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KRTOST ARHEOLOŠKOG SREBRA I GVOŽĐA

EMBRITTLEMENT OF ARCHAEOLOGICAL SILVER AND IRON

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Ključne reči
- arheometrija
- srebro
- gvožđe
- krtost
- konzervacija

Izvod

Krtost izvorno duktilnih arheoloških metala je, ili može biti, složena pojava. Važno je da se razumeju detalji i mehanizmi krtosti da bi se preporučile i izabrale najprikladnije mere sanacije za restauraciju i konzervaciju. U ovom radu je prikazan pregled tehnika koje su primenjene u istraživanju pojave krtosti nekoliko antičkih predmeta od srebra i gvozdene stope stuba sa mosta iz rimskog doba. Primenjene tehnike su omogućile da se odredi najverovatniji mehanizam pojave krtosti, na osnovu čega su date preporuke za očuvanje ovih i drugih krtih predmeta od daljeg oštećenja.

Keywords
- archaeometallurgy
- silver
- iron
- embrittlement
- conservation

Abstract

Embrittlement of originally ductile archaeological metals is, or can be, a complex phenomenon. It is important to understand the details and mechanisms of embrittlement in order to recommend and select the best remedial measures for restoration and conservation. This paper presents a survey of the techniques used to investigate the embrittlement of several ancient embrittled silver objects and an iron pile-shoe from a Roman bridge. These techniques enabled the most probable mechanisms of embrittlement to be determined, leading to recommendations for preserving these and other embrittled objects against further damage.

UVOD

Nekoliko predmeta od srebra veoma različitog porekla, koji su vremenom postali krti, je istraživano u Nacionalnoj vazduhoplovnoj laboratoriji (NLR), Amsterdam, počev od 1994. Ti predmeti su jedna egipatska vaza, ukrasna činija iz Gundestrupa i vizantijska tacna (poslužavnik korišćen prilikom ceremonije pričesta. Sem toga, i krti lom rimske stope stuba koji je nedavno otkriven u koritu reke Maas 1992, je istraživan u saradnji sa druga tri instituta u Holandiji. Stečeno iskustvo iz ovih istraživanja je omogućilo da se odredi najverovatniji mehanizam pojave krtosti, što je dovelo do preporuka kako da se očuvaju ovi i drugi slični predmeti, koji su vremenom postali krti, da bi se predupredila dalja oštećenja, /1-7/.

Neke od tehnika koje su bile potrebne nisu bile dostupne prethodnim generacijama i još nisu potpuno iskorišćene u arheološkim krugovima. U ovom radu je prikazan pregled korišćenih tehnika, i diskutovana njihova prikladnost za postavljanje dijagnoze.

POJAVA KRTOSTI ANTIČKOG SREBRA

Egipatska vaza (Alard Pirson Muzej, Amsterdam)

Slika 1 pokazuje egipatsku vazu iz Ptolomejskog perioda, koja datira iz vremena 300 do 200 godina pre nove ere.

INTRODUCTION

Several embrittled silver objects with widely varying provenance have been investigated by the National Aerospace Laboratory (NLR), Amsterdam, since 1994. These are an Egyptian vase, the Gundestrup Cauldron and a Byzantine paten (a plate used during celebration of the Eucharist). Also, a recent brittle fracture in a Roman pile-shoe recovered from the Maas riverbed in 1992 was investigated in collaboration with three other institutes in the Netherlands. The experience gained from these studies has enabled the most probable mechanisms of embrittlement to be determined, leading to recommendations for preserving these and other similarly embrittled objects against further damage, /1-7/.

Some of the techniques required for these studies were unavailable a generation ago and are not yet fully exploited by the archaeological community. This paper presents a survey of all the techniques used, and discusses their diagnostic capabilities.

ANCIENT SILVER EMBRITTLEMENT

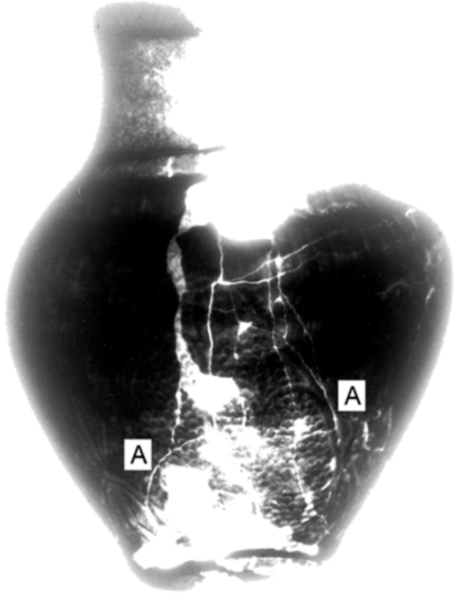
Egyptian vase (Allard Pierson Museum, Amsterdam)

Figure 1 shows the Egyptian vase, which is from the Ptolemaic period and dated to between 300 and 200 BC.

Vaza je ukrašena ugraviranim i utisnutim ukrasima cveća i lotusa i bodljikavog lišća. Radiogram na sl. 2 pokazuje da je vaza detaljno obnovljena (to je stara restauracija, koja datira iz kasnih godina 19.-tog veka). Slika 2 takođe otkriva prsline koje prate spoljnje žlebove gravure i mesta ukrštanja na umreženim prslinama sličnim krtom lomu „ljuske jajeta“.

The vase is decorated with chased and stamped representations of flowers and lotus and acanthus leaves. The X-ray radiograph, Fig. 2, shows that the vase has been much restored (this is an old restoration, done in the late 19th century). Figure 2 also reveals cracks following external chasing grooves and criss-crossing in a brittle similar to the “eggshell” crack pattern.

Slika 1. Egipatska vaza
Figure 1. The Egyptian vase.



Slika 2. Radiogram egipatske vaze: prsline A slede žleb gravure
Figure 2. Egyptian vase radiograph: cracks A follow chasing groove.

Mali uzorci sa ivica i donjeg zida vaze su ispitani primenom skaning elektronskog mikroskopa (SEM) i analize energije disperzije X-zračenja (EDX) u hemijskoj analizi; metalografijom i fraktografijom primenom SEM sekundarnih elektrona (SE) i povratnim rasejanjem elektrona (BSE); i ispitivanjem mikrotvrdoće, /1/.

Analizom EDX je utvrđen sledeći prosečni hemijski sastav, u tež. %: Ag 97,1. Au 0,8; Cu 0,9; Pb 0,7; Bi 0; Sn 0,2; Sb 0,3. Slike 3–6 ilustruju neke od SEM rezultata. Pokazano je da je vaza prauzorna zbog:

- Pojave krtosti izazvane korozijom duž linija klizanja, deformacija na granicama dvojnika i traka segregacija.
- Krtosti izazvane mikrostrukturom; hemijski sastav (0,7% Pb, nema Bi) upućuje na olovo kao glavni uzrok, /1-4, 8/.
- Sinergijska krtost.
- Veze zaostale hladne deformacije i korozijskog oštećenja.

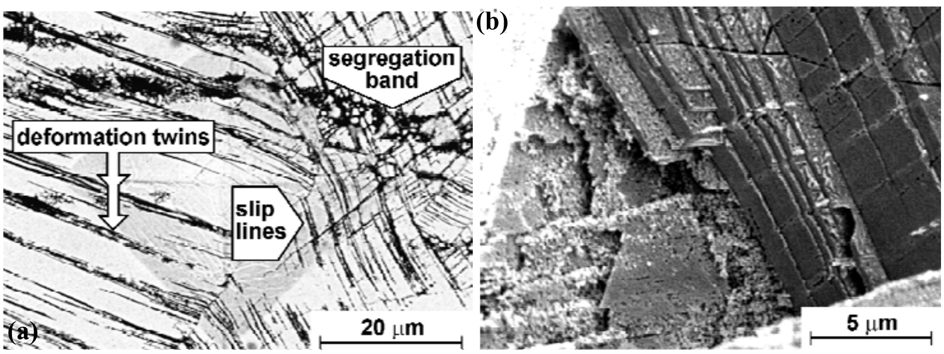
Na slici 6 je prikazana značajna uzajamna povezanost zaostale hladne deformacije i korozije. BSE slike otkrivaju oblik lokalne deformacije. Pridružena shema objašnjava ovaj oblik deformacija na osnovu teorije polja linija klizanja od otiska, /9/. Osim područja pritiska, ova teorija predviđa da se, ako je $t_i/w = 4,4$, formira zona zatezanja na površini suprotno od otiska: utvrđena vrednost t_i/w od 4,2, je dovoljno bliska da se ovakvo tumačenje prihvati. Veoma je značajno pri tom da se u zoni zatezanja pojavljuje korozija i interkristalni lom na i u blizini *unutrašnje površine* vaze, što znači da je izazvano „skriveno“ oštećenje.

Small samples from the lip and lower wall of the vase were subjected to Scanning Electron Microscope (SEM) + Energy Dispersive analysis of X-rays (EDX) chemical analysis; SEM Secondary Electron (SE) and BackScattered Electron (BSE) metallography and fractography; and microhardness testing, /1/.

