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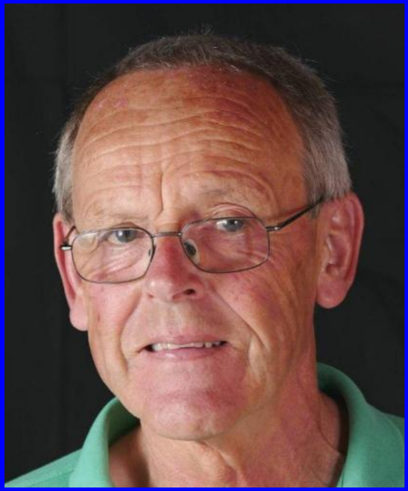


Lecture course on metallurgy, embrittlement and conservation of ancient silver: update 2018

Contents - I

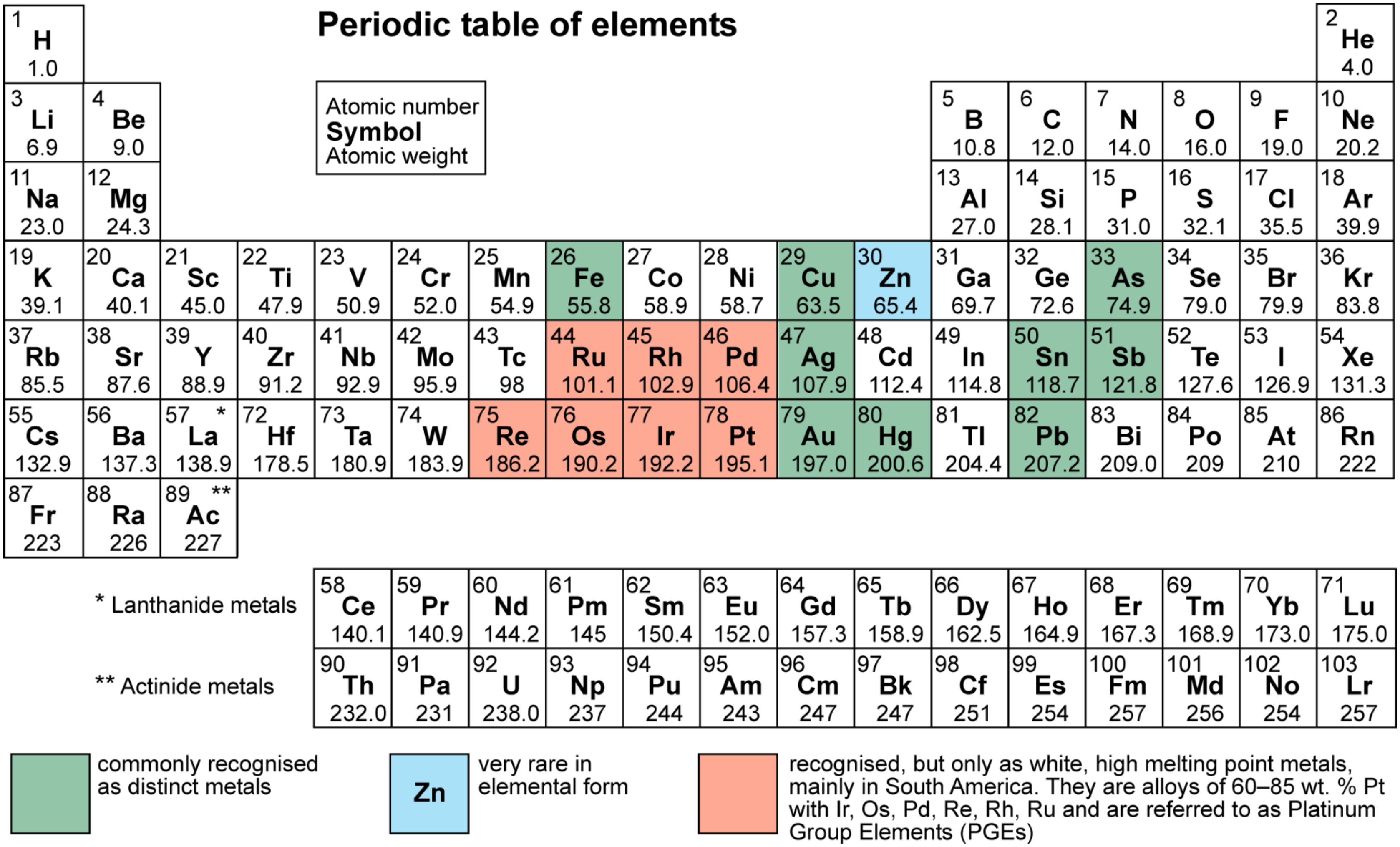
Contents - II

1. Introduction

Archaeometallurgical topics and questions
(after general stylistic identification and provenance)

- **Further identification and provenance**
  - metal/alloy composition
  - origins of metals and ores
- **Manufacturing and craftsmanship**
  - fabrication methods/choices of methods
- **Damage assessment**
  - deformation
  - corrosion
  - embrittlement (cracks)
  - previous restorations
- **Restoration and conservation**
  - methods
- **Authenticity checks**
  - genuine
  - modern fake
  - ancient fake

Metals known in antiquity



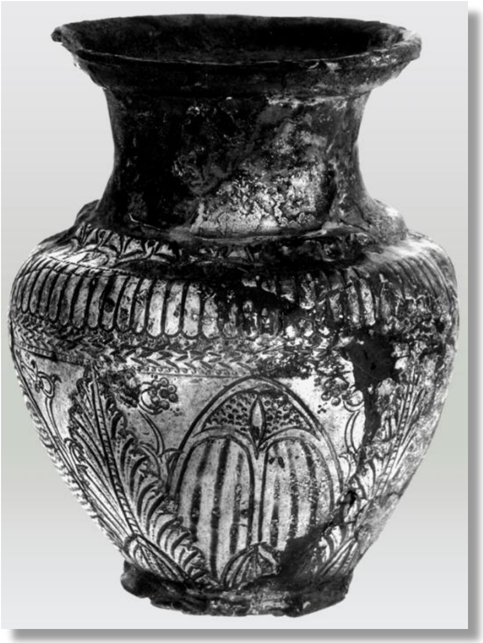
Metals and alloys used in antiquity

Au	unalloyed and alloyed for artefacts and coinage; Au and Ag gilding and plating; Ag–Cu hard solders for joints: see slides 8 and 12 also
Ag	
aurian silver (electrum, **Au–Ag)**	
Cu	Implements, e.g. bronze axe heads, and artefacts; bronzes also used for coinage and plating iron
arsenical copper **(Cu–As)**	
tin bronze **(Cu–Sn)**	
brass **(Cu–Zn)**	not before 2nd century BCE; mainly coinage
meteoric iron **(Fe–Ni)**	implements
Fe	wrought iron and steel implements and artefacts; cast iron artefacts in Far East
Hg	gilding (Hg-Au amalgam); recovery of Au by amalgamation
Pb	artefacts; leaded bronzes and brasses
Sn	bronzes; tinning of bronze, iron, pottery
pewter, soft solders **(Pb–Sn)**	implements and artefacts; soldered joints
Zn	extremely rare: a definite find of zinc sheet, Agora, Athens
As	plating bronze mirrors, daggers and other artefacts
Sb	limited use: artefacts; Cu–Sb castings
Platinum Group Elements **(PGEs)**	small South American artefacts; decorated Egyptian box

Silver in antiquity

- Unalloyed and alloyed (artefacts and coins)
- Gilding and plating
- Ag–Cu hard solder: indicates knowledge of strengthening by additions of copper to silver: see slides 12 and 22 also
- Example artefacts

Gundestrup Cauldron



Egyptian Vase

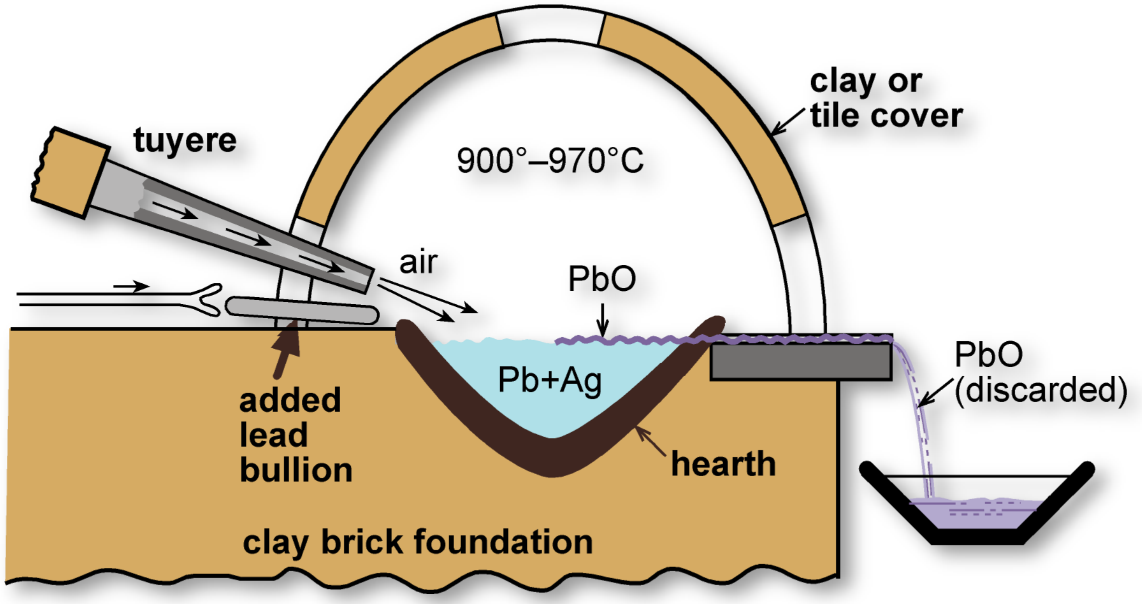
Byzantine Paten

2. Silver production

Silver production - I

- **Main source of silver was pyrometallurgy: lead cupellation (desilverization of lead bullion)**
- **Stage 1**
  - melt ~ 100 kg lead using wood fuel in a *basic* clay hearth, temperature ~ 900°C
  - use bellows + tuyere to oxidise lead to PbO (litharge), which melts at 880°C
  - PbO runs off cupel via a surface groove
  - more lead continually added

Schematic of Stage 1 cupellation ~ 500 BCE (after Conophagos 1980)



Silver production - II

- **Stage 2**
  - silver-enriched lead transferred to second hearth, temperature ~ 1000°C
  - use bellows + tuyere to oxidise lead to PbO
  - remove PbO by repeatedly dipping iron rods* into it, forming layered cones**:**

2 cm

  - this leaves a silver globule resting on the hearth

- **Stage 3**
  - refine silver globules in a third hearth: remaining PbO absorbed by pores in cupel wall
  - silver purity reaches 98.5 – 99.7 wt.%**:** dissolved oxygen suddenly spits out of the molten silver in this purity range. (*Technical note***:** oxygen-free pure silver melting/solidification point is 960.8°C)

**** Possible only after 1000 BCE, when iron became available***

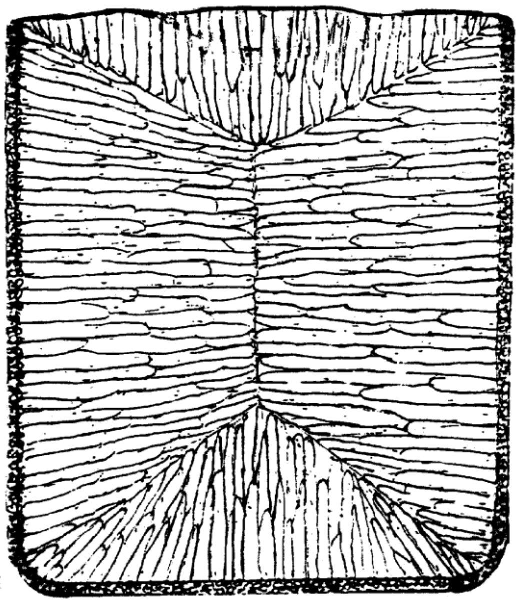
Silver production - III

- **Composition of cupelled silver**
  - **>** 95 wt.% Ag
  - minor-to-trace amounts of Au, Cu, Pb, Bi (generally **<** 1 wt.% for each element)
  - traces of Sb, As, Te, Zn, Ni

N.B: Silver artefacts and coins with > 0.5 –1 wt. % Cu indicate deliberate additions of copper, for strength and wear resistance: Ag–Cu hard solder is also an indication of this. See slides 7, 8 and 22 also

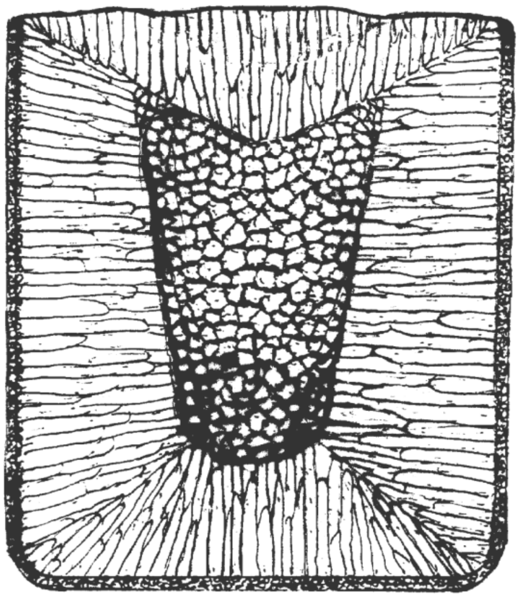
Silver production - IV

- **Cupelled silver globules remelted and cast into ingots**



pure metal

Ingot macrostructures (schematic)

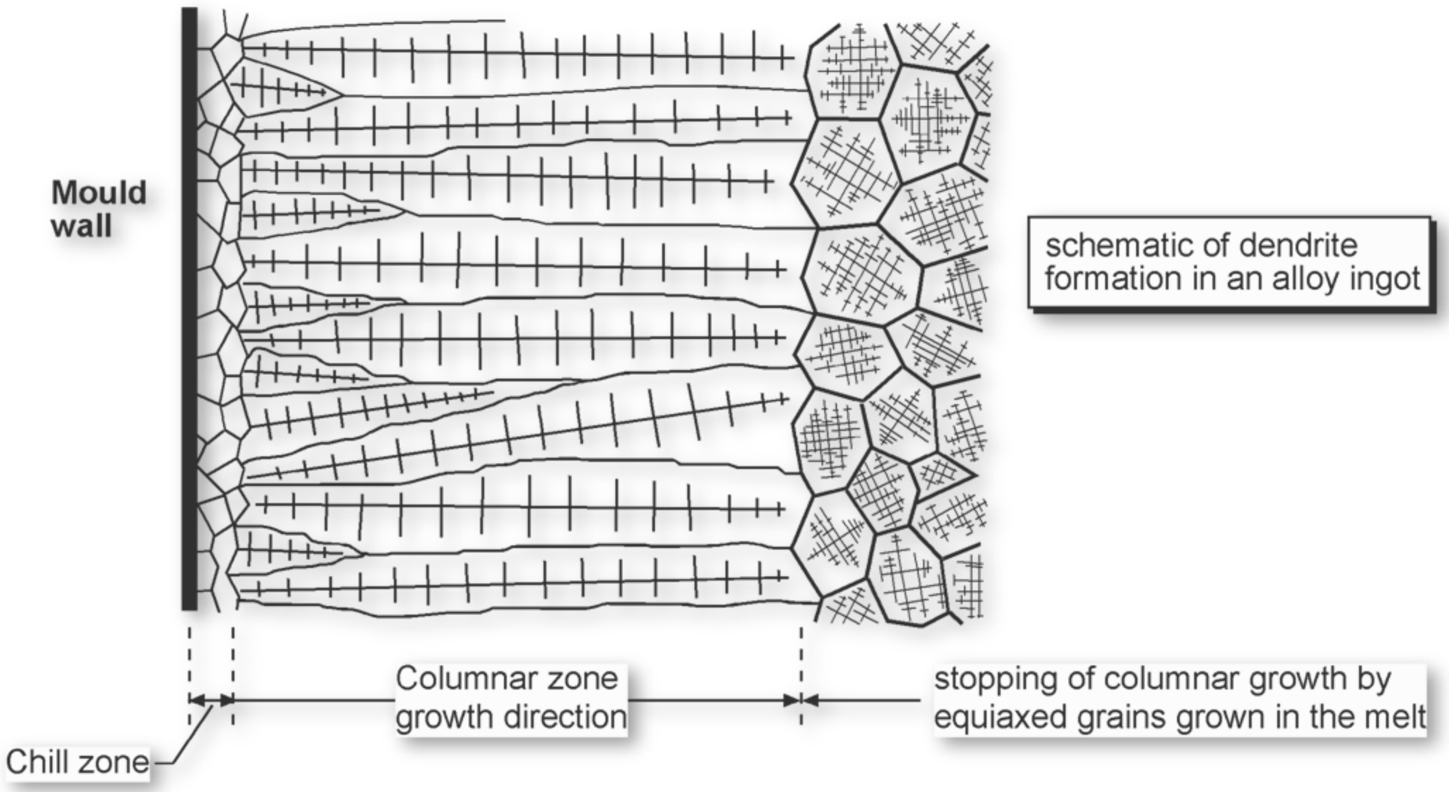


alloy

  - ***chill zone*****:** fine equiaxed grains near mould walls
  - ***columnar zone*** **:** more rapid cooling promotes finer columnar grains
  - ***central equiaxed zone*** (not in pure metals)**:** promoted by increasing amounts of alloying elements

Silver production - V

- **Ingot microstructures: grains and dendrites**

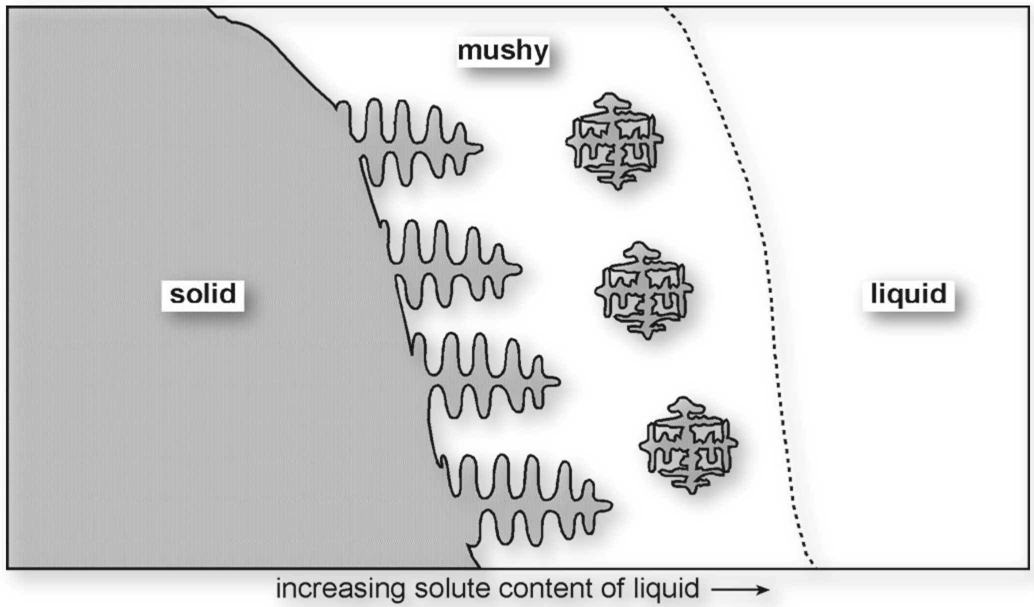


  - ***dendrite*****:** branching treelike crystal form [Greek: *dendron*]
  - ***dendritic growth*****:** common solidification structure, occurring in alloys and sometimes, under special conditions, in pure metals

Silver production - VI

- **Alloys generally solidify over a range of temperature:**

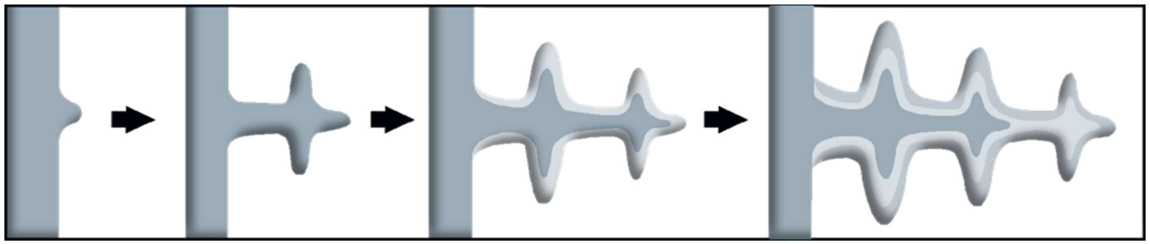
The schematic shows solidification by dendrite formation (left to right) during alloy cooling (after Beckermann and Wang1994)



  - note the general change in solid composition owing to the increasing solute content of the liquid. This occurs even with equilibrium cooling conditions and is explainable with the aid of alloy phase diagrams
  - for high silver content alloys the first part to solidify is richer in Ag, so the melt becomes enriched in solute elements, including Cu

Silver production - VII

- **Dendritic segregation and microsegregation in a silver-rich alloy**

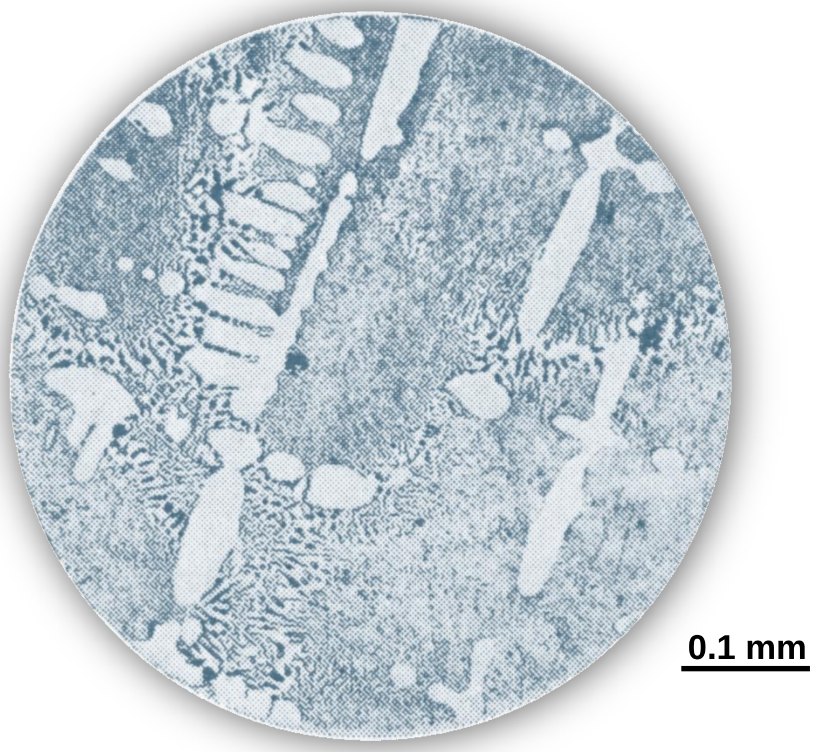


Schematic of dendritic microsegregation (coring) during dendrite formation

- even under ***equilibrium cooling*** conditions the first dendrites to form will be richer in Ag than subsequent ones (dendritic segregation)
- the usual rapid cooling of cast metals occurs under ***non-equilibrium cooling*** conditions and results in
  - dendrites varying in composition between their centres and surfaces (microsegregation, commonly called ***coring***)
  - the final solidifying ***interdendritic*** liquid being rich in solute elements

Silver production - VIII

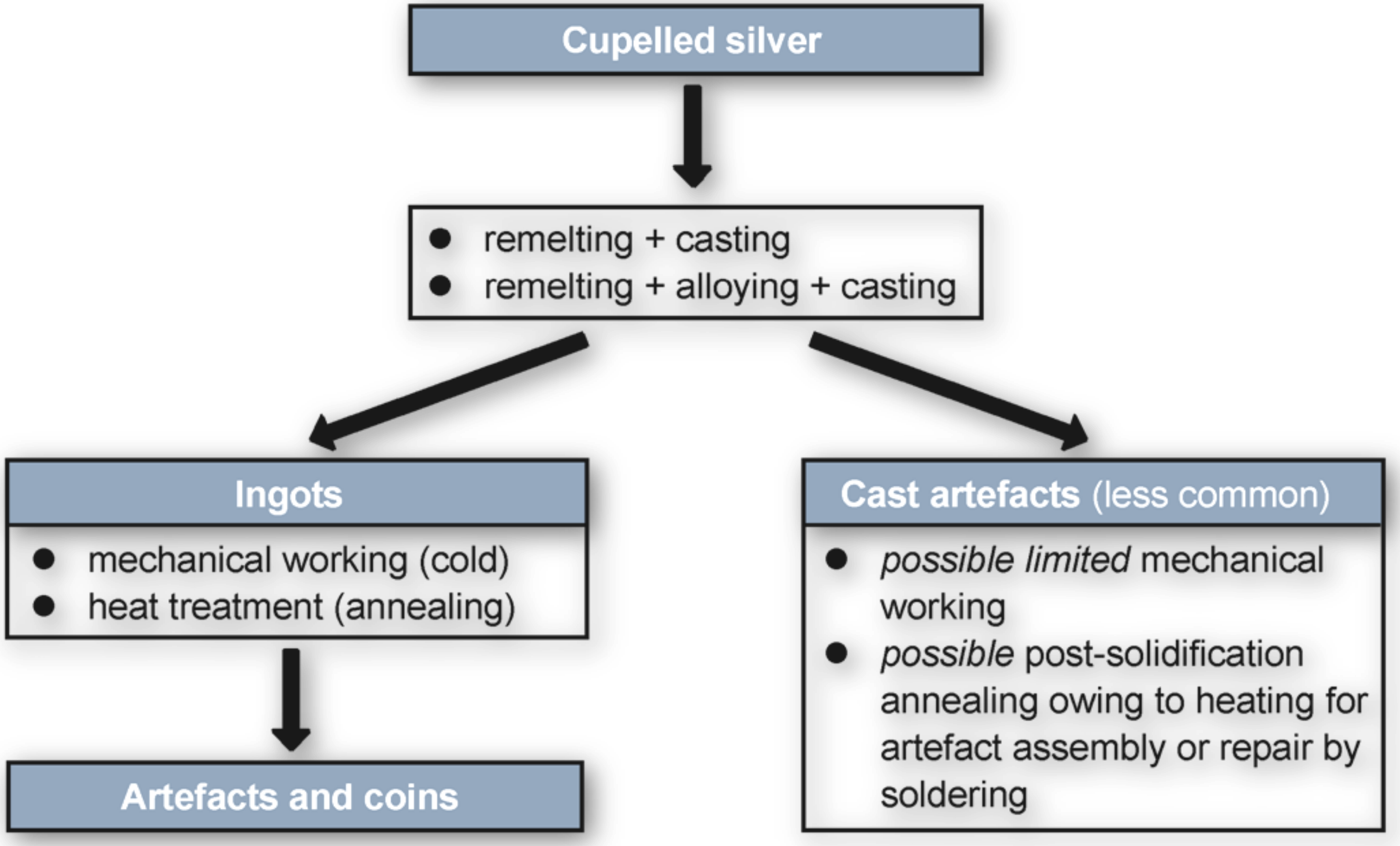
- **Example microstructure of a casting, showing silver-rich dendrites and the finally solidified solute-rich interdendritic phases: coarse and fine *eutectic****



***Greek: *eutēktos* = easily melted**

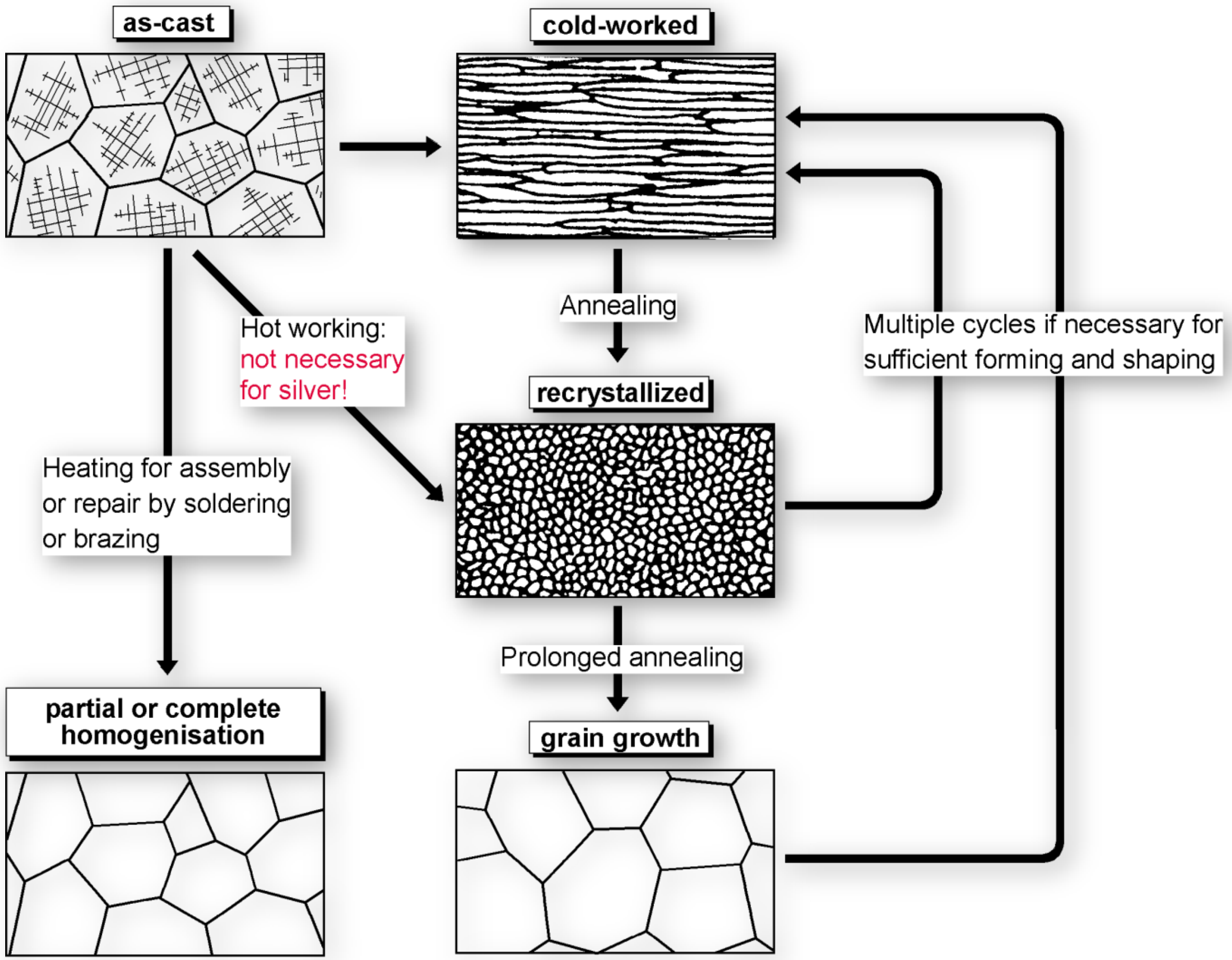
3. Silver processing

Processing overview



N.B: A few artefacts and almost all coins are not annealed after cold-work. This is very important in regard to their long-term condition, as will be seen in the sections on embrittlement of ancient silver and case histories

