Fractography of Ancient Metal Artifacts and Restoration and Conservation

Russell Wanhill, MSc.Tech., PhD (UMIST); Dr. Tech. Sci. (TUD)
Emeritus Principal Research Scientist, Aerospace Vehicles Division
Royal Netherlands Aerospace Centre

Omid Oudbashi, BSc, MA, PhD
Assistant Professor, Department of Conservation of Cultural and Historical Properties, and Head of the Central Laboratory, Art University of Isfahan

Contents

Archeological and archaeometallurgical questions

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

Fractography compared to Metallography

Fractography compared to Metallography

- **Determination of manufactured condition**
  - mechanically worked; mechanically worked + annealed; grain size, segregation bands, slip lines, deformation and annealing twins
  - as-cast; cast and annealed; coring, dendrite and grain sizes; eutectic sizes and distribution
  - alloy phases; matrix and grain boundary precipitates; constituent particles; inclusions; porosity
- **Damage assessment**
  - deformation; formation of internal voids during tensile elongation and ductile fracture
  - surficial and internal corrosion; corrosion layers
  - embrittlement cracks and fractures; microstructurally-induced; corrosion-induced, especially stress corrosion cracking (SCC)

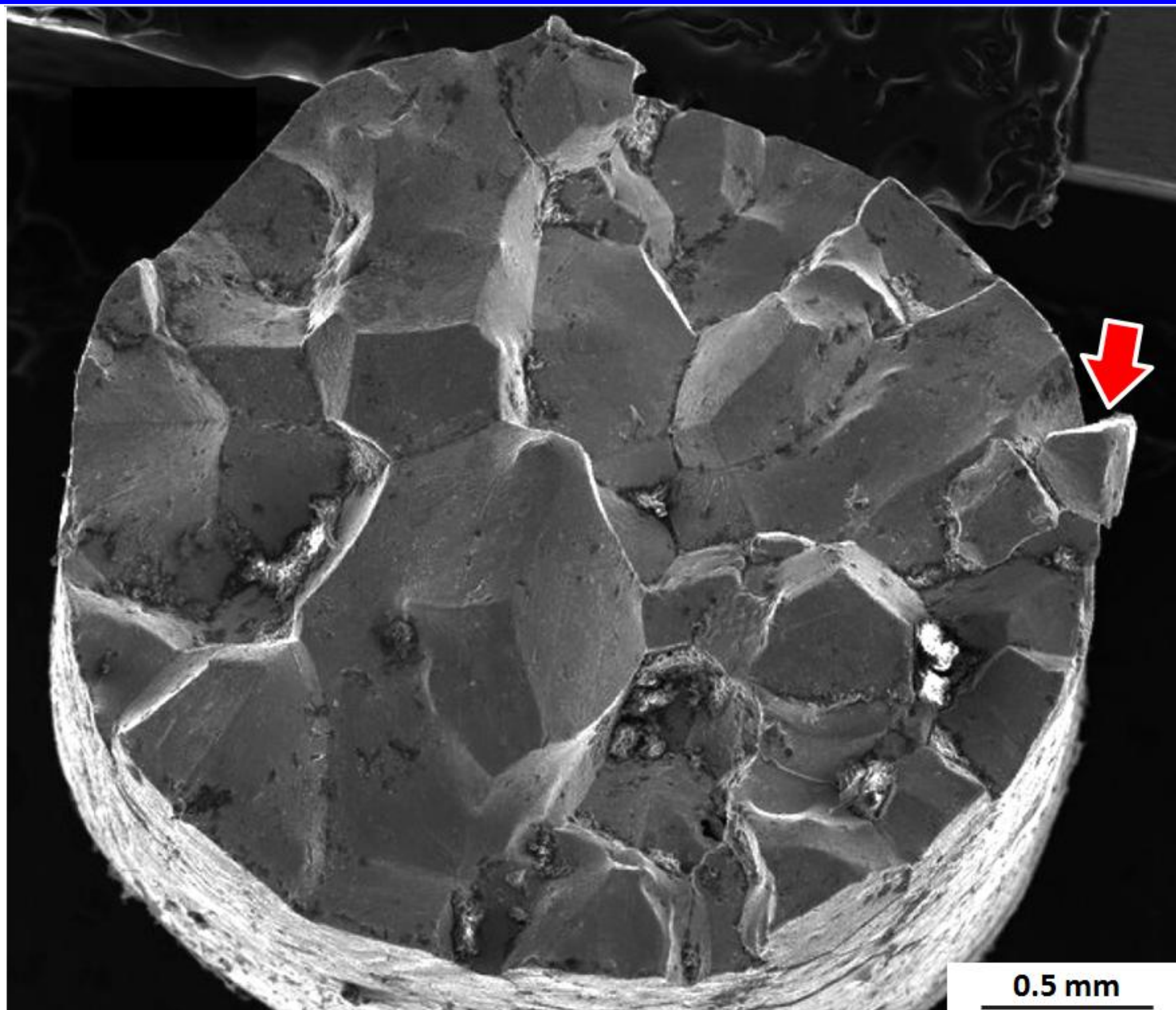
The features in this topic and corrosion damage are mainly investigated using **Metallography.**

The features in this topic (except some corrosion damage) are investigated by **Fractography.**

Case Studies: Gold Alloys

Microstructural embrittlement: 21K gold ring, ca. 300 AD

Original images: Mikkel Storch-Christiansen, Copenhagen, Denmark



- **Intergranular fracture: the arrow points to an almost loose grain.**
- **Coarse grain sizes due to heating from a cremation burial.**
- **Brittleness is likely caused by elemental segregation, e.g. Pb, Bi, K, to the grain boundaries.**