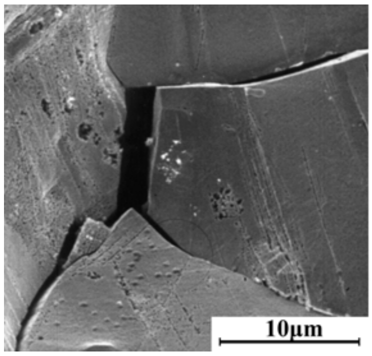
The EDX analyses gave the following average chemical composition, in wt.%: Ag 97.1; Au 0.8; Cu 0.9; Pb 0.7; Bi 0; Sn 0.2; Sb 0.3. Figures 3–6 illustrate some of the SEM results. The vase proved to be archetypal for:

- Corrosion-induced embrittlement along slip lines, deformation twin boundaries and segregation bands.
- Microstructurally-induced embrittlement, chemical composition (0.7% Pb, no Bi) suggests lead as perpetrator, /1-4, 8/.
- Synergistic embrittlement.
- A link between retained cold-work and corrosion damage.

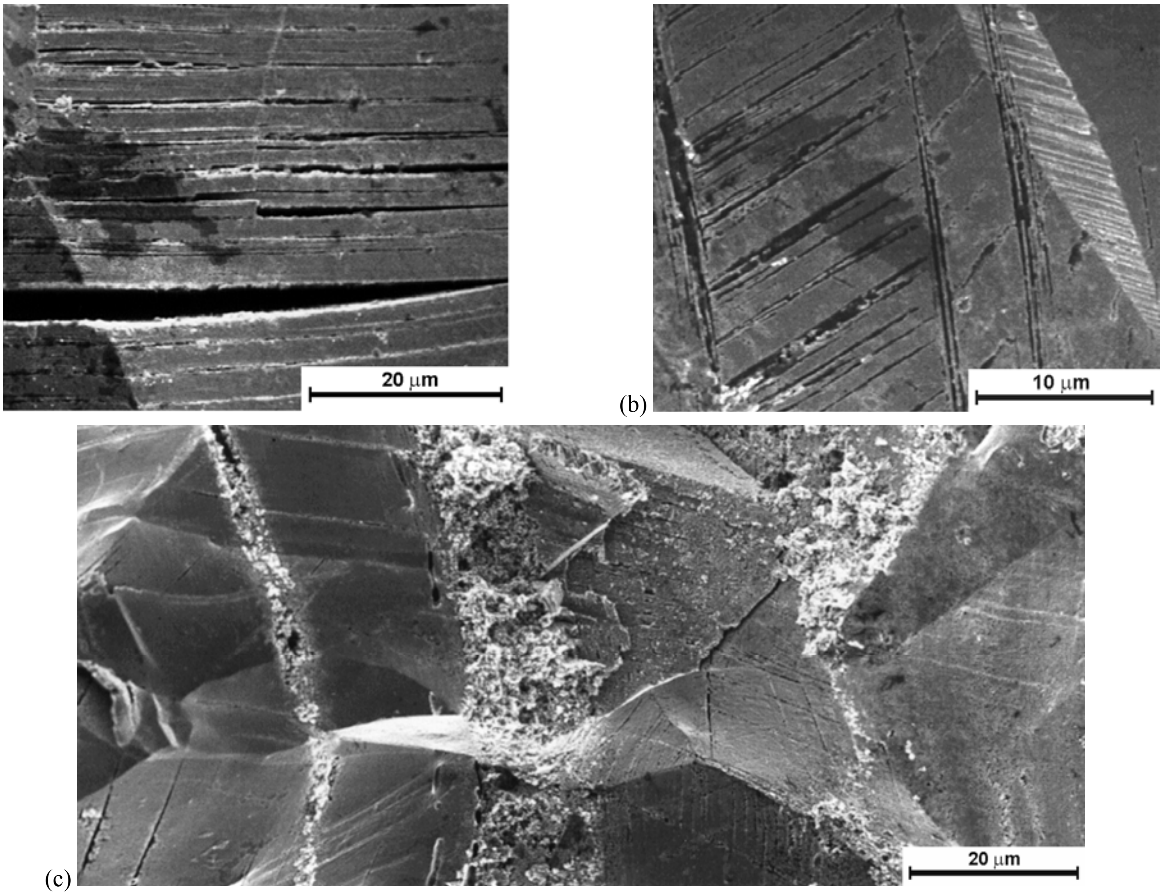
Figure 6 illustrates an especially significant link between retained cold-work and corrosion. The BSE imaging revealed a local deformation pattern. The adjacent schematic interprets this deformation pattern from the slip-line field theory of indentation, /9/. Besides the compression zone, this theory predicts that when $t_i/w = 4.4$ a tension zone forms from the surface opposite the indentation: the actual value of t_i/w is 4.2, close enough to justify the interpretation. The significant point is that the tension zone promoted corrosion and intergranular fracture at and near the *internal surface* of the vase, i.e. it caused “hidden” damage.



Slika 3. Krtost egipatske vaze izazvane korozijom: a) korozija duž linija klizanja, granica dvojnika i traka segregacija; b) kristalografski prelom zbog korozije duž linije klizanja i dvojnika: SEM snimci
Figure 3. Corrosion-induced embrittlement in the Egyptian vase: a) corrosion along slip lines, twin boundaries and segregation bands; b) crystallographic fracture due to corrosion along slip lines and twins: SEM metallograph and fractograph.



Slika 4. Krti interkristalni lom izazvan prisutnom mikrostrukturom egipatske vaze: SEM snimak
Figure 4. Microstructurally-induced brittle intergranular fracture in the Egyptian vase: SEM fractograph.

(a) (b) (c)


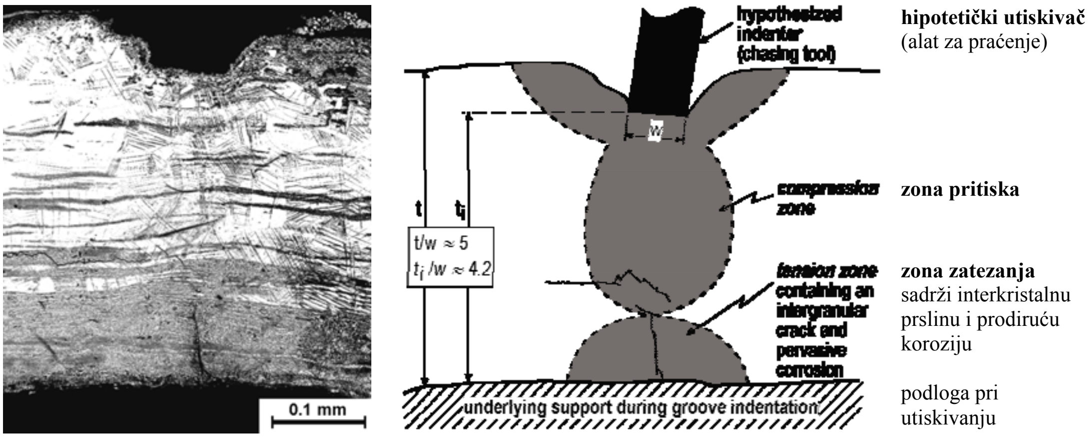
Slika 5. Sinergijska krtost egipatske vaze: a) korozija (uzrok loma) duž linija klizanja preseca fasete granice zrna; b) korozija duž deformacijskih dvojnika preseca granice zrna; c) korozija duž traka segregacija preseca fasete granica zrna; SEM fraktogrami
Figure 5. Synergistic embrittlement in the Egyptian vase: a) corrosion (causing fracture) along slip lines intersecting grain boundary facets; b) corrosion along deformation twin boundaries intersecting a grain boundary; c) corrosion along segregation bands intersecting grain boundary facets: SEM fractographs.

Gundestrup ukrasna činija (Narodni muzej Danske, Kopenhagen)

Slika 7 pokazuje restauriran Gundestrup ukrasni pehar, najveći sačuvani predmet izrađen od srebra iz gvozdene ere Evrope, koji datira iz drugog ili prvog veka pre nove ere.

Gundestrup Cauldron (National Museum of Denmark, Copenhagen)

Figure 7 shows the reassembled Gundestrup Cauldron, which is the largest surviving silverwork object from the European Iron Age, dating to the 2nd or 1st century BC.



Slika 6. Struktura preseka dobijena metalografijom povratnog rasejanja elektrona (BSE) i shematski prikaz žleba spolja graviranog ukrasima na egipatskoj vazi. Uzorak je sa donjeg zida vaze.
Figure 6. Through-thickness BackScattered Electron (BSE) metallograph and schematic of an external chased decorating groove in the Egyptian vase. The sample is from the vase lower wall.

Slika 7. Ukrasni pehar (kondir) Gundestrup
Figure 7. The Gundestrup Cauldron.

Zbog veličine, visokog kvaliteta izrade i ikonografske raznolikosti, pehar je bio predmet brojnih studija, naročito njegov izvorni oblik, koji je još uvek kontroverzan. Pehar se sastoji od dvanaest tanjira i korpe, sve od srebra 95–98%. Hemijska analiza je odredila bakar kao glavni legirajući element (ili nečistoću), /10, 11/.