Schematic of relationships between cast, worked and annealed microstructures for a silver-rich alloy



Possible final microstructures of silver-rich artefacts and coins

- **Castings**
  - inhomogeneous columnar and equiaxed grains containing dendrites**:** inhomogeneity due to ***dendritic segregation***, ***coring*** and ***interdendritic solid rich in solute elements*****:** see slides16 and 17 also
  - partly or completely homogeneous equiaxed grains due to post-solidification heating for soldering assembly or repair
- **Multiple cycle cold-worked and annealed artefacts**
  - homogeneous or inhomogeneous*****equiaxed grains containing annealing twins
- **Finally cold-worked artefacts and coins**
  - homogeneous or inhomogeneous* deformed grains and annealing twins**;** slip lines**;** occasional deformation twins

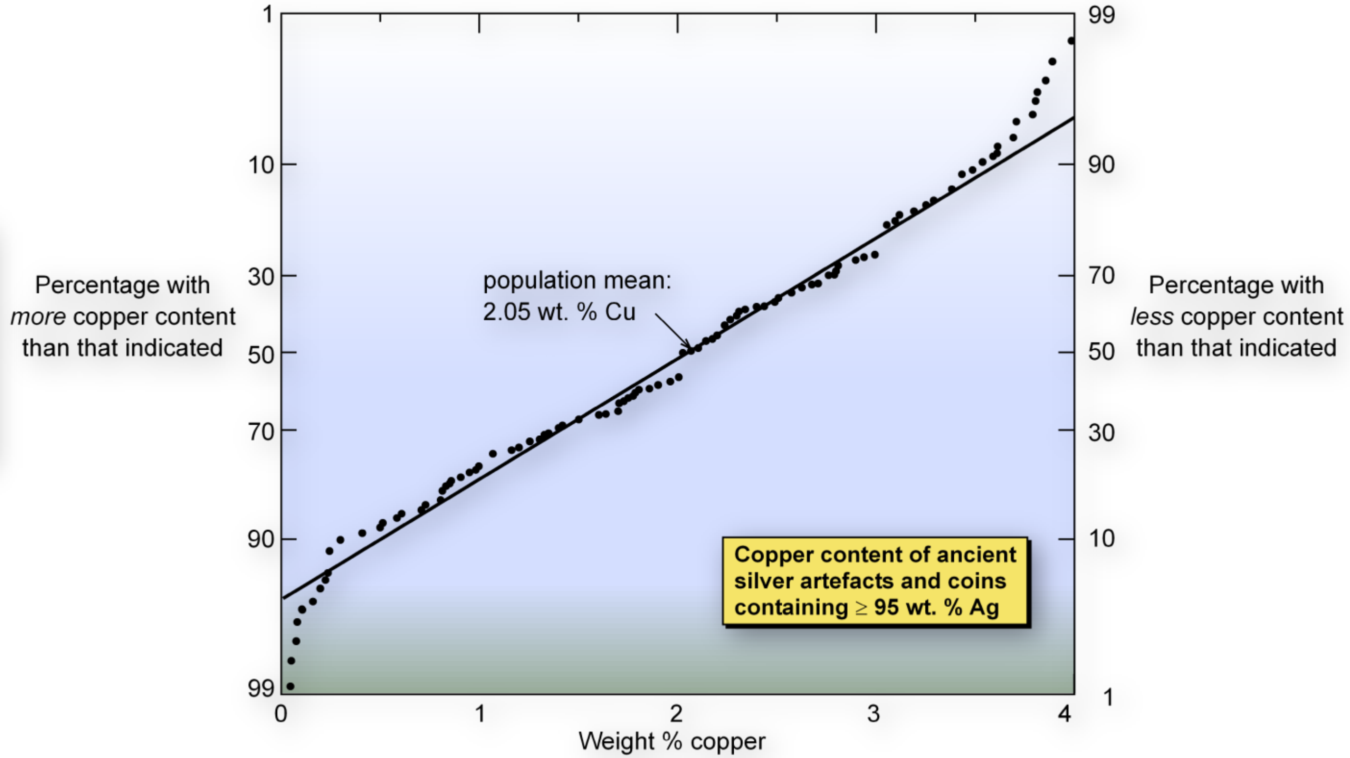
***** Inhomogeneity owing to coring persisting as elongated segregation bands

N.B: Many of these microstructural features will be illustrated in sections 4 –10

Alloying with copper for silver-rich artefacts and coins
(copper is the most important alloying element)

- **Cupellation reduces Cu content to 0.3 – 0.5 wt.%**
- **Cu contents > 0.5 – 1 wt.% are deliberate additions, commencing from about 3000 BCE, to increase strength and wear resistance**

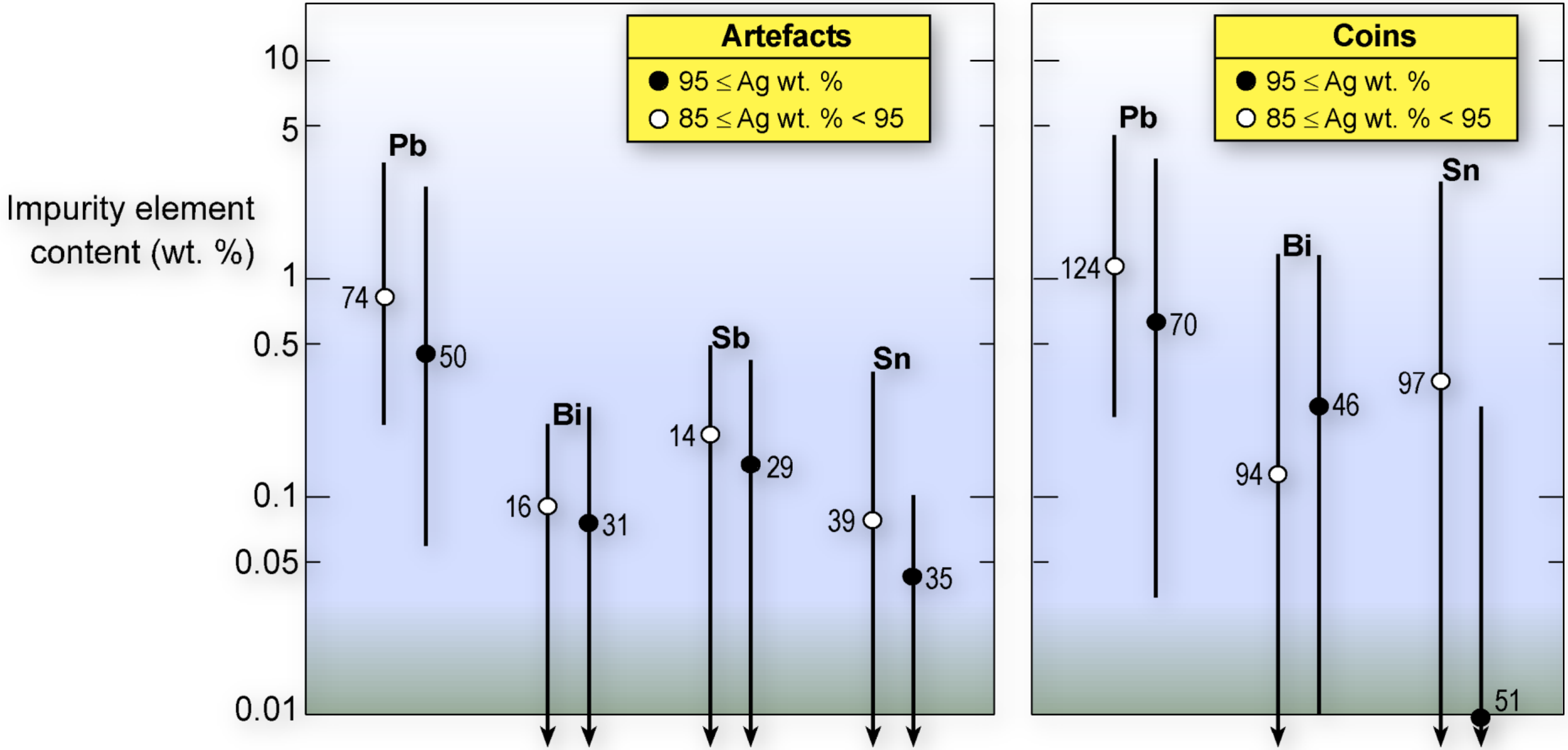
Probability plot of Cu contents for Old World artefacts and coins



- **80 – 90% of objects appear to have had deliberate Cu additions. However, the plot is a *normal* distribution, suggesting non-systematic Cu additions**

Actually and potentially embrittling impurity elements in silver-rich artefacts and coins - I

- **Impurity contents for many Old World artefacts and coins**

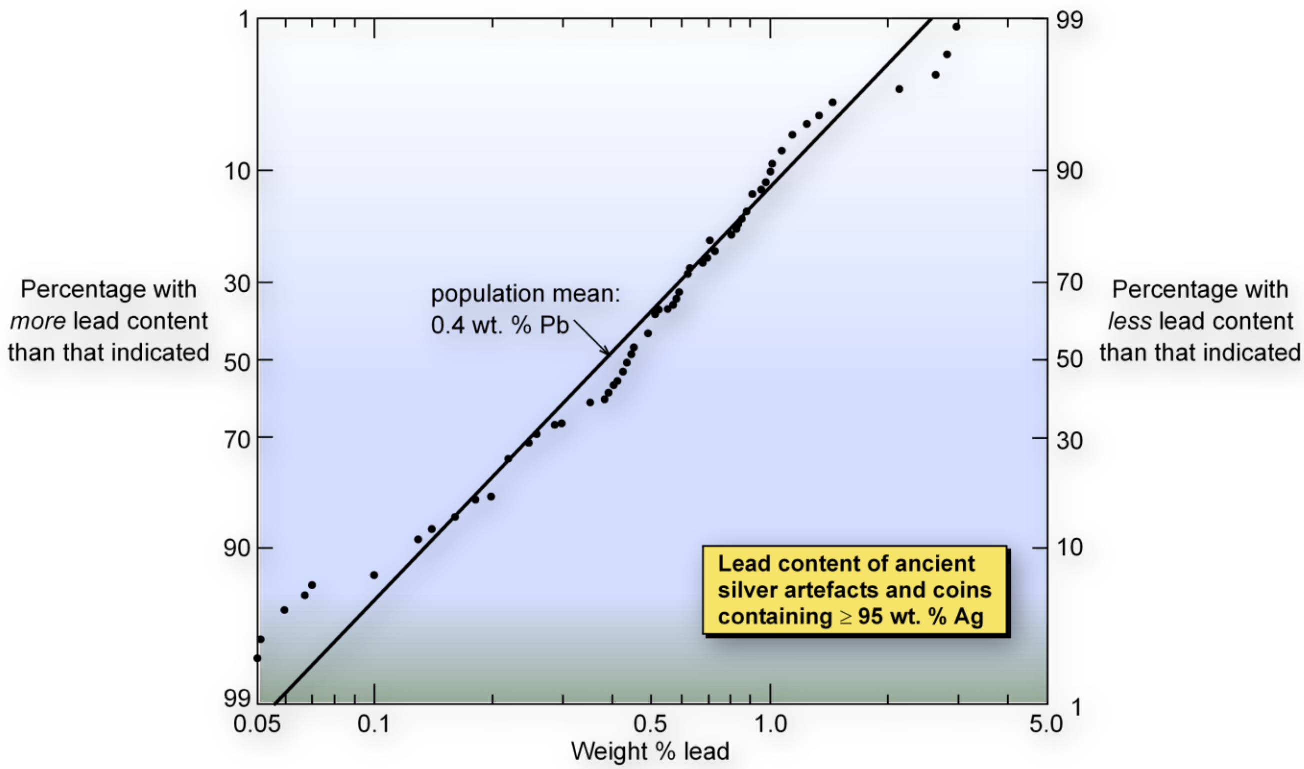


- **Pb is the main impurity, averaging 0.4 – 1 wt.%**
- **Bi, Sb, and Sn generally < 0.5 wt.%**

Actually and potentially embrittling impurity elements in silver-rich artefacts and coins - II

- **Pb is the main impurity (and most probably the most important)**

Probability plot of Pb contents for Old World artefacts and coins



- **This is an approximately *log-normal* distribution, which in this context is characteristic of elemental concentrations in chemical process residues : i.e. the Pb contents simply represent residual Pb after cupellation**

4. Embrittlement of ancient silver

Types of embrittlement

- **Corrosion-induced embrittlement**
  - intergranular* in mechanically worked and fully annealed artefacts
  - intergranular in mechanically worked artefacts with retained cold-work
  - interdendritic in as-cast and nearly as-cast artefacts
  - along segregation bands, i.e. the remains of dendritic microsegregation (coring) and interdendritic segregation that occurred during solidification
  - along slip lines/planes* and deformation twin boundaries in artefacts and coins with considerable retained cold-work
- **Microstructurally-induced embrittlement**
  - intergranular fracture, narrow and sharp cracks; bodily displaced grains
  - most likely due to impurity element segregation to grain boundaries during long-term low temperature ageing
- **Synergistic embrittlement**
  - combinations of corrosion-induced and microstructural embrittlement

***Most probably stress-assisted, i.e. types of stress corrosion cracking* (SCC)**

Corrosion-induced embrittlement - I

- **Intergranular and interdendritic corrosion: optical metallographs**

(a) Intergranular

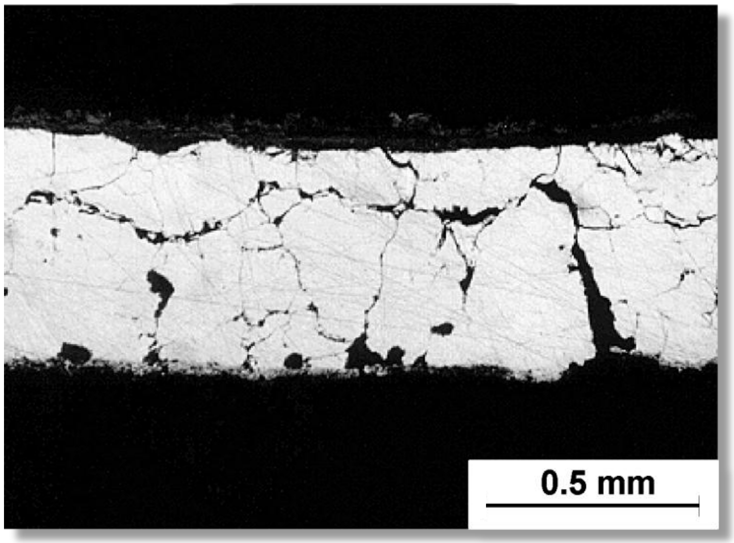


Photo: The British Museum, London

– mechanically worked and annealed silver (Roman Cup). Note wide irregular grain boundary cracks and large grain sizes (0.2 – 0.4mm)

(b) Interdendritic

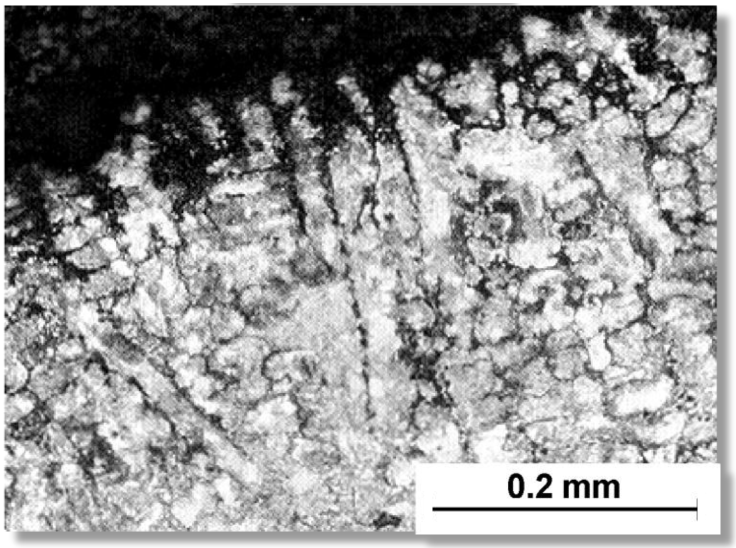
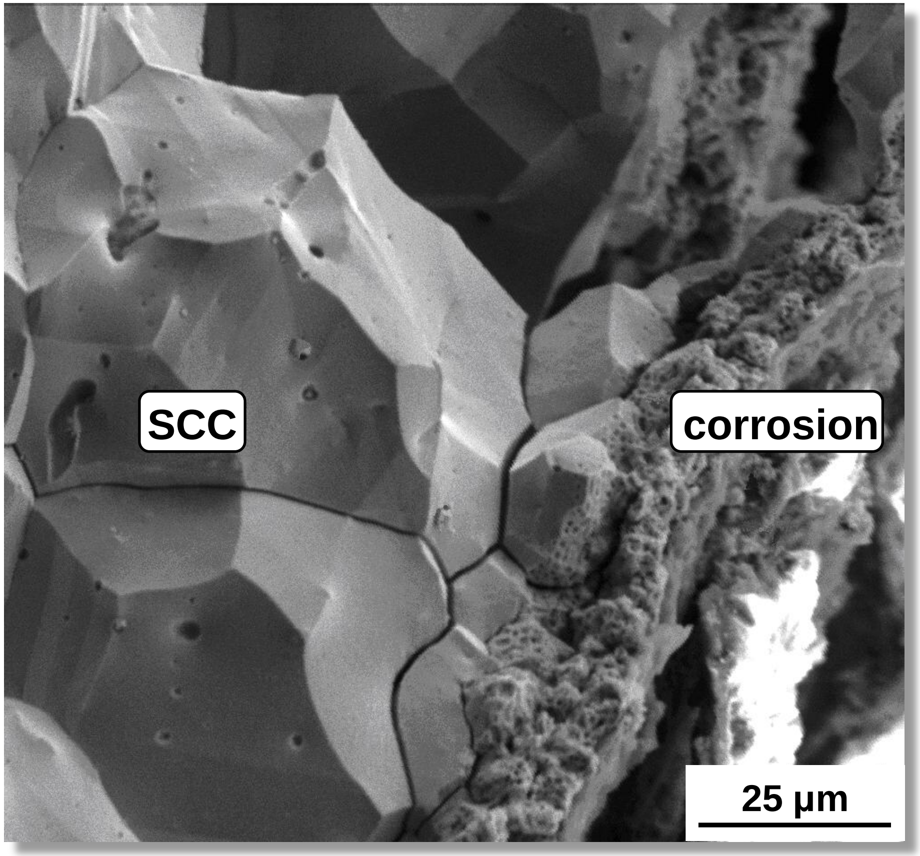


Photo: David Scott, The Getty Institute, Los Angeles

– slightly mechanically worked silver casting from a Sican Tumi (ceremonial knife)

Corrosion-induced embrittlement - II

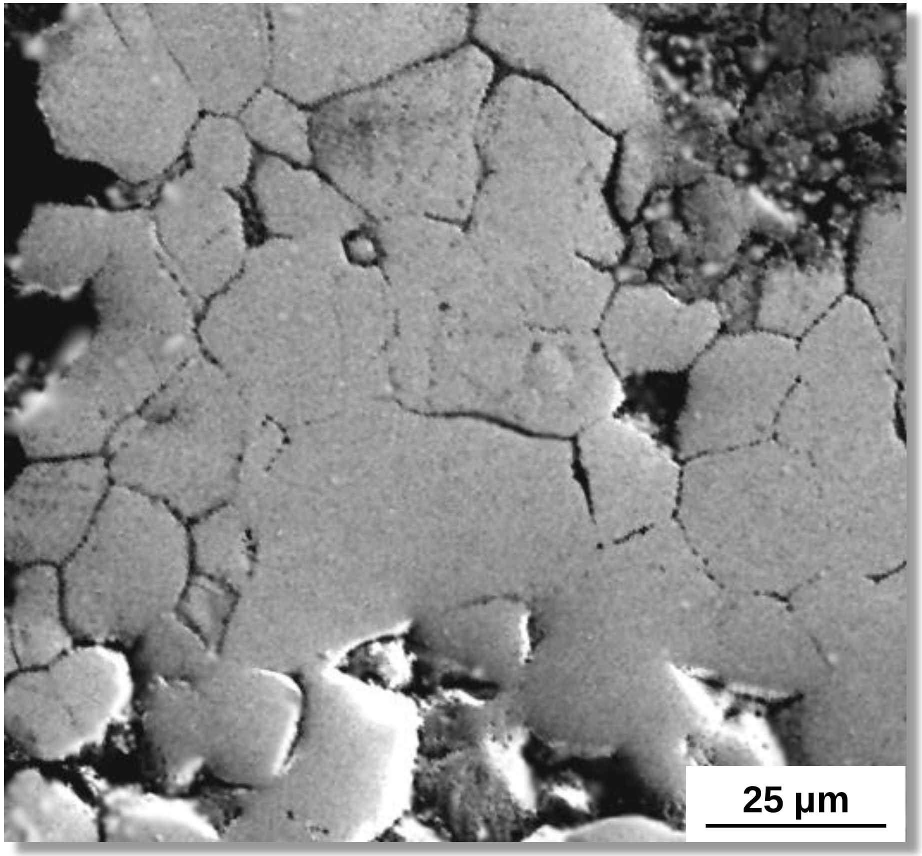
- ***Probable*** **intergranular SCC and** ***subsequent*** **general corrosion: see slide 29 also**
  - Romanesque Kaptorga (small container for relics and amulets)



SEM fractograph: Jarka Vaníčková, Institute of Chemical Technology, Prague

Corrosion-induced embrittlement - III

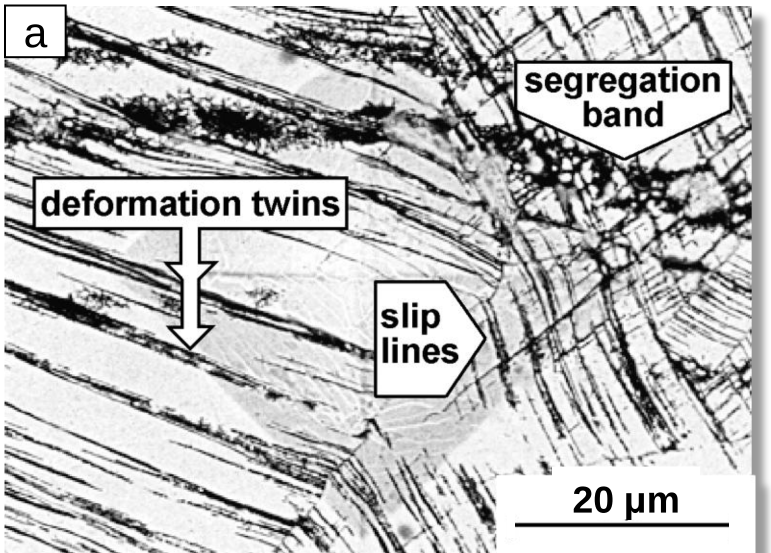
- **Intergranular cracking beginning by corrosion pitting that coalesces into smooth intergranular fracture facets: *probable* intergranular SCC, slide 28**
  - Romanesque Kaptorga (small container for relics and amulets)



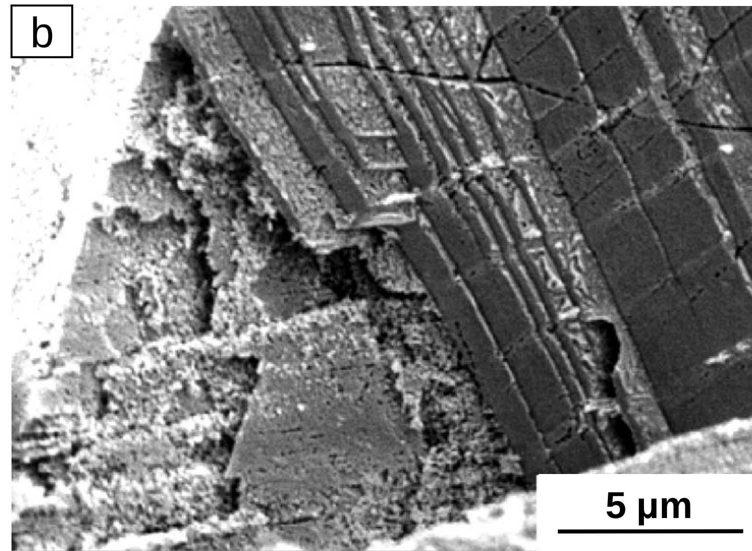
SEM metallograph: Pavel Bartuška, Institute of Physics, Prague

Corrosion-induced embrittlement - IV

- **Corrosion along slip planes, deformation twins and segregation bands**
  - Egyptian Vase, considerable retained cold-work



SEM metallograph: NLR



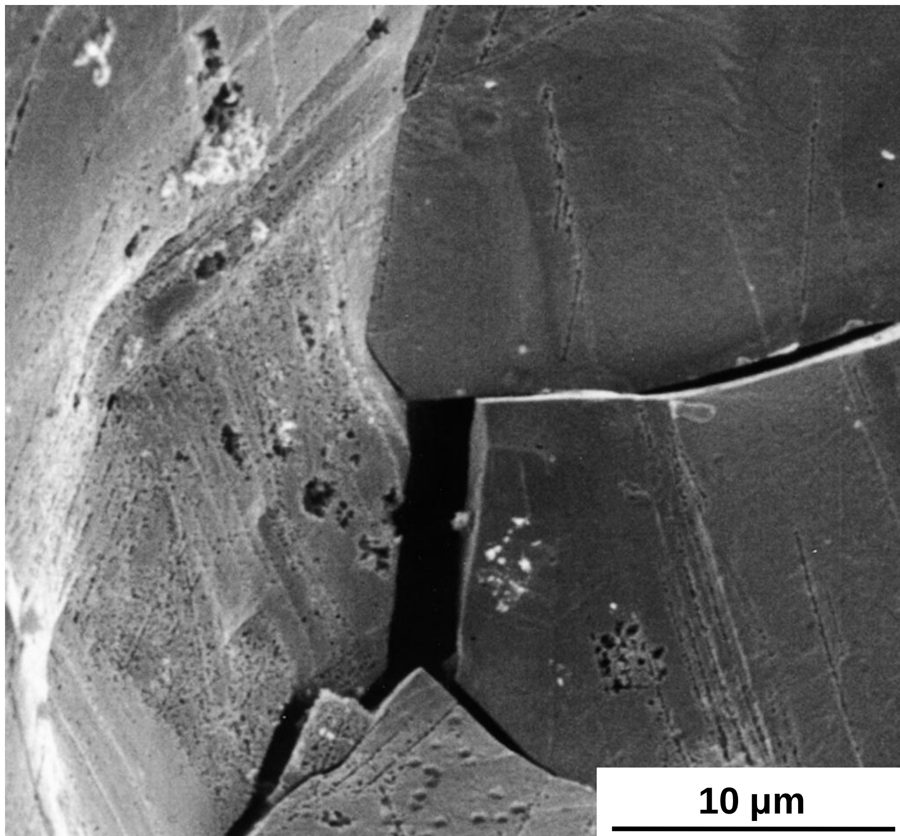
SEM fractograph: NLR

- corrosion attack of slip lines, deformation twin boundaries and segregation bands
- crystallographic fracture due to corrosion and SCC mainly along slip planes

