi postizanja konzervacije uz minimalne intervencije. U radu su opisani tipovi krtosti koji mogu biti izazvani korozijom za slučajeve predmeta i uzoraka od antičkog srebra i modeli i diskutovane mere sanacije, koje su, ili mogu da se primene.

UVOD

Predmeti i kovani novac od antičkog srebra su osetljivi na pojavu krtosti izazvane korozijom i mikrostrukturom, /1-14/. Korozija nastala zbog mikrostrukture je ređa pojava i karakteriše je samo interkristalni lom sa prostorno raspoređenim zrnima /1, 8-12/. Međutim, krtost izazvana korozijom ima više pojavnih oblika, /8-14/.

Ovaj rad sadrži dva glavna dela. Prvi deo opisuje tipove krtosti izazvane korozijom, posebno u svetlu nedavno utvrđenih dokaza da neki tipovi mogu da budu izazvani naponskom korozijom (SCC). Temeljna karakterizacija krtosti je značajna za određivanje najboljeg postupka restauracije i konzervacije predmeta od antičkog srebra. Ovi aspekti su diskutovani u drugom delu rada.

TIPOVI KRTOSTI IZAZVANE KOROZIJOM

Opšta korozija: slika 1

U legurama sa visokim sadržajem srebra je opšta korozija konverzija originalne površine metala ili površine preloma u srebrohlorid, /4, 13-16/.

Hlorid srebra obrazuje krti, finozrni sloj, sl. 1, ali neće uticati na integritet ostalog metala. Sa druge strane, nepovoljni uslovi okoline i dugotrajna zatrpanost (zakopanost) okolnim materijalom mogu dovesti na predmetu do potpune konverzije u hlorid srebra, ponekad pri nepromenjenom obliku, ponekad uz promenu oblika, /4, 15/.

Keywords

- silver
- corrosion
- stress corrosion
- restoration
- conservation

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. The paper describes the types of, and models for, corrosion-induced embrittlement in different ancient silver artefacts, and discusses the remedial measures that are or could be used.

INTRODUCTION

Ancient silver artefacts and coins can be susceptible to microstructurally- 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/. However, corrosion-induced embrittlement has several forms, /8-14/.

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

CORROSION-INDUCED EMBRITTLEMENT TYPES

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, Fig. 1, but does not affect the remaining metal's integrity. On the other hand, unfavourable environmental conditions and longevity of interment (burial) may result in an object being completely converted to silver chloride, sometimes retaining its shape, sometimes not, /4, 15/.

Interkristalna ili interdendritska korozija, slike 2-6

Interkristalna korozija je najčešći tip korozije, jer se ona javlja na mehanički obrađenim i otpuštenim starim predmetima, koji čine većinu otkrivenih starina. Ovaj tip korozije je delom pripisan niskoj temperaturi segregacije bakra, /2, 3, 6, 13, 14/, koji je često sadržan u antičkom srebru. Naročito se smatraju vrlo štetnim takozvani diskontinualni talozi bakra, /2/. Ovi talozi u stvari izgledaju kao amorfni, a ne kao diskontinualni, i ponekad stvaraju utisak da granice zrna imaju meanderski izgled. Međutim, interkristalna korozija ne mora da se pojavi duž meandriranih granica zrna, ali se javlja duž granica na kojima se ne uočavaju diskontinualni talozi, /12-14/. Sledeći značajan uticaj potiče od zaostale (sačuvane) hladne obrade, koja može da poveća osetljivost, kako prema interkristalnoj tako i prema transkristalnoj koroziji, /8-12/. Primeri koji pokazuju sve navedene uticaje dati su na sl. 2-5.

Interdendritska korozija može da se pojavi u odlivcima, koji se retko nalaze, posebno iz Starog veka. Primer iz Perua, iz doba pre Inka, prikazan je na sl. 6.

Transkristalna korozija: slike 7 i 8

Korozija duž granica linija klizanja i dvojnika deformacija može da se pojavi u predmetu koji nije otpušten posle (završne) mehaničke obrade. To je tipično za kovani novac, /1/, i predmete ukrašene grecanjem i utiskivanjem, /8, 12/.

U unutrašnjosti metala ovi tipovi korozije mogu izazvati dodatnu koroziju duž traka segregacija. One su izrazito modifikovani ostaci segregacije elemenata rastvorenih na visokoj temperaturi (jezgro) i interdendritske segregacije, koje se javljaju tokom očvršćavanja ingota ili čišćenja dragocenih predmeta. Primeri za ove tipove korozije egipatske vaze su dati na sl. 7 i 8. Opšta korozija je napala i delimično razorila leve delove površine preloma.

Prikaz transkristalne korozije izazvane naponom (naponskom korozijom – SCC): slika 9

Krtost antičkog srebra, zbog naponske korozije (SCC), je već ranije prikazana, /8, 17/, a da nije potpuno jasno istaknuto da je u pitanju SCC. U oba slučaja pojava krtosti je pripisana zaostaloj hladnoj deformaciji, posle čega je došlo do transkristalnih prslina.