Četiri mala metalografska uzorka iz različitih delova pehara su ustupljena NLR od strane Peter Northovera, Univerzitet Oksford. Uzorci su ispitani FEG-SEM skening elektronskim mikroskopom visoke rezolucije sa emisijom elektrona u polju u kombinaciji sa automatizovanom opremom sa difrakcijom elektrona povratnog rasejanja (EBSD). Ovo je moćna EBSD tehnika za mikrostrukturnu analizu. Utvrđeno je da su za uzorke Gundestrup pehara najkorisnije sledeće opcije, /12/:

– Inverzne polarne slike (IPF) kodirane bojom.
– Mape zakrivljenja rešetke na granicama zrna (ugao dezorijentacije susednih zrna).
– Mape zajedničkih mesta u rešetki (CSL).

Slike 8-12 ilustruju dve grupe rezultata EBSD analize:

(1) Uzorak 366: Ovaj uzorak je u stvari otpušten i nije korodirao, on je slučajno raspoređene mikroteksture, sl. 8a, i razvijenih granica zrna taloga bakra, što granicama zrna daje razuđen meandarski izgled, sl. 8b. Detalji na sl. 9 dokazuju da su u pitanju isprekidani talozi, /13–15/.

Owing to its size, high quality workmanship and iconographic variety, the Cauldron has been the subject of many studies, particularly its origin, which is still controversial. The Cauldron consists of twelve plates and a bowl, all of 95–98% silver. Chemical analyses showed copper to be the main alloying (or impurity) element, /10, 11/.

Four small metallographic samples from different parts of the Cauldron were lent to the NLR by Peter Northover, Oxford University. The samples were examined using a Field Emission Gun Scanning Electron Microscope (FEG-SEM) combined with automated Electron BackScatter Diffraction (EBSD) equipment. This EBSD is a powerful technique for microstructural analysis. For the Cauldron samples the following options were of most use, /12/:

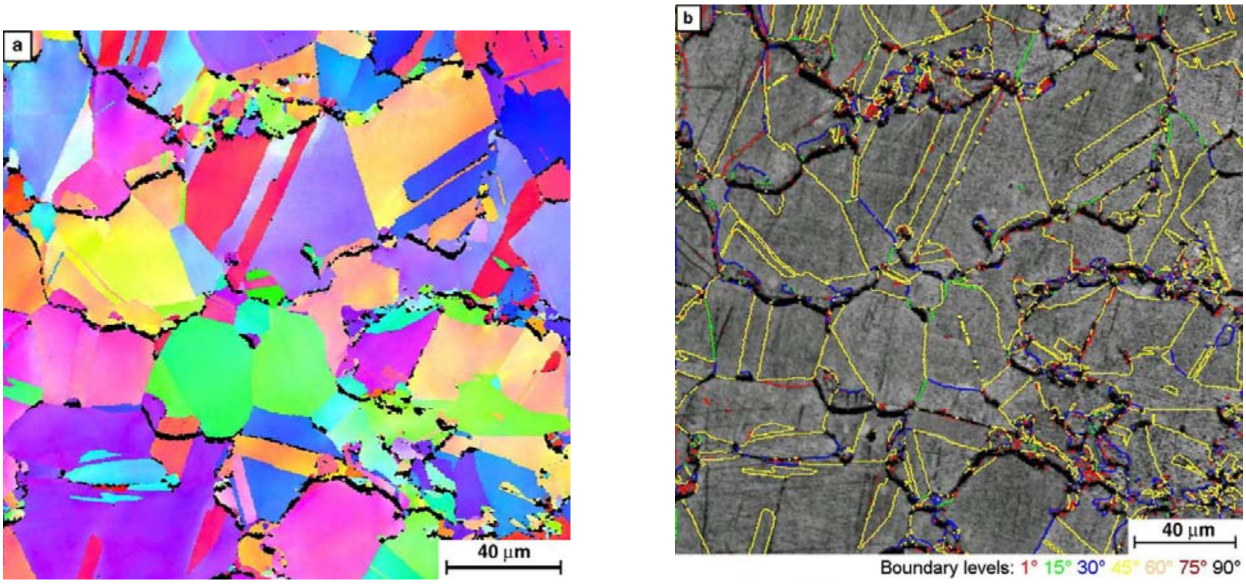
– Inverse Pole Figure (IPF) colour-coded maps.
– Boundary rotation angle maps.
– Coincidence Site Lattice (CSL) maps.

Figures 8-12 illustrate two groups of EBSD results:

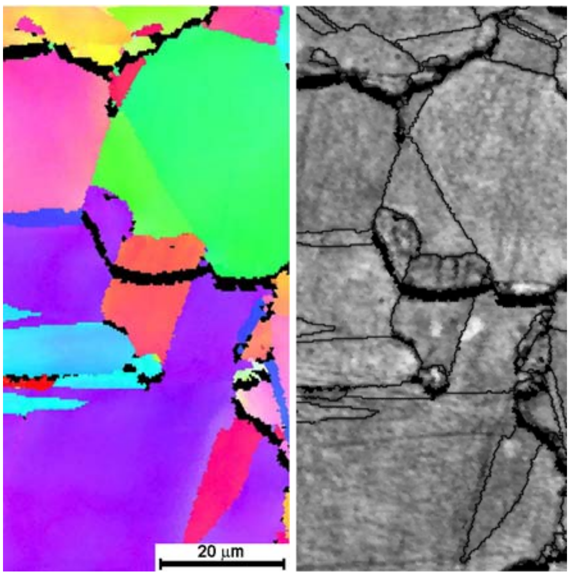
(1) Sample 366: This sample was essentially annealed and corrosion-free, of a random microtexture, Fig. 8a, and extensive grain boundary precipitation of copper, giving the grain boundaries a meandering appearance, Fig. 8b. The details in Fig. 9 prove discontinuous precipitations, /13–15/.

(2) Uzorci 361, 363, 365: Nađen povećani udeo zaostale hladne deformacije i korozijskog oštećenja. Na sl. 10-12 je zaostala hladna deformacija crveno područje (klizanje) i žuto područje nepravilne granice (dvojnici). Korozijska oštećenja su crna područja, koja predstavljaju uglavnom interkristalne prsline, ali i transkristalne prsline (bolje se vidi na sl. 12a). Međutim, nema dokaza o isprekidanom talogu.

(2) Samples 361, 363, 365: Increasing amounts of retained cold-work and corrosion damage is found. In Figs. 10-12 the retained cold-work are red regions (slip) and irregular yellow boundaries (twins). The corrosion damage are black regions, representing mainly intergranular cracks, but also transcrystalline cracks (best seen in Fig. 12a). However there was no evidence of discontinuous precipitation.

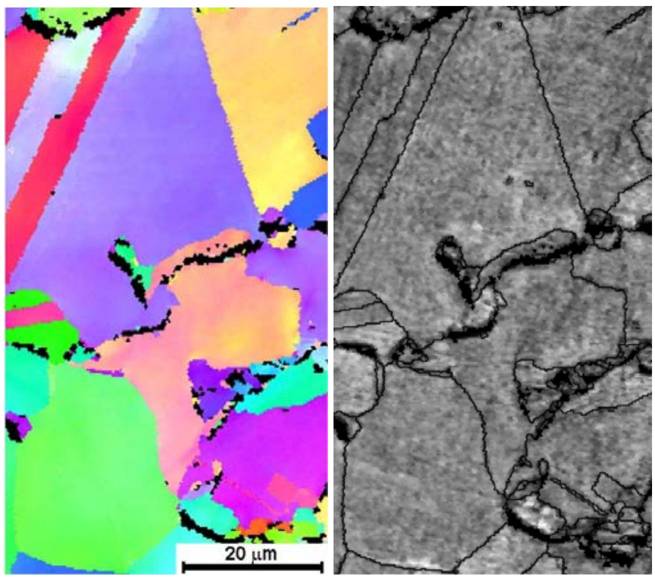


Slika 8. IPF kodirana mapa u boji i mapa ugla orijentacije granica za uzorak 366. Žute granice su uglavnom otpušteni dvojnici
Figure 8. IPF colour-coded map and boundary rotation angle map for sample 366. The yellow boundaries are mainly annealing twins.



Talog se stvara na prvobitnoj granici „zelenog“ zrna, raste u „zeleno“ zrno, menja orijentaciju rešetke ka susednom zrnu „purpurne“ matrice i „crvenkasto-mrkom“ otpuštenom dvojniku.