N.B: Deformation twins in silver are narrow with lenticular end points

Microstructurally-induced embrittlement - I

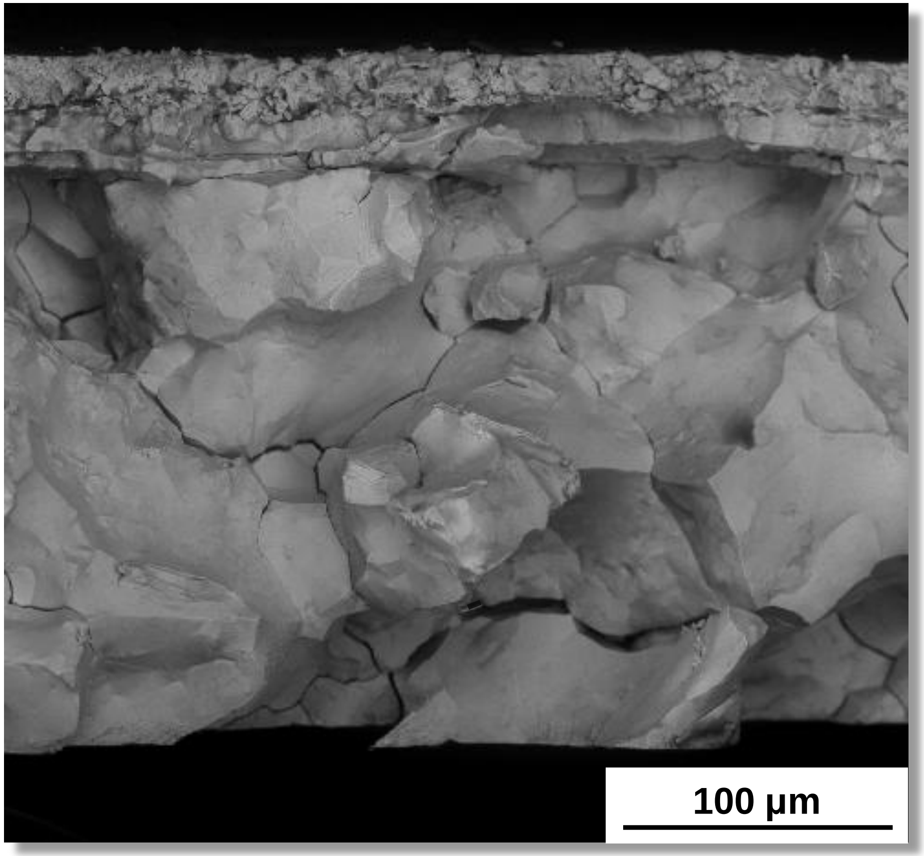
- **Intergranular fracture, narrow and sharp cracks, bodily displaced grains**
  - Egyptian Vase, retained cold-work**:** some corrosion pitting along slip lines



SEM fractograph: NLR

Microstructurally-induced embrittlement - II

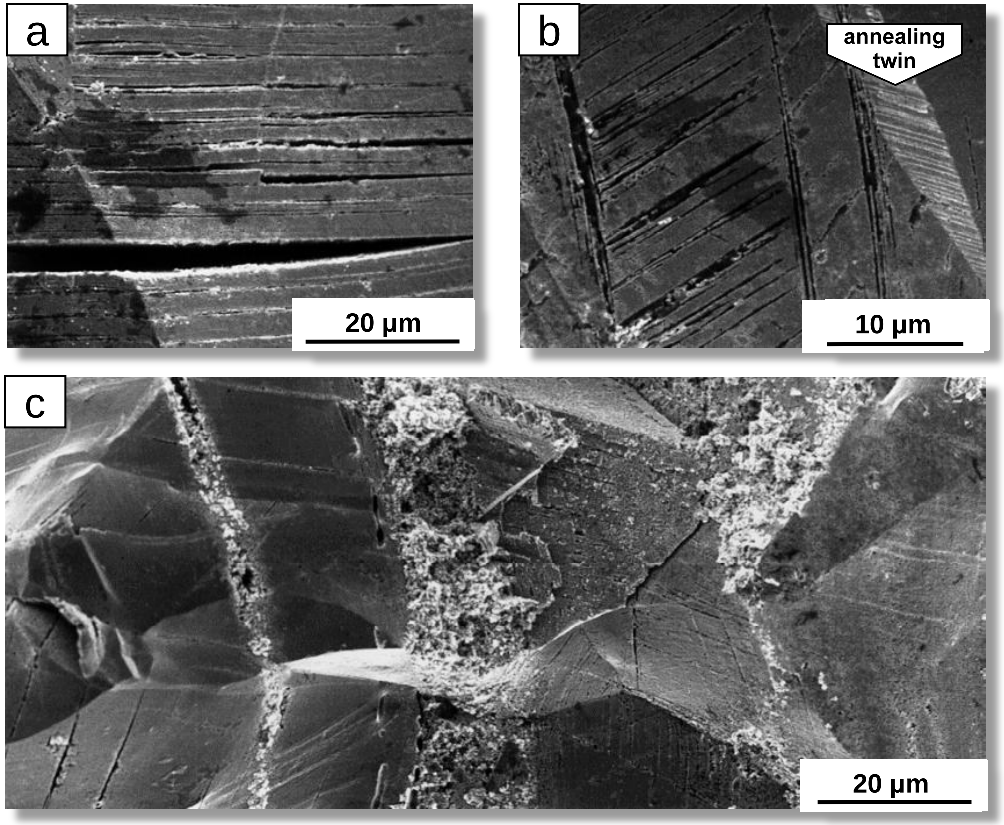
- **Intergranular fracture, narrow and sharp cracks, bodily displaced grains**
  - Roman Kantharos**:** recrystallized surface grains due to planishing, see slide 60



SEM fractograph: Netherlands Institute for Cultural Heritage, Amsterdam

Synergistic embrittlement

- **SEM fractographs (NLR) of finally cold-worked silver from an Egyptian Vase**



(a) corrosion and SCC causing fracture along slip planes intersecting grain boundary facets
(b) corrosion along deformation twin boundaries intersecting a grain boundary**:** note the almost uncorroded annealing twin with internal slip lines
(c) corrosion along segregation bands intersecting grain boundary facets

5. Case history #1: Gundestrup Cauldron

Gundestrup Cauldron (Denmark)

- **2000 years old masterpiece of European Iron Age silverwork**

National Museum of Denmark, Copenhagen

  – reassembled from 12 plates and a bowl, 95 – 98 wt.% silver: main alloying element is copper

Gundestrup Cauldron analysis techniques: SEM+EBSD metallography (NLR)

- **Field Emission Gun Scanning Electron Microscope (FE-SEM) combined with Electron BackScatter Diffraction (EBSD) equipment**

- **EBSD is a powerful technique for microstructural analysis, with many options. For the Gundestrup Cauldron the following options were of most use:**
  - Inverse Pole Figure (IPF) colour-coded maps
  - Boundary rotation angle maps
  - Coincidence Site Lattice (CSL) maps

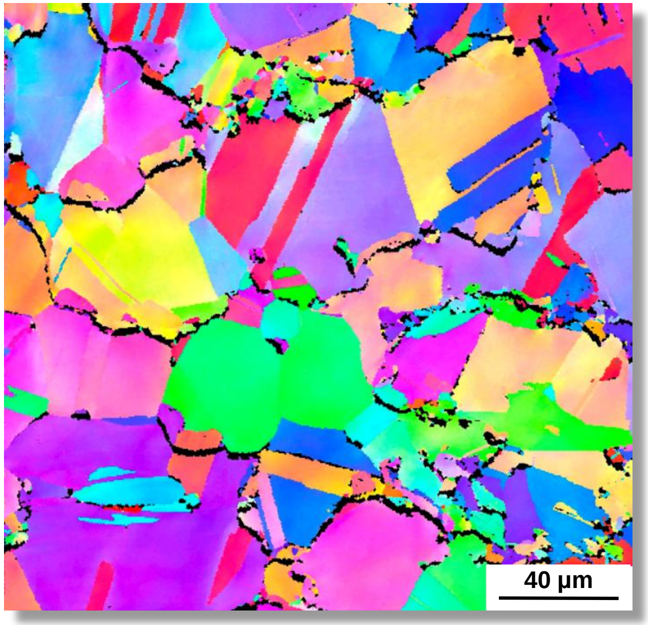
- **Four samples with previously determined chemical compositions (wt.%)*:**

Sample	Cu	Au	Pb	Bi	Traces
361	4.64	0.29	0.39	0.07	Fe,Ni
363	1.76	0.35	0.52	0.13	Fe,Zn
365	2.17	0.33	0.58	0.11	Fe,Ni,Zn
366	3.44	0.36	0.64	0.11	Fe,Ni,Zn

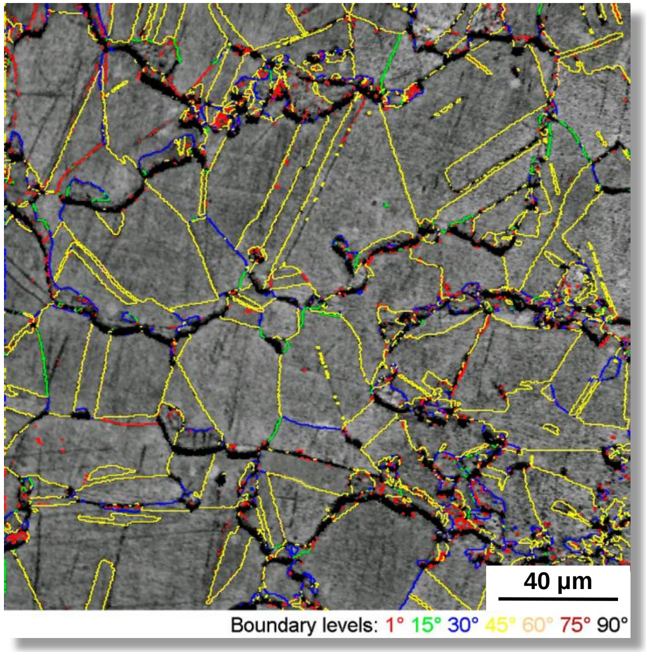
*Peter Northover, University of Oxford, Electron Probe MicroAnalysis (EPMA) + Energy Dispersive analysis of X-rays (EDX)

Gundestrup Cauldron sample 366: annealed microstructure

IPF colour-coded map

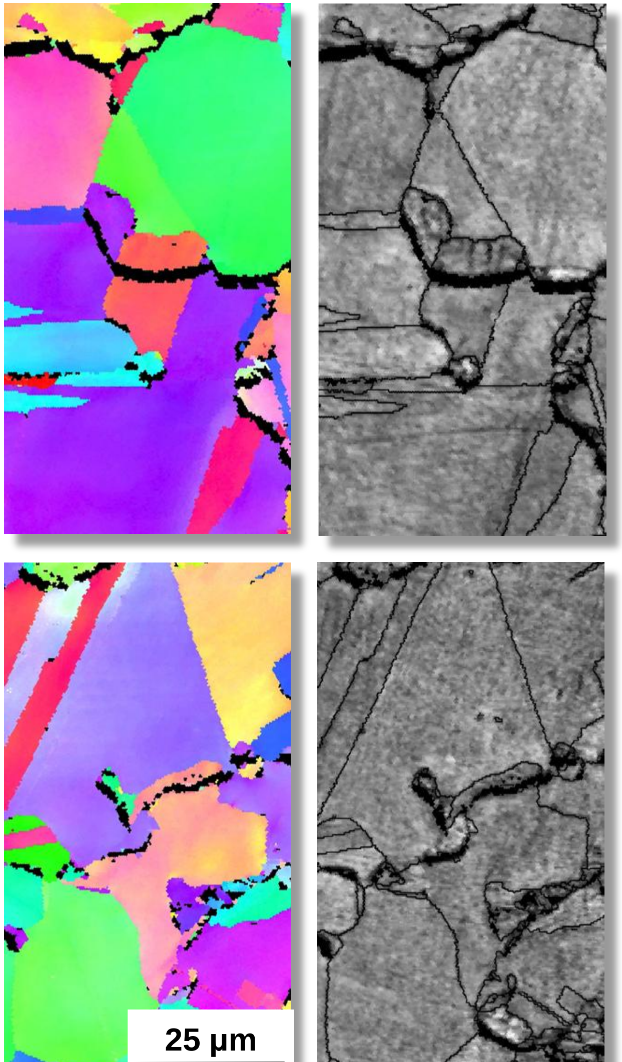


Boundary rotation angle map



- No corrosion
- Equiaxed randomly oriented grains**;** annealing twins (yellow-coded boundaries)
- Discontinuous precipitation of copper at grain boundaries, giving meandering or “wiggly” grain boundary appearances**:** see slide 38 also

Gundestrup Cauldron sample 366: discontinuous precipitation of copper



Precipitate behaviour

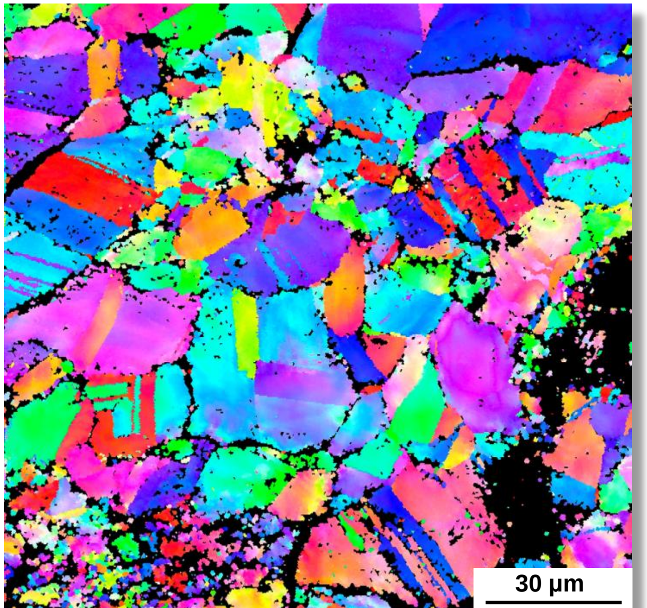
- nucleation at original "green" grain boundary
- growth into "green" grain, changing its lattice orientation to that of the contiguous grain with the "purple" matrix and "red" annealing twin

Precipitate behaviour

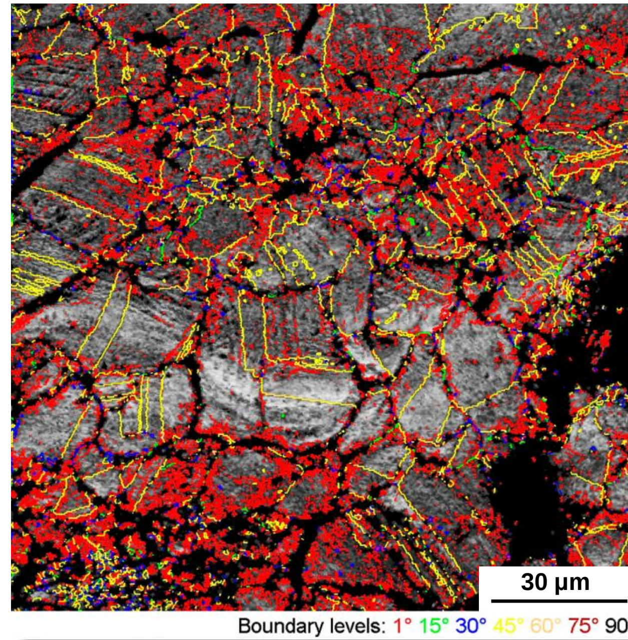
- two nucleations at original grain boundary between "purple" and "pink" grains
- growth in opposing senses**:** (a) into the "pink" grain, changing its lattice orientation to that of the contiguous "purple" grain **;** (b) into the "purple" grain, changing its lattice orientation to that of the contiguous "pink" grain

Gundestrup Cauldron sample 361: remanent cold-work and corrosion

IPF colour-coded map



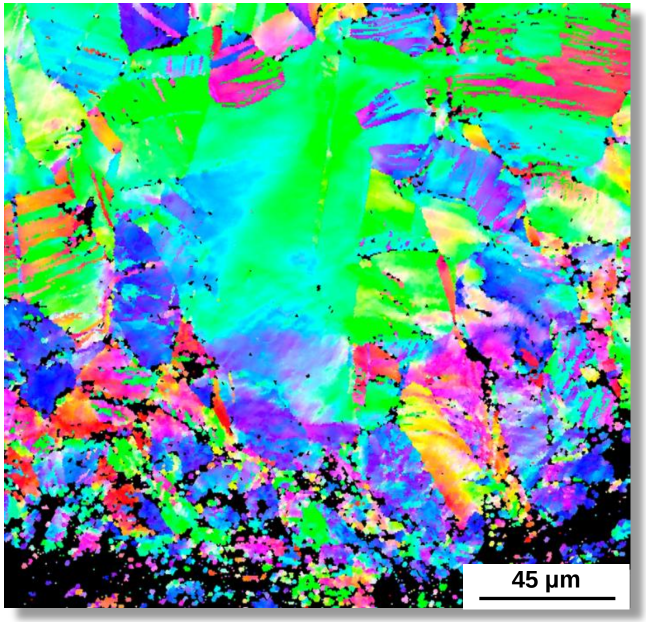
Boundary rotation angle map



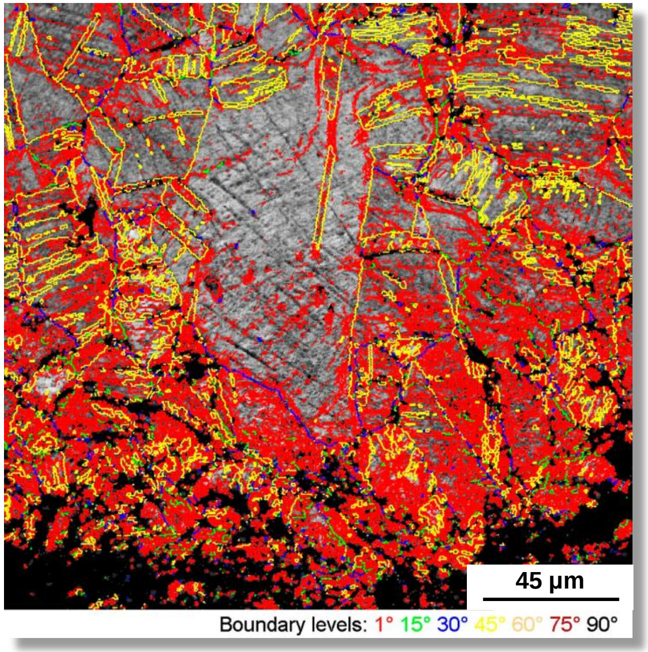
- Corrosion**:** black areas, mainly grain boundary cracks
- Equiaxed grains with colour shifts**;** annealing twins
- Retained cold-work visible on Boundary rotation angle map as dislocations (red) and deformation twins (narrowly-spaced irregular yellow boundaries)
- Corrosion preferentially associated with cold-work
- No discontinuous precipitation of copper

Gundestrup Cauldron sample 363:
localised remanent cold-work and corrosion

IPF colour-coded map



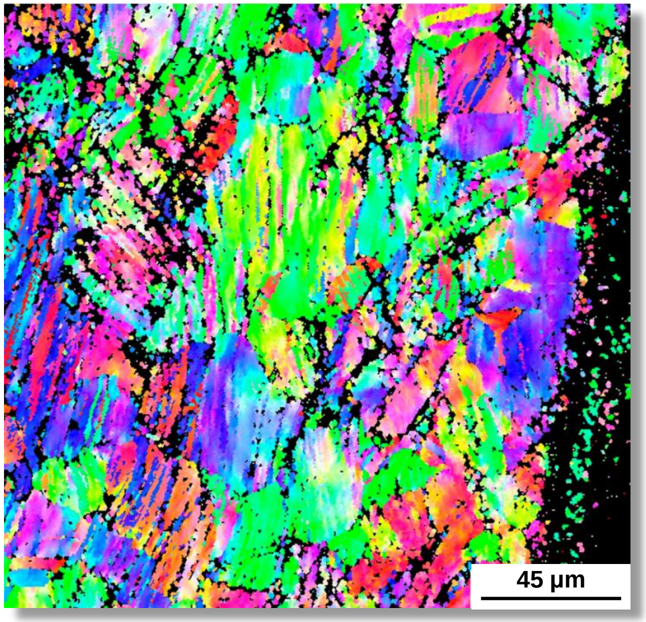
Boundary rotation angle map



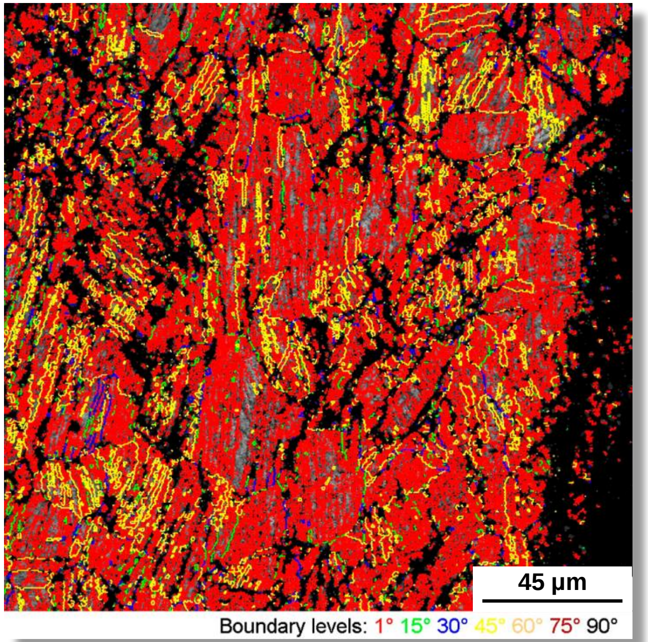
- Corrosion: black areas, mainly grain boundary cracks
- Equiaxed grains with significant colour changes; a few annealing twins
- Retained cold-work visible on Boundary rotation angle map as dislocations (red) and deformation twins (narrowly-spaced irregular yellow boundaries)
- Corrosion preferentially associated with cold-work
- No discontinuous precipitation of copper

Gundestrup Cauldron sample 365: extensive remanent cold-work and corrosion

IPF colour-coded map



Boundary rotation angle map



- Corrosion: black areas, grain boundary and *transgranular* cracks
- Distorted grains with significant colour changes
- Retained cold-work visible on Boundary rotation angle map as dislocations (red) and deformation twins (narrowly-spaced irregular yellow boundaries)
- No discontinuous precipitation of copper

Gundestrup Cauldron case history conclusions

- **Corrosion-induced damage and embrittlement of 3 out of 4 samples**
- **Retained cold-work primarily responsible for corrosion***
- **Discontinuous precipitation of copper in annealed microstructure was innocuous.This is important because the eminent metallurgist C.S. Smith stated that discontinuous precipitation renders grain boundaries highly susceptible to corrosion. Clearly, this need not always be the case**
- **Probable link between retained cold-work and (non-)occurrence of discontinuous precipitation, e.g.**
  - sample 366**:** annealed, **3.44 wt.% Cu**, extensive precipitation
  - sample 361**:** cold-work, **4.64 wt.% Cu**, no precipitation

**** See case history #2, Egyptian Vase, also***

6. Case history #2: Egyptian Vase

Egyptian Vase

- **Rare survivor from the Ptolemaic period, between 300 and 200 BCE**
  - the designs and form blend cultural traditions, notably Egyptian and Persian
  - extensively restored (old restoration)
  - 97 wt.% silver

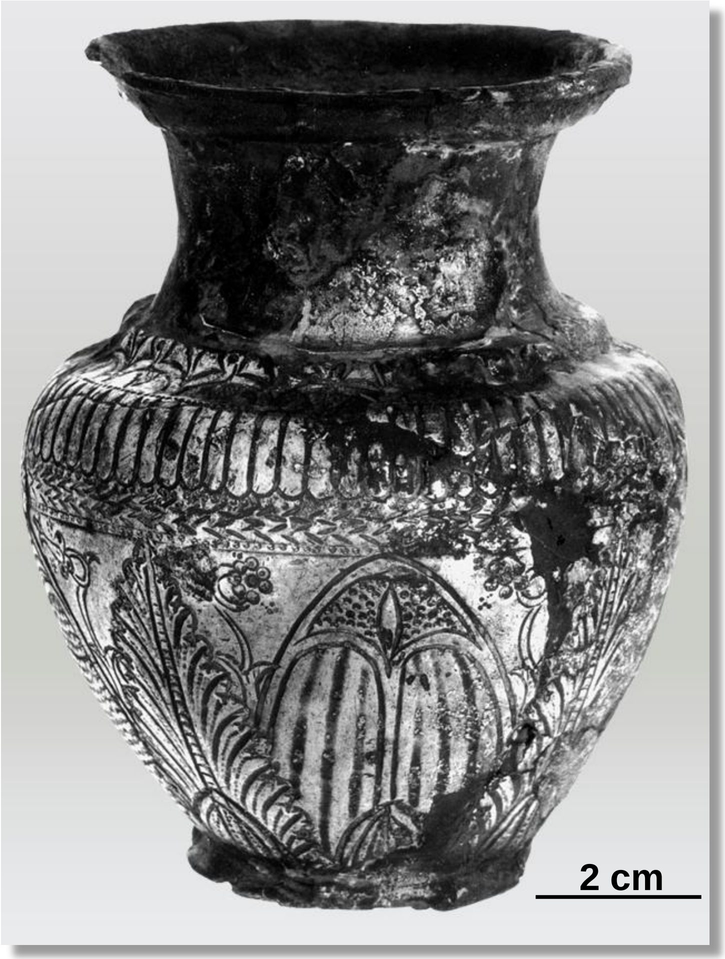


Photo: Allard Pierson Museum, Amsterdam

Egyptian Vase analysis techniques

- **X-ray radiography**

- **Metallography on fragments**
  - Scanning Electron Microscope (SEM)
    - Secondary Electron (SE) and BackScattered Electron (BSE) imaging
    - Energy Dispersive analysis of X-rays (EDX)
  - microhardness testing

- **Scanning Electron Microscope (SEM) fractography on fragments**

- **EDX analyses of three fragments gave the following average chemical composition (wt.%):**

Cu	Au	Pb	Bi	Sb	Sn
0.9	0.8	0.7	0	0.3	0.2

Egyptian Vase: X-ray radiography

- **Example X-ray image: reveals external and internal damage, especially missing pieces and through-thickness cracking**
  - extensive restoration
  - note hairline cracks and brittle "eggshell" crack pattern at upper centre
  - hairline cracks $\boxed{\text{A}}$ follow external chased decorating grooves: see slide 51 also

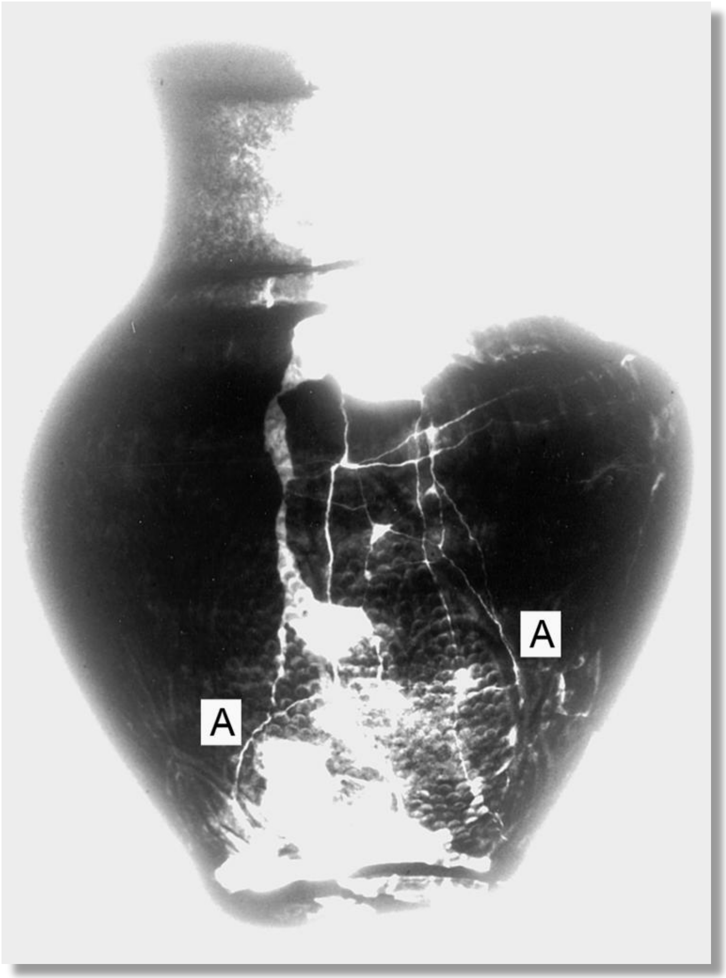
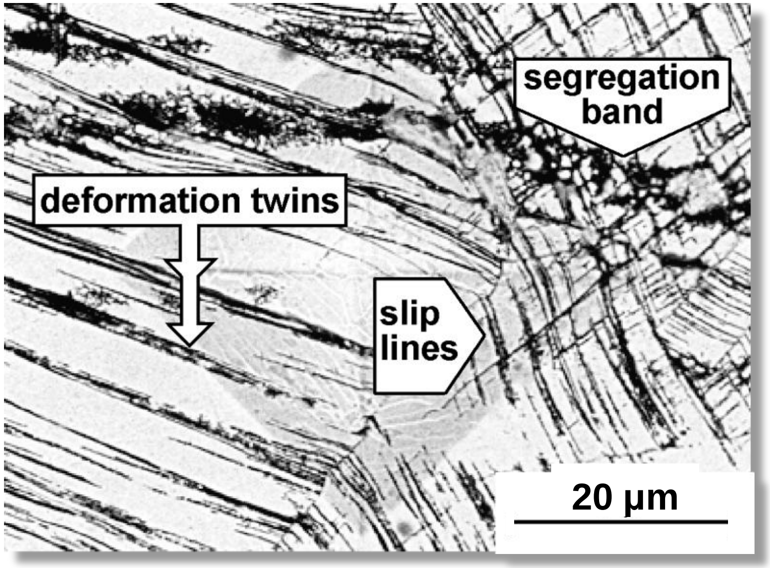