Slika 9 pokazuje: (a) koroziju linija klizanja, (b) pojavu prslina, i (c) rezultujući kristalografski lom uočen na egipatskoj srebrnoj vazi, /8, 9/. Na vazi je takođe došlo do mikrostrukturne krtosti, što je omogućilo da se vide transkristalne prsline, koje su se nadovezale na interkristalni lom, sl. 9a i b.

Prikaz interkristalne korozije izazvane naponom (naponskom korozijom – SCC): slike 2 i 10

Interkristalna SCC se često javlja u metalima i legurama, /24, 26/, ali ipak ograničena samo na materijale visoke čvrstoće. Predloženo je nekoliko mehanizama, ali nema opšte saglasnosti, čak ni za pojedine vrste legura.

Međutim, u opštem izgledu interkristalne SCC, fasete granica zrna deluju relativno čisto. Ovakav izgled je ovde iskorišćen kao podloga za analogiju da i u antičkom srebru može da dođe do interkristalne SCC.

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 (often present in ancient silver), /2, 3, 6, 13, 14/. In particular, so-called discontinuous precipitation of copper can be very detrimental, /2/. This precipitation actually looks amorphous, not discontinuous, and sometimes causes the grain boundaries to appear meandering. 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 Figs. 2-5.

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

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. This is typical of struck coins, /1/, and artefacts decorated 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 in an Egyptian vase, are given in Figs. 7 and 8. General corrosion has attacked the left-hand fracture surfaces.

Evidence for transgranular Stress Corrosion Cracking - SCC: Figure 9

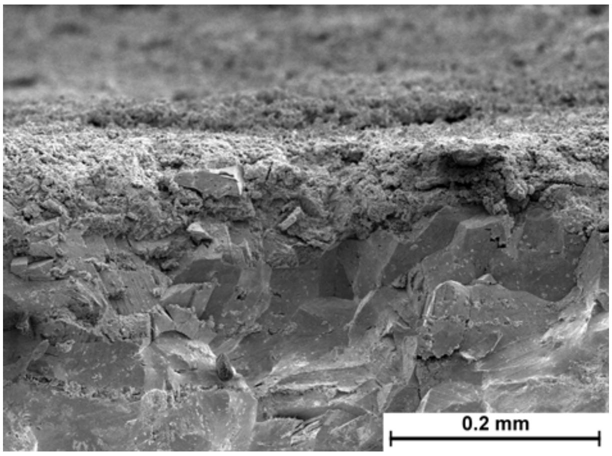
Stress-assisted corrosion-induced embrittlement of ancient silver was previously reported, /8, 17/, without explicitly implicating SCC. In both cases the embrittlement was attributed to residual cold-work, which resulted in transgranular cracking.

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 Figs. 9a and 9b.

Evidence for intergranular Stress Corrosion Cracking - SCC: Figures 2 and 10

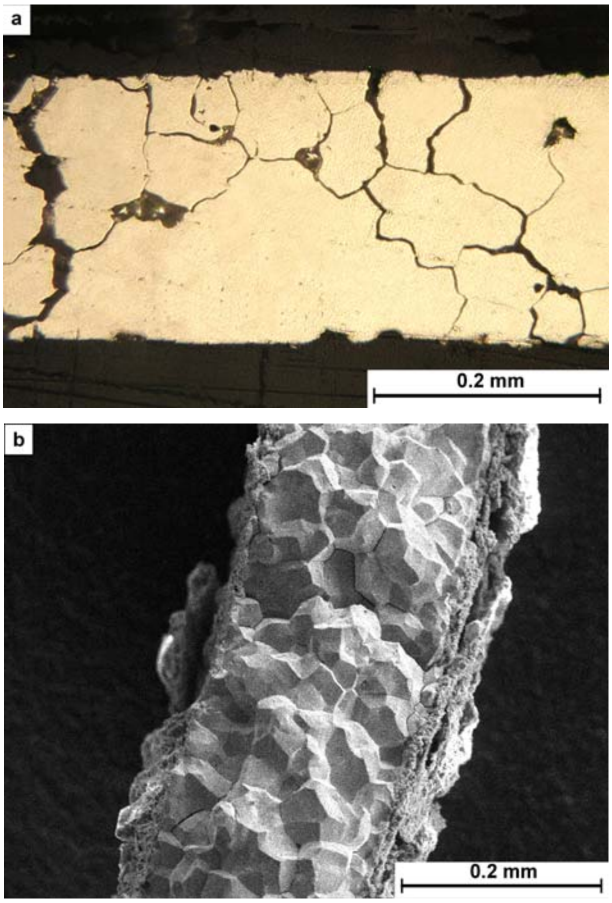
Intergranular SCC is a widespread phenomenon in metals and alloys, /24, 26/. Several mechanisms have been proposed, but there is no overall consensus, even for a particular class of alloys.

However, common features of intergranular SCC are the relatively clean-looking grain boundary facets. In this paper these features are used by analogy to suggest that intergranular SCC can occur in ancient silver.