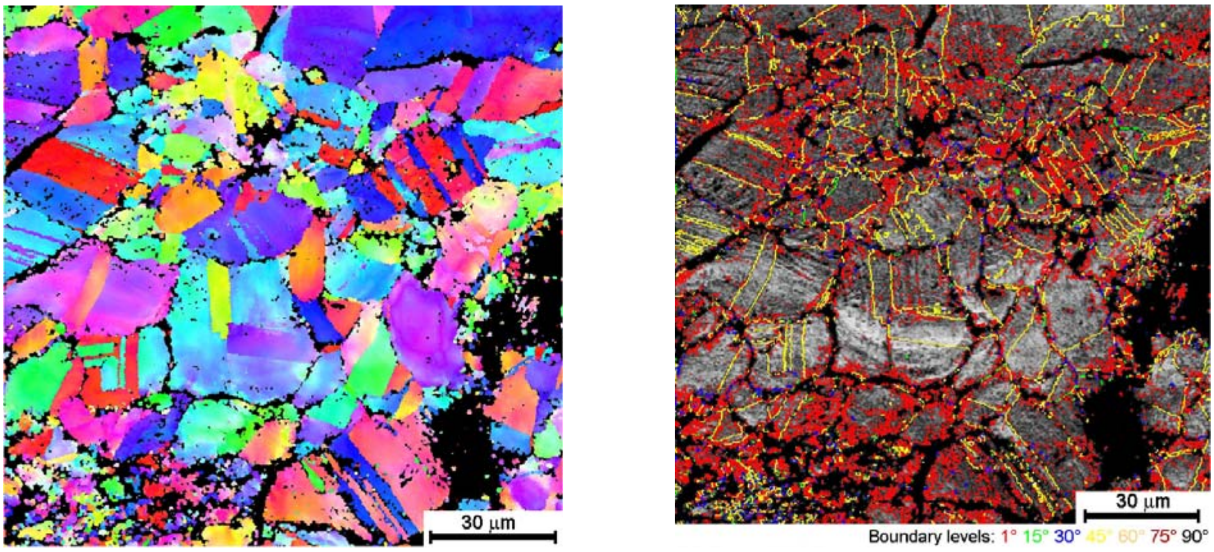
Precipitate behaviour: nucleation at original “green” grain boundary, growth into “green” grain, changing its lattice orientation to that of the contiguous grain having the “purple” matrix and “reddish-brown” annealing twin.



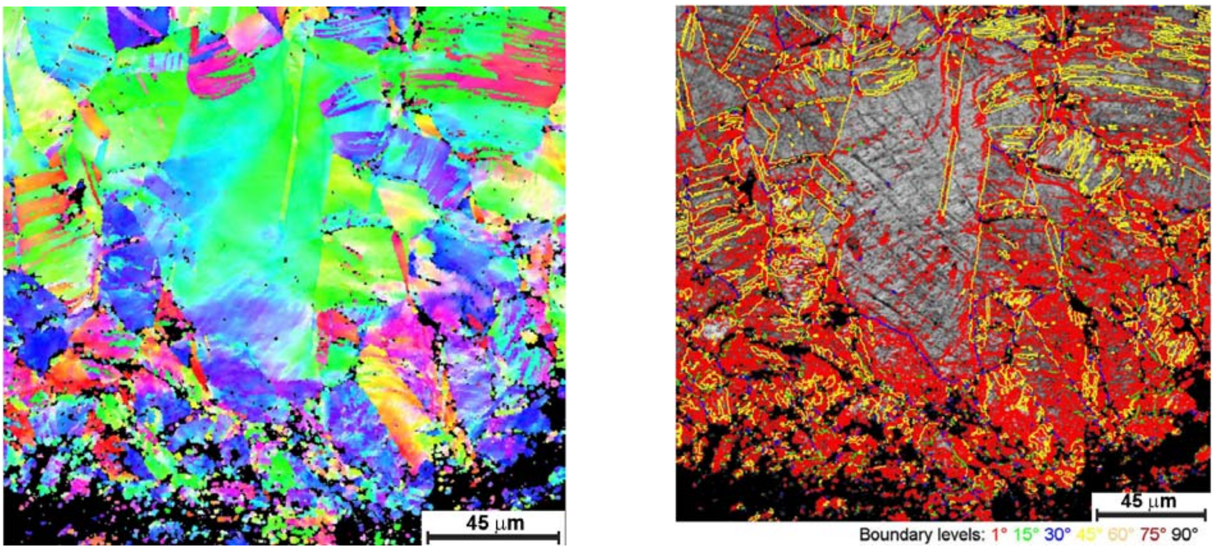
Talozi se posebno stvaraju na prvobitnoj granici „purpurnih“ i „ružičastih“ zrna, rastu u suprotnim smerovima: jedan u „ružičasto“ zrno, menja pravac rešetke ka susednom „purpurnom“ zrnu; a drugi u „purpurno“ zrno, pravac ka susednom „ružičastom“ zrnu.

Precipitate separate nucleations at boundary between “purple” and “pink” original grains, growth in opposing senses: one into the “pink” grain, changing its lattice orientation to contiguous “purple” grain; one into the “purple” grain, orientation to contiguous “pink” grain.

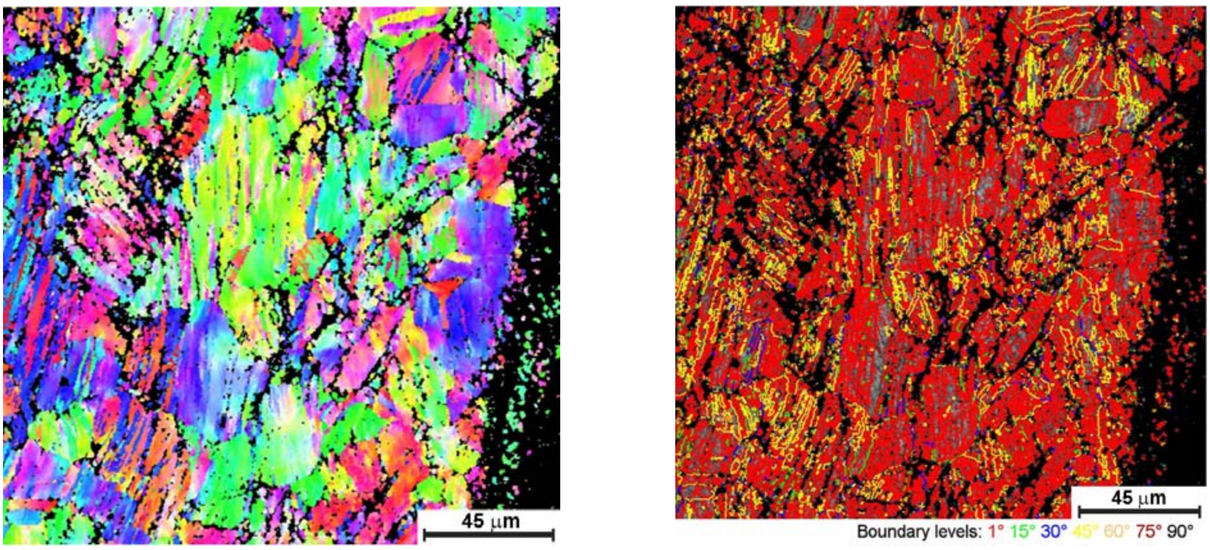
Slika 9. Detalji stvaranja i rasta taloga u uzorku 366 činije Gundestrup
Figure 9. Details of precipitate nucleation and growth in Gundestrup Cauldron sample 366.



Slika 10. IPF kodirana mapa u boji i mapa ugla orijentacije granica za uzorak 361
Figure 10. IPF colour-coded map and boundary rotation angle map for sample 361.



Slika 11. IPF kodirana mapa u boji i mapa ugla orijentacije granica za uzorak 363
Figure 11. IPF colour-coded map and boundary rotation angle map for sample 363.



Slika 12. IPF kodirana mapa u boji i mapa ugla zakretanja granica za uzorak 365
Figure 12. IPF colour-coded map and boundary rotation angle map for sample 365.

Vizantijski nafornjak (Kolekcija Menil, Hjuston)

Slika 13 prikazuje vizantijski nafornjak, koji datira oko 600. godine. Nafornjak je redak i visoko kvalitetan liturgijski predmet iz oltara. Značajna središnja ploča je dobro očuvana, ali je na obimnom kružnom žlebu sa ukrasima došlo do intenzivnog loma.

Mali uzorak sa nafornjaka je ispitan SEM metalografijom i pomoću EDX analize u prethodnom istraživanju Holandskog instituta za kulturno nasleđe (ICN) iz Amsterdama. Na uzorku je jasno vidljiva površinska (plitka) interkristalna korozija, sl. 14a, a pri većim uvećanjima se vide i isprekidani talozi bakra na granicama zrna, sl. 14b. Ovi talozi daju granicama zrna razuđen meandarski izgled, sličan onom na sl. 8b.

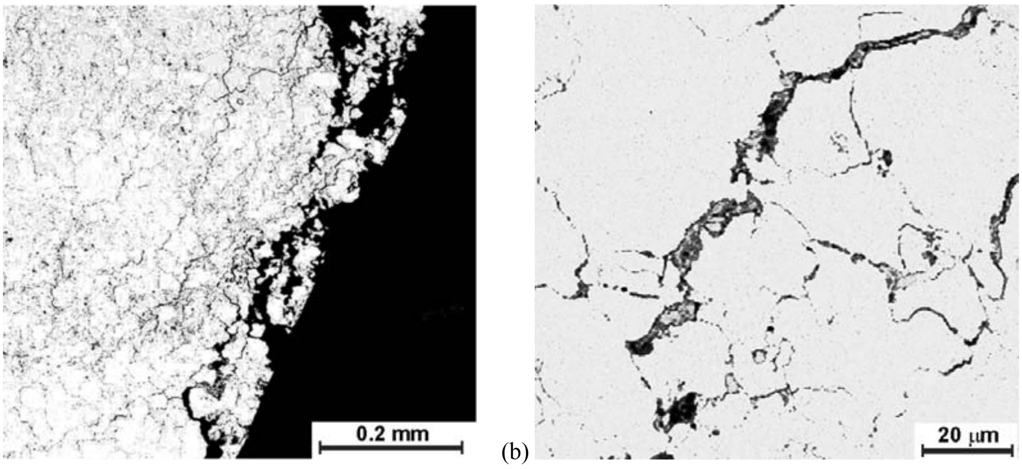
Slika 13. Vizantijski nafornjak: fotografija je vlasništvo Kolekcije Menil, Hjuston
Figure 13. The Byzantine paten: photograph courtesy of The Menil Collection, Houston.