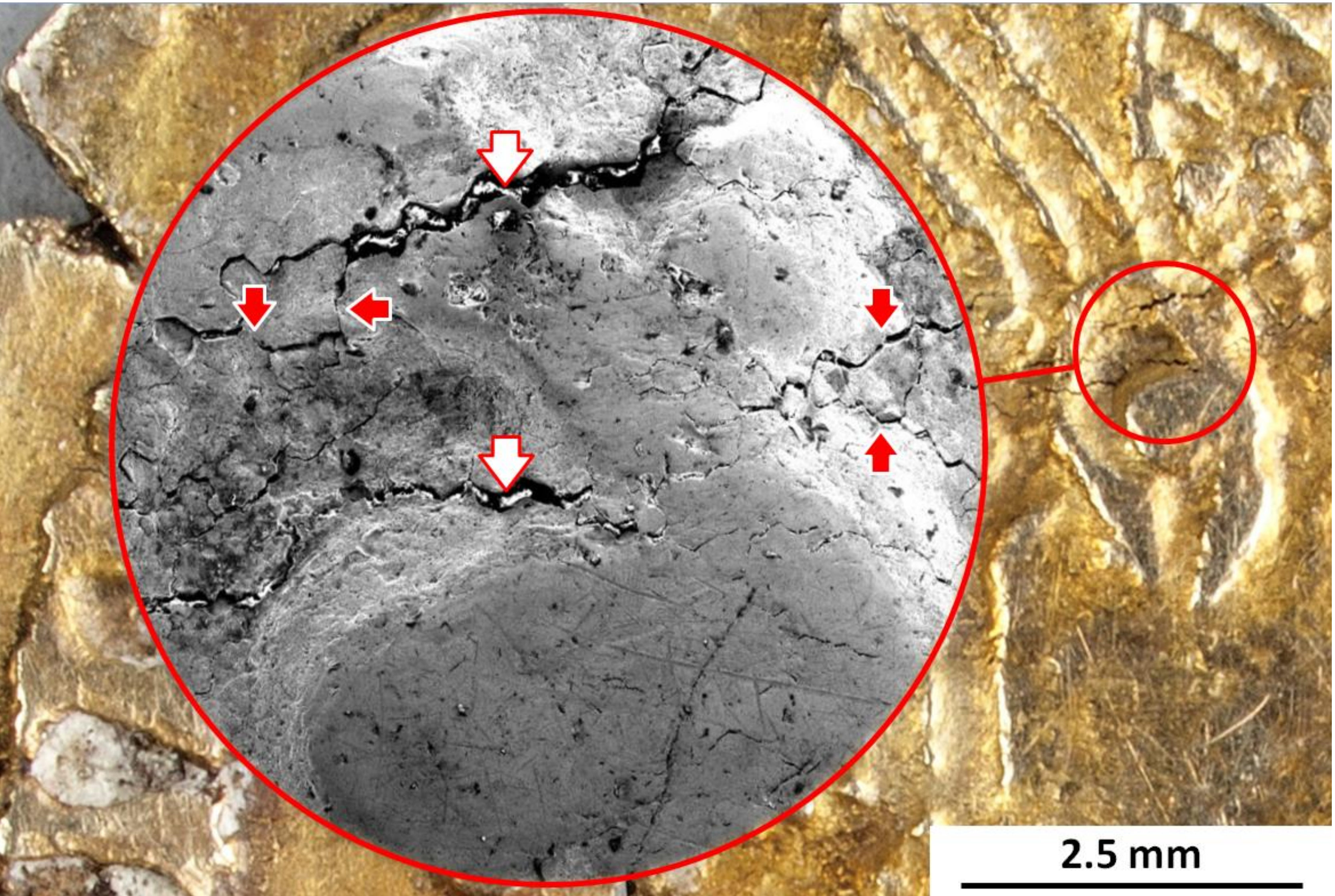
SCC embrittlement I: 13K Runic coin, 5^{th} -7^{th} Century AD

Original image: Fries Museum, Leeuwarden, The Netherlands

- **Fracture has been crudely 'repaired' by using a glue.**

SCC embrittlement II: 13K Runic coin, 5th -7th Century AD

Original images: Fries Museum, Leeuwarden; NLR, Marknesse; The Netherlands

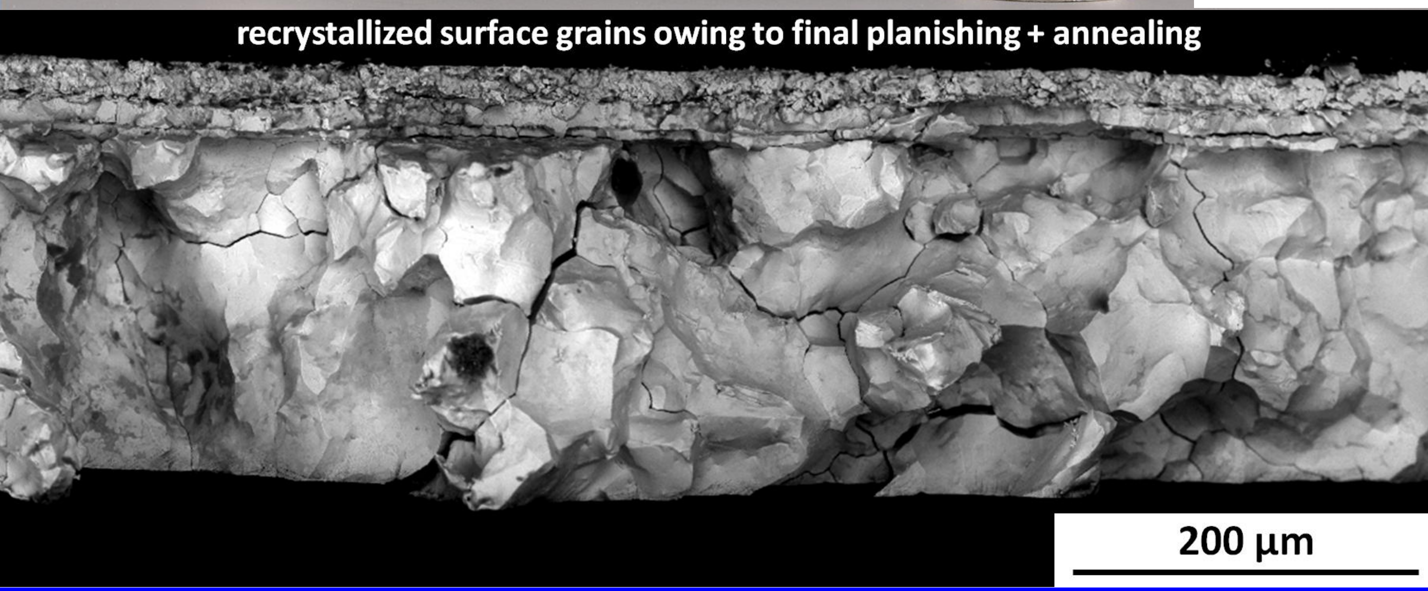


- Intergranular fracture: the white arrows point to glue infiltrated by accident.
- Small arrows point to grain boundaries incompletely separated by SCC.

Case Studies: High-Silver Alloys

Microstructural embrittlement: Roman Kantharos, 100 BCE – 100 AD

Original images: Museum Het Valkhof, Nijmegen; Ineke Joosten, ICN, Amsterdam, The Netherlands



- **The arrow points to a large crack in the inner cup. Both cups are impregnated by an epoxy resin.**

- **Intergranular cracks and fracture: a few almost loose grains.**
- **Brittleness is likely caused by lead (Pb) segregation to grain boundaries.**