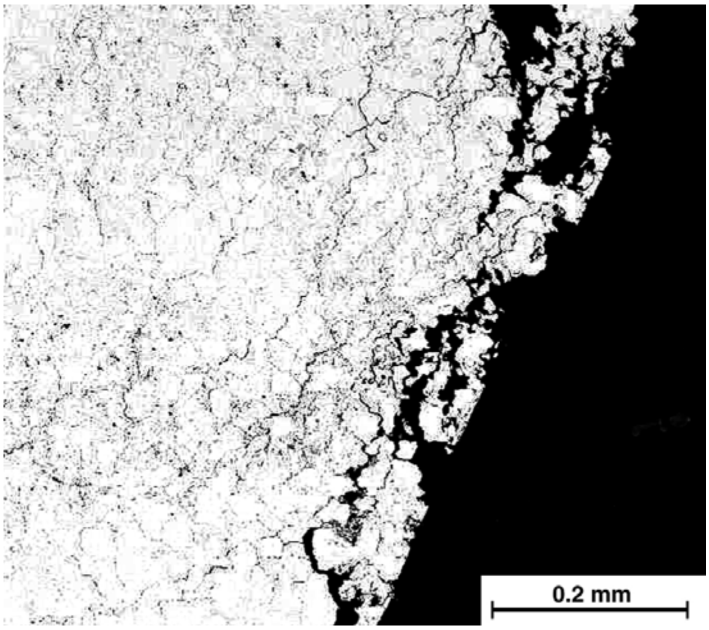
Slika 1. SEM snimak opšte (površinske) korozije preko interkristalnog loma egipatske vaze, /8/: vidi i sl. 2b

Figure 1. SEM fractograph of general corrosion overlying intergranular fracture in an Egyptian vase, /8/: see Fig. 2b also.



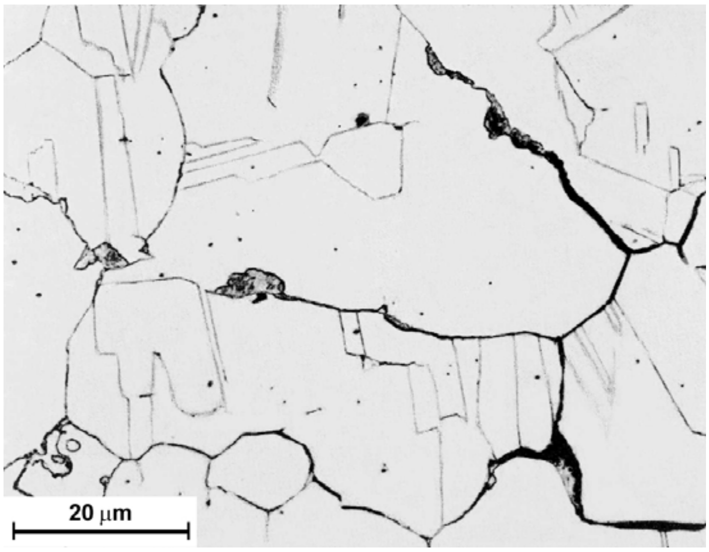
Slika 2. Optička metalografija (a) i SEM snimak površine preloma (b) interkristalnog loma kaptorge (posude za relikvije i amajlije), /13/. Nema diskontinualnog taloga bakra na granicama zrna. Vidi se opšta (površinska) korozija, uporedi sa sl. 1

Figure 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 of copper at grain boundaries. Note the general (surface) corrosion in the fractograph, cf. Fig. 1.



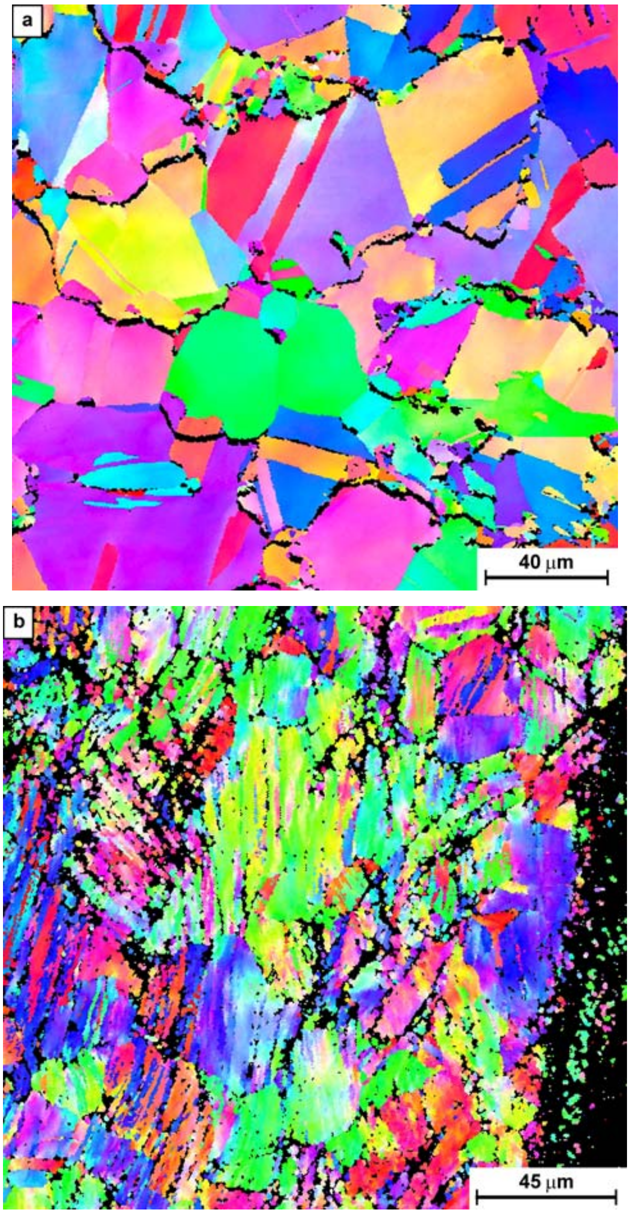
Slika 3. SEM metalografija interkristalnog loma izazvanog korozijom vizantijskog nafornjaka (oltarski poslužavnik). Postoje izraženi diskontinualni talozi bakra na granicama zrna, koji se ne vide pri datom uvećanju