Byzantine paten (The Menil Collection, Houston)

Figure 13 shows the Byzantine paten, which has been dated to about 600 AD. The paten is a rare and high-quality liturgical altar object. The important central tableau is well preserved, but there has been extensive breakage along the surrounding circular decorating grooves.

A small sample from the paten was examined by SEM metallography and EDX in a preliminary investigation at the Netherlands Institute for Cultural Heritage (ICN) in Amsterdam. The sample showed surficial (shallow) intergranular corrosion, Fig. 14a, and at higher magnifications discontinuous precipitation of copper at the grain boundaries, Fig. 14b. This precipitation gave the grain boundaries a meandering appearance, similar to that in Fig. 8b.

(a) (b)



Slika 14. Interkristalna korozija (a) i isprekidani talog bakra na granicama zrna (b) na vizantijskom nafornjaku. EDX analiza je pokazala u prvom redu srebro na lokaciji 1, a srebro i bakar na lokacijama 2-4. SEM snimci i analiza ljubaznošću Ineke Justen, ICN
Figure 14. Intergranular corrosion (a) and discontinuous precipitation of copper at grain boundaries (b) in the Byzantine paten. EDX analyses showed primarily silver at location 1, and silver and copper at locations 2-4. SEM metallographs and analyses courtesy of Ineke Joosten, ICN.

Tipovi krtosti i njen značaj

Od uočena tri tipa krtosti, izazvane korozijom, prisutnim mikrostrukturama i kao sinergijska krtost, najčešće se javlja krtost izazvana korozijom /3, 4/, i njen značaj je veoma različit. Preliminarna ispitivanja rimskog kondira (bogato ukrašenog pehara), /19/, pokazuju da mikrostrukturna krtost može biti vrlo značajne oštrine, ali je izgleda mnogo ređa. To je upravo tako, jer je kombinacija sinergijske i korozijske krtosti izuzetno štetna, uslovljavajući da predmet bude ne samo lomljiv, već i trošan. Konzervaciji takvih predmeta treba posvetiti posebnu pažnju, /1/.

Types of embrittlement and their severity

Of the three types of embrittlement, corrosion-induced, microstructurally-induced, and synergistic, corrosion-induced embrittlement is much more common, /3, 4/, and its severity varies widely. Preliminary examination of a Roman kantharos (a highly ornamented beaker), /19/, indicates that microstructurally-induced embrittlement can be severe, but it seems to be much rarer. This is just as well, since its synergistic combination with corrosion is very detrimental, rendering an object not only frangible but friable. Special care should be taken to conserve such objects, /1/.

Koroziono oštećenje, zaostala hladna deformacija i diskontinuirano taloženje

Sve u svemu, a posebno na osnovu rezultata Gundestrup pehara, izgleda da je zaostala hladna deformacija načelno glavni uzrok za koroziju, dok i intenzivno diskontinuirani talozi mogu biti bez značaja. To je različito od mišljenja poznatog metalurga Siril Stenli Smita, koji je sugerisao da isprekidani talozi čine granice zrna izuzetno osetljivim prema koroziji, /16/. Međutim, prikazani rezultati su potpuno saglasni sa iskustvom koje je stekao Petar Northover, /17/.

On je uočio interkristalnu koroziju i pojavu prslina u antičkom Baktrijan srebru i pored sadržaja bakra ispod 1%, koji je suviše nizak da izazove pojavu diskontinuiranog taloženja, /2/.

Bilo kako bilo, vrlo je moguće postojanje zavisnosti između zaostale hladne deformacije i pojave diskontinuiranog taloženja. Hladna deformacija može da smanji početnu brzinu rasta diskontinuiranih taloga u legurama srebro-bakar na povišenim temperaturama, što je posledica pojave deformacijom izazvanog diskontinuiranog taloženja, /18/. Sličan uticaj može da se pojavi i kod uzoraka kotla 361, 363 i 365, čak do nivoa da se spreči pojava isprekidanog taloga. Potvrda za ovu pojavu može se očekivati od transmisione elektronske mikroskopije (TEM) tankih folija pripremljenih iz malih uzoraka, što je tehnički izvodljivo primenom opreme sa usmerenim mlazom jona (FIB) ili sa dvojnim mlazom.

Značajan aspekt koji se odnosi naročito na restauraciju i konzervaciju, što je ilustrovano egipatskom vazom i vizantijskim nafornjakom. To je uticaj dekorativnog graviranja ili utiskivanja na korozijsko oštećenje. Prsline duž žleba gravure na sl. 2, tumačenje sl. 6, i pojava loma duž kružnog žleba na nafornjaku ukazuju da tankozidni predmeti sa ugraviranim ili utisnutim ukrasima treba da se ispitaju na korozijsko oštećenje posebno na odgovarajućim lokacijama na *unutrašnjim* ili *leđnim površinama*. Ako je to tako, moguće mere sanacije se sastoje u nanošenju zaštitnih prevlaka na te površine, /4/.

Pregled tehnika za dijagnostiku

Zbog složenosti pojave krtosti, njeno utvrđivanje kod antičkog srebra zahteva brojne tehnike dijagnostike. Pregled tih tehnika, koje su raspoređene u četiri glavne grupe, je dat u tab. 1:

(1) *Vizuelni pregled:* On je očigledan, ali ipak osnovni. Samo vizuelni pregled daje opšti utisak o stanju predmeta. On treba da se dokumentuje fotografijama, koje treba da budu u boji kao značajna mogućnost kada su u pitanju korodirani predmeti, na primer /20/.

(2) *Radiografija X-zračenjem:* Ona može da otkrije kako spoljnja tako i unutrašnja „skrivena" oštećenja i restauraciju. (Ona može da pomogne u utvrđivanju kako je sklopljen složeni predmet, npr. navedeni rimski pehar, /21/.)

(3) *Metalografija, EBSD, EDX ili WDX, mikrotvrdoća:* Metalografija je najvažnija tehnika dijagnostike, naročito u kombinaciji SEM sa EBSD i hemijskom analizom pomoću EDX ili WDX. Ispitivanje mikrotvrdoće povezano sa SEM metalografijom može pomoći u određivanju tipa i značaja krtosti, /1, 2, 4/, kao što je dato na sl. 15.

Corrosion damage, retained cold-work and discontinuous precipitation

On balance, and especially in view of the Gundestrup Cauldron results, it appears that retained cold-work is generally responsible for corrosion, while extensive discontinuous precipitation can be innocuous. This differs from the opinion of the eminent metallurgist Cyril Stanley Smith, who suggested that discontinuous precipitation makes grain boundaries highly susceptible to corrosion, /16/. However, the present results are consistent with the experience of Peter Northover, /17/.

He observed intergranular corrosion and cracking in ancient Bactrian silver despite copper contents bellow 1%, too low for discontinuous precipitation to occur, /2/.

Be that as it may, there is a possible link between retained cold-work and the occurrence of discontinuous precipitation. Cold-deformation can reduce the early growth rate of discontinuous precipitation in silver-copper alloys at elevated temperatures, and this could be due to deformation-induced continuous precipitation within the grains, /18/. A similar effect may have occurred in the Cauldron samples 361, 363 and 365, even to the extent that discontinuous precipitation was prevented. Verification of this would require Transmission Electron Microscopy (TEM) of thin foils prepared from small samples, which is technically possible using Focussed Ion Beam (FIB) or Dual Beam equipment.

An important aspect particularly relevant to restoration and conservation is illustrated by the Egyptian vase and the Byzantine paten. This is the effect of decorative chasing and stamping on the corrosion damage. The cracks along the chasing grooves in figure 2, the interpretation of figure 6, and the breakages along the circular grooves of the paten, suggest that all thin-walled objects with chased or stamped decorations should be examined for corrosion damage especially at the corresponding *internal* or *rear surface* locations. If this is so, a possible remedial measure is to apply a protective coating to these surfaces, /4/.

Survey of diagnostic techniques

Owing to its complexity, the embrittlement of ancient silver requires a number of diagnostic techniques for its assessment. Table 1 surveys these techniques, classified into four main topics:

(1) *Visual inspection:* This is obvious, but nevertheless essential. Only visual inspection gives an overall impression of an object's condition. This should be photographically documented, with colour photography as an important option for corroded objects, e.g. /20/.

(2) *X-ray radiography:* This can reveal both external and internal "hidden" damage and evidence of restorations. (It can also help to determine how a complex object is assembled, e.g. the Roman kantharos mentioned earlier, /21/.)