SCC embrittlement I: Romanesque Kaptorga, 10th Century AD

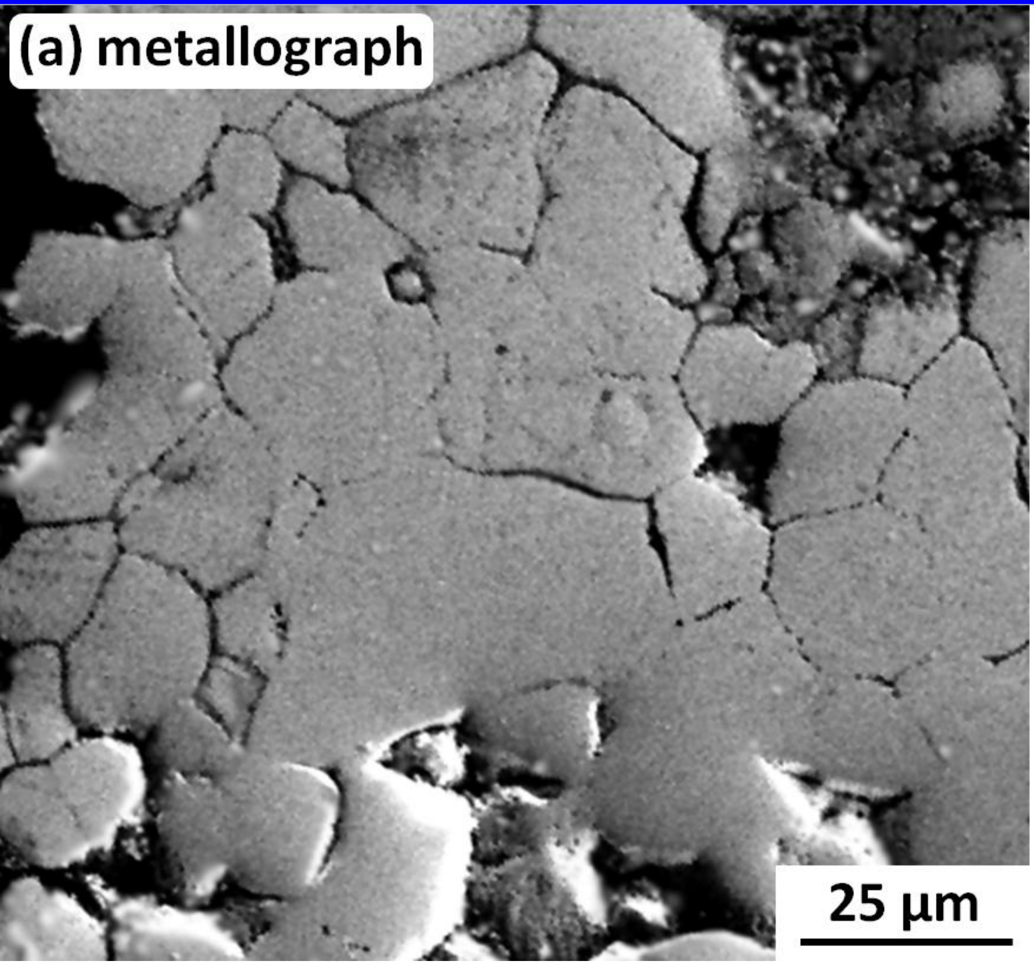
Original images: Jiří Děd, ICT; IACAS; Prague, Czech Republic

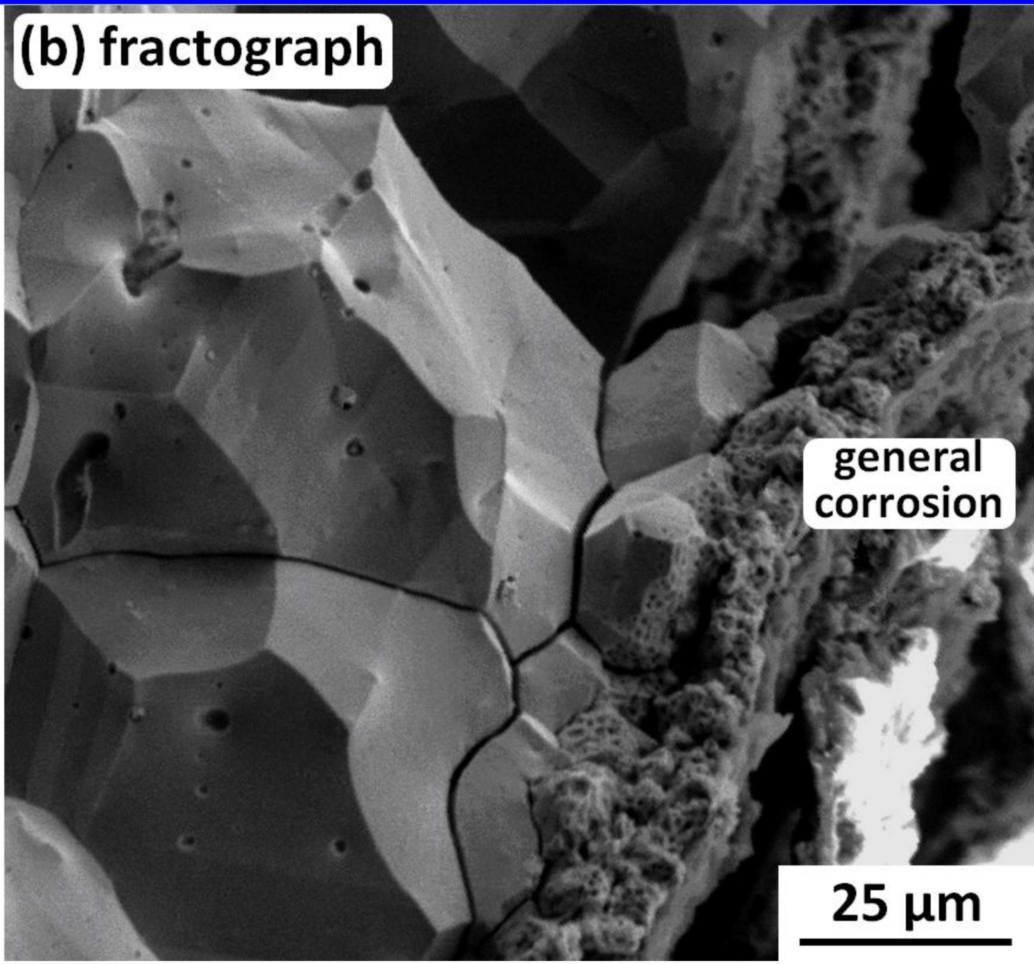
- As-found: extensively broken and fragile.

- Restoration is irreversible owing to the fragility of the fragments.