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



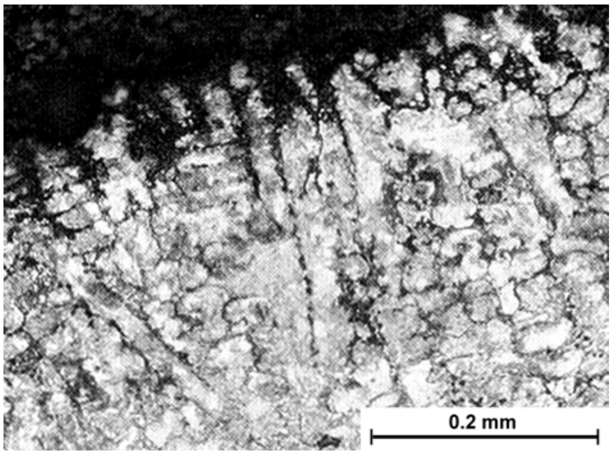
Slika 4. Optička metalografija interkristalnog loma izazvanog korozijom glave persijskog kralja, izrađene iskivanjem sa leđne strane, /2/. Vide se prsline diskontinualnog taloga bakra na granicama nekih zrna

Figure 4. Optical metallograph of corrosion-induced intergranular fracture in a repoussé Sassanian head, /2/. Note the cracking associated with discontinuous precipitation of copper at some grain boundaries.

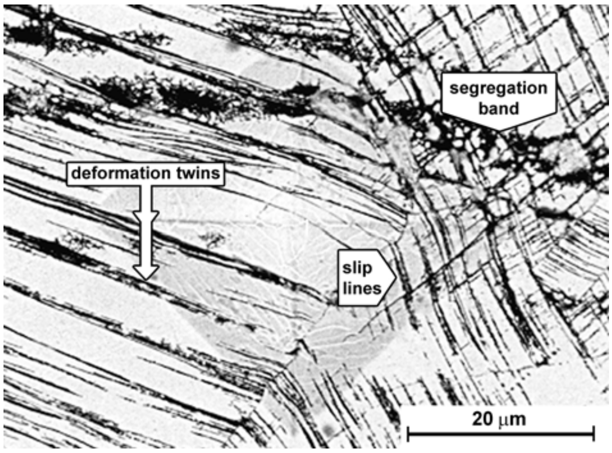


Slika 5. Mapa kodirana u bojama povratnog rasejanja elektronske difrakcije IPF, inverzne slike kraka (IPF), otpuštenog (a), i izrazito hladno deformisanog uzorka od Gundestrup pehara (kondira), /12/. Otpušteni uzorak nije korodirao i pored izraženog diskontinualnog taloga bakra (obeleženog linijom od crnih tačaka) na granicama zrna. Hladno obrađeni uzorak nema diskontinualnog taloga bakra na granicama zrna, ali se lako uočava intenzivno izražen interkristalni i transkristalni lom (unutrašnje površine jasno istaknutih crnih tačaka)

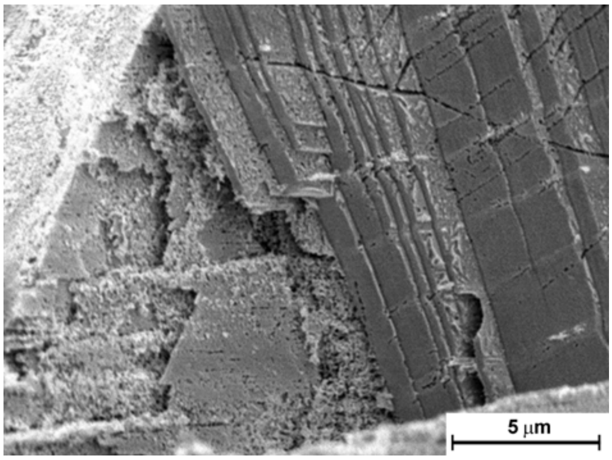
Figure 5. Electron Backscatter Diffraction IPF (Inverse Pole Figure) colour-coded maps of (a) annealed and (b) heavily cold-worked samples from the Gundestrup cauldron, /12/. The annealed sample was uncorroded despite extensive discontinuous precipitation of copper (delineated by the black dots) at grain 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).