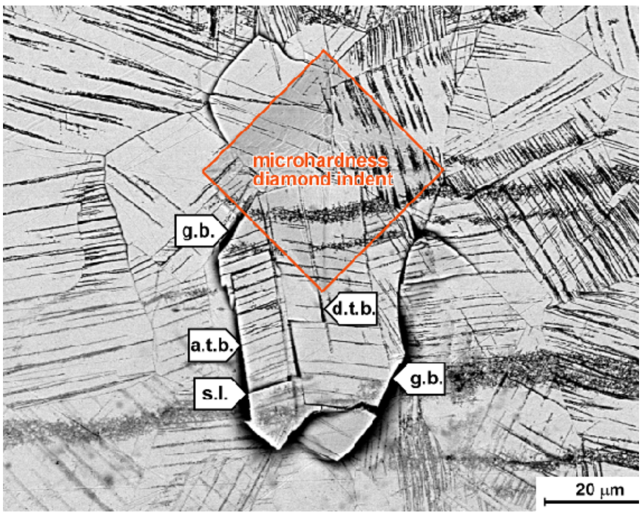
(3) *Metallography, EBSD, EDX or WDX, microhardness:* Metallography is the most important diagnostic technique, especially when SEM is combined with EBSD and chemical analysis by EDX or WDX. Microhardness testing coupled to SEM metallography can help in determining embrittlement types and severity, /1, 2, 4/, as given in Fig. 15.

(4) *Fraktografija:* To je osnovna dopuna metalografije sa ciljem da se napravi razlika između tipova krtosti. Detaljna fraktografija podrazumeva značajnu obučenost i iskustvo u tumačenju, /2/.

(4) *Fractography:* This is an essential adjunct to metallography for distinguishing between the types of embrittlement. Detailed fractography requires considerable interpretative skill and experience, /2/.

Tabela 1. Tehnike ispitivanja pojave krtosti u arheološkom srebru, /2, 4/

Vizuelno ispitivanje ×1–×10, golim okom ili lupom	Rendgenska radiografija ×1, ograničeno uvećanje	Optička ×10–×1000, i SEM ×10–×30.000 metalografija, EBSD, EDX ili WDX, i ispitivanje mikrotvrdoće (HV)	SEM fraktografija ×10–×30.000
Svrha: osnovno stanje objekta	Svrha: „skrivena“ oštećenja	Svrha: stanje prerade, hemijska analiza, unutrašnja oštećenja i pojava krtosti	Svrha: tip krtosti
• nominalno neoštećen • restauriran - raspored makro-prslina - nedostajući delovi • fragmentisan - raspored makro-prslina - nedostajući delovi	• nominalno neoštećen, restauriran ili fragmentisan - mikroprsline - makroprsline - prsline koje prate utisnute ukrase • restaurirana - nedostajući delovi	• stanje prerade - plastično deformisan } veličina zrna, segregacije, linije - plastično deformisan i žaren } klizanja, dvojnici deformacije i žarenja - liveno (dendritna struktura) } jezgro, eutektički sloj - liveno i žareno • hemijska analiza (SEM + EDX ili WDX) - poreklo: olovo-čistoća, prirodno srebro ili sa tragovima zlata - sadržaj olova, kalaja, bizmuta, antimona, arsena i talijuma: povezano je sa krtošću izazvanom mikrostrukturama - sadržaj bakra - visoka čistoća (nizak sadržaj bakra) mogu biti povezani sa zaostalom deformacijom - namerni dodatak bakra za povećanje čvrstoće - neravnomerno taloženje na granicama zrna u toku dužeg vremena • krtost izazvana korozijom (SEM + EBSD) - površinska - interkristalne prsline: usled hladne plastične deformacije ili neravnomernog taloženja bakra - međudendritna - transkristalna korozija duž traka segregacije - transkristalna korozija i prsline usled hladne plastične deformacije: traka klizanja, granica deformacionih dvojnika i oblasti traka klizanja ispod utisnutih ukrasa • krtost izazvana mikrostrukturom - uske interkristalne prsline - zrna raspoređena po celom komadu • ispitivanje mikrotvrdoće (HV) - žareno } HV vrednosti zavise i od hemijskog - zaostala plastična deformacija } sastava, naročito sadržaja bakra - korozija } HV vrednosti i mogući nastanak - krtost mikrostrukture } novih prslina	• krtost izazvana korozijom - površinska korozija - korodirane površine loma sa finozrnim izgledom kao površinska korozija - transkristalni lom (kristalografski) duž traka klizanja i granica dvojnika deformacije, verovatno i duž dvojnika žarenja • krtost izazvana mikrostrukturom - uglavnom čiste granice zrna (bez segregacija): mogu pokazati lokalnu koroziju gde trake klizanja, deformacioni dvojnici i segregacije presecaju površinu preloma - uske interkristalne prsline - zrna raspoređena po celom komadu



Slika 15. Ispitivanje tvrdoće za krtost srebra: egipatska vaza, SEM snimak (oznake prslina: b.g.– na granici zrna; s.l.– na liniji klizanja; d.t.b.–na granici deformacionog dvojnika; a.t.b.–na granici otpuštenog dvojnika). Tekst na slici: mikrotvrdoća otisak dijamanta.
Figure 15. Microhardness test for silver brittleness: Egyptian vase, SEM metallograph (key: b.g.–grain boundary crack; s.l.–slip line crack; d.t.b.–deformation twin boundary crack; a.t.b.–annealing twin boundary crack).

Table 1. Diagnostic techniques for archaeological silver embrittlement /2, 4/.

Visual inspection ×1–×10, unaided eye and hand lens	X-ray radiography ×1 limited enlargement	Optical , ×10–×1000, and SEM, ×10–×30,000, metallography, EBSD, EDX or WDX, and microhardness testing (HV)	SEM fractography ×10–×30,000
Purpose: Object Basic Condition	Purpose: "Hidden" Damage	Purpose: Manufactured Condition, Chemical Analysis, Internal Damage and Embrittlement	Purpose: Embrittlement Types
• nominally intact • restored - macrocrack patterns - missing pieces • fragmented - macrocrack patterns - missing pieces	• nominally intact, restored, or fragmented - hairline cracks - macrocracks - cracks following indented decorations • restored - missing pieces	• manufactured condition - mechanically worked; - mechanically worked and annealed } grain size, segreg. bands, slip lines, deformation and annealing twins - as-cast (dendritic); - cast and annealed } coring, eutectic distribution • chemical analysis (SEM + EDX or WDX) - source: lead cupellation, native silver or aurian silver - lead, bismuth, antimony, tin, arsenic and thallium contents: linked to microstructurally-induced embrittlement - copper content - high purity (low copper) may be linked to retained cold-work - intentional additions of copper for strength - long-term discontinuous precipitation along grain boundaries • corrosion-induced embrittlement (SEM + EBSD) - surficial - intergranular cracks: linked to cold-work or discontinuous precipitation of copper - interdendritic - transgranular corrosion along segregation bands - transgranular corrosion and cracking linked to cold-work: slip lines, deformation twin boundaries, and slip-line fields below indented decorations • microstructurally-induced embrittlement - narrow intergranular cracks - bodily displaced grains • 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	• embrittlement - surficial corrosion - corroded fracture surfaces with fine granular appearance like surficial corrosion - transgranular fracture (crystallographic) along slip bands and deformation twin boundaries, possibly also along annealing 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 - narrow intergranular cracks - bodily displaced grains

Mere sanacije

Intenzivne diskusije o merama sanacije pri restauraciji i konzervaciji krtog antičkog srebra su izložene u radovima /2–4/. Ovde je dat zaključak:

– Detaljna analiza slučaja je suštinska za određivanje najboljeg postupka restauracije i konzervacije krtih predmeta.
– Najbolje mere sanacije, sa aspekta očuvanja predmeta, nisu uvek takve da se komad može vratiti u prethodno stanje. Ovo je kontroverzna tema!
– Sve mere sanacije imaju *za* i *protiv*: svaki slučaj se mora proučiti posebno s obzirom na etiku i tehničke mogućnosti.

KRTOST RIMSKE STOPE STUBA

Utvrđeno je ranih devedesetih prošlog veka da su prepreke u koritu reke Maas, blizu Cuijka u Holandiji, ruševine rimskog mosta. Programom sanacije su nađeni i uklonjeni mnogi kameni blokovi i ostaci od više od 100 hrastovih stubova. Neki od stubova su na donjem zašiljenom kraju još uvek bili pokriveni gvozdenom stopom stuba. Svaka stopa stuba je izrađena od četiri gvozdene šipke, spojene u sklop zagrevanjem i kovačkim zavarivanjem. Stubovi i stope stubova datiraju između 340. i 400. godine, /22/.

Stubovi i pričvršćene stope stubova su preneti radi čuvanja u velikom skladištu sa betonskim podom. Na jednoj stopi stuba su nađena tri slomljena štapa, od kojih je bar jedan slomljen nedavno. U pitanju je bio udarni lom izaz

Remedial measures

Extensive discussions of the remedial measures for restoration and conservation of embrittled ancient silver are provided in References /2–4/. A summary is given here:

– Detailed case histories are essential for determining the best ways to restore and conserve embrittled objects.
– The best remedial measures, in regard preserving the objects, are not always reversible. This is a controversial topic!
– All remedies have *pros* and *cons*: each case must be considered in the light of ethics and technical capabilities.