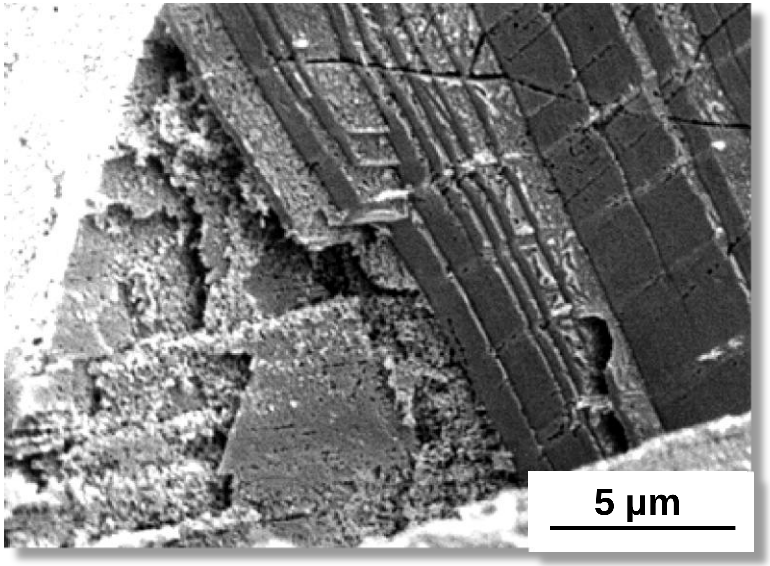
Photo: Roel Jansen, University of Amsterdam

Egyptian Vase: corrosion-induced embrittlement

- **Corrosion along slip lines/planes and deformation twin boundaries (retained cold-work) and segregation bands**



SEM metallograph: NLR

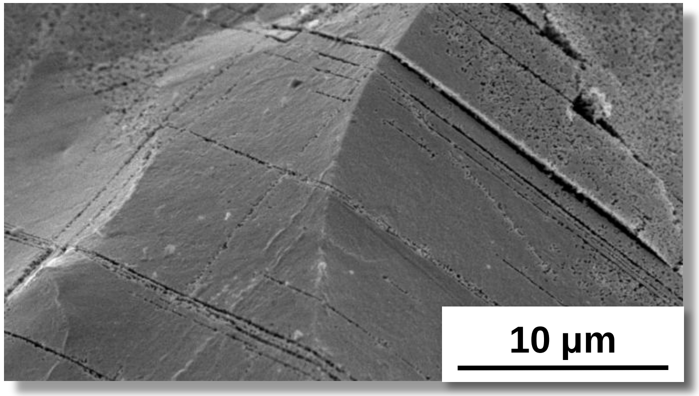


SEM fractograph: NLR

- corrosion attack of slip lines, deformation twin boundaries and segregation bands
- crystallographic fracture due to corrosion and SCC along slip planes

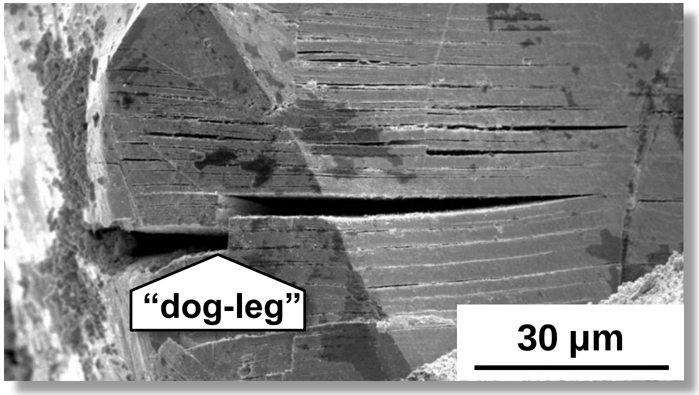
Egyptian Vase: corrosion ⟶ transgranular SCC

(a) Corrosion pitting along slip lines*



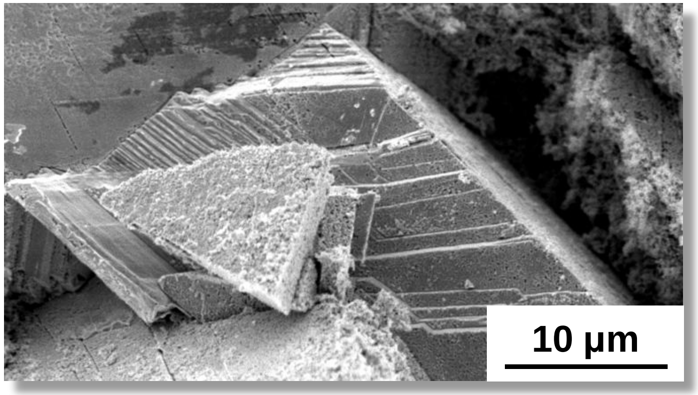
SEM fractograph: NLR

(b) Slip plane and “dog-leg” cracking



SEM fractograph: NLR

(c) Transgranular fracture steps/blocks

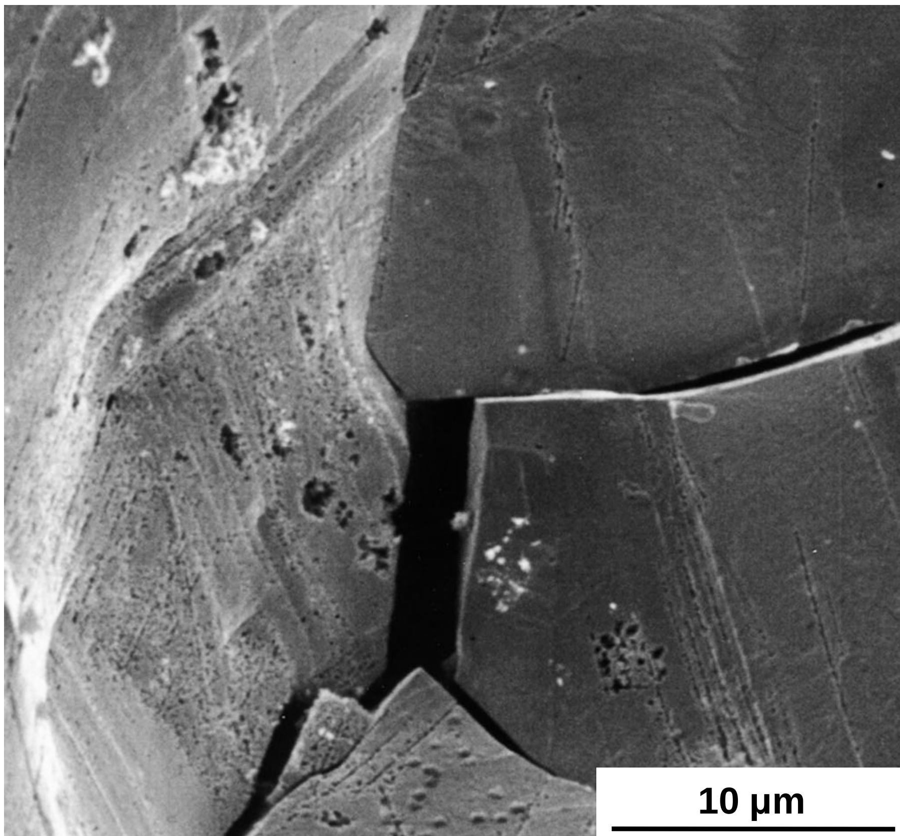


SEM fractograph: NLR

Revealed by intergranular fracture due to microstructural embrittlement

Egyptian Vase: microstructurally-induced embrittlement

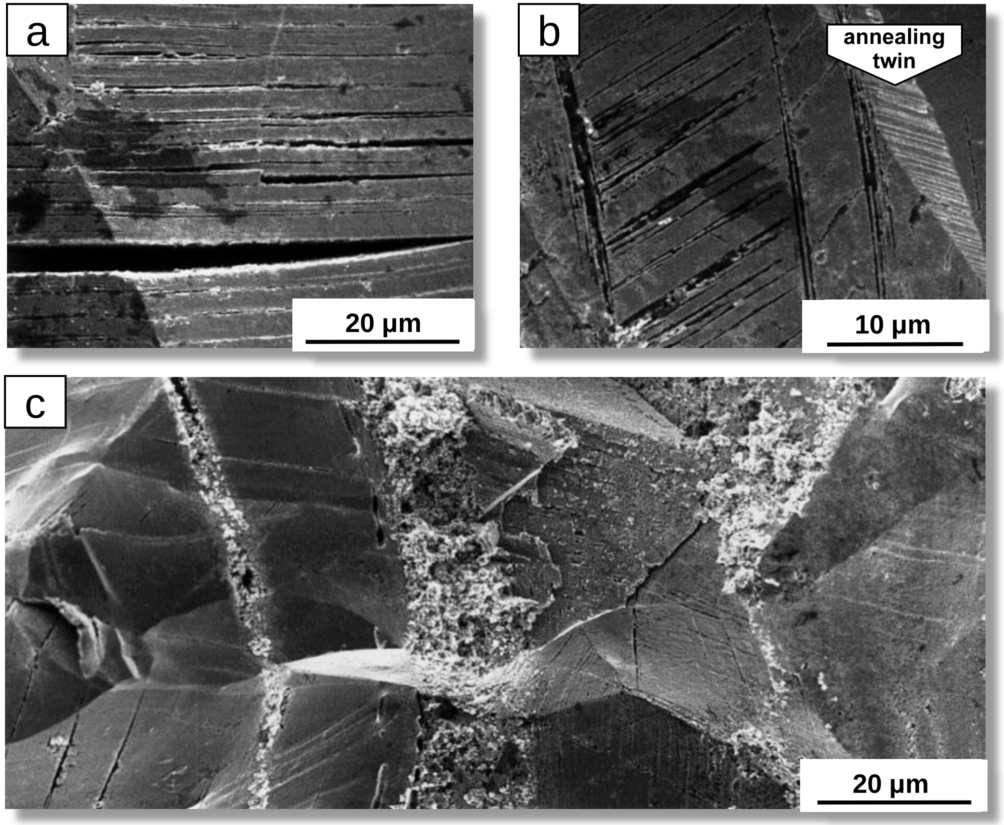
- **Intergranular fracture, narrow and sharp cracks, bodily displaced grains**
  - retained cold-work resulted in some corrosion pitting along slip lines



SEM fractograph: NLR

Egyptian Vase: synergistic embrittlement

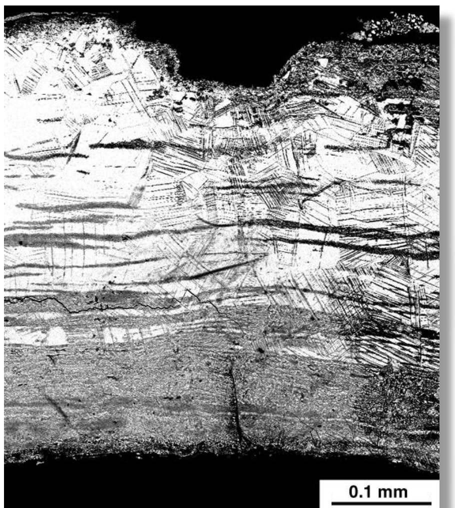
- **SEM fractographs (NLR)**



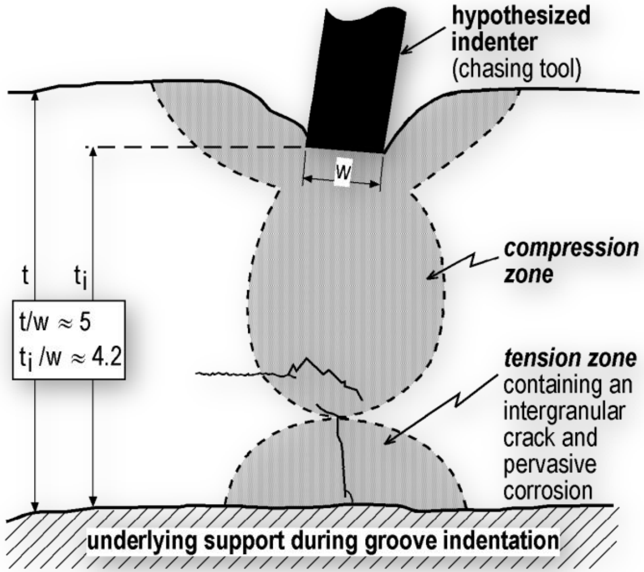
(a) corrosion and SCC causing fracture along slip planes intersecting grain boundary facets
(b) corrosion along deformation twin boundaries intersecting a grain boundary**:** note the almost uncorroded annealing twin with internal slip lines
(c) corrosion along segregation bands intersecting grain boundary facets

Egyptian Vase: retained cold-work and corrosion

- **Cross-section of external chasing groove in lower wall of vase**



SEM metallograph: NLR



schematic suggests a deformation "pattern" from the slip-line field theory of indentation: the theory predicts a tension zone opposite the indented (chased) groove when $t_i/w = 4.4$ (close to actual value)

– microhardness in *tension* zone **<** 20 HV: indicates weakening by corrosion

N.B: Because corrosion-induced cracking is on the opposite surface to the groove, it is inside the vase and hidden from visual inspection. See the X-ray radiograph in slide 46 also

Egyptian Vase case history conclusions

- **Vase archetypal for**
  - corrosion at slip lines, deformation twin boundaries and segregation bands
  - transgranular SCC mainly along slip planes but with "dog-legs" also
  - link between retained cold-work and widespread***** and localised****** (chased decorations) corrosion damage
  - microstructurally-induced embrittlement, whereby the Vase's composition (0.7 wt.% Pb, no Bi) suggests lead to be the most likely perpetrator*******
  - synergistic embrittlement

- **Vase metal now fragile owing to synergistic embrittlement**

- **Thin-walled artefacts with chased decorations should be examined for damage at and near corresponding *internal* or *rear surface* locations**

**** See case history #1, Gundestrup Cauldron***

***** See case history #3, Byzantine Paten***

****** See case history #4, Roman Kantharos***

7. Case history #3: Byzantine Paten

Byzantine Paten (Eastern Roman Empire)

- **Rare and high quality liturgical altar object, dated to about 600 AD**
  - extensive breakage along annular decorating grooves
  - about 95 wt.% silver : main alloying element is copper
  - earlier measured chemical composition (wt.%) of one sample*:

Cu	Au	Pb	Bi	Traces
5.33	0.58	0.86	0.06	Fe,Ni,Co,Zn

Photo: The Menil Collection, Houston

*Peter Northover, University of Oxford, Electron Probe MicroAnalysis (EPMA) + Energy Dispersive analysis of X-rays (EDX)

Byzantine Paten analysis techniques: SEM + EDX metallography of sample

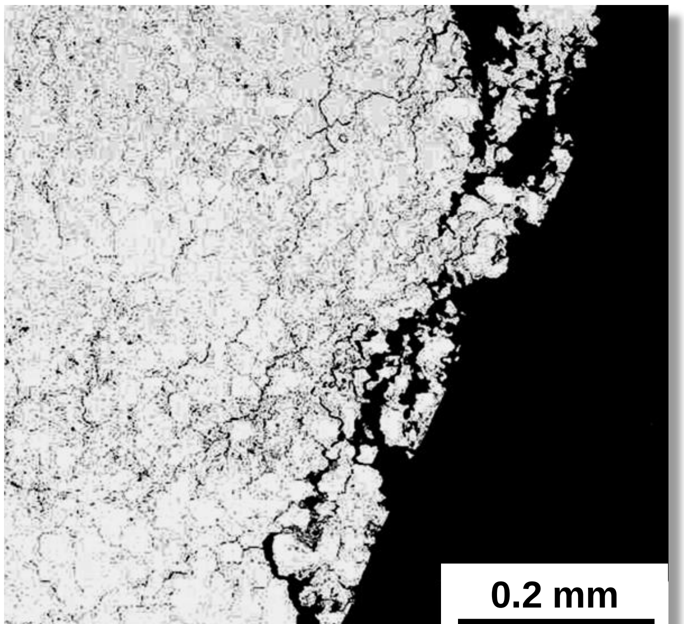
- **Metallography: Netherlands Institute for Cultural Heritage (ICN), Amsterdam**
  - Scanning Electron Microscope (SEM)
  - Secondary Electron (SE) imaging
  - Energy Dispersive analysis of X-rays (EDX) for local chemical compositions

N.B: Only a limited investigation was possible. Nevertheless, some important conclusions were drawn by analogy with case history #2 (Egyptian Vase), ***see slide 57***

Byzantine Paten: SEM + EDX metallography results

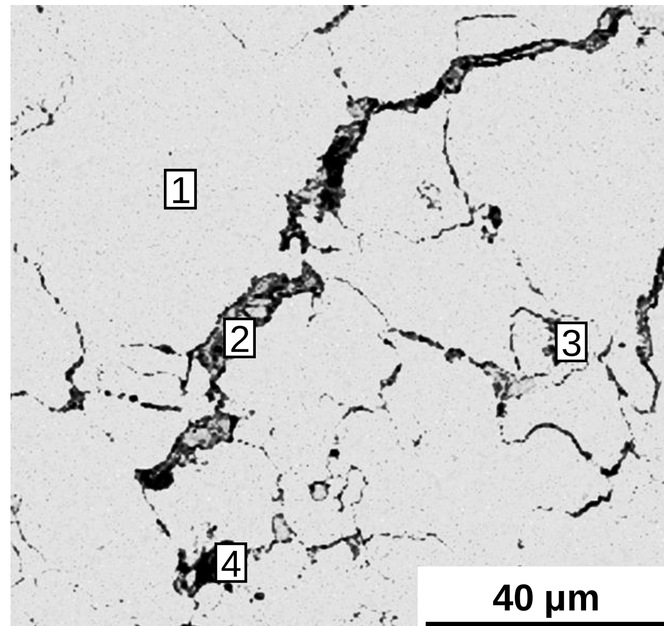
- **Intergranular corrosion and cracking; discontinuous precipitation of copper at grain boundaries**

(a) Corrosion and cracking



SEM metallograph: Ineke Joosten, ICN, Amsterdam

(b) Precipitation of copper



SEM metallograph: Ineke Joosten, ICN, Amsterdam

- EDX spot 1 : Ag
- EDX spots 2, 3, 4 : Ag,Cu

Byzantine Paten case history conclusions

- **Sample showed**
  - intergranular corrosion and cracking
  - discontinuous precipitation of copper, ***not necessarily*** associated with cracking
- **By analogy with case history #2, Egyptian Vase:**
  - breakage along the Paten's annular decorating grooves is probably caused by localised corrosion due to retained cold-work in them
  - the annular grooves on the intact part of the Paten should be assessed for damage on both the front and rear surfaces, ***but especially the rear side***. A possible remedial measure is to apply a protective coating to the rear surface, see slides 135–140 for more information on coatings, specifically slide 139

8. Case history #4: Roman Kantharos

Roman Kantharos - I

- **Superb drinking cup, partially gilded, dated to between 100 BCE and 100 AD**
  - found in 1934 during dredging the Maas riverbanks near Stevensweert, the Netherlands
  - inner and outer cups, with cast foot riveted to the outer cup: originally two handles as well
  - extensive cracks in both cups: see slide 60 also
  - > 97 wt.% silver

Photo: Museum Het Valkhof, Nijmegen

Roman Kantharos - II

- **Inner cup**
  - severely embrittled**:** arrow points to visibly large crack
  - exterior surface shows planishing marks (light hammering) that deformed only the surface grains
  - cup restoration and conservation included cleaning with acetone**;** use of an epoxy resin to glue the narrow cracks*****; repeat cleaning**;** and applying a protective resin

***<u>Irreversible</u> and only partly effective, see second main conclusion in slide 65**

Photo: Museum Het Valkhof, Nijmegen

Roman Kantharos inner cup analysis techniques

- **Fractography: NLR; Netherlands Institute for Cultural Heritage (ICN), Amsterdam**
  - Scanning Electron Microscopy (SEM) on two fragments
    - Secondary Electron (SE) and BackScattered Electron (BSE) imaging

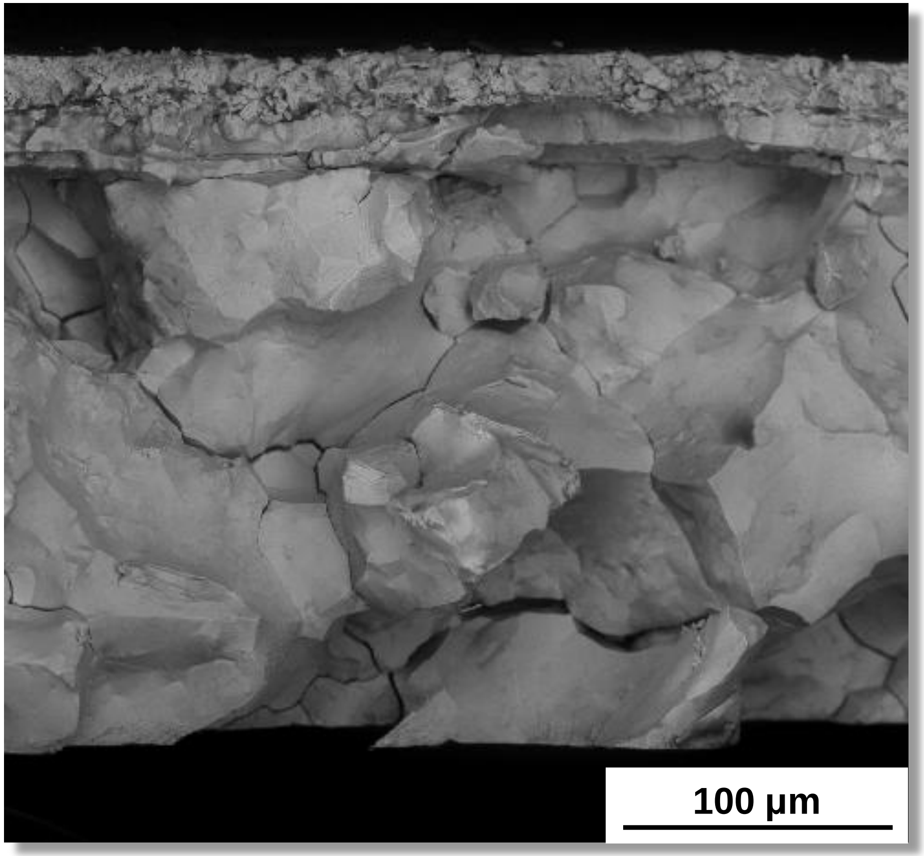
- **Chemical analysis: DSM Research, Geleen; ICN, Amsterdam**
  - X-ray Fluorescence (XRF)

Cu	Au	Pb	Sn
0.45 – 0.63	0.58 – 0.63	0.16 – 0.25	0 – 0.29

N.B: Only a limited investigation was possible. Nevertheless, important conclusions were obtained, see slide 65

Inner cup: microstructurally-induced embrittlement

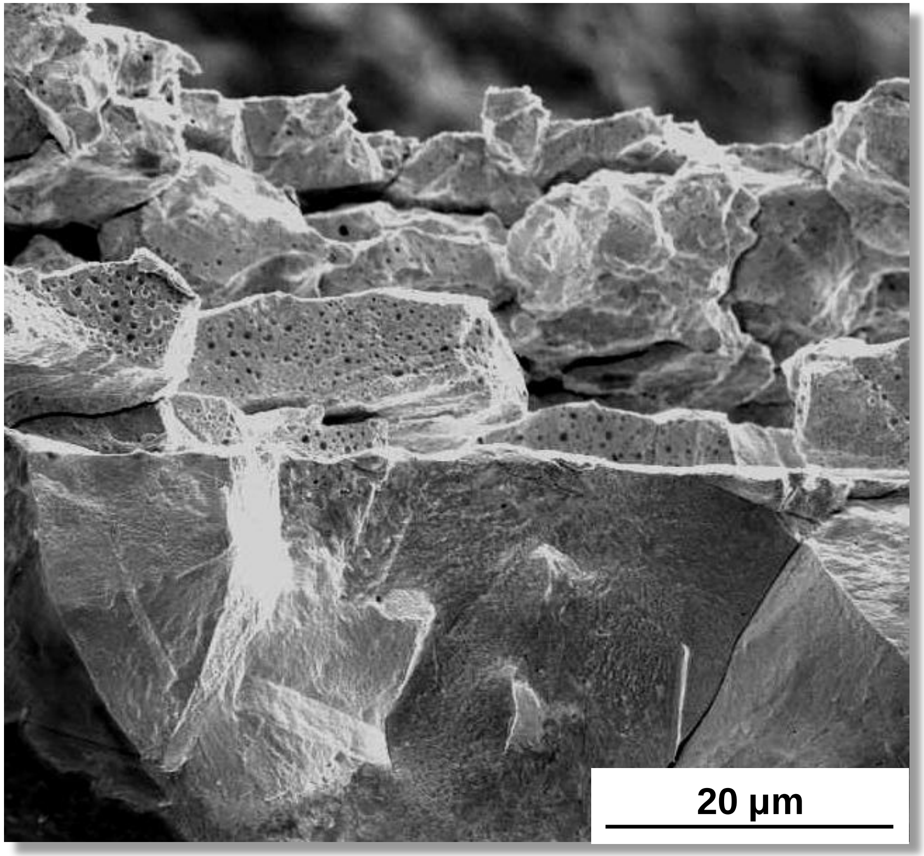
- **Intergranular fracture, narrow and sharp cracks, bodily displaced grains**
  - recrystallized surface grains due to planishing, see slide 60



SEM fractograph: Netherlands Institute for Cultural Heritage, Amsterdam

Inner cup: corrosion pitting of recrystallized surface grains

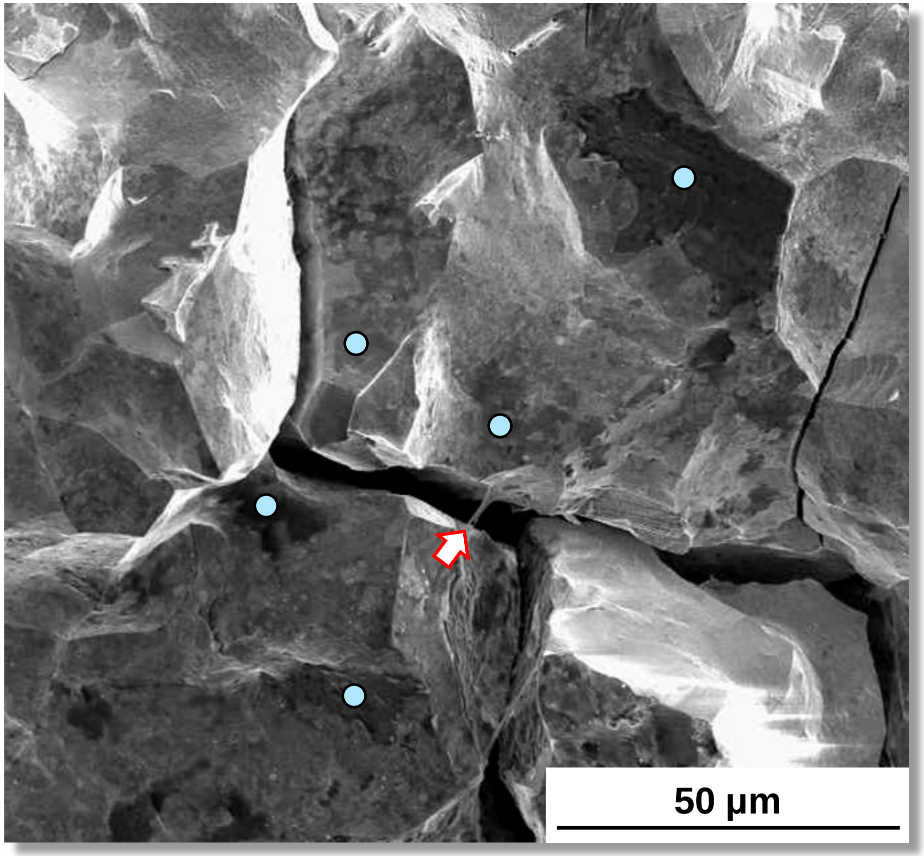
- **Most probably the result of attack around cuprite (Cu_2O) crystallites formed by internal oxidation at the annealing temperature (~ 700ºC)**



SEM fractograph: NLR

Inner cup: traces of epoxy resin

- **Circles indicate some examples of epoxy resin on grain boundary fracture facets, and the arrow points to a thread of epoxy resin "bridging" a crack**



SEM fractograph: NLR

Roman Kantharos inner cup case history conclusions

- **Fragments showed**
  - microstructurally-induced embrittlement, whereby the cup's composition (0.16 – 0.25 wt.% Pb) suggests lead to be the perpetrator*
  - corrosion (localised pitting) only in recrystallized surface grains
  - traces of epoxy resin suggesting incomplete penetration into cracks
- **Inner cup is fragile even though impregnated with epoxy resin, which probably did not penetrate into many narrow cracks, e.g. the internal ones in slide 62**

**** See case history #2, Egyptian Vase***

9. Case history #5: Romanesque Kaptorga

Romanesque Kaptorga (Czech Republic)

- **Small container for relics and amulets, dated to 10th Century AD**
  - found in Klecany, near Prague, Czech Republic, ***in a grave****: extensively broken and fragile, easily fragmented by handling
  - restored with ***removable*** external backing of silk and acrylic lacquer, followed by ***irreversible*** internal backing of glass cloth and epoxy resin**;** external backing removed with acetone
  - about 94 – 95 wt.% silver