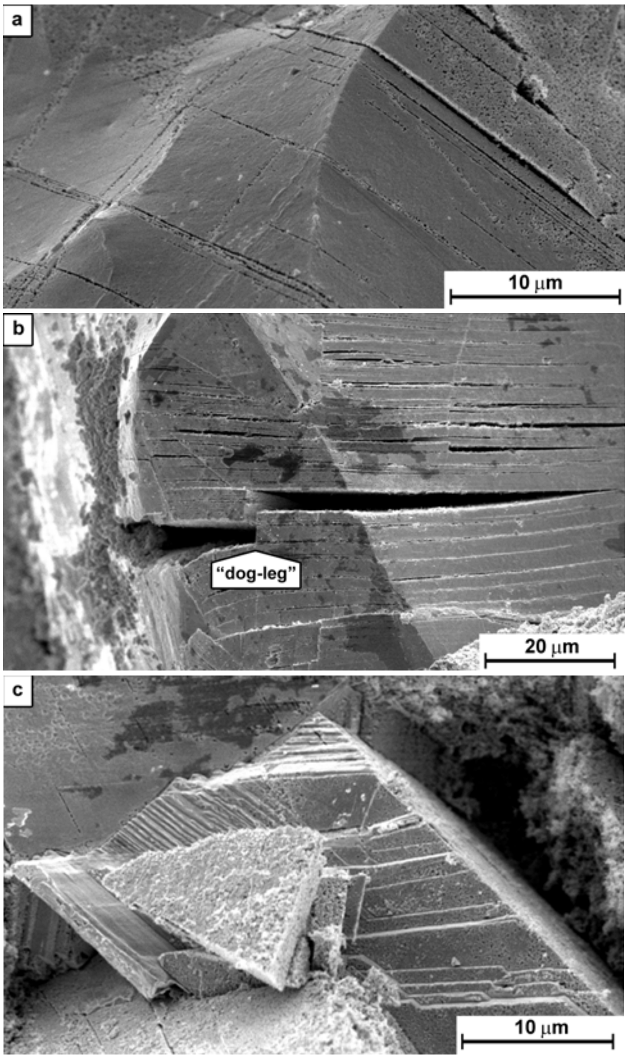
Slika 6. SEM metalografija interdendritske korozije koja prodire u virtualni liveni uzorak obrednog tumi noža Sika, /16/
Figure 6. SEM metallograph of interdendritic corrosion penetrating into a virtually as-cast sample from a Sican tumi (knife), /16/.



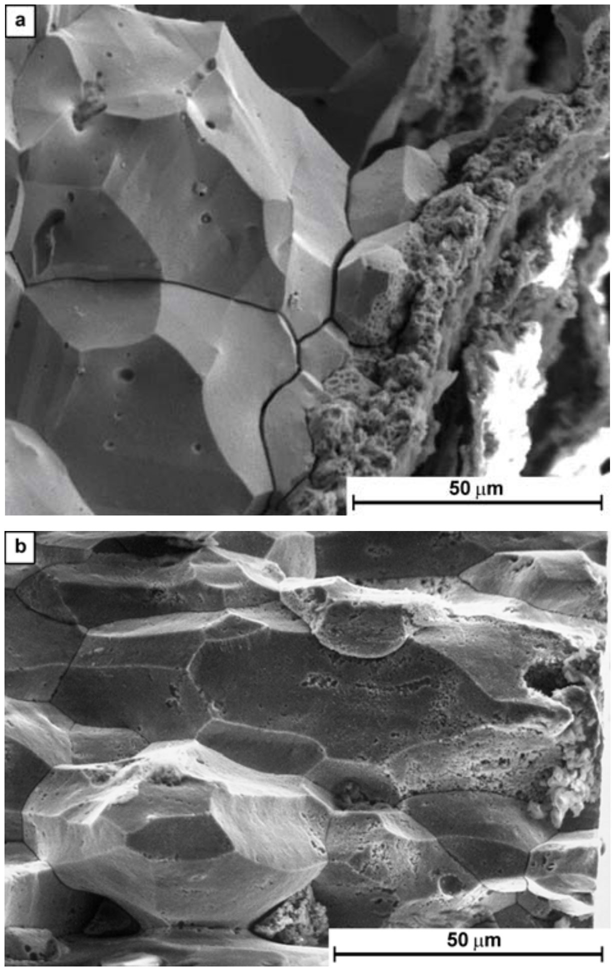
Slika 7. SEM snimak korozije duž linija klizanja, deformacija dvojnika i traka segregacije u egipatskoj vazi, /8, 12/. Korozija se bolje vidi i zbog senke otiska od izmerene mikrotvrdoće
Figure 7. SEM metallograph of corrosion along slip lines, deformation twins and segregation bands in an Egyptian vase, /8, 12/. The diamond-shaped shadow is due to a microhardness indentation that rendered the corrosion more visible.



Slika 8. SEM snimak loma od korozije duž ravni klizanja i dvojnika deformacije egipatske vaze, /8, 12/. Opšta korozija je napala i delimično razorila levi deo površine preloma
Figure 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 surfaces.



Slika 9. SEM snimci loma od (a) korozije duž linija klizanja, (b) rastvaranja ravni klizanja i prslina i (c) topografije kristalografskog loma egipatske vaze, /9/
Figure 9. SEM fractographs of (a) slip line corrosion, (b) slip plane dissolution and cracking, and (c) crystallographic fracture topography in an Egyptian vase, /9/.