SCC embrittlement II: Romanesque Kaptorga, 10th Century AD

Original images: Pavel Bartuška, Institute of Physics: Jaroslava Vaníčková, ICT; Prague, Czech Republic



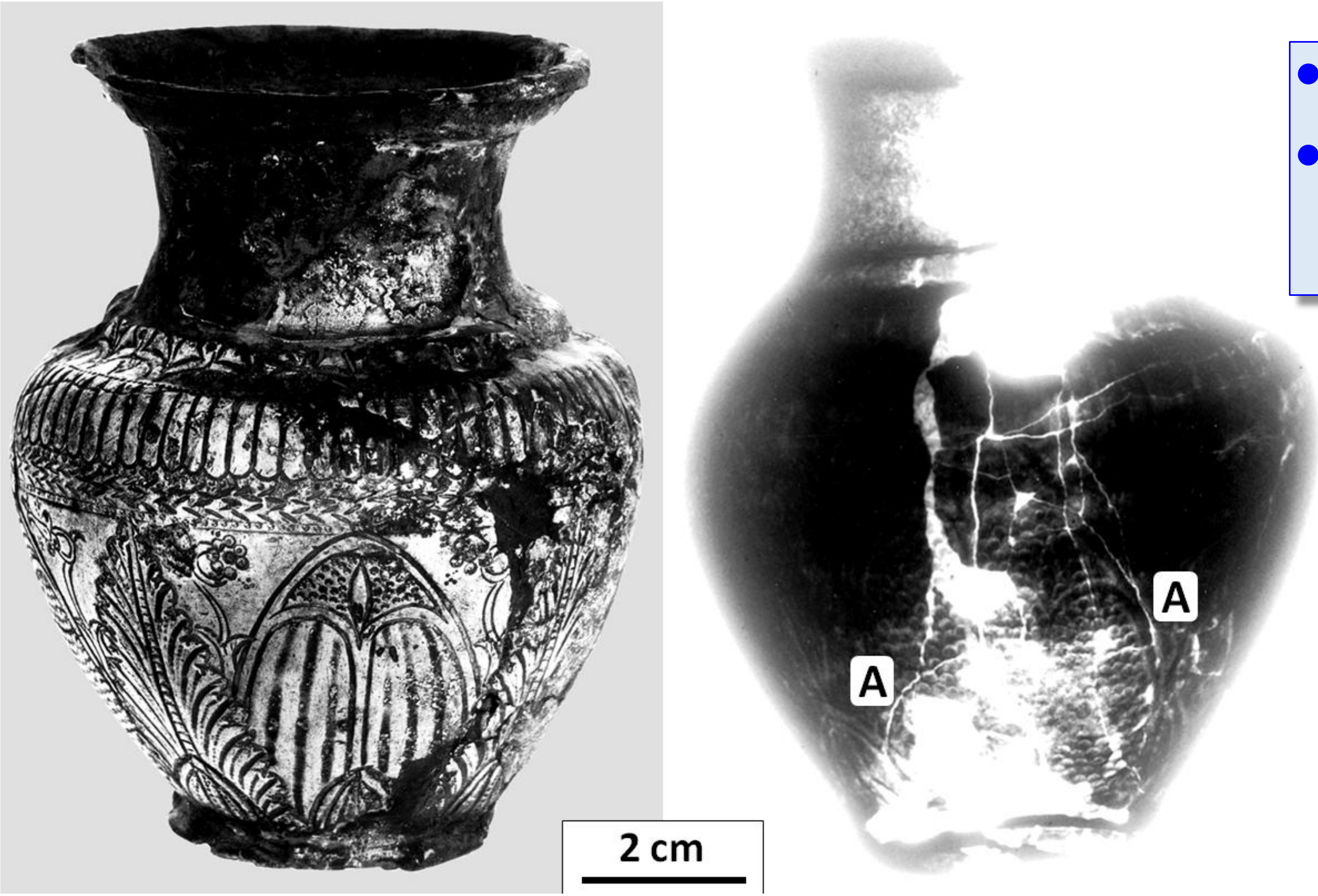


- **Corrosion pitting coalescing to form intergranular cracks.**

- **Intergranular SCC being destroyed by corrosion.**

Synergistic embrittlement I: Egyptian Vase, 3rd Century BCE

Original images: Ron Leenheer, Allard Pierson Museum; Roel Jansen, University of Amsterdam; The Netherlands



- **Heavily restored (old restoration).**
- **Severe cracking, some along the external chasing, (A).**

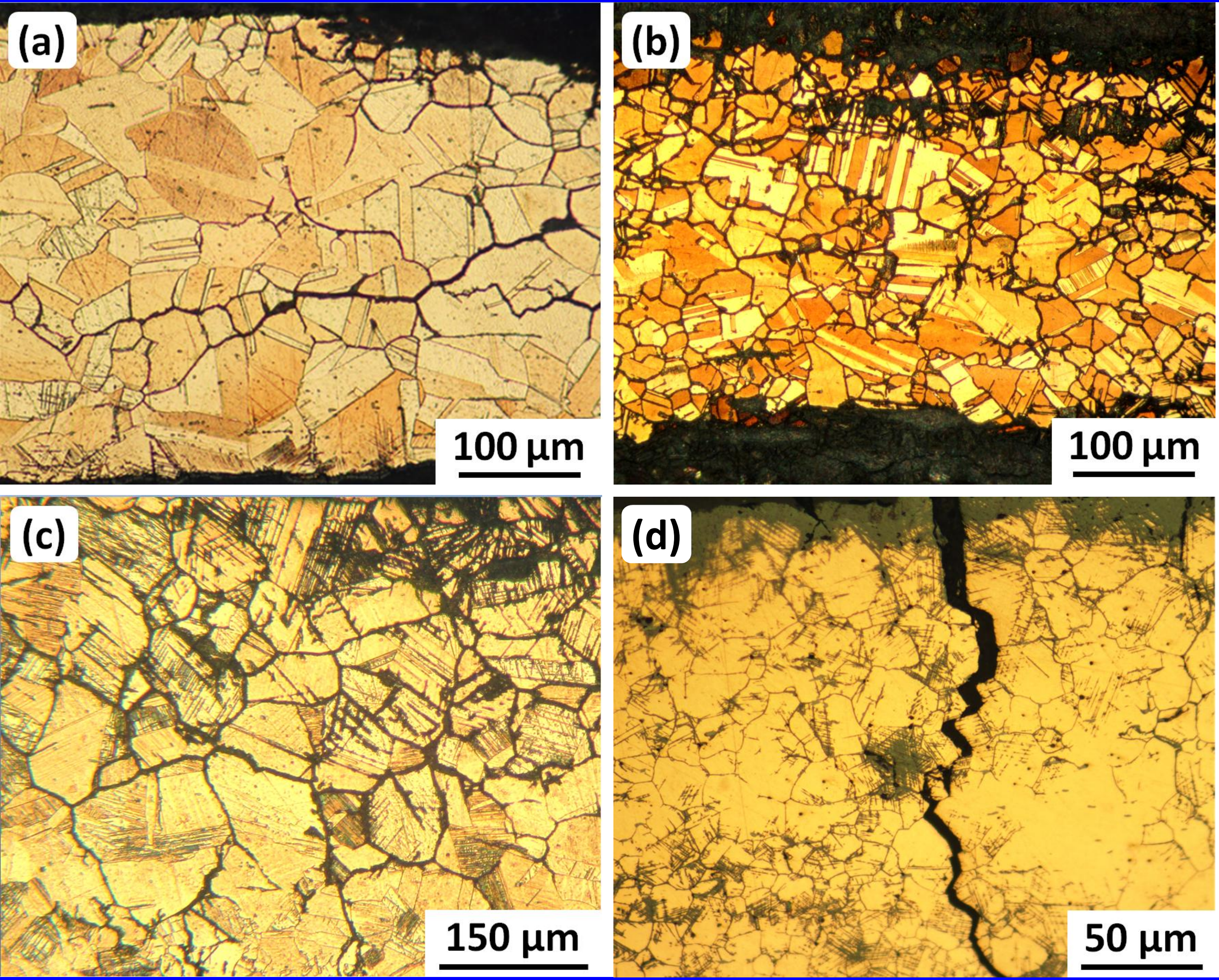
Synergistic embrittlement II: Egyptian Vase, 3rd Century BCE