Grave environments can be bad owing to human decomposition

Photo: Institute of Archaeology, Prague

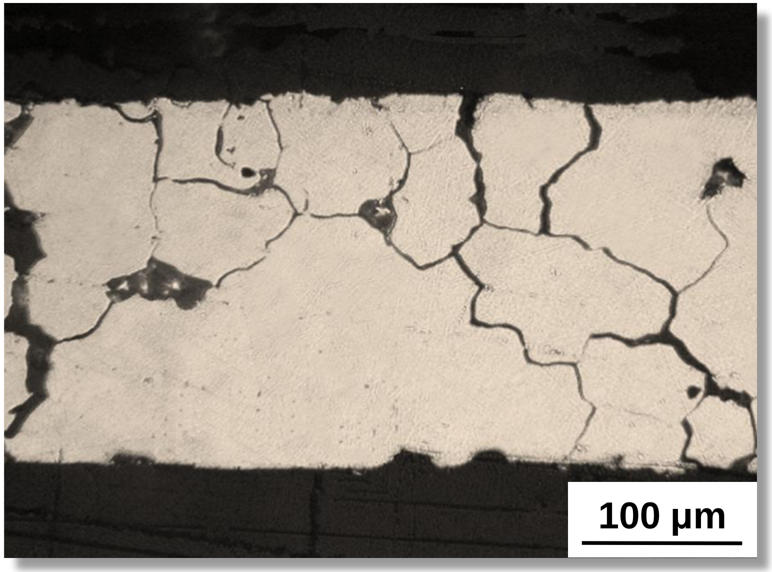
Romanesque Kaptorga analysis techniques

- **Institute of Chemical Technology (ICT), Prague; Institute of Physics, Academy of Sciences of the Czech Republic (ASCR), Prague**
- **Metallography on fragments**
  - optical microscopy
  - Scanning Electron Microscope (SEM)
    - Secondary Electron (SE) imaging
    - Energy Dispersive analysis of X-rays (EDX) for local chemical compositions
- **Scanning Electron Microscope (SEM) fractography on fragments**

Romanesque Kaptorga: intergranular cracks and fracture

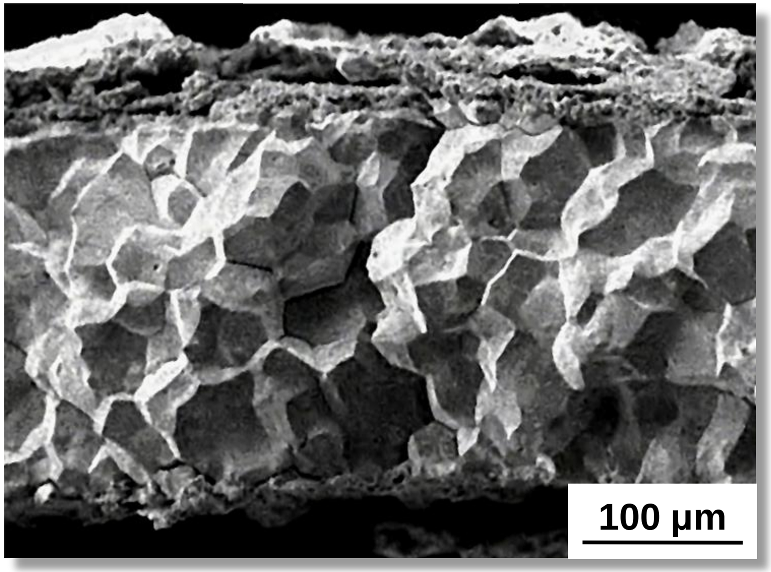
- Intergranular cracking and fracture in a *fully annealed* microstructure
- No grain boundary precipitation or EDX-detectable copper segregation
- Surface general corrosion and some internal corrosion

(a) cracking



Optical metallograph: Jarka Vaníčková, ICT, Prague

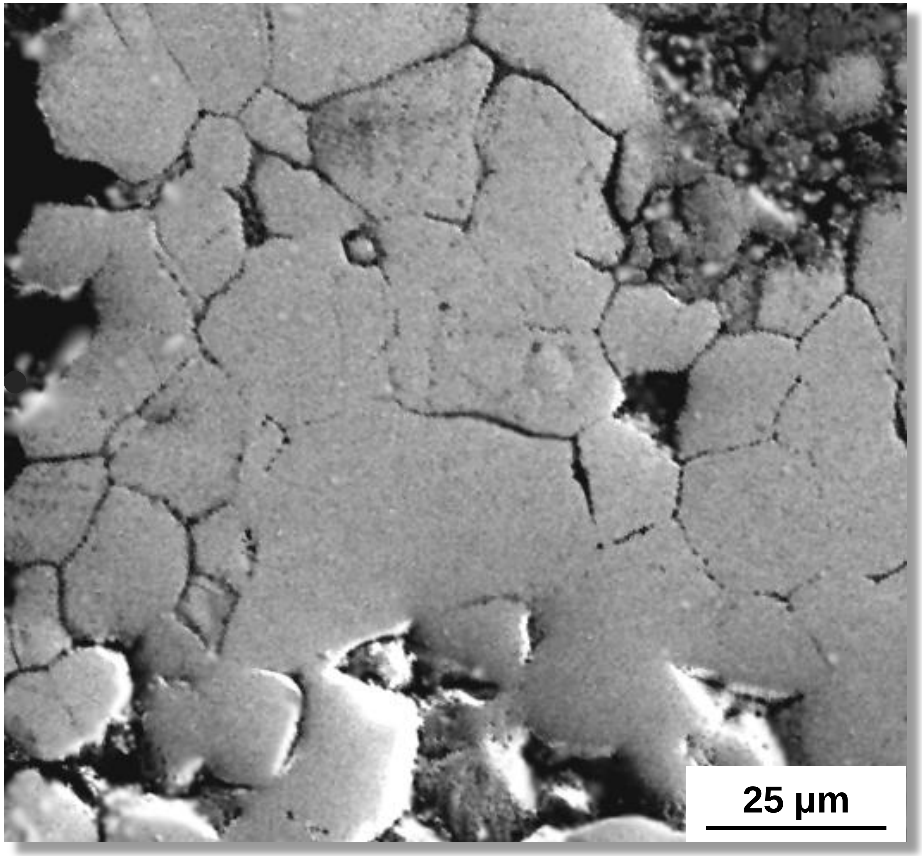
(b) fracture



SEM fractograph: Jarka Vaníčková, ICT, Prague

Romanesque Kaptorga: beginning of intergranular cracking

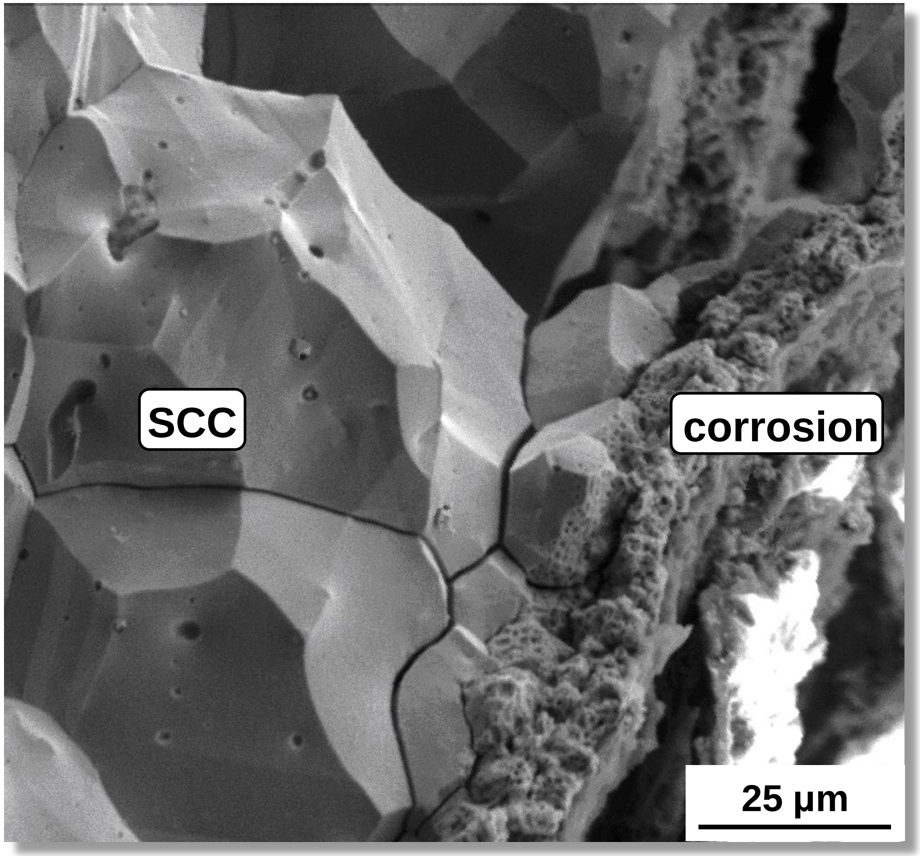
- **Intergranular cracking began with corrosion pitting that coalesced to form smooth intergranular fracture facets**



SEM metallograph: Pavel Bartuška, Institute of Physics, Prague

Romanesque Kaptorga: NLR interpretation of fractography

- **Intergranular SCC *due to external forces* and *subsequent* general corrosion that proceeded slowly inwards from both side surfaces**



SEM fractograph: Jarka Vaníčková, ICT, Prague

Romanesque Kaptorga case history conclusions

- **Fragments showed**
  - extensive intergranular cracking and fracture ***(NLR interpretation: SCC)***
  - no precipitation or EDX-detectable segregation of copper
  - main alloying elements only Cu (3.3 – 3.5 wt.%) and Au (2.3 – 2.5 wt.%)
  - no other elements at EDX-detectable levels
  - surface and internal corrosion products mainly silver chloride (AgCl)

- **Intergranular fracture in the fully annealed condition suggests SCC due to external forces (soil weighing on a hollow object) and a very adverse grave environment: high salinity from body decomposition**

10. Case history #6: Sasanian King's Head

Sasanian King's Head (Iran)

- **Portrait, partially gilded, dated to 4th Century AD**
  - hammered from *one* piece of metal to 1 – 1.8 mm thick; details obtained with tracers and punches on internal (repoussé) and external (chasing) surfaces
  - extensively embrittled: large cracks in R.H. neck area; replacement L.H. neck area
  - restoration and conservation: many large cracks and dents left alone; **some bent areas straightened by hand pressure and hammering, including 650ºC annealing of broken-off pieces of R.H. neck and beard***; exterior corrosion was removed by rubbing after soaking for weeks in distilled water; more resistant black underlayer locally removed with solvents; final polishing
  - 94 – 95 wt.% silver

Heilbrunn Timeline of Art History, www.metmuseum.org

Irreversible

Sasanian King's Head analysis techniques*

- **Visual observations:**
  - Metropolitan Museum of Art (MMA), New York
- **Optical metallography and microhardness testing**
  - Massachusetts Institute of Technology (MIT), Cambridge
- **Chemical analysis:**
  - Spectrographic analysis of the metal (semi-quantitative)**:** National Spectrographic Laboratories Inc., Cleveland
  - X-ray diffraction of internal and external surface corrosion products**:** Smithsonian Institution Museum of History and Technology Conservation Analytical Laboratory, Washington; New York University, New York

***K.C. Lefferts: Technical Notes, *The Metropolitan Museum of Art Bulletin*, Vol. 25 (3), pp. 147–151, 1966**

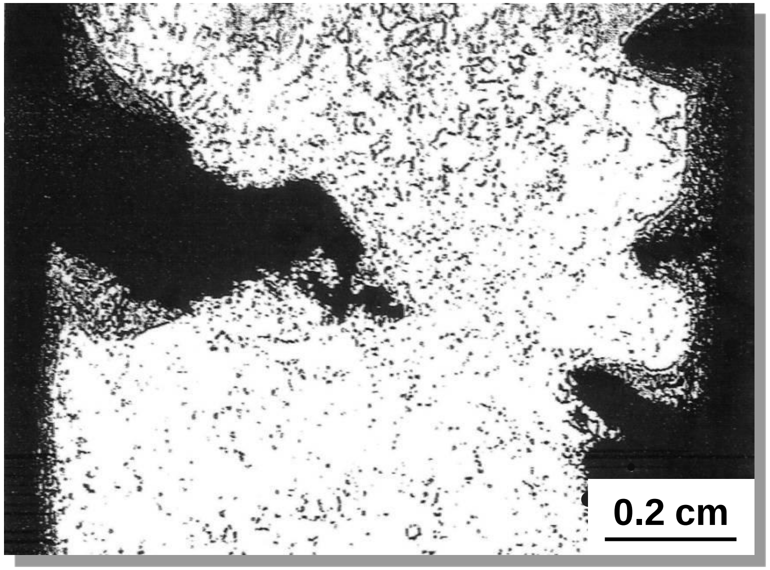
Sasanian King's Head: visual and metallographic observations - I

- **MMA observations and interpretations**
  - intergranular surface cracks
  - intergranular through cracks
  - intergranular cracking during fabrication
  - grain boundary precipitation of copper
  - retained cold-work**:** distorted annealing twins, strain markings; microhardness 84 HV

- **NLR comments and interpretations**
  - ***no evidence*** **:** probably inferred
  - ***yes*****:** Lefferts' figure 1
  - ***no*****:** transgranular tearing owing to ductility exhaustion, see slide 77a
  - ***most probably*** **:** see slide 77b
  - ***yes*****:** "strain markings" are actually deformation twins, see slide 77b

Sasanian King's Head: visual and metallographic observations - II

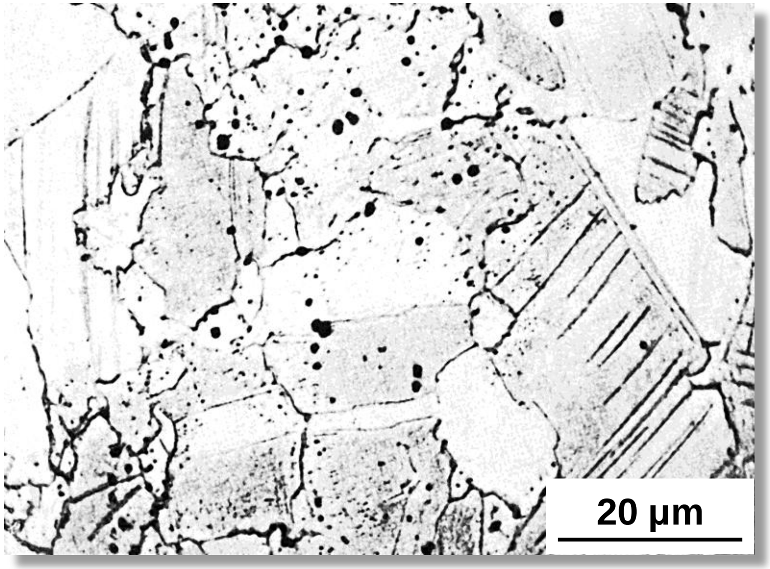
(a) Tearing during fabrication



Optical metallograph: K.C. Ruhl, MIT, Cambridge

- blunt tearing cracks
- darker areas rich in copper oxide (owing to oxidation during annealing) following the tear contours

(b) Retained cold-work; precipitation



Optical metallograph: K.C. Ruhl, MIT, Cambridge

- distorted annealing twins
- deformation twins
- beginning of discontinuous precipitation of copper at some grain boundaries

Sasanian King's Head case history conclusions

- **Extensively embrittled**
- **By analogy with case history # 1, Gundestrup Cauldron, the retained cold-work was most probably responsible for:**
  - intergranular corrosion and cracking
  - hindering or suppressing discontinuous precipitation of copper
- **Chemical composition (wt.%):**

Cu	Au	Pb,Si	Bi,Fe,Ca	Traces
~ 5	0.1 – 1	0.05 – 0.5	0.01 – 0.1	Sn,Ni,Zn,Al,Mg,Ti,Na,K,Li

- **Surface corrosion products mainly silver chloride (AgCl)**

11. Case history #7: Polovtsian Khan Cup

Polovtsian Khan Cup

- **Superb decorated cup, partially enamelled and gilded, dated to 13th Century AD**

  - found in the Ukraine ***in a grave**:** extensively broken and fragile

  - restored using *removable* external backing of glass cloth and Mecosan adhesive, followed by a *removable* internal backing of glass cloth and Mecosan or "Super Glue"**;** external backing removed with acetone

Grave environments can be bad owing to human decomposition

Photo: Gerhard Stawinoga, Archaeological Landesmuseum, Schleswig

Polovtsian Khan Cup assessment (NLR)

- Brittle fracture*, especially along external decorating grooves
- Some ductility in uncracked fragments, since these could be bent back to shape*

- Intergranular corrosion and fracture due to both retained cold-work under decorating grooves and external forces (soil weighing on a hollow object), and an adverse grave environment: high salinity from body decomposition

*G. Stawinoga: Die Tasse des Khans – Die Restaurierung einer mittelalterlichen Silbertasse, *Arbeitsblätter für Restauratoren*, Vol. 30 (2), pp. 137–142, 1997

12. Mechanisms of corrosion-induced embrittlement

Survey of case history corrosion embrittlement results†

Observations		Cauldron	Vase	Paten	Kaptorga	Head
Intergranular embrittlement		3 samples		•	•	•
Transgranular embrittlement		1 sample	•			
Annealed microstructure		1 sample		•*	•	
Retained cold-work		3 samples	•			•
Discontinuous precipitation of copper		1 sample		•		b.d.
Chemical composition (wt.%):	Cu	1.76 – 4.64	0.9	5.33	3.3 – 3.5	~ 5
	Au	0.29 – 0.36	0.8	0.58	2.3 – 2.5	0.1 – 1
	Pb	0.39 – 0.64	0.7	0.86	n.d.	0.05 – 0.5
	Bi	0.07 – 0.13	n.d.	0.06	n.d.	0.01 – 0.1
Surface corrosion product mainly AgCl			•		•	•

*Cold-work probably in decorating grooves; n.d. = not detectable; b.d. = barely detectable

†***N.B: Khan cup omitted because only visually assessed***

Survey of Gundestrup Cauldron corrosion embrittlement results

Observations	Sample 361	Sample 363	Sample 365	Sample 366
Intergranular embrittlement	●	●	●	
Transgranular embrittlement			●	
Annealed microstructure				●
Retained cold-work*	●	●	●	
Discontinuous precipitation of Cu				●
Copper content (wt.%)	4.64	1.76	2.17	3.44

*Increasing retained cold-work in the order 361 < 363 < 365

Types of corrosion-induced embrittlement

- **Intergranular* in mechanically worked and fully annealed artefacts**
- **Intergranular in mechanically worked artefacts with retained cold-work**
- **Interdendritic in as-cast and nearly as-cast artefacts**
- **Along segregation bands, i.e. remains of dendritic microsegregation (coring) and interdendritic segregation occurring during solidification**
- **Along slip lines/planes* and deformation twin boundaries in artefacts and coins with considerable retained cold-work**
- **Examples are given in slides 27–30, 33; 39–41 (case history #1); 47, 48,50 (case history #2); 56 (case history #3); 69–71 (case history #5)**

Most probably stress corrosion cracking (SCC), see slides 86, 87, 89–93

Intergranular corrosion: scenarios from case histories

- ***Can*** **occur in fully annealed artefacts (Kaptorga) but not necessarily, see Cauldron sample 366**

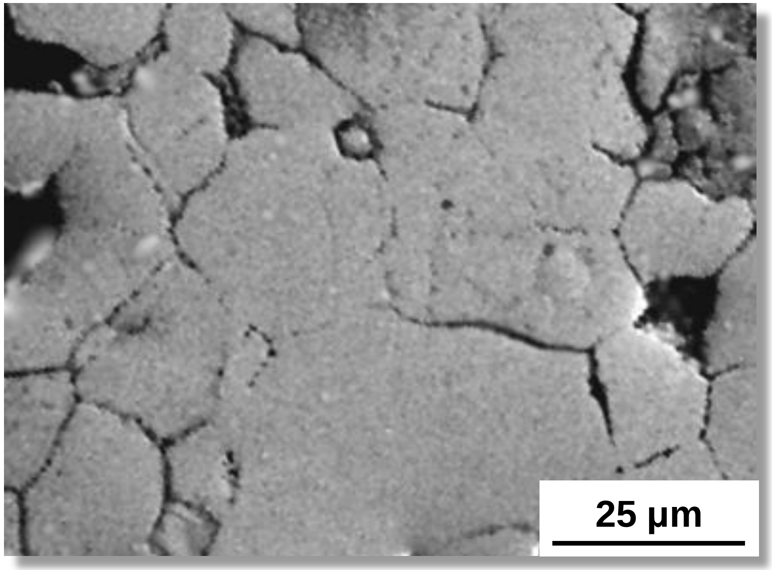
- **Occurs in artefacts with retained cold-work: Cauldron samples 361, 363, 365 and King's Head; *probably* also in Paten and Cup decorating grooves**

- **Not necessarily *(or even at all?)* mechanistically associated with discontinuous precipitation of copper: see Cauldron sample 366**

- **Probable/possible mechanisms:**
  - fully annealed**:** **SCC** from external forces and very adverse environment
  - retained cold-work**:** **SCC** from internal stresses, possible external forces and adverse environment
  - galvanic corrosion**:** in moisture-containing environments the more noble (copper-depleted) silver matrix acts as cathode and the copper-enriched grain boundaries dissolve anodically

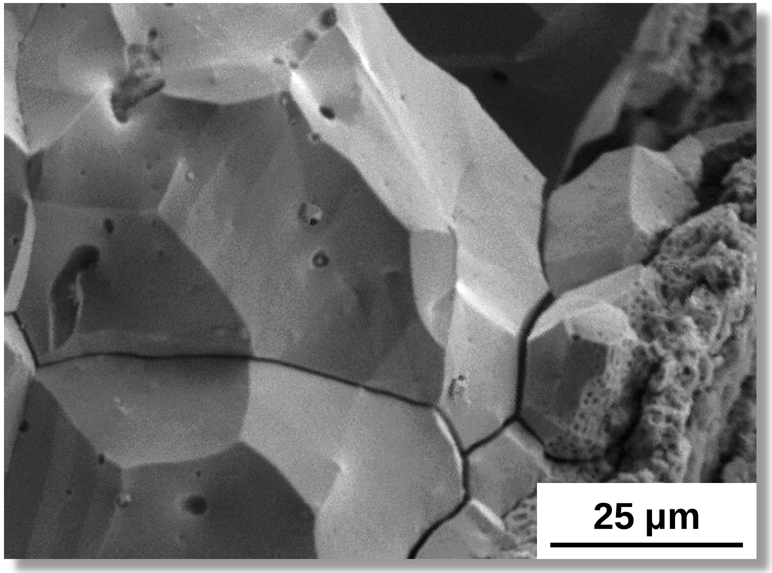
Stages of probable intergranular SCC (Romanesque Kaptorga)

(a) Corrosion pitting at grain boundaries and pit coalescence to form cracks



SEM metallograph: Pavel Bartuška, Institute of Physics, Prague

(b) "Clean" intergranular fracture, followed by general corrosion



SEM fractograph: Jarka Vaníčková, ICT, Prague

- external forces from burial required (fully annealed microstructure)
- probably very adverse environment (human grave with high salinity)
- pitting and SCC occur because grain boundaries are anodically active due to ***local*** strains and compositional variations (notably Cu content)

Interdendritic and segregation band corrosion

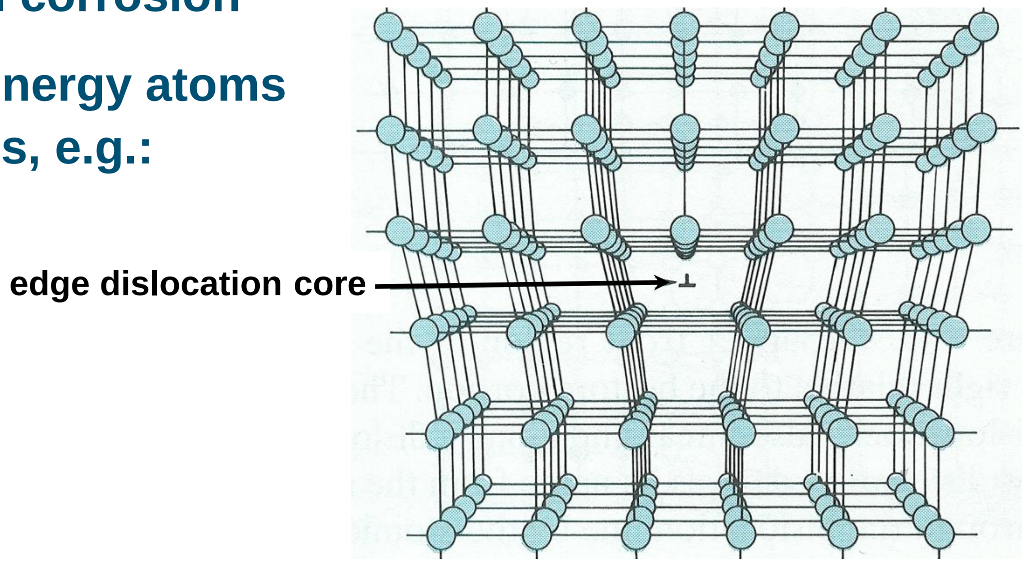
- **Segregation-induced corrosion due to *high-temperature* segregation of copper during alloy solidification**

- **Segregation occurs during dendrite formation, whereby gradients in copper content occur in the dendrites themselves and between the dendrites and the final solidifying liquid: see slides 14–17**

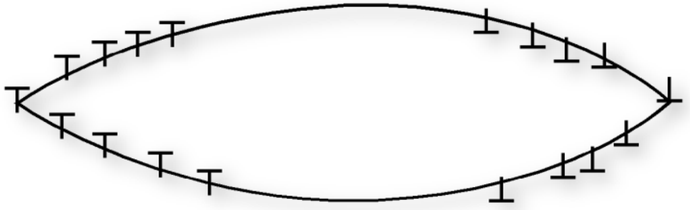
- **Mechanism is local galvanic attack in moisture-containing environments:**
  - in castings silver-rich dendrites act as cathodes and interdendritic copper-enriched metal dissolves anodically, see slide 27b
  - in mechanically-worked artefacts the lower copper content silver matrix acts as cathode and the higher copper content silver in the segregation bands dissolves anodically, see slides 30a and 33c

Corrosion along slip lines/planes and deformation twin boundaries - I

- **Slip and deformation twinning involve locally high strains, whereby some atoms are in non-equilibrium higher energy positions. These atoms are susceptible to preferential corrosion**
- ***In both cases*** **the higher energy atoms surround dislocation cores, e.g.:**



- **In deformation twins the dislocations are confined to noncoherent regions of twin/matrix interfaces, e.g.:**

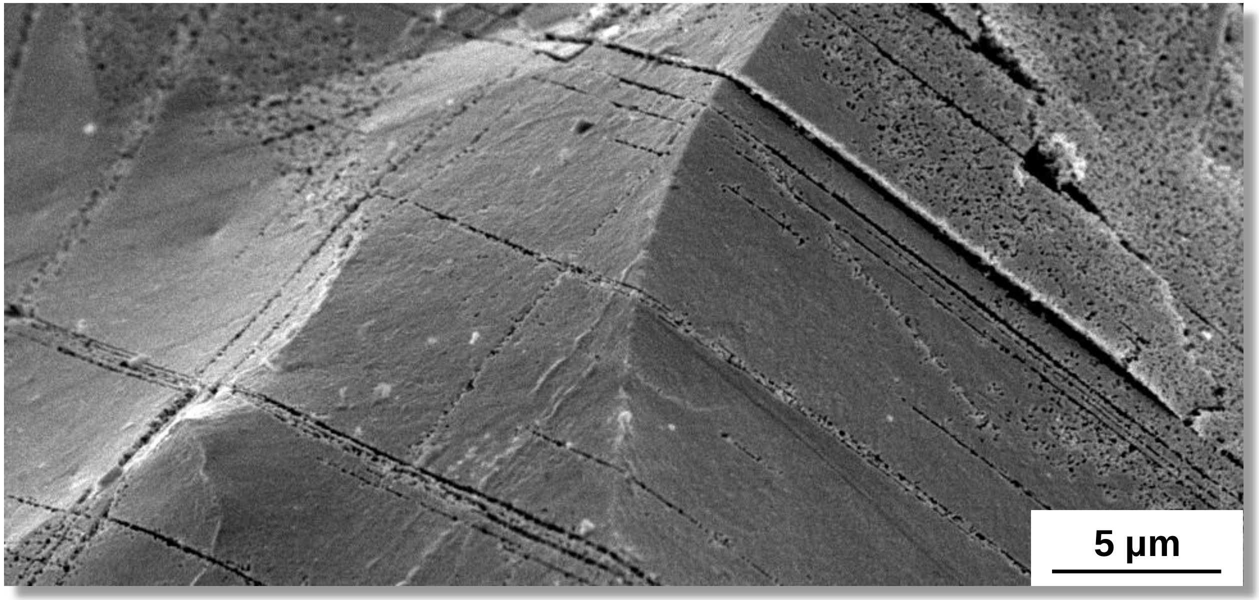


Corrosion along slip lines/planes and deformation twin boundaries - II

- **For silver there are particular factors that could promote corrosion along slip lines/planes and deformation twin boundaries:**
  - low stacking fault energy, resulting in a tendency for planar slip and greater concentrations of dislocations in bands of localised slip
  - narrow deformation twins (see slides 30a and 33b) and hence higher local strains in the noncoherent regions
  - in ***archaeological*** silver the possibility of long-term segregation of solute and impurity elements to the highly strained regions