Slika 10. SEM snimci (a) interkristalnog loma od korozije i opšte korozije srebrne kaptorge (detalj sl. 2b) i (b) granica između SCC i interkristalne korozije legure aluminijum-litijum, /27/
Figure 10. SEM fractographs of (a) corrosion-induced intergranular fracture and general corrosion in a silver kaptorga (detail of Fig. 2b) and (b) the boundary between SCC and intergranular corrosion in an aluminium-lithium alloy, /27/.

Slike 2 i 10 predstavljaju primere interkristalnog loma izazvanog korozijom. Slika 10a je detalj sa sl. 2b, a sl. 10b je izgled preloma izazvanog interkristalnom korozijom i SCC u leguri aluminijum-litijum, /27/.

Na sl. 10a se vidi prelaz od opšte korozije do konačnog razaranja korozijom izazvanog interkristalnog loma srebrne kaptorge, /13/. Interkristalni prelom izgleda vrlo čisto, uz samo izolovane jamice pitinga. Slika 10b pokazuje prelaz od interkristalne korozije sa korodiranim (nagriženim) fasetama do interkristalne SCC sa fasetama jakog pitinga, /27/. Na drugim snimcima preloma se vidi jači piting, uglavnom u području interkristalne korozije, /27/.

Iako površine preloma i prelaza na sl. 10a i b nisu istog izgleda, njihova sličnost upućuje na to da interkristalni lom izazvan korozijom na sl. 10a može biti SCC. U tom slučaju razlog pojave potrebnih napona i deformacija mogu biti spoljnje sile unete pri zatrpavanju pre nego zaostala hladna deformacija, jer kaptorga ima rekristalisanu mikrostrukturu velikih otpuštenih zrna, /13/.

Figures 2 and 10 give examples of corrosion-induced intergranular fracture. Figure 10a is a detail of Fig. 2b, and Fig. 10b is a fractograph of intergranular corrosion and SCC in an aluminium-lithium alloy, /27/.

Figure 10a 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 10b 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, mainly affected the intergranular corrosion area, /27/.

Although the fracture surfaces and transitions in Figs. 10a and 10b do not look identical, their similarity suggests that the corrosion-induced intergranular fracture in Fig. 10a is SCC. In this case the source of the necessary stresses and strains is external force due to interment rather than residual cold-work, since the kaptorga had a recrystallized microstructure with large annealed grains, /13/.

MODELI LOMA IZAZVANOG KOROZIJOM

Modeli koji povezuju koroziju linija klizanja sa transkristalnom SCC postoje za legure koje imaju istu površinski centriranu kubnu (FCC) kristalnu rešetku kao srebro, /18-23/. Ovi modeli razmatraju dve faze pojave prslina.

(1) Korozija duž linija klizanja i poništavanja ravni klizanja: Kod nekoliko klasa FCC legura javlja se korozija duž linija klizanja, /21, 22, 24/. Korozija počinje na pitingu visoko napregnutih kristalnih rešetki u jezgru ravanski povezanih dislokacija. Jamice prodiru u proreze koji mogu da se spoje u ravni poništavanja i prsline. Kako su u FCC metalima ravni klizanja {111}, ove inicijalne prsline su u {111} ravnima.

(2) Transkristalna SCC:

U ovoj fazi razvoja prsline se razlikuju u prosečnim raspoloživim kristalografskim ravnima loma i u topografiji loma. Najčešće ravni loma su obično {110} u legurama bakra, /18-20/ i {100} u austenitnim nerđajućim čelicima, /21/, iako se prosečne {110} prsline javljaju i u tim čelicima, /22/. Kao detalj topografije loma otkrivaju se mikrofasete. Na površini preloma legura bakra vide se mikrofasete {110}, /19/, a površina preloma nerđajućeg čelika se delom ili potpuno sastoji od {111} mikrofasete, /21, 22/.

Modeli su „cepanje izazvano korozijom“, /18-20/; njegov nastavak, „poništavanje izazvano deformacijom“, /23/; i „plastičnost izazvana korozijom“, /21, 22/. Detaljna diskusija modela i njihova primenljivost na antičko srebro su već ranije dati, /9/. Kako je model cepanja izazvan korozijom napušten, /23/, a model plastičnosti izazvane korozijom zahteva prisustvo vodonika, koji se ne pojavljuje kada srebro korodira, /25/, ostaje samo model poništavanja izazvano deformacijom, koji može da se primeni za objašnjenje oblika prikazanih na sl. 9.

Shema modela poništavanja izazvano deformacijom je dat na sl. 11. Predložen (a ovde skraćeno prikazan) redosled pojava je:

(a) Gomilanje dislokacija kao prepreke u ravni klizanja.

(b, c) Inicijacija i rast prslina poništavanjem ravni klizanja, koji su izazvani deformacijom od lokalnog normalnog napona, σ_{n1}. Poništavanje ravni klizanja se nastavlja sve dok je σ_{n1} veći od lokalnog normalnog napona, σ_{n2}, na naizmeničnim kristalografskim ravnima.