Original image: NLR, Marknesse, The Netherlands

Case Studies: Bronzes

SCC embrittlement I: Metallographs from Iranian bronze artifacts

Original images: Omid Oudbashi, Art University of Isfahan, Isfahan, Iran

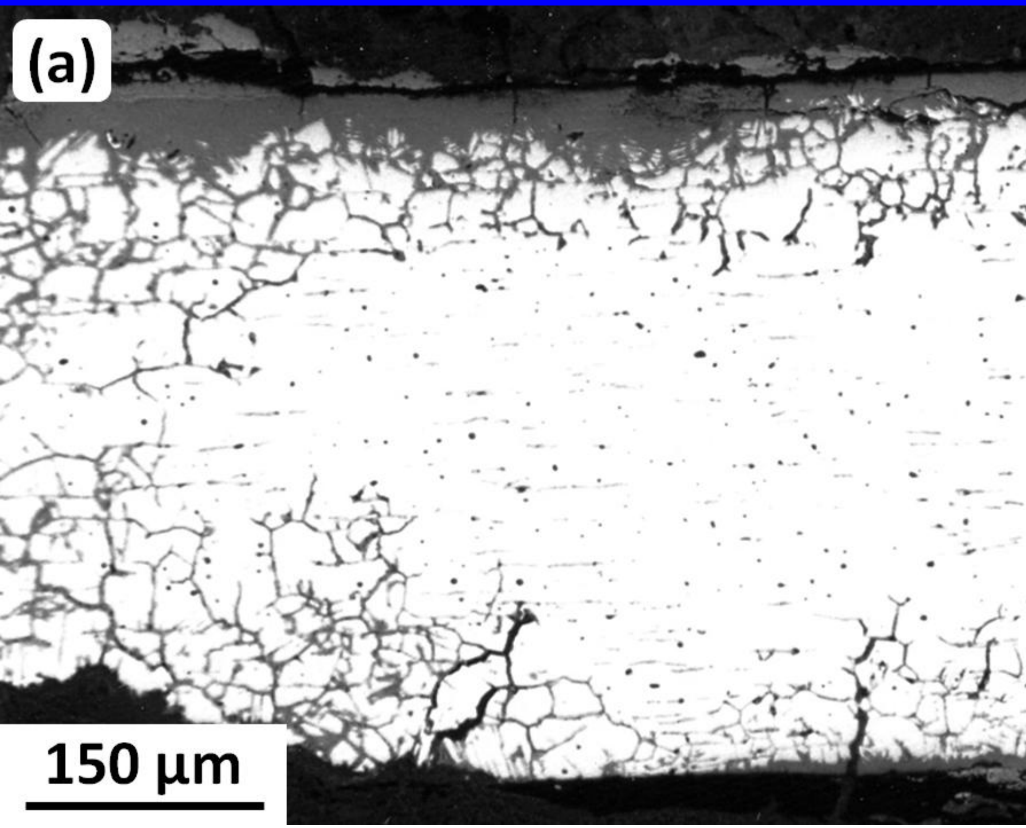


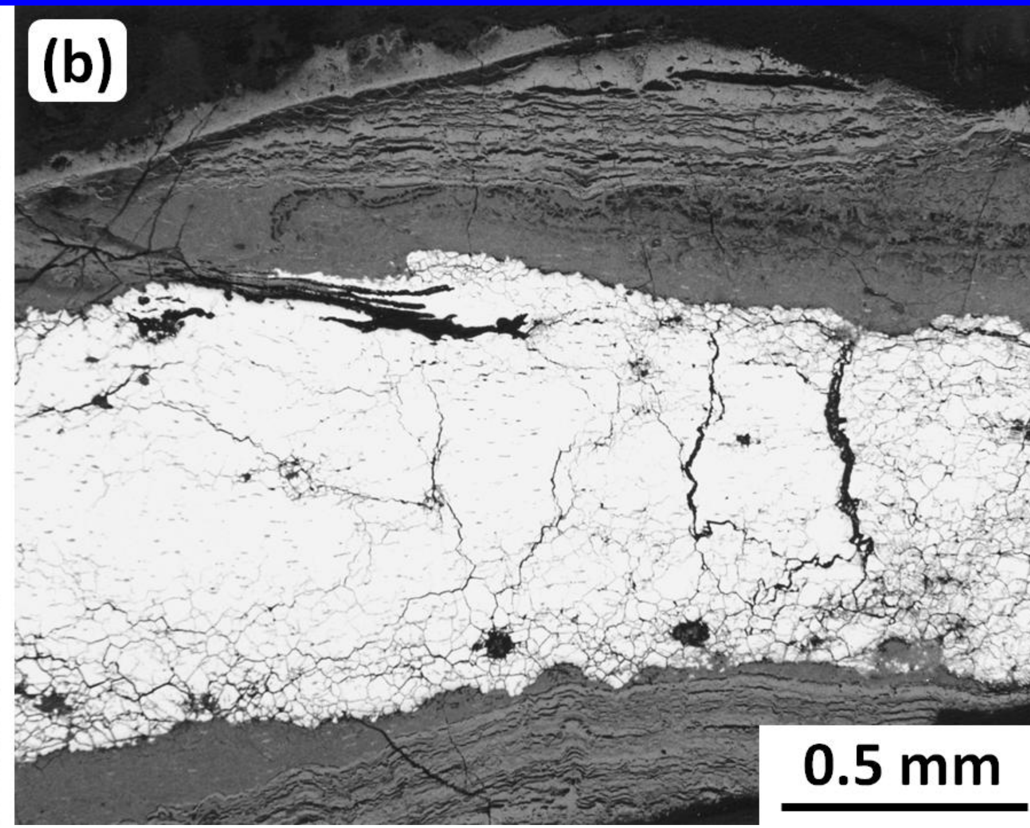
17a	Vessel: Marlik: 14th-10th Century BCE
17b	Vessel: Deh Dumen: 25th-20th Century BCE
17c	Vessel: Deh Dumen: 25th-20th Century BCE
17d	Button: Baba Jilan: 8th Century BCE

- **All artifacts experienced cold-work and annealing cycles, leaving residual stresses and therefore SCC susceptibility during their burial.**
- **Severe intergranular SCC led to fragility and some breakages.**