Detailed explanation of corrosion-induced embrittlement along slip lines/planes - I

- **First stage: corrosion pitting along slip lines, revealed by synergistic embrittlement of the Egyptian Vase (case history #2)**



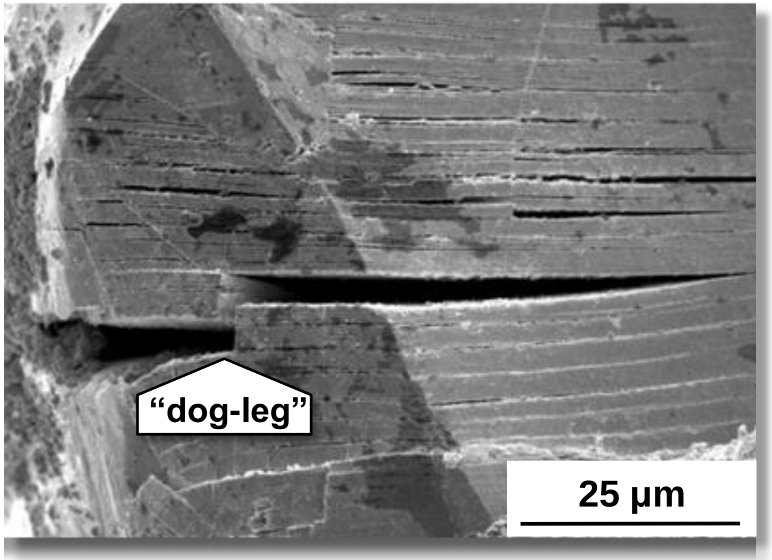
SEM fractograph: NLR

  - pitting begins at and around surface-connected dislocation cores
  - pits coalesce and develop into slots, causing slip plane dissolution

Detailed explanation of corrosion-induced embrittlement along slip lines/planes - II

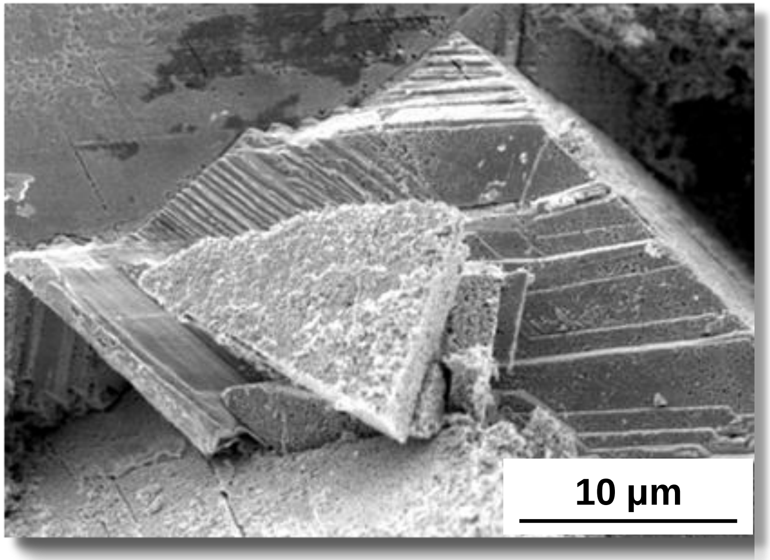
- **Second and third stages: transgranular SCC, mainly on {111} slip planes**

Slip plane and "dog-leg" cracking



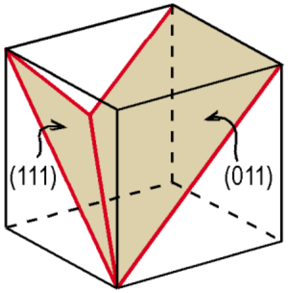
SEM fractograph: NLR

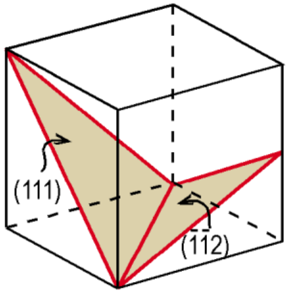
Transgranular fracture steps/blocks



SEM fractograph: NLR

– "dog-leg" cracks ***perpendicular*** to slip plane cracks must be on other types of plane, e.g. {110} or {112}, as in the examples shown here





Detailed explanation of corrosion-induced embrittlement along slip lines/planes - III

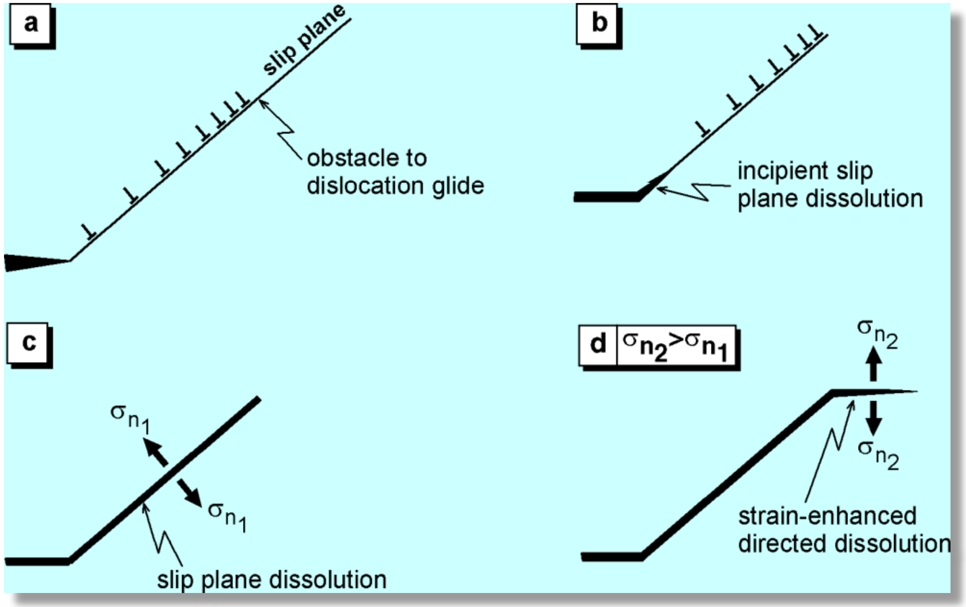
- **Slip plane and "dog-leg" cracking best explained by the *strain-enhanced dissolution* model of SCC (Lichter *et al*. 2001)**

- **Proposed sequence of events**

  a : dislocation emission from crack tip and pile up at an obstacle

  b,c : slip plane dissolution, enhanced by the strain associated with the local normal stress, σ_{n_1}

  d : strain-enhanced directed dissolution on alternative plane ("dog-leg") when local normal stress, σ_{n_2}, exceeds σ_{n_1} but is insufficient to blunt the crack tip by dislocation emission



Corrosion-induced embrittlement summary - I

- **Corrosion-induced embrittlement is a slow process, taking many centuries**
- **There are several types and probable / possible mechanisms. Case histories show the importance of retained cold-work:**

Embrittlement	**Mechanisms***	**Retained cold-work**	**Case histories****
Intergranular	LGA; LGA during SCC	important (not #5)	#1, #3, #5, #6, #7
Interdendritic	LGA	not required	Sican Tumi (Scott 1996)
Segregation bands	LGA	not required	#2
Transgranular	LGA during SCC	essential	#1, #2

* LGA = local galvanic attack; SCC = stress corrosion cracking

** #1: Gundestrup Cauldron; #2: Egyptian Vase; #3: Byzantine Paten; #5: Romanesque Kaptorga; #6: Sasanian King's Head; #7: Polovtsian Khan Cup

- **Intergranular and transgranular embrittlement are linked via the absence or presence and amount of retained cold-work, see slide 95**

Corrosion-induced embrittlement summary - II

Rationale linking intergranular and transgranular embrittlement

- **Intergranular pitting and cracking (SCC) caused by local strains (and compositional variations) at and near grain boundaries. The local strains derive from external forces (case history #5, Kaptorga) and / or retained cold-work (case histories #1, 3, 6, 7: Cauldron, Paten, Head, Cup)**

increased retained cold-work (case histories #1 and #2: Cauldron, Vase)

- **Transgranular cracking (SCC) caused by local strains owing mainly to dislocation pile-ups on slip planes. Some contribution from local strains on “dog-leg” crystallographic planes and deformation twin boundaries (case histories #1, 2: Cauldron, Vase)**

13. Mechanism(s) of microstructurally-induced embrittlement

Survey of case history microstructural embrittlement results

Observations		Vase	Kantharos
Intergranular embrittlement		●	●
Annealed microstructure			●
Retained cold-work		●	
Discontinuous precipitation of copper			
Chemical composition (wt.%):	Cu	0.9	0.45 – 0.63
	Au	0.8	0.58 – 0.63
	Pb	0.7	0.16 – 0.25
	Bi	n.d.	n.d.
	Sn	0.2	0 – 0.29

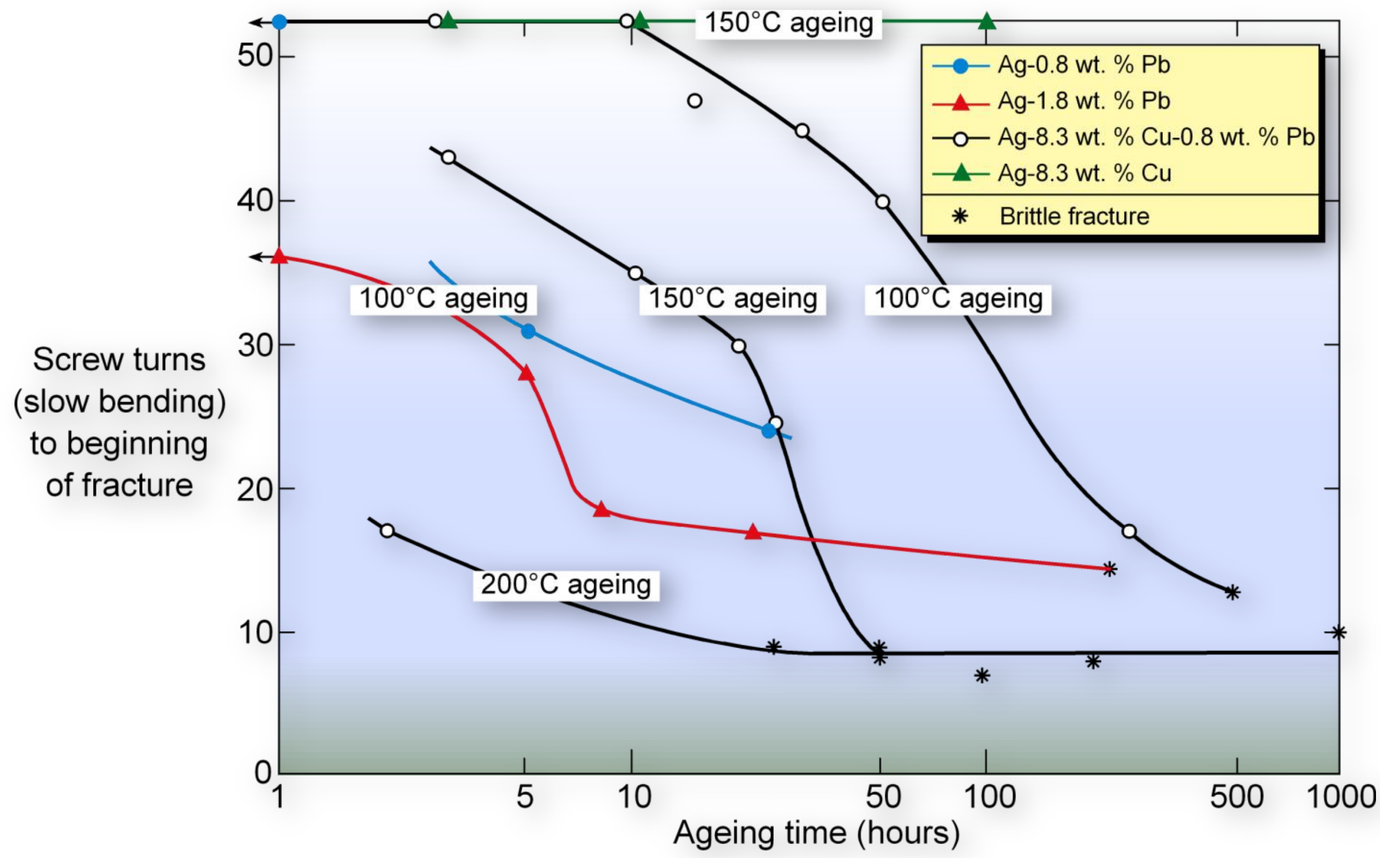
n.d. = not detectable

Suggested causes of microstructurally-induced embrittlement

- **Lead precipitation at grain boundaries (Thompson and Chatterjee 1954)**
- **Discontinuous precipitation of copper at grain boundaries (Smith 1965; Werner 1965; Schweizer and Meyers 1978)**
- **Atomic segregation of lead to grain boundaries (Wanhill *et al*. 1998)**
- **Atomic segregation of lead and / or bismuth to grain boundaries (Wanhill 2002)**

Evidence for embrittlement by lead precipitation - I

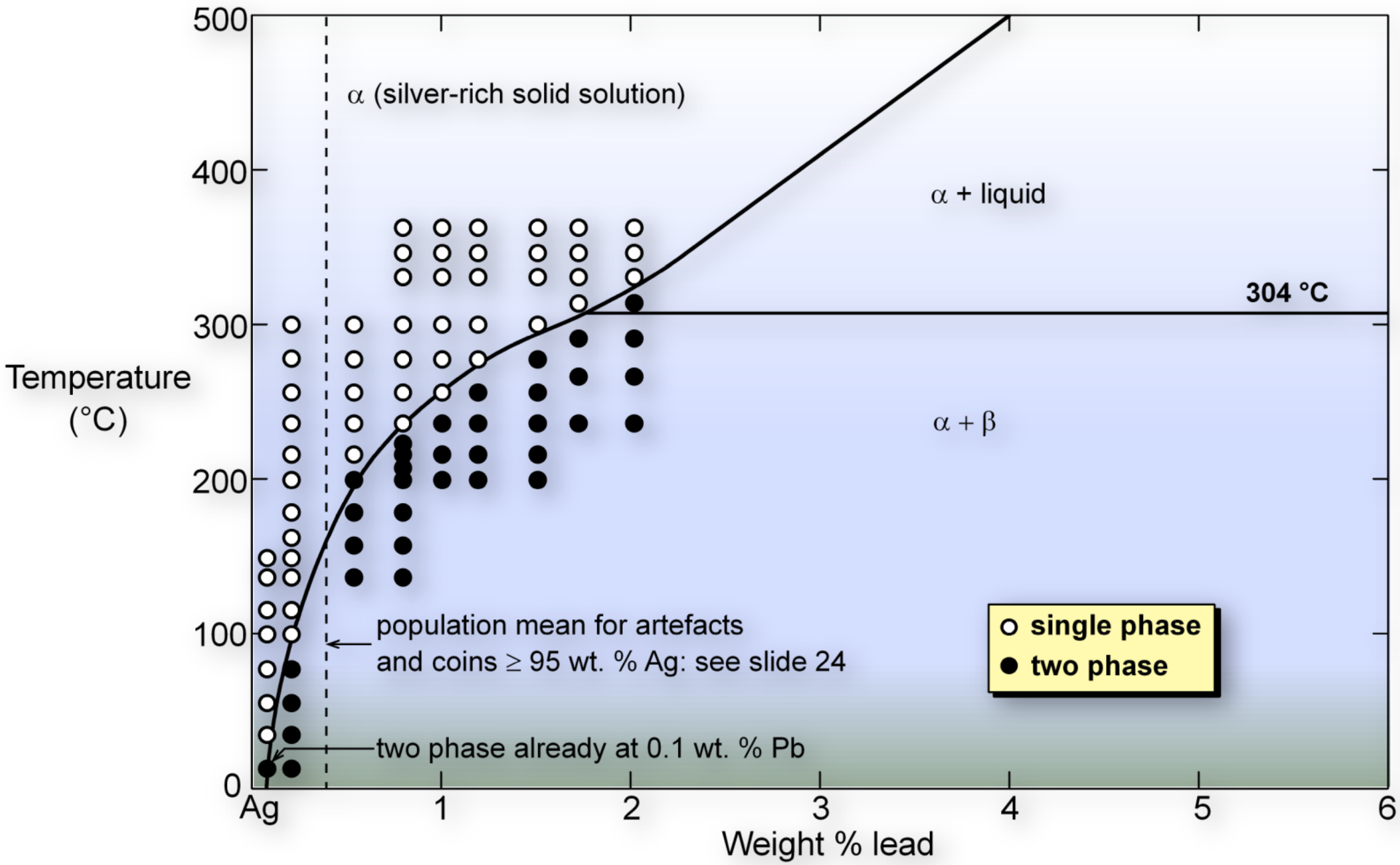
- **Age-embrittlement of cast, solution treated and aged Ag-Pb and Ag-Cu-Pb alloys (Thompson and Chatterjee 1954)**



N.B: Ag-Cu alloy bending resistance unaffected by ageing: see slide 101 also

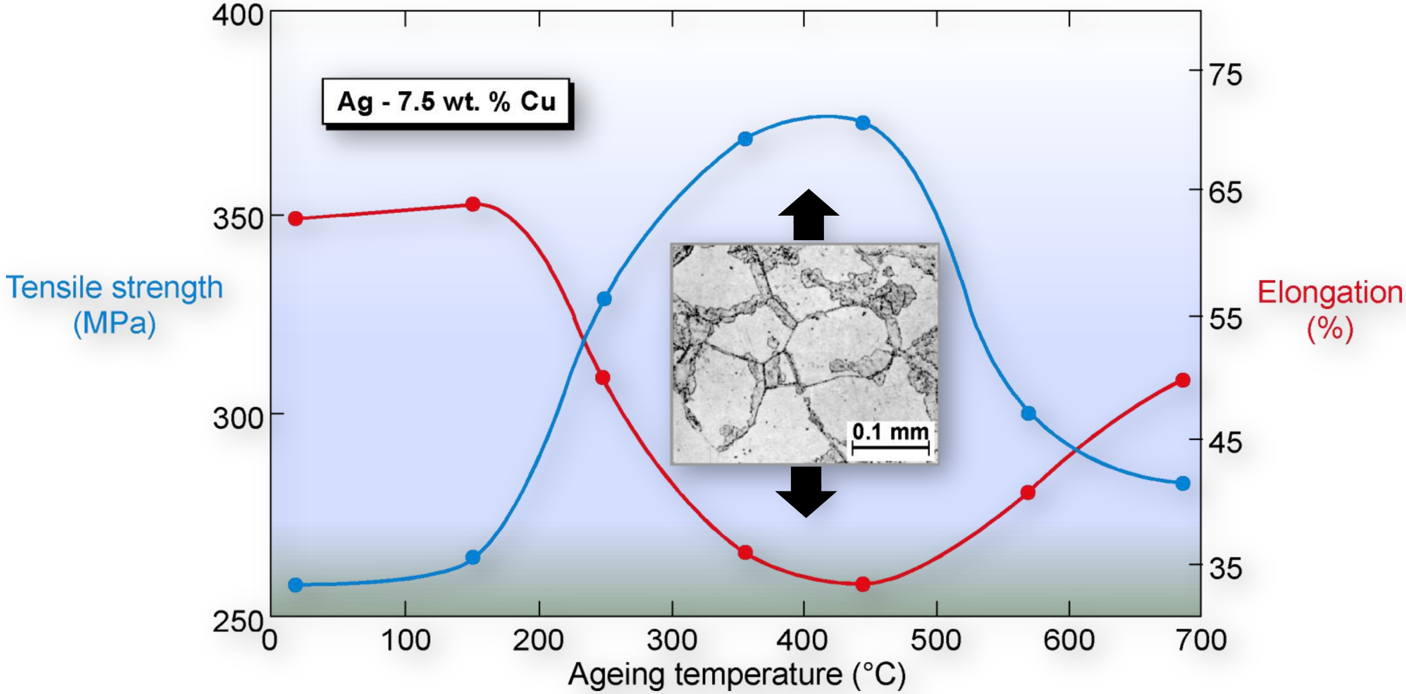
Evidence for embrittlement by lead precipitation - II

- **Long-term low temperature ageing of silver-rich Ag-Pb alloys, resulting in lead-rich β phase precipitates (Thompson and Chatterjee 1954)**



Effect of copper precipitation on mechanical properties

- **Discontinuous precipitation due to 30 minutes ageing of 720 °C solutionised and quenched standard silver (Norbury 1928)**

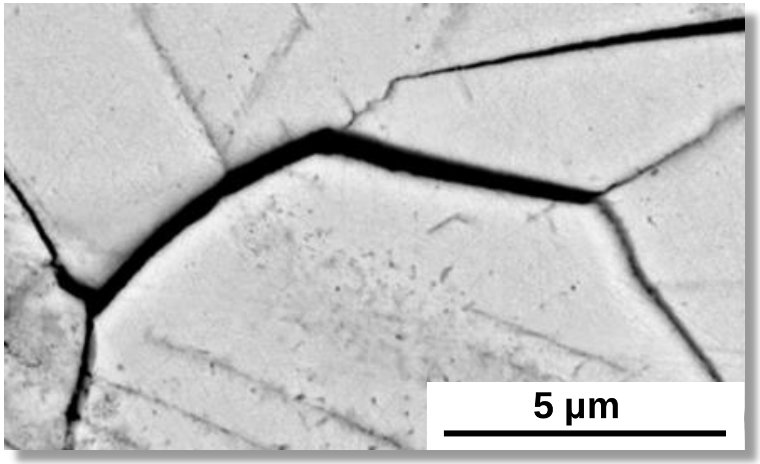


  - minimum tensile elongation ~ 34%: still highly ductile
  - results consistent with longer time ageing of Ag-Cu alloy, see slide 99

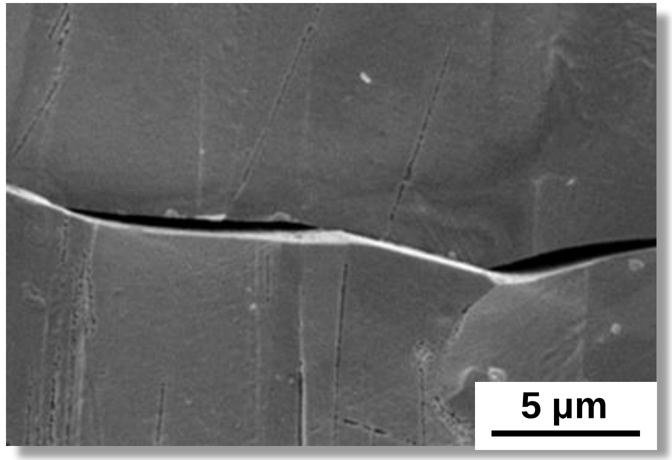
- **Conclusion: copper *does not* cause microstructural embrittlement of silver**

Evidence for embrittlement without (lead) precipitation

- “Clean” intergranular fracture: case history #2, Egyptian Vase



SEM metallograph: NLR



SEM fractograph: NLR

- These magnifications should have revealed any grain boundary precipitates, especially by metallography. Features on the grain facets in the fractograph are due to corrosion pits along slip lines

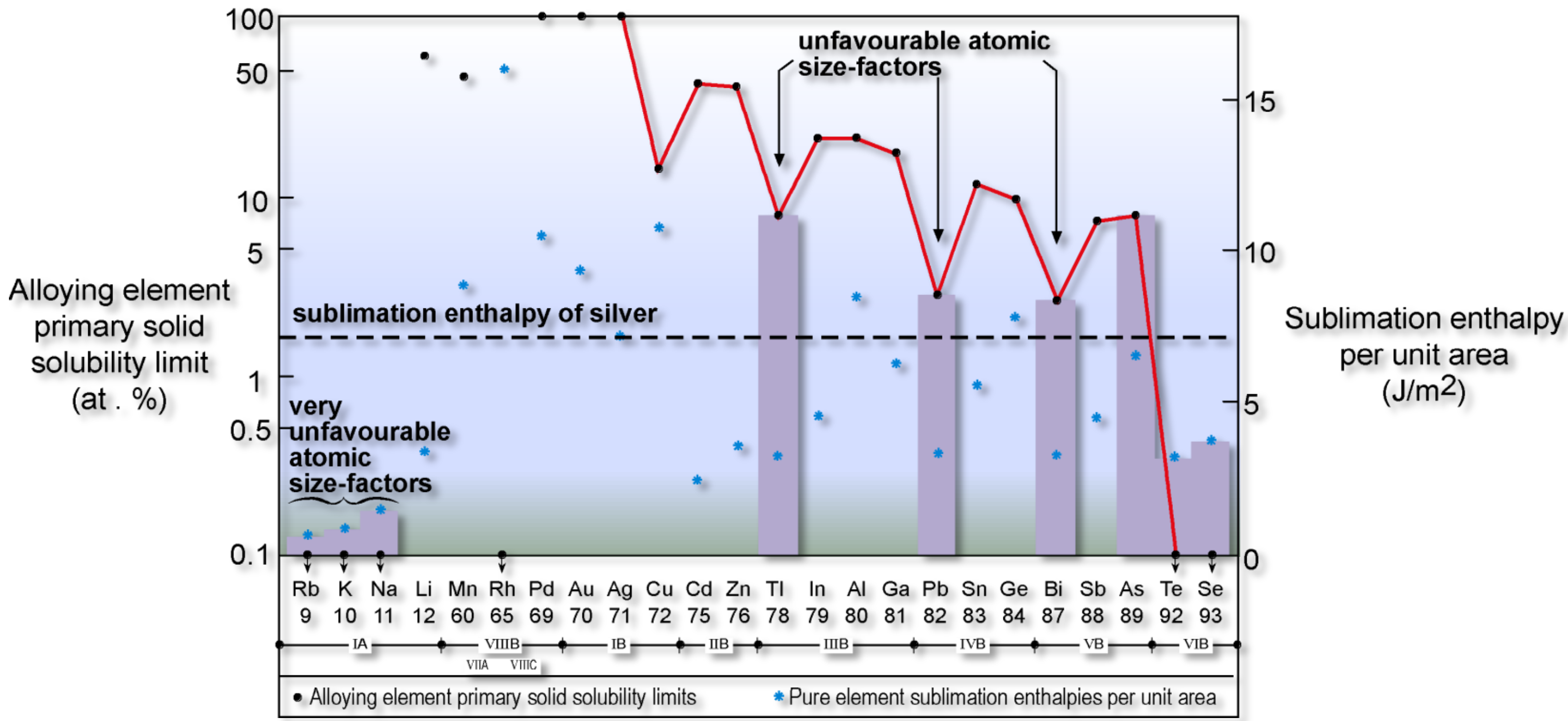
Metallurgical concepts involved in microstructurally-induced embrittlement*

- Alloy phase diagrams, especially Primary Solid Solubility Limits (PSSL)
- Equilibrium grain boundary segregation
- Grain boundary types: high-angle random boundaries most susceptible to solute segregation

* R.J.H. Wanhill, Archaeological Silver Embrittlement: a Metallurgical Inquiry, NLR-TP-2002-224, National Aerospace Laboratory NLR, Amsterdam, 2002

Predicted microstructurally-embrittling elements for silver - I

- **Predictions considering PSSL (linked to atomic size factors), grain boundary segregation (sublimation enthalpies) and solute contents < 5 at.%**



N.B: Thallium (Tl) and arsenic (As) included, and tin (Sn) and antimony (Sb) excluded due to phase diagram considerations. However, tin and antimony can embrittle silver (Ercker 1574; Gowland 1918) at higher solute contents

Predicted microstructurally-embrittling elements for silver - II

- **Impurity elements in amounts $\lesssim$ 5 at. %**
  - as-cast ingots and archaeological artefacts**:** Bi, Na, Pb, Rb, Se, Te*
  - cold-worked and annealed artefacts } long-term segregation**:**
  - finally cold-worked artefacts and coins } As, Bi, Pb*, Tl

  * known embrittlement, but not proven for archaeological objects

- **Evidence favouring microstructural embrittlement by lead**
  - many Old World artefacts and coins, slide 23, show that Pb is the main impurity
  - Egyptian Vase and Roman Kantharos contained Pb ***but no*** Bi, see slide 97

Microstructurally-induced embrittlement: summary

- **Most likely mechanism for archaeological silver objects**
  - long-term low-temperature ageing, whereby atomic segregation of an impurity element, or elements, occurs to grain boundaries, resulting in brittle intergranular fracture

N.B: (1) Atomic segregation could be followed by precipitate formation at grain boundaries, see slide 100, but this does not seem to be necessary for embrittlement