(d) Rast prsline usmeren poništavanjem ravni klizanja na naizmeničnoj ravni na kojoj je lokalni normalni napon, σ_{n2}, veći od σ_{n1} ali nije dovoljno veliki da zatupi vrh prsline uvođenjem dislokacija.

Pod pretpostavkom da ravni loma ne moraju uvek biti ravni klizanja, što je utvrđeno za legure bakra i austenitne nerđajuće čelike, /18-22/, ovaj model daje objašnjenje za transkristalni oblik loma na sl. 9b i c. Slika 9b pokazuje prslinu „naglog pregiba“ od 90°, koja ne može biti u {111} ravni, već se mora naći u ravni {110} ili {112}. Slika 9c pokazuje sličan „nagli pregib“ zbog kojeg se javljaju strme stepenice (pod velikim uglom) na površinama preloma u ravni klizanja. Nisu nađene mikrofasete slične onim uočenim kod legure bakra, /19/, i nerđajućeg čelika, /21, 22/, ali je to ionako promenljivo, vidi opis faze, /2/.

MODELS OF FRACTURE INDUCED BY CORROSION

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, the 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 Fig. 9.

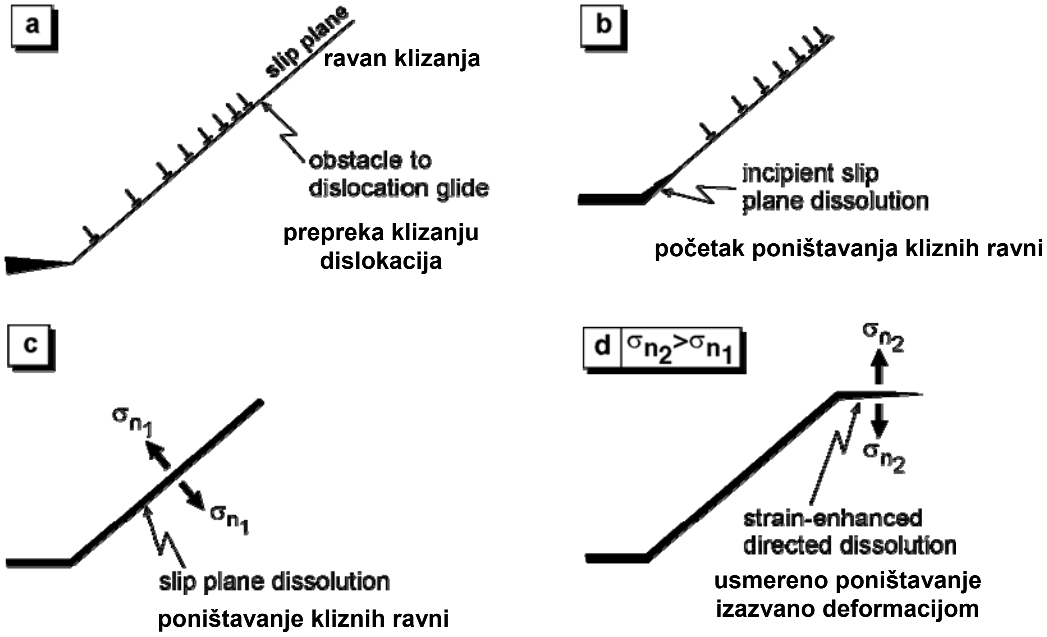
A schematic of the strain-enhanced dissolution model is given in Fig. 11. The proposed (and here abbreviated) sequence of events is:

(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 Figs. 9b and 9c. Figure 9b shows a 90° “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 found for copper alloys, /19/, and stainless steels, /21, 22/, but this was variable anyway, see stage (2) above.



Slika 11. Model transkristalne SCC „rastvaranja ubrzanog deformacijom“, /23/
Figure 11. The “strain-enhanced dissolution” model of transgranular SCC, /23/.

RESTAURACIJA I KONZERVACIJA

Moderna restauracija i konzervacija moraju uzeti u obzir tehničke i etičke aspekte. To znači da prednost imaju *reverzibilni* postupci sanacije kod kojih je važan integritet predmeta. Međutim oni nisu uvek praktični, /4, 6, 7/. To je izraženo u slučaju vrlo krtih i rasparčanih predmeta od antičkog srebra, za koje je od suštinskog značaja trajno oblikovanje, /4, 28/.

Postupak sanacije predmeta od antičkog srebra, izrazito krtih zbog korozije, zavisi od njihovog stanja, /9, 12/:

(1) Celovit (ali sa prslinom) ili ranije saniran predmet može da se očisti, izduva do suve površine prsline i otklone bilo kakvi zaostali produkti korozije, i da se osloji providnim organskim slojem, *koji se može skinuti*. I u tom slučaju treba razmotriti postupke čišćenja i nanošenja sloja, /4, 29/.

Klasičnim postupcima čišćenja obnavlja se površina završnim blagim poliranjem, čišćenjem i ispiranjem u demineralizovanoj vodi i alkoholu, i predmet se suši, najbolje u okolini niske vlažnosti, npr. u eksikatoru.