SCC embrittlement II: Metallographs from Iranian bronze artifacts

Original images: George Vander Voort, Wadsworth, IL 60083-9293, USA



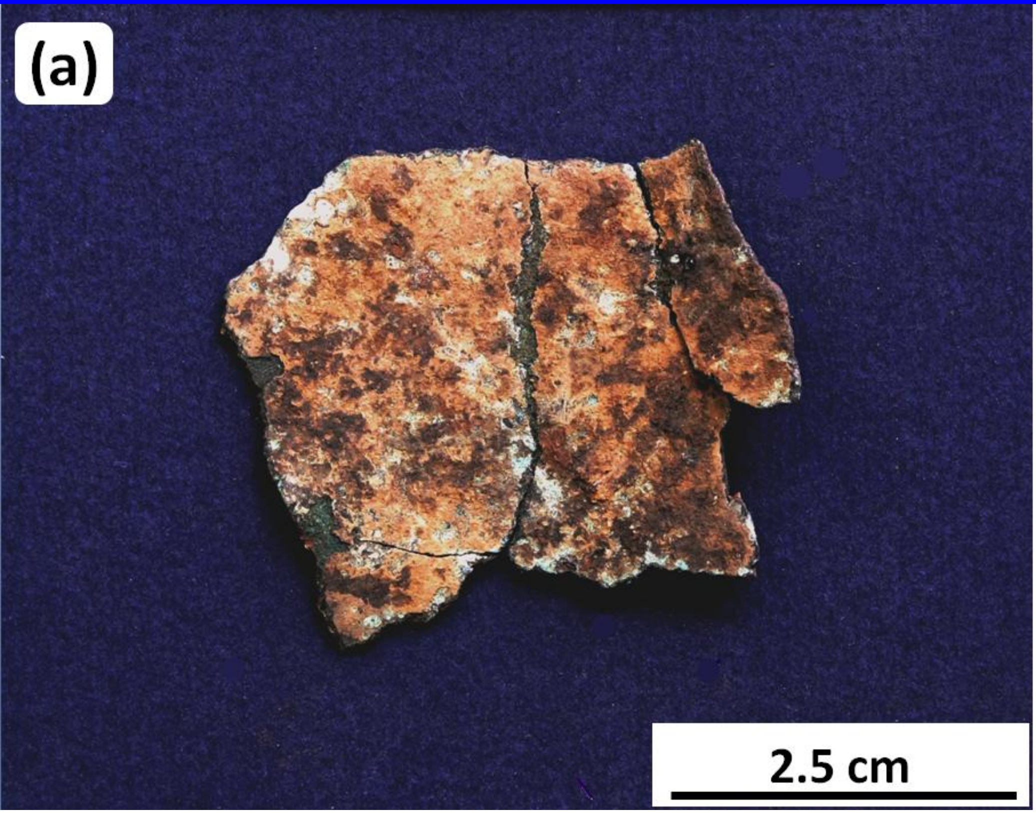


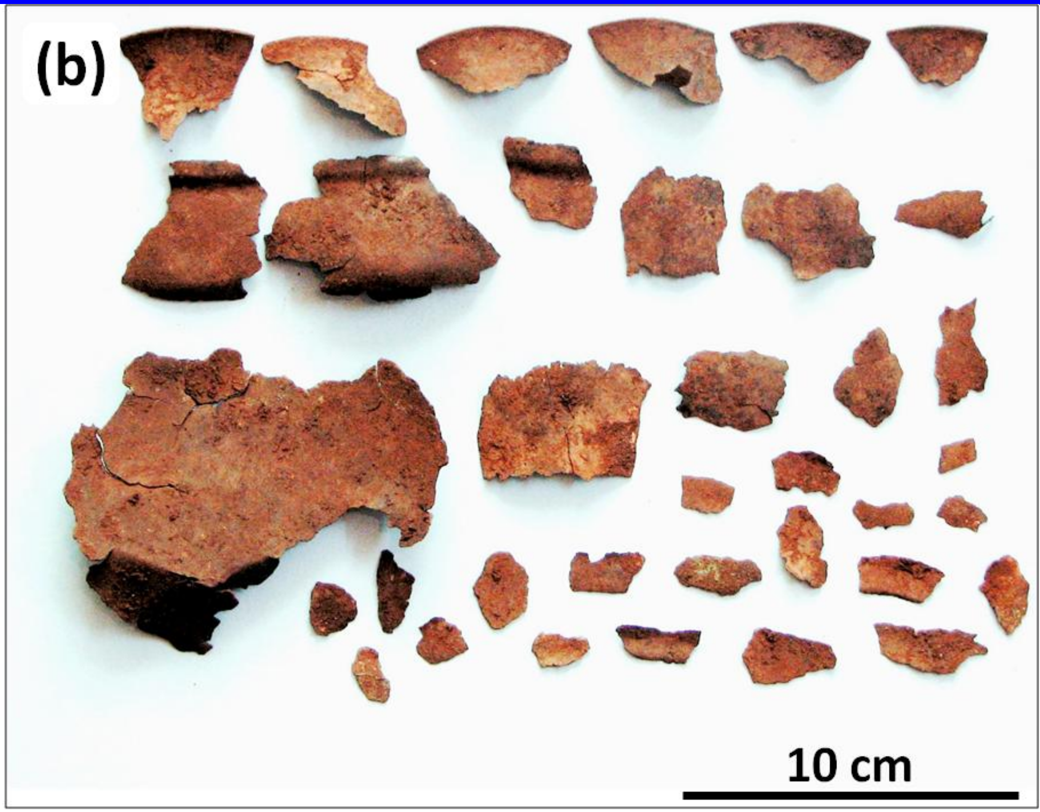
- **Metallographs illustrating progressive external corrosion destroying evidence of SCC - and *eventual* fracture surfaces - in Luristan vessels from the 8th-7th Century BCE: (a) Cu-9.5wt.%Sn-0.33wt.%As; (b) Cu-18.2 wt.%Sn-0.06wt.%As.**

NOTE: **This is broadly similar to destruction of SCC evidence in high-silver alloys, slide 13.**