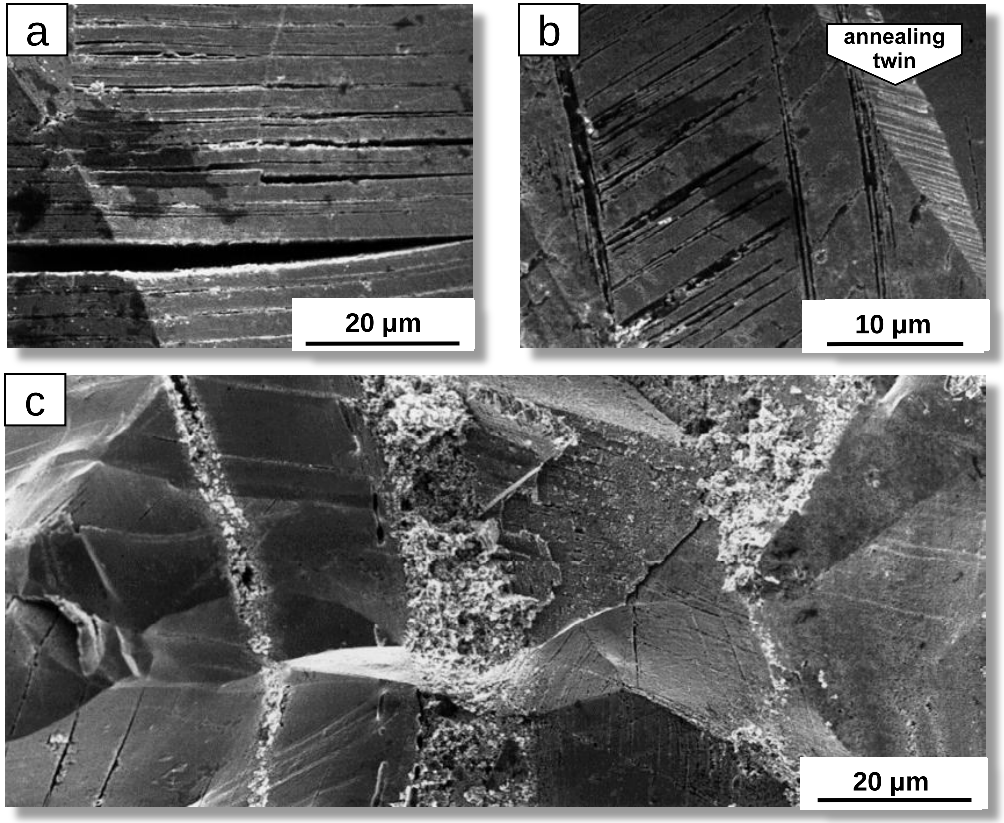
2) Co-segregation of embrittling elements, resulting in conjoint embrittlement, could occur at the low impurity concentrations typical of Old World artefacts and coins, see slide 23

- **Primary embrittling impurity most probably lead**

14. Mechanisms of synergistic embrittlement

Synergistic embrittlement examples - I

- **Case history #2, Egyptian Vase, see slides 33 and 50 also**

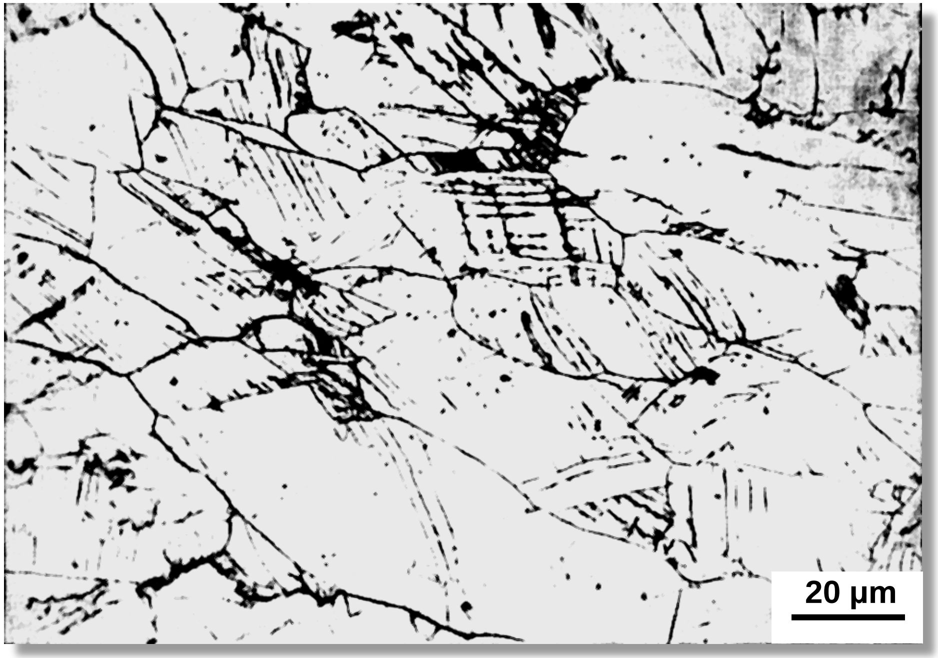


SEM fractographs: NLR

(a) corrosion and SCC causing fracture along slip planes intersecting grain boundary facets
(b) corrosion along deformation twin boundaries intersecting a grain boundary: note the almost uncorroded annealing twin with internal slip lines
(c) corrosion along segregation bands intersecting grain boundary facets

Synergistic embrittlement examples - II

- **Indian silver coin (severely embrittled)**



Optical metallograph: F.C. Thompson and A.K. Chatterjee 1954

  - corrosion along slip lines, possibly also along deformation twin boundaries
  - intergranular cracks

N.B: This is a probable case of synergistic embrittlement

Synergistic embrittlement mechanisms

- Corrosion occurs along slip lines/planes, deformation twin boundaries and segregation bands
- The corrosion develops into cracks owing to internal residual stresses and/or external forces
- Under the action of external forces these cracks then initiate fracture along microstructurally-embrittled grain boundaries (which may fracture anyway, though possibly less easily)
- In turn, intergranular fractures expose more slip lines/planes, deformation twins and segregation bands to the environment and therefore increase the opportunities for corrosion

Synergistic embrittlement: summary

- **Combinations of corrosion-induced and microstructural embrittlement**

- **Very damaging: synergistic embrittlement renders an artefact**
  - frangible (easily broken), ***or even***
  - friable (easily crumbled)

- **Example: case history #2, the Egyptian Vase *(so far unique)***

15. Effects of grain size

Silver grain sizes

- **Ancient silver sometimes has large grains > 0.1 mm, e.g. the Roman Cup, slide 27a, and Romanesque Kaptorga, slide 69a**
- **Large grains are due to (prolonged) annealing, resulting not only in recrystallization but also grain growth, see slide 20**
- **Ancient metalsmiths would likely over-anneal to ensure malleability and ductility during further cold-working and finishing***
- **It follows that large grains *are not a primary cause* of embrittlement, since they improve the workability of an object**
- **However, large grains *are an important secondary factor*: the large grains cause *increased* embrittlement when it is occurring**

Insufficient ductility results in tearing during fabrication, see slide 77a

Grain size and embrittlement of ancient silver

- **Large grains in ancient silver increase embrittlement in several ways, by**

  (1) facilitating penetration of intergranular corrosion, e.g. the Roman Cup in slide 27a, and possibly also increasing the corrosion rate

  (2) facilitating grain boundary microcrack initiation owing to
  - longer dislocation pile-ups
  - increased concentrations of impurities (segregants) at grain boundaries, thereby lowering the grain boundary fracture energy

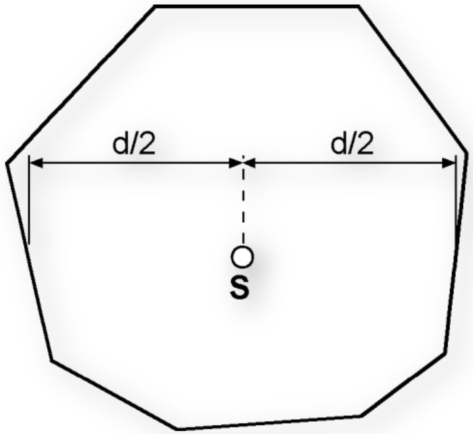
  (3) providing easy fracture paths for microcracks to become macrocracks

- **Further discussion and summary in slides 115-121**

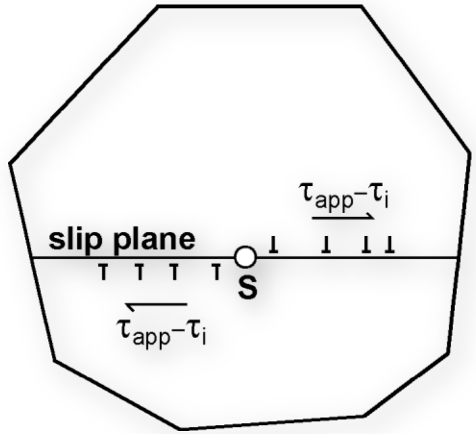
Grain boundary crack initiation in ancient silver - I

Model a

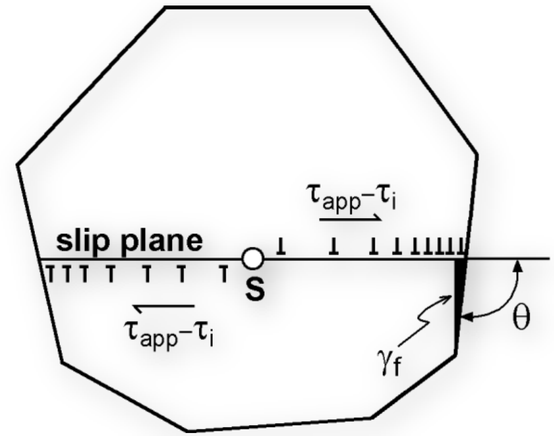
Classical dislocation pile-up model: "applicable" to corrosion-induced or microstructural embrittlement ***but not synergistic embrittlement***



- dislocation source in a grain



- applied shear stress, opposed by lattice friction stress, causes source to emit dislocations along a slip plane



- dislocations pile-up at grain boundaries, and a microcrack initiates at a boundary weakened by corrosion or impurity element segregation

S = dislocation source
d = grain diameter

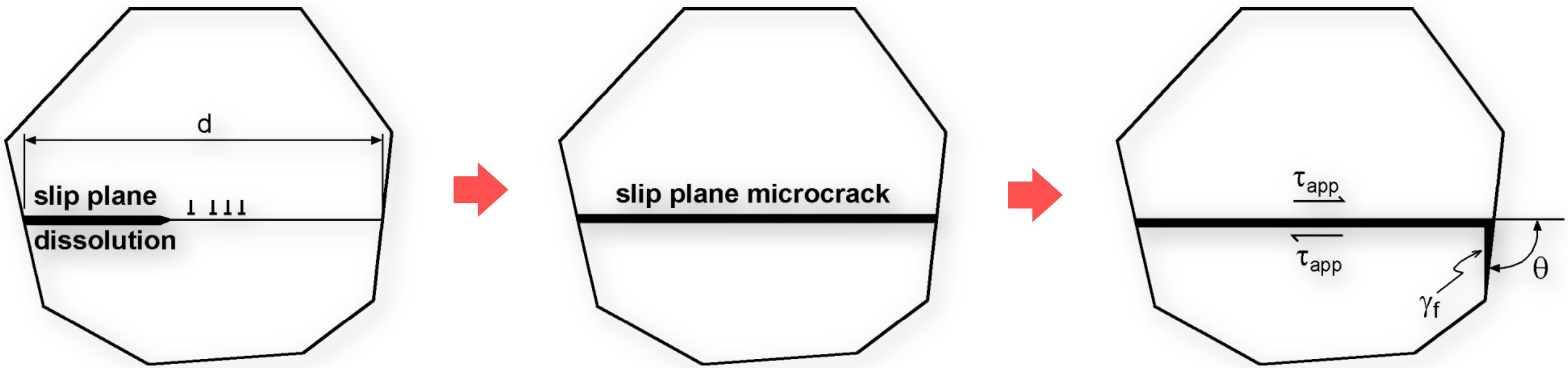
τ_{app} = applied shear stress
τ_i = lattice friction stress
$\perp, \top$ = edge dislocations of opposite sign

γ_f = fracture energy of weakened grain boundary
θ = angle between slip plane and microcrack

Grain boundary crack initiation in ancient silver - II

Model b

Corrosion-induced slip plane dissolution, leading to crack initiation at a grain boundary weakened by corrosion or impurity element segregation: "applicable" to corrosion-induced and synergistic embrittlement



- slip plane being corroded away to form a microcrack
- slip plane dissolution and microcrack formation completed
- applied shear stress causes crack initiation at weakened grain boundary

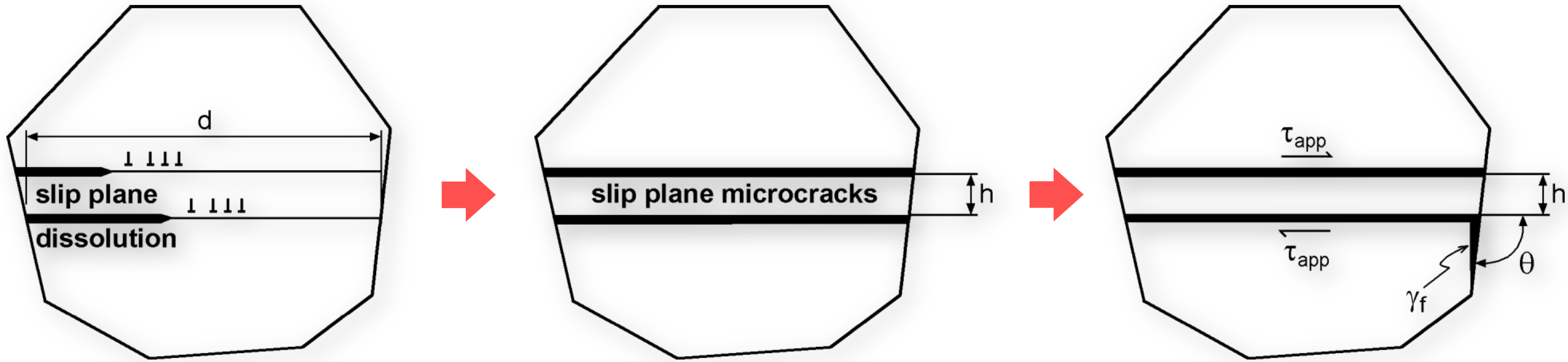
d = grain diameter
$\perp$ = edge dislocations

τ_{app} = applied shear stress
γ_f = fracture energy of weakened grain boundary
θ = angle between slip plane and microcrack

Grain boundary crack initiation in ancient silver - III

Model c

Corrosion-induced slip plane dissolution, leading to crack initiation at a grain boundary weakened by corrosion or impurity element segregation: "applicable" to corrosion-induced and synergistic embrittlement



- slip planes being corroded away to form microcracks

  d = grain diameter
  $\perp$ = edge dislocations

- slip plane dissolution and microcracks formation completed

  h = distance between parallel slip plane cracks

- applied shear stress causes crack initiation at weakened grain boundary

  τ_{app} = applied shear stress
  γ_f = fracture energy of weakened grain boundary
  θ = angle between slip plane and microcrack

Grain boundary crack initiation in ancient silver - IV

- **Model criteria and general result**

a $$\tau_{app} - \tau_i \geq \sqrt{\frac{2\pi\mu\gamma_f}{(1-\nu)\,d}} \bullet \frac{1}{\sqrt{F(\theta)}}$$

b $$\tau_{app} \geq \sqrt{\frac{2\pi\mu\gamma_f}{(1-\nu)\,d}} \bullet \frac{1}{\sqrt{F(\theta)}}$$

c $$\tau_{app} \geq \sqrt{\frac{2\pi\mu\gamma_f}{(1-\nu)\,d}} \bullet \frac{1}{\left(\sqrt{\frac{3h}{\pi d}} \bullet \left(\frac{d}{h} + 0.2865\right)\right)} \bullet \frac{1}{\sqrt{F(\theta)}}$$

general result

$$\tau_{app} \propto \frac{1}{\sqrt{d}}, \gamma_f$$

i.e. the stress required for microcrack initiation is reduced by increased grain size and a decrease in grain boundary fracture energy

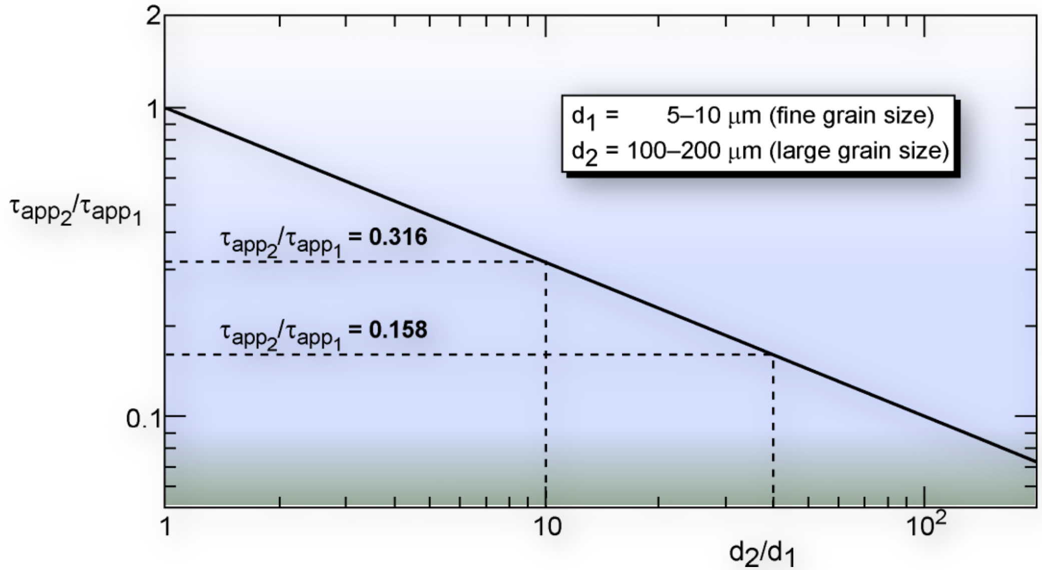
τ_{app} = applied shear stress
γ_f = grain boundary fracture energy
d = grain diameter and slip plane crack length

τ_i = lattice friction stress
ν = Poisson's ratio
h = distance between parallel slip plane cracks

μ = shear modulus for the slip plane
$F(\theta)$ = angular function

Grain boundary crack initiation in ancient silver - V

- **The relationship $\tau_{app} \propto \frac{1}{\sqrt{d}}$ indicates a significant effect of grain size on the stress required for grain boundary crack initiation, e.g.**



  – τ_{app_1} and τ_{app_2} are the respective applied shear stresses required to initiate grain boundary microcracks in fine-grained (d_1) and large-grained (d_2) silver
  – τ_{app_2} is only 1/3 – 1/6 of τ_{app_1}

Grain boundary crack initiation in ancient silver - VI

- **The relationship $\tau_{app} \propto \gamma_f$ indicates a significant effect of grain boundary fracture energy on the stress required for grain boundary crack initiation**

- **Larger grain size can have two effects that decrease γ_f and hence τ_{app} (see slide 114 also):**
  - facilitation of intergranular corrosion
  - increased concentrations of impurities (segregants) at grain boundaries, since there are fewer boundaries, thereby lowering the grain boundary fracture energy

Effects of grain size: summary

- **Ancient silver sometimes has large grain sizes, more than 0.1 mm**
- **Large grains are *an important secondary factor* that increases**
  - corrosion-induced embrittlement
  - microstructurally-induced embrittlement
  - synergistic embrittlement

by several possible mechanisms

16. Diagnostic techniques for ancient silver embrittlement

List of techniques

- **Visual inspection**
- **X-ray radiography**
- **Metallography**
  - optical (light microscopy)
  - **Scanning Electron Microscope (SEM)**
    - Secondary Electron (SE) and BackScattered Electron (BSE) imaging
    - Electron BackScatter Diffraction (EBSD) imaging
    - Energy Dispersive analysis of X-rays (EDX)

      or
    - Wavelength Dispersive analysis of X-rays (WDX)
  - microhardness testing
- **Scanning Electron Microscope (SEM) fractography**
- **Chemical analysis other than EDX and WDX**

Diagnostic techniques used in the case histories†

Techniques	Cauldron	Vase	Paten	Kantharos	Kaptorga	Head
Visual inspection	*	●	*	●	●	●
X-ray radiography		●		●		
Optical metallography					●	●
SEM metallography						
– SE and/or BSE imaging	●	●	●		●	
– EBSD	●					
– EDX	●	●	●		●	
Vickers microhardness (HV)		●				●
SEM fractography		●		●	●	
Chemical analysis**	●		●	●		●

* Assumed

** EPMA (Cauldron, Paten); XRF (Kantharos); semi-quantitative spectroscopy (Head)

†***N.B: Khan cup omitted because only visually assessed***

Visual inspection

- **Unaided eye and hand lens (×1 –×10); stereobinocular (×10 –×50)**
- **Purpose: artefact basic condition**
  - nominally intact
  - restored
    - missing pieces
    - macrocrack patterns
  - fragmented
    - missing pieces
    - macrocrack patterns

N.B: Examination with a stereobinocular can be particularly informative

X-ray radiography

- **Limited enlargement possible**
- **Purpose: “ hidden damage”, see slide 46**
  - nominally intact, restored or fragmented
    - hairline cracks
    - macrocracks
    - cracks following indented decorations (chasing and stamping)
  - restored
    - missing pieces

N.B: Access to X-ray equipment can be a problem: especially for CAT-scans

Metallography - I: manufactured condition

- **Optical, SEM, SEM + EBSD**
  - **mechanically worked and annealed**
    - grain size
    - segregation bands**:** SEM–BSE
    - annealing twins
    - grain and twin orientations (texture)**:** SEM + EBSD
  - **final mechanical working**
    - grain size
    - segregation bands: SEM–BSE
    - annealing and deformation twin distinctions
    - grain and annealing twin texture changes
    - density of plastic deformation (dislocations)

    SEM + EBSD
  - **as-cast (dendritic); cast and annealed**
    - coring
    - eutectic distribution

Metallography - II: embrittlement

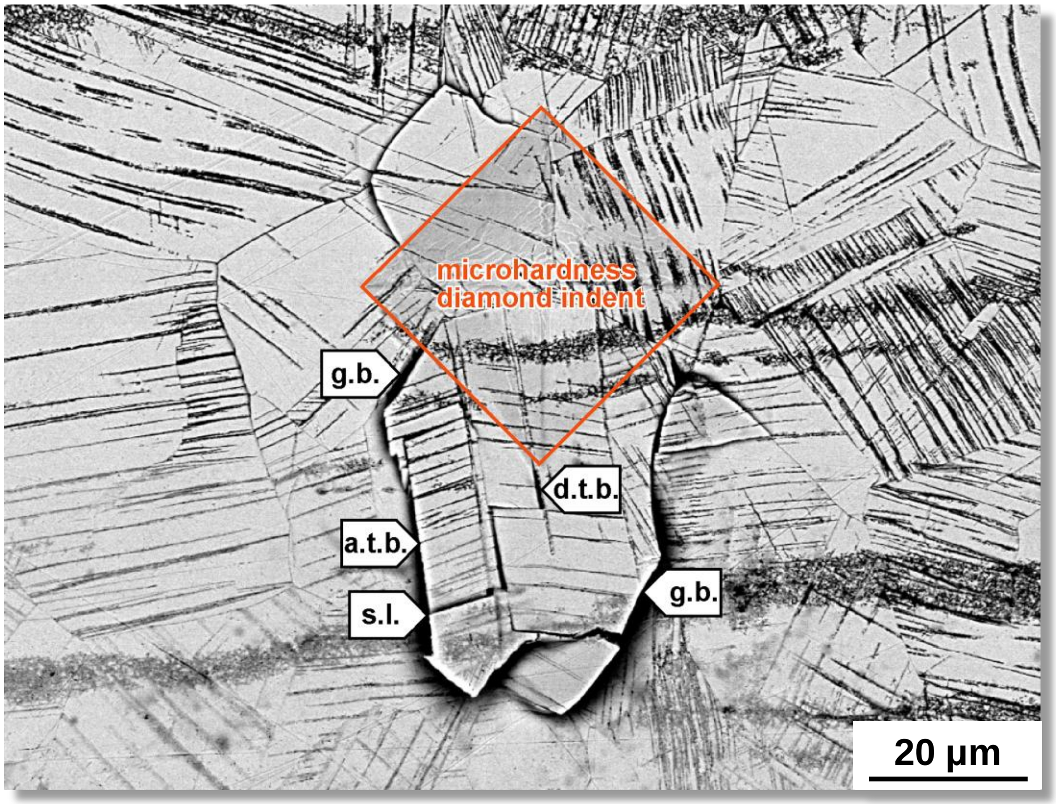
- **Corrosion-induced embrittlement**
  - surficial corrosion (slow general destruction)
  - intergranular pitting and cracks**:** with or without discontinuous precipitation of Cu
  - interdendritic
  - along segregation bands, slip lines, deformation and/or annealing twin boundaries**;** and in ***slip line fields*** below indented decorations } SEM–BSE, EBSD
  - identification of discontinuous precipitation of Cu**:** optical,SEM, SEM + EBSD

- **Microstructurally-induced embrittlement**
  - narrow intergranular cracks
  - bodily displaced grains

- **Microhardness testing (HV)**
  - annealed
  - retained cold-work } HV depends on alloying, notably Cu content, and cold-work
  - corrosion**:** detected by low HV and possible nucleation of new cracks
  - microstructural embrittlement**:** nucleation of new intergranular cracks
  - synergistic embrittlement**:** nucleation of several types of cracks, see slide 129

Metallography - III: microhardness test-induced cracking

- **Synergistic embrittlement cracking: case history #2, Egyptian Vase**



SEM metallograph: NLR

Key	
g.b.	: *grain boundary crack*
s.l.	: *slip line crack*
d.t.b.	: *deformation twin boundary crack*
a.t.b.	: *annealing twin boundary crack*

N.B: The embrittlement is very severe

Metallography - IV: chemical analysis

- **SEM + EDX or SEM + WDX**
  - **source**
    - lead cupellation
    - native silver
    - aurian silver

    unlikely
  - **copper content**
    - high purity silver (low Cu) may be linked to retained cold-work
    - alloying additions of Cu for strength and wear resistance
    - long-term discontinuous precipitation at grain boundaries
  - **actual or potential embrittling impurity elements**
    - Pb, Bi, Sb, Sn, As, Tl (Sb and Sn most unlikely embrittlers)

SEM fractography: types of embrittlement

- **Corrosion-induced embrittlement**
  - surficial corrosion (slow general destruction)
  - corroded fracture surfaces with fine granular appearance like surficial corrosion
  - “clean” intergranular fracture suggestive of SCC
  - transgranular fracture along slip lines / planes and deformation twin boundaries, ***possibly*** also along annealing twin boundaries

- **Microstructurally-induced embrittlement**
  - clean intergranular fracture ***if corrosion absent*** **:** see synergistic embrittlement also
  - generally narrow intergranular cracks ***except in the case of :***
  - bodily displaced grains

- **Synergistic embrittlement**
  - combinations of fractographic features from corrosion-induced and microstructural embrittlement

17. Remedial measures for ancient silver embrittlement

Introduction: ethical and technical considerations

- **Modern restorations and conservation are concerned with both ethical and technical aspects:**
  - an artefact's integrity, meaning ***veracity***, should be respected
  - remedial measures should be ***reversible***

- **However, reversibility is not always practicable:**
  - integrity, meaning ***wholeness***, may require remedial measures that are ***irreversible***

- **Thus remedial measures, which may be much-needed, can be controversial**

Potential remedial measures for embrittled ancient silver

- **Nominally intact artefacts and coins**
  - undeformed
    - corrosion protection
  - deformed
    - corrosion protection
    - ***heat-treatment of coins*** (flattening-out and reading inscriptions**;** removing microstructural embrittlement) followed by corrosion protection
- **Restored artefacts**
  - old restoration
    - corrosion protection
    - ***disassembly***, reassembly with non-hygroscopic adhesives and fillers, and corrosion protection
  - modern restoration
    - corrosion protection
- **Fragmented artefacts and coins**
  - assembly, corrosion protection
  - ***heat-treatment***, assembly, corrosion protection

N.B: (1) Corrosion protection needs careful consideration: see slides 135–140
(2) Disassembly, even if feasible, should be avoided if at all possible
(3) Heat-treatment is highly controversial: see slide 141
(4) Coins are small and easier to heat-treat (also probably less rare)

Corrosion protection - I: overview

- **The most complete and effective corrosion protection measures for embrittled ancient silver would be**
  - cleaning
  - outgassing to dry out crevices and crack surfaces and any entrapped corrosion products
  - application of a protective coating in a low-humidity environment
- **Cleaning is *obviously irreversible* (a point sometimes forgotten)**
- **Ideally, coating application should be *reversible*. This could be difficult or impossible, depending on the embrittlement severity and choice of coating, see slide 139**

Corrosion protection - II: cleaning suggestions

- **Choice of cleaning methods will depend on an artefact's condition, and hence requires much forethought and care. Suggestions are :**

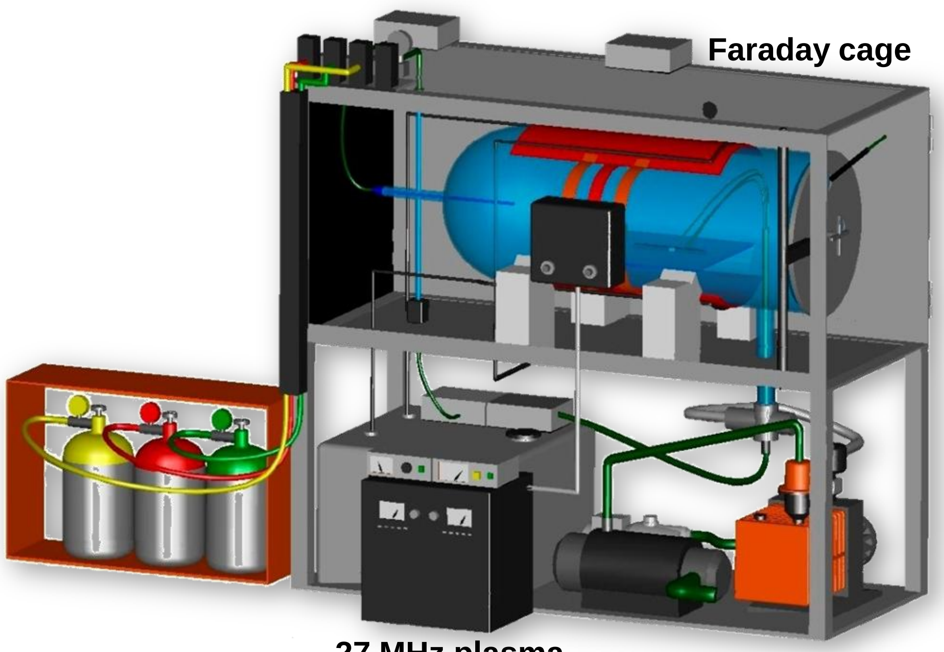
- **"Traditional" cleaning**
  - restore surface finish, if necessary, by ***light*** polishing
  - clean and rinse successively in demineralised water and ethanol
  - allow to dry, preferably in a low-humidity environment (desiccator)