ROMAN PILE-SHOE EMBRITTLEMENT

Obstacles in the Maas riverbed near Cuijk, the Netherlands, were recognised in the early 1990s to be the remains of a Roman bridge. A recovery programme found and removed many stone blocks and the remains of more than 100 oak piles. Some of the pointed lower ends of the piles were still covered by iron pile-shoes. Each pile-shoe was made from four iron bars, joined by heating and hammer-welding to form a point. The piles, and hence the pile-shoes, were dated to between 340 and 400 AD, /22/.

The piles and attached pile-shoes were transported for storage in a large concrete-floored shed. One pile-shoe was found to have three broken bars with at least one recent fracture. This was an impact fracture caused by a fall to the floor of the shed. The pile-shoe was sent to the Museum van padom na betonski pod. Stopa stuba je poslata u muzej Het Valkhof u Nijmegenu, gde je isečen komad na kojem je očuvana površina nedavnog loma.

Na sl. 16 je detalj stope stuba, gde se vide tri polomljena štapa i odsečeni deo, na kojem je gornja površina nedavnog loma. „N“ označava glavu eksera za pričvršćenje za drveni stub. Na sl. 17 je makrofotografija donje površine preloma. Tokom vekova, u koritu reke, štap je neravnomerno korodirao do oko 0,5 mm. Velika unutrašnja površina preloma se sastojala od svetlih nekorodiralih faseta, neke od njih su bile do 3 mm u prečniku. Ovaj neobični i očigledno krti lom je odmah proučen zajedničkim istraživanjem, primenom nekoliko tehnika za dijagnostiku.

Zajedničko istraživanje

Odsečeni komad, sl. 16, je čekićem udaren na bočnoj površini, što je dovelo do krtog loma u veće fragmente. Tako je potvrđena udarna krtost na temperaturi okoline na mestu inicijalnog preloma. Fragmenti su zatim podvrgnuti istraživanju, tab. 2.

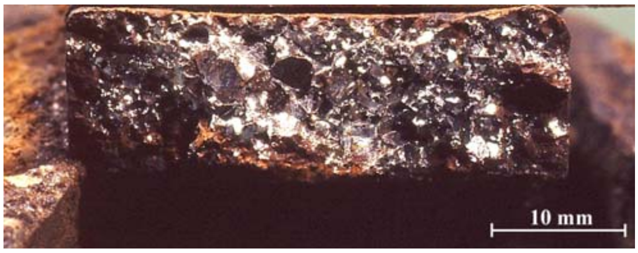
Het Valkhof in Nijmegen, where a slice containing one of the recent fracture surfaces was sawn off.

Figure 16 is a detail of the pile-shoe, showing all three broken bars and the sawn-off slice, which included the upper fracture surface of the recent breakage. “N” indicates nail head attaching it to the wooden pile. Figure 17 is a macrophotograph of the lower fracture surface. During the centuries in the riverbed the bar corroded evenly to about 0.5 mm. The large internal fracture consisted of shiny uncorroded facets, some of which up to 3 mm in diameter. This unusual and obviously brittle fracture prompted a collaborative investigation using several diagnostic techniques.

The collaborative investigation

The sawn-off slice, Fig. 16, was struck on a side surface with a hammer, resulting in brittle fracture to large fragments. This confirmed the ambient temperature impact brittleness at the location of the original breakage. The fragments were then used for the investigation, Table 2.

Slika 16. Prelomljena stopa sa odsečenim delom i gornjom prelomljenom pvršinom nedavnog loma
Figure 16. The broken pile-shoe with a sawn-off slice with the upper fracture surface of the recent break.



Slika 17. Donja površina preloma nedavnog loma
Figure 17. The lower fracture surface of the recent break.

Tabela 2. Tehnike ispitivanja pojave krtosti stope stuba, /6, 7/

Tehnika	Specifični aspekti i razlozi	Organizacija
Fraktografija		
• Makrofraktografija	krti lom, korozija	Het Valkhof
• SEM / FEG-SEM	interkristalni lom + lom cepanjem	PR-MA / NLR
Optička metalografija	mikrostruktura, tvrdoća	CORUS, NLR
Hemijska analiza		
<u>Matrica</u>		
Difrakcija X zracima (XRD)	gvožđe i sloj površinske korozije	PR-MA
Fluorescentna spektroskopija X zracima (XRF)	sastav gvožđa	CORUS
Sagorevanje + infracrvena (IR) detekcija	sadržaj ugljenika i sumpora u gvožđu	CORUS
<u>Metalografske površine</u>		
SEM + EDX, Electron Probe MicroAnalysis	sastav gvožđa i uključaka	CORUS / PR-MA
(EPMA) + WDX	raspodela fosfora i kiseonika	
<u>Površine preloma</u>		
Fotoelektronska spektroskopija X zracima (XPS)	segregacije na granicama zrna	PR-MA

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

Izbor tehnika za dijagnostiku je dopunjavan kako se razvijao postupak istraživanja. Na primer, postalo je očigledno da, ako je moguće, treba ispitati sveže, nezagađene površine, da bi se dokazale segregacije fosfora na granicama zrna. Nažalost, uzorci nisu mogli biti pripremljeni u vakuumu za ispitivanje loma i korišćenjeOže elektronske spektroskopije (AES).

Choice of the diagnostic techniques developed as the investigation proceeded. For example, it became clear that fresh, uncontaminated fracture surfaces should be examined, if possible, for evidence of phosphorus segregation to grain boundaries. Unfortunately, specimens could not be made for *in vacuo* fracture and examination by Auger Electron Spectroscopy (AES).

Umesto toga, uzorci su lomljeni u inertnoj atmosferi i površine preloma ispitivane fotoelektronskom spektroskopijom pomoću X zraka (XPS). To nije dalo zadovoljavajuće rezultate i nije omogućilo izvođenje zaključaka, /6, 7/.

Sumirani rezultati za glavna područja u tab. 2. su:

(1) *Fraktografija:* Na sl. 18 su FEG-SEM krtog loma, koji je gotovo potpuno interkristalan na, i u blizini spoljnje površine, i mešoviti interkristalni lom i lom cepanjem prema centru štapa. Veličina zrna je varirala između 0,25 mm do preko 2 mm.

(2) *Metalografija:* na sl. 19 je poprečni presek, uključujući površinu preloma. Tri zone su rezultat zavarivanja tri gvozdene trake u jedinstveni štap. Mikrostruktura se sastoji od velikih nedeformisanih zrna ferita, nešto deformisanih dvojnika u blizini spoljnjih površina i neuobičajenog uticaja nagrizanja, izraženog u zoni 2. Ovo je uticaj segregacija fosfora i tipičan je za antičko gvožđe sa fosforom, /23, 24/.

(3) *Hemijska analiza:* Ona je pokazala da je štap od gvožđa sa fosforom (0,25–0,52 tež. % P) sa vrlo malim sadržajem silicijuma, mangana i sumpora; i izuzetno malim sadržajem ugljenika (0,0033 tež. % C) na mestu prvobitnog loma, /6, 7/. Analiza XRD je takođe pokazala da je korodirani površinski sloj akaganeitne strukture, koja može da se obrazuje posle sanacije stope stuba iz korita reke, /6, 7, 25/.

Instead, recourse was made to breaking a sample in a nominally inert atmosphere and interrogating the fracture surface by X-ray Photoelectron Spectroscopy (XPS). This was unsatisfactory and inconclusive, /6, 7/.

Summarised results for the main topics in Table 2 are:

(1) *Fractography:* Figure 18 shows FEG-SEM images of the brittle fracture, which was almost entirely intergranular at, and near the outside surfaces, and a mixture of intergranular and cleavage fracture towards the centre of the bar. The grain size varied from 0.25 mm to more than 2 mm.

(2) *Metallography:* Figure 19 shows a cross-section including the fracture surface. The three zones are the result of hot-welding three strips of iron together to form the bar. The microstructure consists of large undeformed ferrite grains, some deformation twinning close to the outside surfaces, and an unusual etching effect especially in zone 2. This effect is due to phosphorus segregation and typically occurs in ancient phosphoric iron, /23, 24/.

(3) *Chemical analyses:* These showed that the bar is a phosphoric iron (0.25–0.52 wt.% P) with very low silicon, manganese and sulphur contents; and extremely low carbon content (0.0033 wt.% C) at the location of the original breakage, /6, 7/. The XRD analyses also showed that the surface corrosion layer was akaganeite, which would have formed after recovery of the pile-shoe from the riverbed, /6, 7, 25/.

Table 2. Diagnostic techniques for the pile-shoe embrittlement, /6, 7/.