Novi postupak čišćenja je redukcija plazmom vodonika, /30/. To zahteva manje od jednog sata na temperaturi 40–100°C, što smanjuje ili isključuje značajne promene mikrostrukture predmeta. Plazma vodonika otklanja produkte korozije sa površine metalnog srebra.

(2) Ako je krtost izrazita, može biti potrebno da se sastavi rasparčan predmet. Obično se to izvodi impregnacijom sa, ili potapanjem u lak ili smolu, /28/, i spajanjem očišćenih parčadi lepljenjem ili tekstilnom trakom sa lepljivom stranom, /7/. Ovi postupci se ne mogu ponoviti.

Dodatna teškoća se javlja ako su parčad prekrivena produktima korozije i/ili deformisana, u kom slučaju može biti potrebno termički ih obraditi pre sastavljanja, /6, 7/. I ovaj postupak se ne može ponoviti, a postoji i opasnost od daljeg oštećenja.

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/:

(1) 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, 29/.

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 newly developed cleaning method is hydrogen plasma reduction, /30/. This requires less than an hour, at temperatures 40–100°C, which minimises or avoids significant alterations to an object’s microstructure. The hydrogen plasma reduces surface corrosion products to metallic silver.

(2) If the embrittlement is severe it may be necessary to consolidate fragmented objects, usually by impregnating with, or soaking in, lacquers or resins, /28/, and joining the cleaned fragments with adhesives and adhesive-impregnated backing cloths, /7/. These treatments are irreversible.

An additional difficulty is added if the fragments are covered in corrosion products and/or deformed, in which cases it may be necessary to heat-treat them before consolidation, /6, 7/. Again, this is irreversible, and not without risk of further damage.

Moguća alternativa za spajanje lakom ili smolim je čišćenje praćeno korišćenjem Parilen prevlake. Na primer, predmet može prvo da se očisti u plazmi vodonika, koji može da prodre u povezane površinske prsline, kao i da očisti površinu. U tom smislu površina interkristalnog loma koja izgleda relativno čista, kao na pr. kaptorga, sl. 10a, ukazuje da će mnogobrojne interkristalne prsline biti očišćene za kratko vreme. Posle čišćenja, predmet treba da se podvrgne postupku oslojavanja Parilenom, /31/.

Parilen prevlake imaju posebne osobine i prednosti, jer se primenjuju u parnoj fazi, u atmosferi sniženog pritiska, /31/. Njihova debljina se može kontrolisati, dobro prodiru u duboke šupljine (ili prsline), i nema pojave tačkastih rupica. Vlaga je uglavnom uklonjena u atmosferi sniženog pritiska (13,3 Pa, 0,1 torr) u komori za nanošenje prevlake. Sledeća prednost je mogućnost „modeliranja“ debljine prevlake da ispuni prsline, što obezbeđuje lepljenje površina loma i bolje sastavljanje.

Nedostaci primene Parilen prevlake su što se ona ne može skinuti na temperaturi ispod 150-175°C, tj. ona može biti ustvari potpuno nepovratan postupak za antičko srebro, i da se za primenu zahteva specijalna oprema. Međutim, ova oprema na mora da se kupi, već može da se unajmi za manje prevlake.

Pošto je Kanadski institut za konzervaciju u Otavi već konzervirao krte i lomljive predmete korišćenjem Parilen prevlaka, razumno je da se nastavi istraživanje mogućnosti njene upotrebe za konzervaciju antičkog srebra izražene krtosti.

ZAKLJUČNE NAPOMENE

Antičko srebro može biti osetljivo na nekoliko tipova krtosti izazvanih korozijom. Dati su primeri više starina, veoma različitog vremenskog perioda, porekla i oblika: jedna egipatska vaza, kaptorga iz Češke Republike, vizantijski nafornjak, glava persijskog kralja (Sasanida), iskivana sa leđne strane, Gundestrup kondir, i tumi obredni nož Sika. Pokazano je da su neke od ovih pojava krtosti posledica naponske korozije (SCC).

Oštećenja mogu biti tako velika da treba primeniti trajnu restauraciju i konzervaciju. U ovim postupcima treba pažljivo razmotriti tehnički i etički aspekt da bi se smanjio obim intervencija. u tom smislu detaljni prikazi izvedenih primera, /1, 5, 8, 12-14, 32/, koji karakterišu pojavu krtosti, su od velike koristi.

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A possible alternative to consolidation using lacquer or resins is cleaning followed by the use of Parylene coatings. For example, an object could first 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, Fig. 10a, suggests that many intergranular cracks would be cleaned after a short time. Following cleaning, the object could undergo a Parylene coating procedure, /31/.

Parylene coatings have special properties and advantages, since they are applied in the vapour phase in a reduced-pressure environment, /31/. They have controllable thickness, high crevice (or crack) penetration, and are pinhole-free. Most moisture would be removed by the reduced-pressure environment (13.3 Pa, 0.1 torr) in the coating chamber. It is also possible to “tailor” the coating thickness to fill cracks, thereby providing adhesion between the fracture surfaces and consolidation.

Disadvantages of using Parylene coatings are that they are not removable below 150-175°C, 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 hired 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.

CONCLUDING REMARKS

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

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, 32/, to characterize embrittlement are most useful.

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