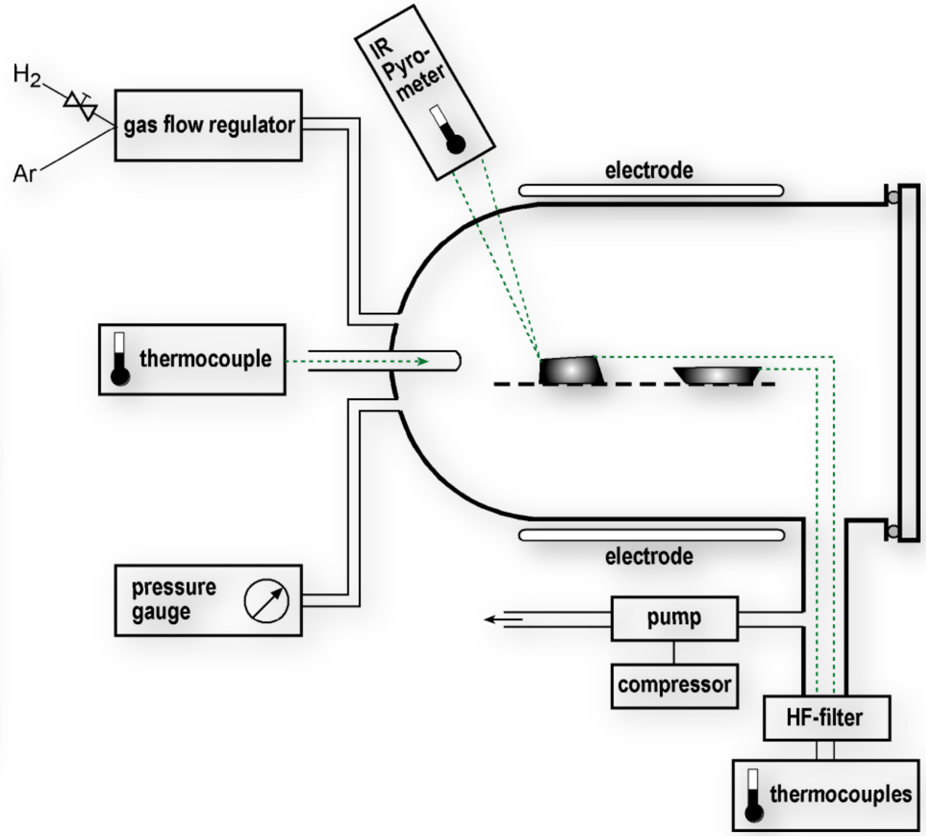
- **Hydrogen plasma reduction of surface corrosion (AgCl) to silver**
  - artefact(s) in vacuum chamber
  - up to 1 hour in low-pressure hydrogen plasma at 40 – 100°C **:** this low-temperature range avoids microstructural changes in the silver during the treatment

N.B: This is a possible alternative to heat-treatment for artefacts severely embrittled by corrosion. Such heat-treatments require unacceptably high temperatures ≥ 700°C, see slide 142

Corrosion protection - III: hydrogen plasma cleaning

- **Musée Suisse plasma equipment : courtesy Katharina Schmidt–Ott**





Corrosion protection - IV: coating requirements and types

- **Coating requirements**
  - ambient temperature application: preferable or essential
  - colourless and transparent
  - conformal (uniform and closely controllable thickness) and pinhole-free
  - high crevice and crack penetration
  - low permeability to moisture and corrosive gases (e.g. atmospheric H_2S)
  - long-term stability
  - removable, i.e. ***reversible*: preferable or essential

- **Candidate coating types**
  - acrylic resins
  - aliphatic polyurethanes
  - cellulose nitrate “Frigilene”

    } liquid phase application

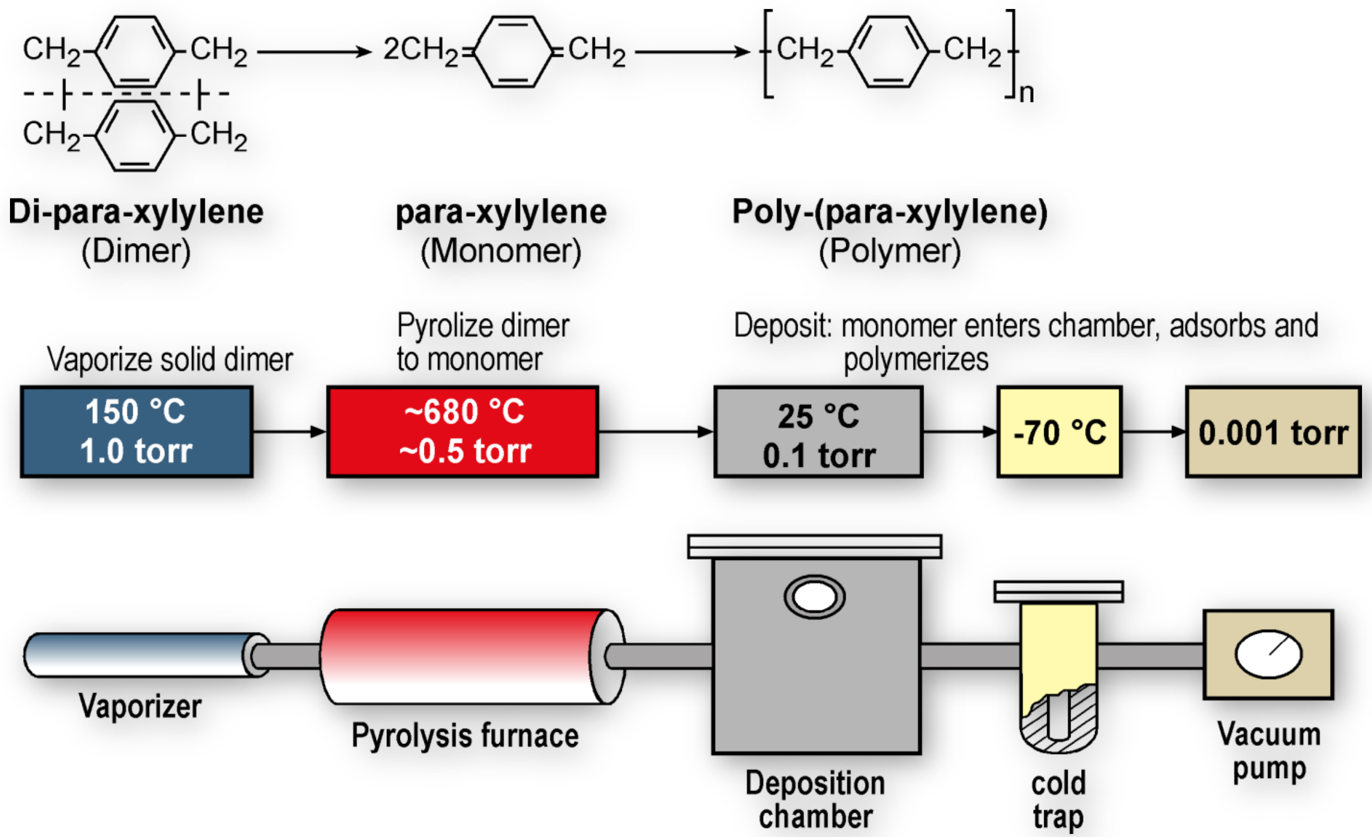
  - “Parylenes” } vapour phase application
  - wax } solid phase application

Corrosion protection - V: coating choice

Coating type	Application conditions	Pros	Cons
• acrylics • polyurethanes • cellulose nitrate • wax	• liquid phase except wax • normal air environment	• removable with some difficulty (most probably unfeasible for severely cracked objects)	• thickness variations, possible pinholes • poor crevice / crack penetration • entrapped moisture
• Parylenes	• vapour phase • reduced pressure environment	• controllable thickness, pinhole-free • high crevice / crack penetration • most moisture removed by reduced pressure environment	• effectively irreversible (not removable below 150 –175 °C) • special equipment, see slide 140

- **Coating choice also requires much forethought and care. Suggestions:**
  - nominally intact artefacts**:** removable coatings to prevent tarnishing
  - severely cracked artefacts**:** Parylene-type coating to prevent further corrosion-induced or synergistic embrittlement
  - Byzantine Paten, case history #3**:** removable coating on rear surface to inhibit progression of any localised corrosion

Corrosion protection - VI: parylene deposition process



N.B: (1) Parylenes used for brittle and fragile objects, despite irreversibility (Canadian Conservation Institute, Ottawa)

(2) Equipment available for small coating runs: (SCS Cookson Electronics)

Remedial heat-treatments - I: pros and cons

- **Pros:**
  - alleviation of handling / studying / conservation problems
  - restoration of severely embrittled and fragmented objects

- **Cons:**
  - ***irreversible***
  - microstructural changes causing loss of information and possibly misleading for future investigators
  - risk of further damage
  - limited technical and scientific information for guidance, slide 142

Remedial heat-treatments - II: current knowledge

- **Corrosion-induced embrittlement (Werner 1965; Ravich 1993)**
  - 0.5 hour at 300 – 400°C in hydrogen (pre-treatment) to convert AgCl to Ag
  - 5 – 10 minutes at 700°C, minimum, in inert environment or under charcoal

- **Microstructurally-induced embrittlement (Thompson and Chatterjee 1954). Heat treatments in an inert environment:**
  - 1 hour at 200 – 250°C for Ag–0.8 wt.% Pb
  - 0.5 – 1 hour at 500°C for Ag–0.8 wt.% Pb–8.3 wt.% Cu**: *suggestion only***

N.B: Low-temperature hydrogen plasma cleaning is a possible alternative to heat-treatment for objects severely embrittled by corrosion, see slides 136, 137

Remedial heat-treatments - III: potentially sanctionable usages

- **Alleviation of corrosion-induced, microstructurally-induced and synergistic embrittlement of**
  - deformed coins, to enable flattening-out and reading inscriptions
  - deformed artefacts, to enable restoring original shapes
  - fragmented coins and artefacts to alleviate handling and studying, and also to enable restoration

Remedial measures used in the case histories

Remedial measures	Cauldron	Vase	Paten	Kantharos	Kaptorga	Head	Cup
Cleaning	*	●	*	●	●	●	●
Surface corrosion removal	*	●	*	*	●	**	●
Heat-treatment (***irreversible***)					●	***	
Reassembly							
— reversible	●					●	
— ***effectively irreversible***		●			●		●
Consolidation (***irreversible***)				●			
Coating (reversible)				●			●

* Assumed**;** ** external surface only**;** *** broken-off pieces (***ungilded***)

Remedial measures case history #5, Kaptorga

- Restored with *removable* external backing of silk and acrylic lacquer, then an *irreversible* internal backing of glass cloth and epoxy resin: external backing removed with acetone

As-found: extensively broken and fragile, easily fragmented by handling

Photo: Jiří Děd, ICT, Prague

Photo: Institute of Archaeology, Prague

Remedial measures case history # 7, Khan Cup - I : as-received*

- **Extensively broken: this was a grave burial. Crude joining of some fragments using *two* adhesives, one resistant to organic solvents**

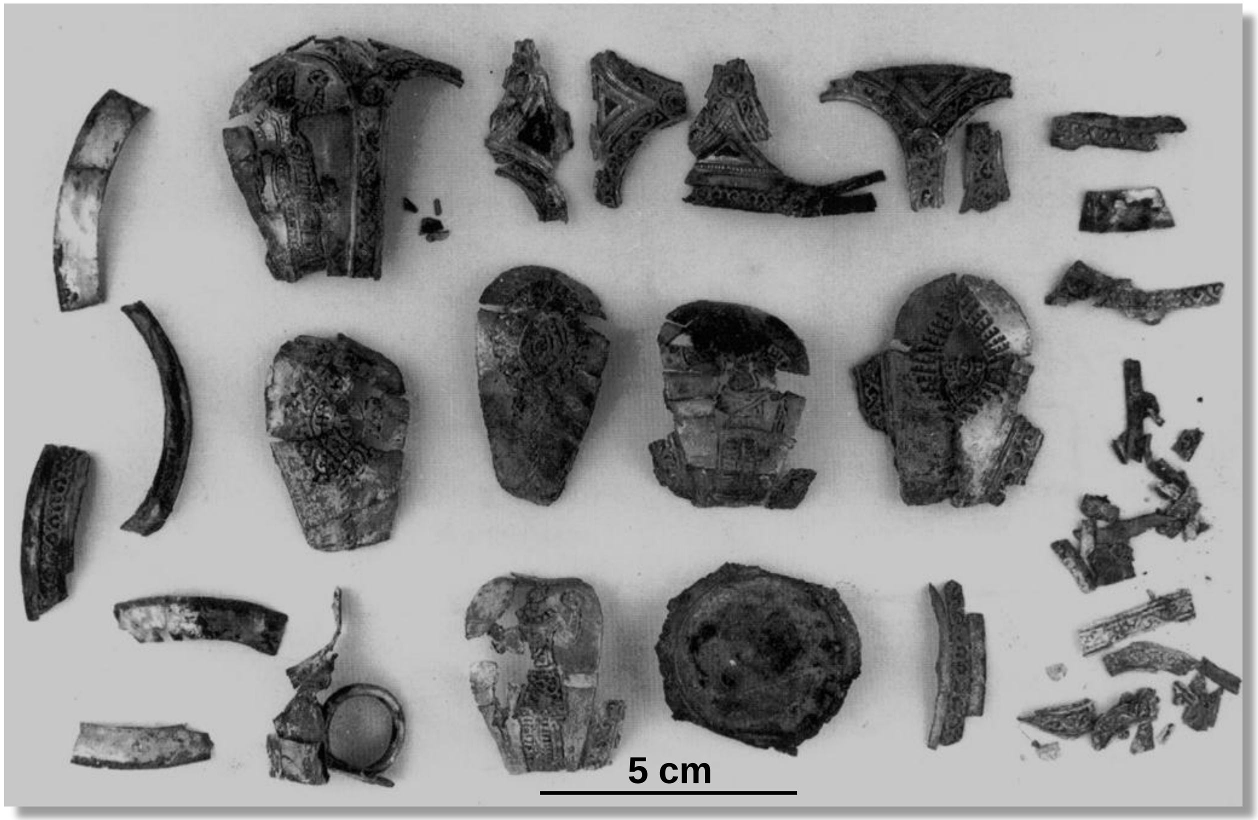


Photo: Gerhard Stawinoga, Archaeological Landesmuseum, Schleswig

****Received and restored at the Archaeological Landesmuseum, Schleswig***

Remedial measures for the Khan Cup - II: restoration procedure*

- **Joined fragments disassembled: one adhesive was dissolvable in acetone, the other had to be mechanically removed**
- ***154* fragments for reassembly: corrosion removed with silver polish, followed by rinsing in distilled water and drying with alcohol**
- **Strongly deformed fragments were supported by rubber backing and partially or wholly reshaped by applying light pressure with burnishing tools (steel or hardwood)**
- **External *fixation***
  - **partial assembly:** fragments fixed using strips of adhesive tape (Tesapack)
  - **full assembly** required joining under stress using wooden clamps**:** this needed fixation with glass silk impregnated by Mecosan adhesive (removable with acetone)
- **Internal *joining* (partial and full assembly) using glass silk and Mecosan or "Super Glue"**
- **After full assembly, removal of external fixation using acetone**
- **Exposed glass silk (internally covering gaps in the full assembly) pigmented using silver powder mixed with Paraloid B 72, a clear non-yellowing lacquer removable with acetone and toluene**
- **Final coating of the restored Cup with Paraloid B 72 dissolved in toluene**

***G. Stawinoga: Die Tasse des Khans – Die Restaurierung einer mittelalterlichen Silbertasse, *Arbeitsblätter für Restauratoren*, Vol. 30 (2), pp. 137–142, 1997**

Remedial measures for the Khan Cup - III: completed restoration

Photo: Gerhard Stawinoga, Archaeological Landesmuseum, Schleswig

besides enabling the Cup to be aesthetically appreciated, the restoration also showed how it had been fabricated *

***G. Stawinoga: Die Tasse des Khans – Die Restaurierung einer mittelalterlichen Silbertasse, *Arbeitsblätter für Restauratoren*, Vol. 30 (2), pp. 137–142, 1997**

Remedial measures: summary comments

- **Remedial measures for restoring and conserving embrittled ancient silver are not always *reversible*. Heat-treatments are *irreversible* and particularly controversial**

- **Remedies are always mixtures of *pros* and *cons*. Each case must be considered on its own merits, accounting for an artefact's condition, ethical aspects and current technical capabilities**

- **Detailed case histories are illustrative and important for determining the best ways to restore and conserve embrittled artefacts**

- **Low-temperature studies of microstructurally-induced embrittlement (especially Ag-Pb and Ag-Cu-Pb alloys) could be very worthwhile for determining how to minimise microstructural changes when heat-treating to alleviate microstructural and synergistic embrittlement**

18. Extent of the embrittlement problem

"Setting the scene"

- **Opinions on seriousness of ancient silver embrittlement differ widely**
  - often extremely brittle (Schweizer and Meyers 1979; Kallfass *et al*. 1985)
  - certain objects very brittle (Thompson and Chatterjee 1954; Werner 1965)
  - small proportion of artefacts and coins badly embrittled (Northover 1999)

- **From the case histories and mechanism discussions, sections 5 –14 of this Lecture Course, there appear to be four primary factors:**
  - copper content
  - lead content
  - retained cold-work
  - adverse environment, especially graves

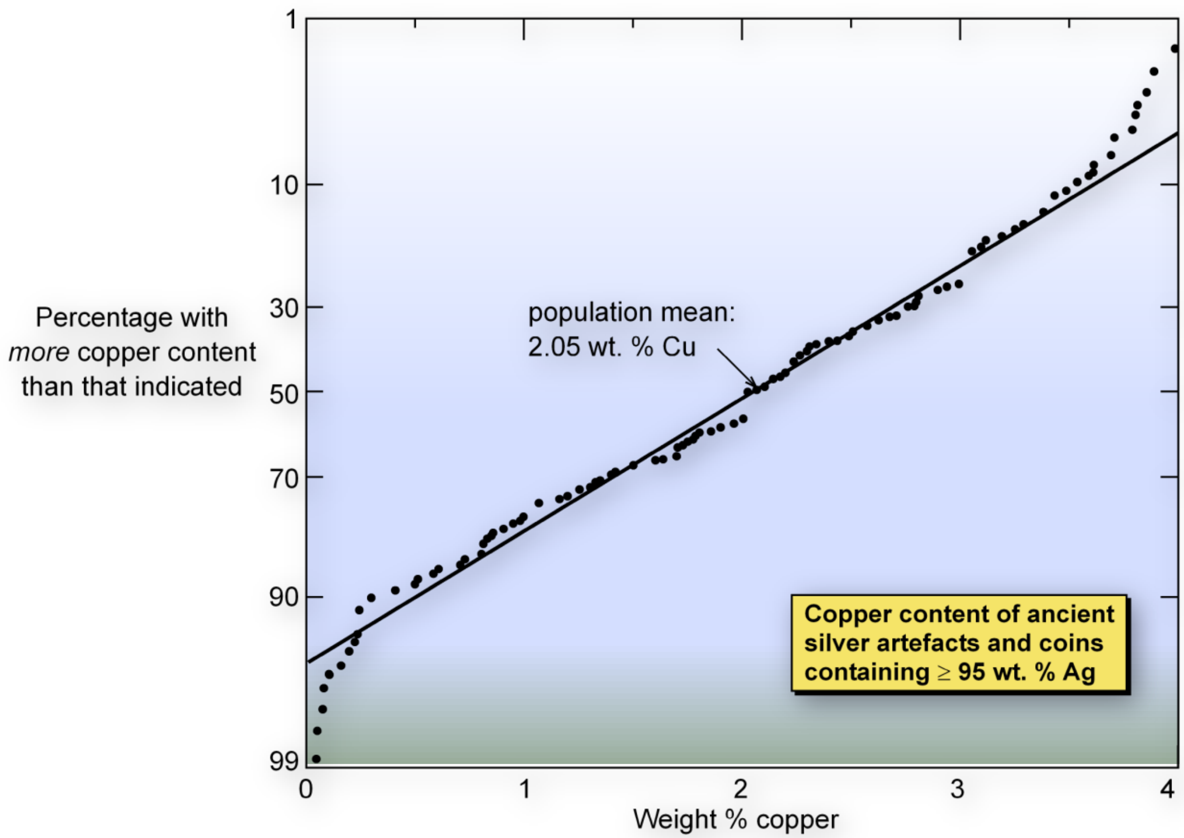
By considering these factors it is possible to make some statements, *with caution*, about the extent of the embrittlement problem

Corrosion-induced embrittlement: cold-work, copper content and the burial environment

- ***Case history*** **artefacts contain local (#1, 2, 3, 7) and/or widespread (#2, 6) retained cold-work**

- **From slide 22: 50% of artefacts and coins contain < 2 wt.% Cu; retained cold-work likely to add strength**

- **Corrosion – induced embrittlement could be widespread in high-purity ancient silver, especially in grave burial objects**

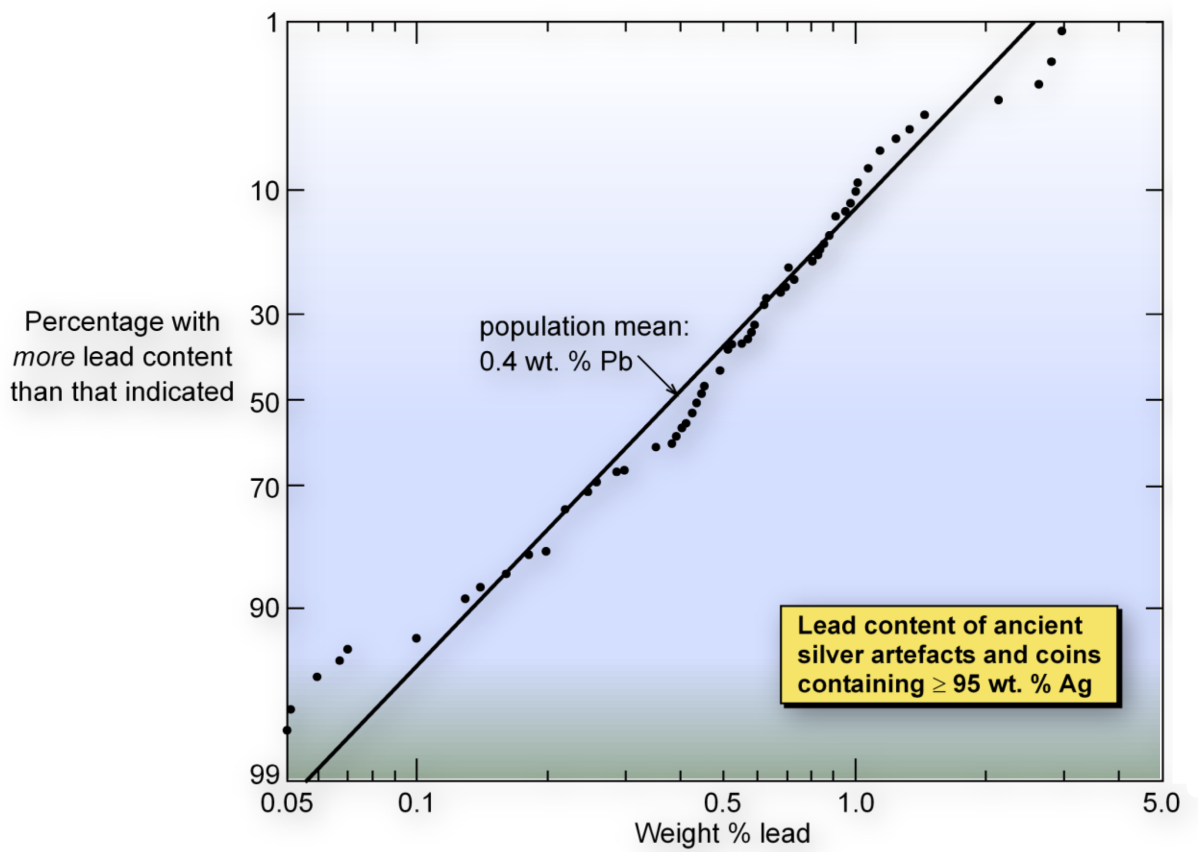


Microstructurally-induced embrittlement: lead

- ***Case history*** **artefacts (#2, 4) contain 0.7 wt.% and 0.16 – 0.25 wt.% Pb**

- **From slide 24: ~ 70% of artefacts and coins contain > 0.25 wt.% Pb**

- **Assuming lead is the culprit, investigation of other artefacts and coins should reveal more cases, possibly in combination with corrosion– induced embrittlement, slide 154**



Synergistic embrittlement: hypothesis

- **From the case histories *it appears that* corrosion-induced embrittlement is more frequent than microstructurally-induced embrittlement**

Hence

- **Synergistic embrittlement might be more likely than microstructurally-induced embrittlement alone**

However

- **Case history #2, the Egyptian Vase, is so far unique**

N.B: As mentioned in section 14 (slide 111) of this Lecture Course, synergistic embrittlement is very damaging. It is important to recognise synergistically-embrittled artefacts because their conservation requires special care (Wanhill et al. 1998)

Extent of embrittlement: summary

- **Ancient silver often contains enough copper and lead to allow corrosion-induced, microstructurally-induced and synergistic embrittlement; and some artefacts and most coins will contain retained cold-work**

But

- **Northover's examination of hundreds of silver artefacts and coins has shown only a small proportion to be badly embrittled**

Hence

- **A combination of adverse factors is necessary for severe embrittlement. These factors include**
  - Cu, Pb contents and distribution (segregation, precipitation)
  - manufactured condition, notably retained cold-work**:** also large grain sizes
  - burial time and environment, especially grave burials

19. General conclusions: importance of case histories

Types of embrittlement - I

- **Current knowledge enables identifying and providing explanations of types of embrittlement of ancient silver**
  - corrosion-induced embrittlement: case histories* #1, 2, 3, 5, 6, 7
  - microstructurally-induced embrittlement: case histories* #2, 4
  - synergistic embrittlement: case history* #2

* #1**Cauldron** #2**Vase** #3**Paten** #4**Kantharos** #5**Kaptorga** #6**King's Head** #7**Khan Cup**

- **Several types and probable/possible mechanisms of corrosion-induced embrittlement. Case histories show the importance of retained cold-work:**

Embrittlement	Mechanisms**	Retained cold-work	Case histories*
Intergranular	LGA; LGA during SCC	important (not #5)	#1, #3, #5, #6, #7
Interdendritic	LGA	not required	Sican Tumi (Scott 1996)
Segregation bands	LGA	not required	#2
Transgranular	LGA during SCC	essential	#1, #2

** LGA = local galvanic attack; SCC = stress corrosion cracking

Types of embrittlement - II

- Case histories #2 , Vase, and #4, Kantharos, show that microstructurally-induced embrittlement is characterised by intergranular fracture with narrow and sharp cracks and bodily displaced grains. The most likely mechanism is long-term low-temperature ageing, whereby lead (Pb) segregates to grain boundaries

- Synergistic embrittlement is combinations of corrosion-induced and microstructurally-induced embrittlement, so far found only from case history #2, the Vase. Synergistic embrittlement is very damaging, making an artefact frangible and even friable

Restoration and conservation

- **Detailed case histories are important for determining the best ways to restore and conserve embrittled ancient silver**

- **Remedial measures for restoring and conserving embrittled artefacts and coins fall into two main categories**
  - corrosion protection
  - heat-treatment

- **Corrosion protection**
  - generally applicable
  - requires much prior consideration

- **Heat-treatment**
  - difficult to justify, but could be essential for some severely embrittled and fragmented objects

Extent of embrittlement problem

- **Ancient silver often contains enough copper and lead to allow corrosion-induced, microstructurally-induced and synergistic embrittlement; and some artefacts and most coins will contain retained cold-work, which is strongly linked to corrosion-induced embrittlement**

But

- **Northover's examination of hundreds of silver artefacts and coins has shown only a small proportion to be badly embrittled**

Hence

- **A combination of adverse factors is necessary for severe embrittlement. These factors include**
  - Cu, Pb contents and distribution (segregation, precipitation)
  - manufactured condition, notably retained cold-work: also large grain sizes
  - burial time and environment, especially grave burials with high salinity from body decomposition

20. Bibliography

Selected references

- **G. Stawinoga: Die Tasse des Khans – Die Restaurierung einer mittelalterlichen Silbertasse, *Arbeitsblätter für Restauratoren*, Vol. 30 (2), pp. 137–142, 1997.**

- **R.J.H. Wanhill: Case Histories of Ancient Silver Embrittlement, *Journal of Failure Analysis and Prevention*, Vol. 11 (3), pp. 178-185, 2011.**

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- **R.J.H. Wanhill: Stress Corrosion Cracking in Ancient Silver, *Studies in Conservation*, Vol. 58 (1), 2013.**