Techniques	Specific Aspects and Purposes	Organisation
Fractography		
• Macrofractography	brittle fracture, corrosion	Het Valkhof
• SEM / FEG-SEM	intergranular + cleavage fracture	PR-MA / NLR
Optical metallography	microstructure, hardness	CORUS, NLR
Chemical analysis		
Bulk		
X-Ray Diffraction (XRD)	iron and surface corrosion layer	PR-MA
X-Ray Fluorescence (XRF) spectroscopy	iron composition	CORUS
Combustion + InfraRed (IR) detection	carbon and sulphur content of iron	CORUS
Metallographic surfaces		
SEM + EDX, Electron Probe MicroAnalysis (EPMA) + WDX	iron and inclusion compositions, phosphorus and oxygen line scans	CORUS / PR-MA
Fracture surfaces		
X-ray Photoelectron Spectroscopy (XPS)	grain boundary segregation	PR-MA

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

Mehanizmi razvoja krtosti

Krtost šipke je pripisana lokalno ekstremno niskom sadržaju ugljenika u kombinaciji sa relativno visokim sadržajem fosfora, /6, 7/. Značajna veličina feritnih zrna upućuje na to da je do niskog sadržaja ugljenika došlo zbog lokalnog razugljeničavanja tokom konačne izrade stope stuba, /26/. Ovaj niski sadržaj ugljenika je omogućio visoko temperaturnu segregaciju fosfora po granicama zrna, i posledičnu osetljivost na krti udarni lom na temperaturi okoline, /27–30/. Faktor koji doprinosi krtosti je uticaj zareza zbog neravnomernog razvoja korozije koja prodire u štap.

Konzervacija ostalih stopa stuba

Postoje dva aspekta konzervacije ostalih saniranih stopa stuba. Kao prvo, mora se očekivati postojanje površinskog sloja korozije koji sadrži akaganeit. Kako je akaganeit higroskopan, korozija će napredovati sve dok se aktivno ne spreči isušivanjem slojeva korozije ili skladištenjem stopa

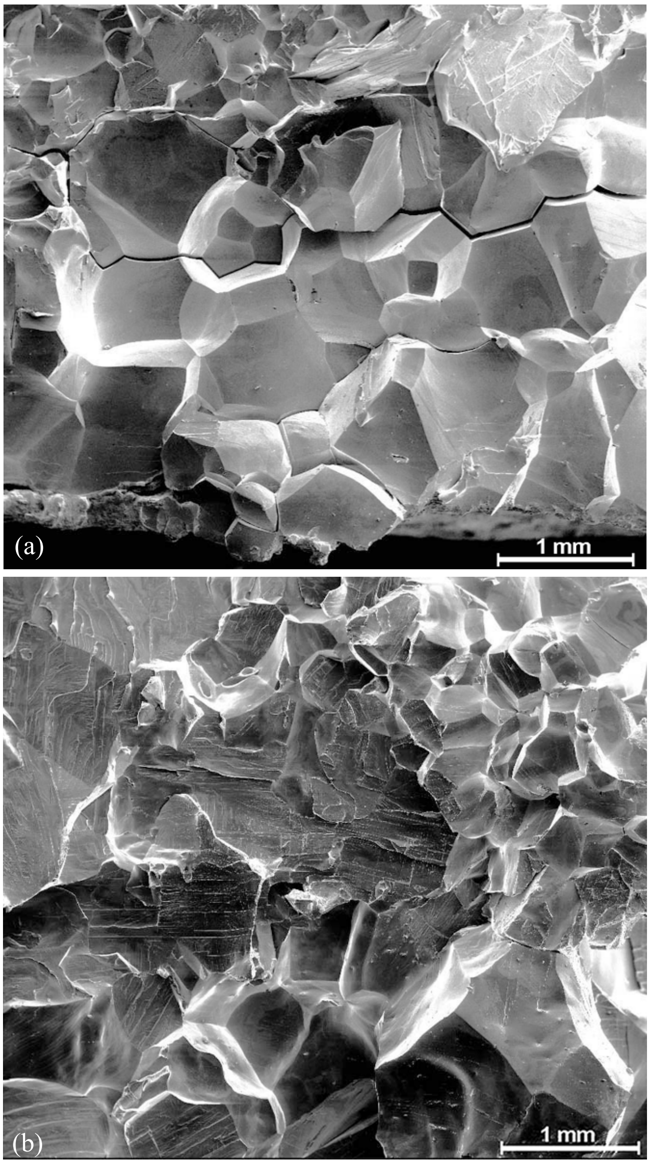
Embrittlement mechanisms

Embrittlement of the bar was attributed to the *locally* extremely low carbon content combined with the relatively high phosphorus content, /6–7/. The large ferrite grain sizes suggest that the low carbon content was due to local decarburisation during final manufacture of the pile-shoe, /26/. This low carbon content enabled high-temperature segregation of phosphorus to the grain boundaries, resulting in susceptibility to brittle impact fracture at ambient temperatures /27–30/. A contributing factor to the brittleness is a notch effect owing to non-uniform corrosion developed in the bar.

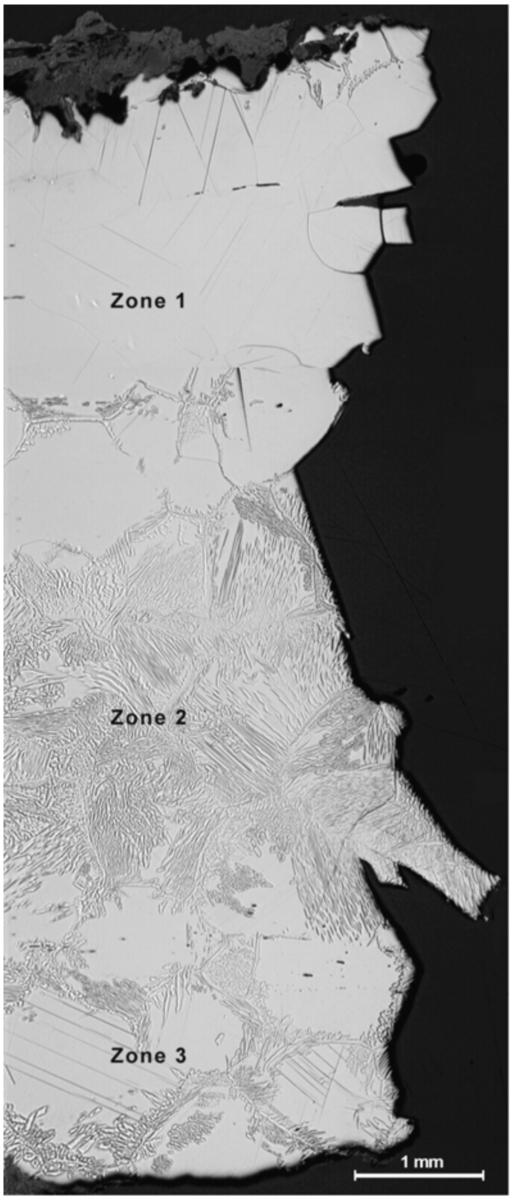
Conservation of other pile-shoes

There are two aspects to conserving the other recovered pile-shoes. Firstly, these must be expected to have surface corrosion layers containing akaganeite. Since akaganeite is hygroscopic, corrosion will continue unless actively prevented by drying out the corrosion layers and either storing stuba u okruženje niske vlažnosti, /25/, ili primenom zaštitnih (organskih) prevlaka. Kao drugo, neke ili nekoliko ovih stopa stuba mogu imati ekstremno nizak sadržaj ugljenika na sličnim lokacijama duž štapova. Na taj način, ako se neke stope iznesu iz skladišta, ili ako su ili nisu pričvršćene za stubove, sa njima se mora pažljivo rukovati i moraju se transportovati vrlo pažljivo kako bi se izbegao lom.

the pile-shoes in a low-humidity environment, /25/, or applying a protective (organic) coating. Secondly, some or many of these pile-shoes could have extremely low carbon contents at similar locations along the bars. Thus if any are to be removed from storage, and whether or not they are still attached to piles, they should be handled and transported with care to avoid breakages.



Slika 18. FEG-SEM fraktografije uzorka odsečenog dela: (a) na, i blizu spoljnje površine, (b) bliže centru
Figure 18. FEG-SEM fractographs of a sample from the sawn-off slice: (a) at, and near the external surface, (b) nearer the centre.



Slika 19. Mikrostruktura po debljini slomljenog uzorka: gornja i donja ivica su prvobitne površine: SEM metalografski snimak
Figure 19. Through-thickness microstructure of a broken sample: top and bottom edges are the original surfaces: SEM metallograph.

ZAKLJUČNE NAPOMENE

Ovaj rad je pokazao da savremene tehnike dijagnostike, naročito metalografija i hemijska analiza, obezbeđuju da se bolje razume krtost u antičkim predmetima od srebra i objasni pojava krtosti i korozije u gvozdenim stopama stuba rimskog mosta. Stečeno znanje može da se koristi za predlaganje i primenu optimalnih mera sanacije za restauraciju i konzervaciju ovakvih i sličnih predmeta povećane krtosti.

CONCLUDING REMARKS

This paper has shown that modern diagnostic techniques, especially metallography and chemical analysis, enable improved understanding of embrittlement in ancient silver objects and explanation of embrittlement and corrosion of a Roman bridge iron pile-shoes. This knowledge can be used to propose and use the optimum remedial measures for restoration and conservation of such and similar embrittled objects.

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