SCC embrittlement III: Iranian bronze vessel fragments

Original images: Omid Oudbashi, Art University of Isfahan, Isfahan, Iran



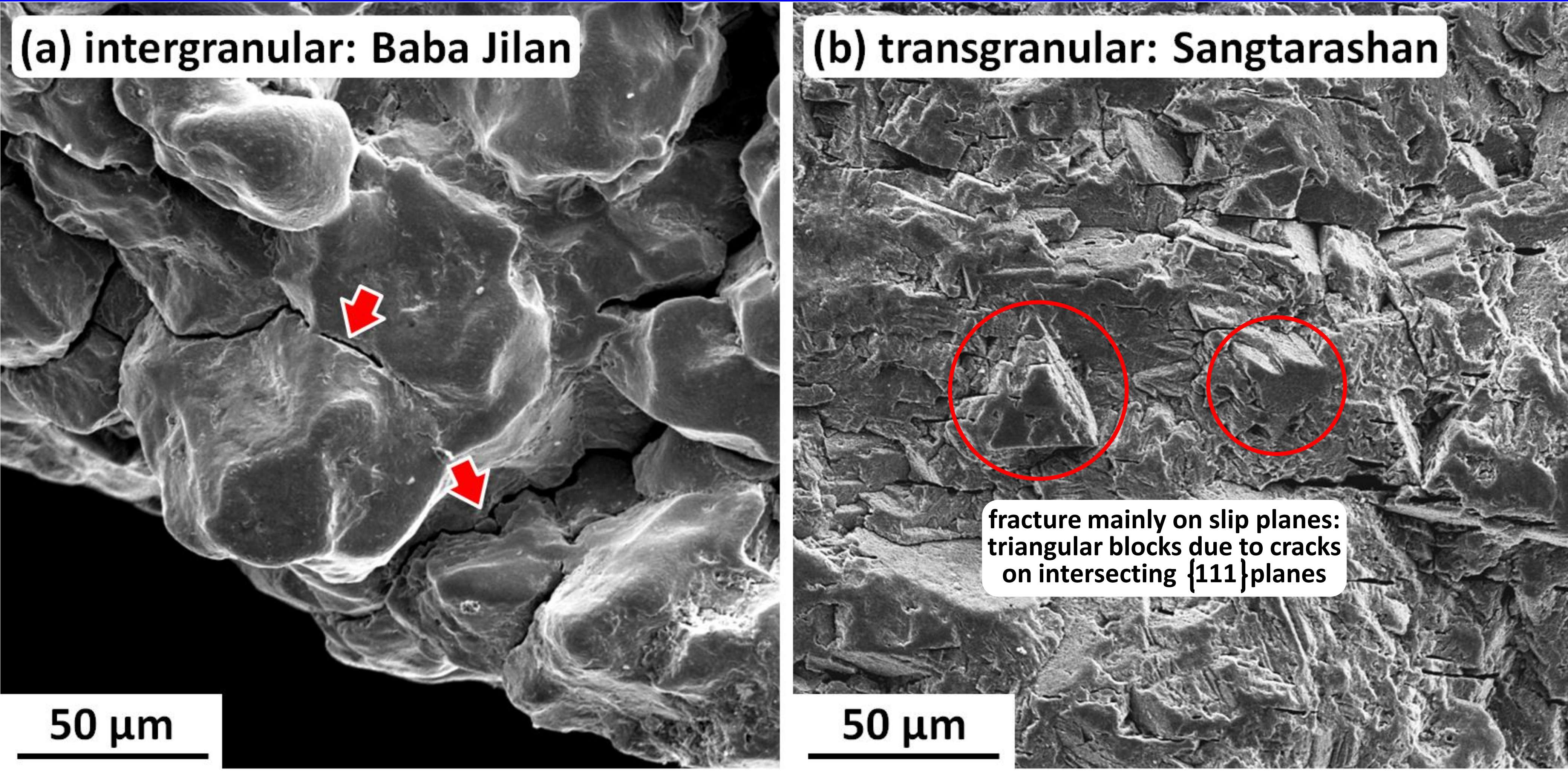


- **Baba Jilan, 8th Century BCE: Cu-10.71wt%Sn-0.42wt%P.**

- **Sangtarashan, 8th-7th Century BCE: Cu-10.97wt%Sn-0.45wt%Cu.**

SCC embrittlement IV: Fractographs from Iranian bronze vessel fragments

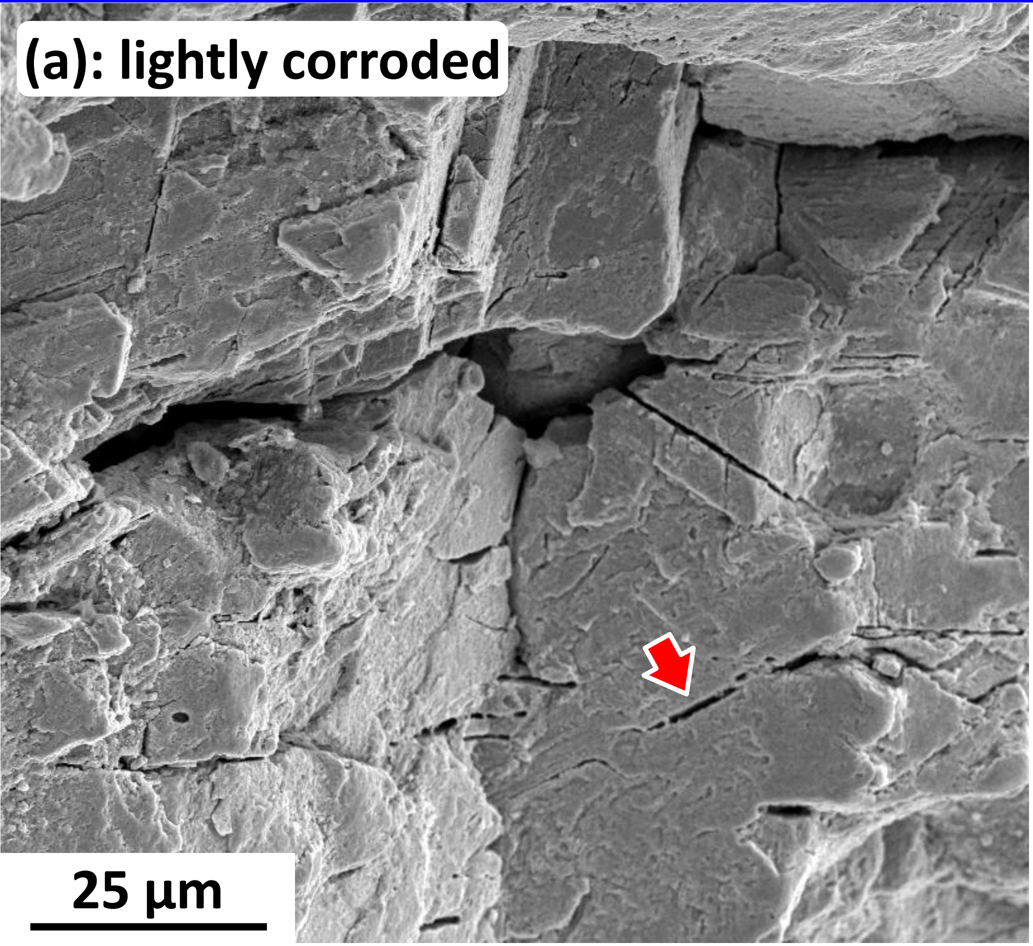
Original images: Omid Oudbashi, Art University of Isfahan, Isfahan, Iran

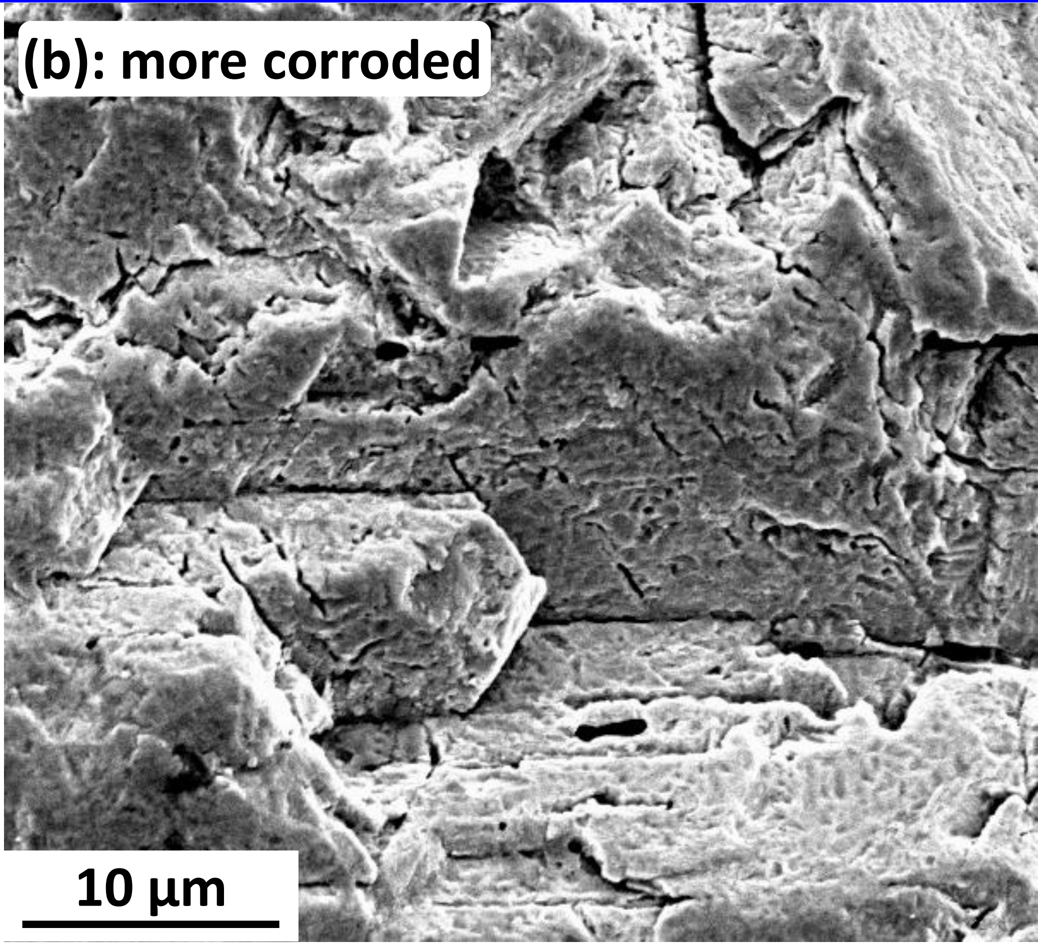


- ⬇ ***Apparently* discontinuous and irregular cracking: corrosion layer effect.**

SCC embrittlement V: Fractographs from Iranian bronze vessel fragments

Original images: Omid Oudbashi, Art University of Isfahan, Isfahan, Iran





- **Transgranular fracture and cracking mainly along slip planes, and SCC initiation by corrosion pitting and pit coalescence (arrowed).**

Case Studies: Wrought Irons

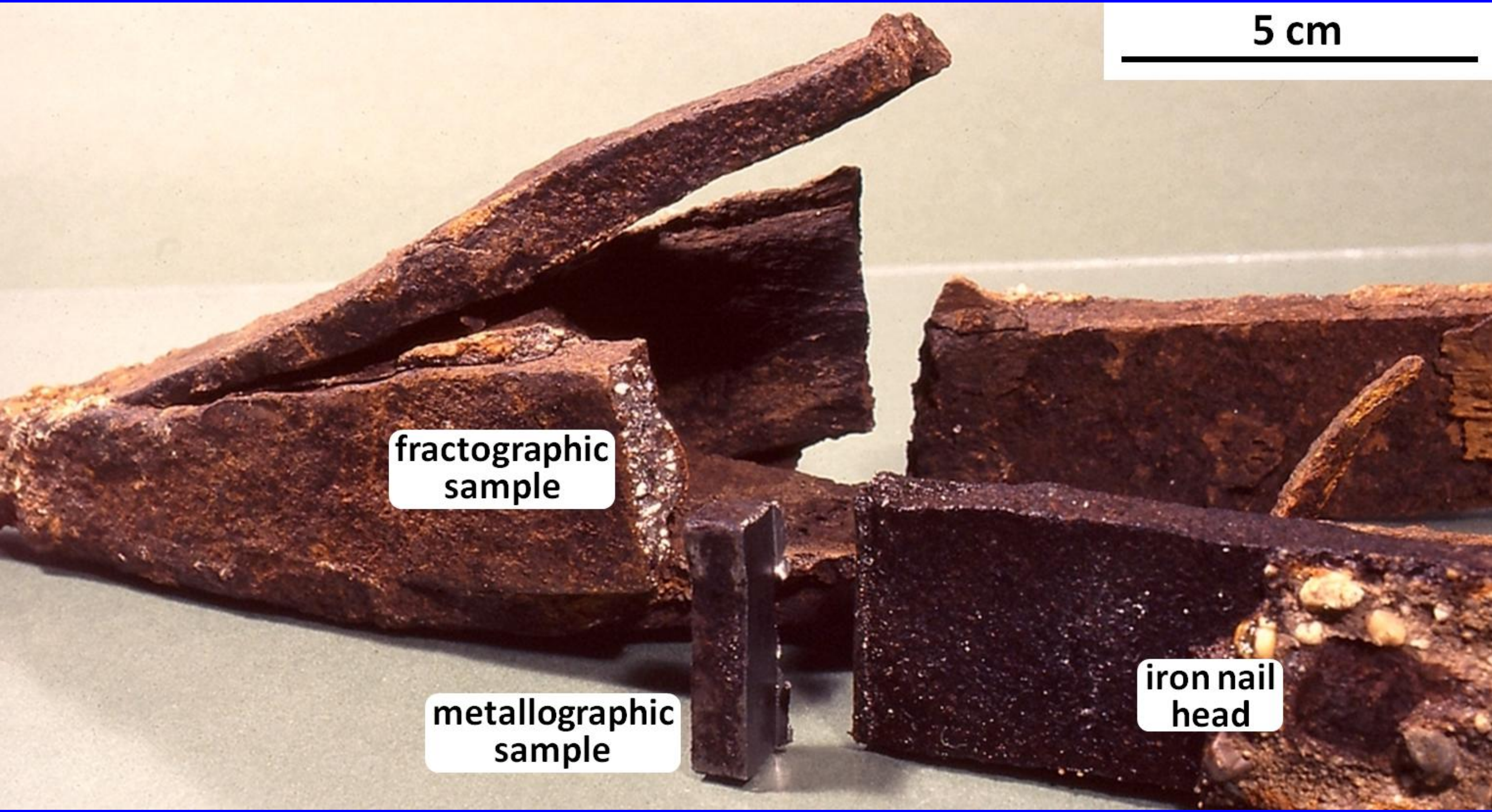
Microstructural embrittlement I: Roman Pile-shoe, 4th Century AD

Original image: Mergor in Mosam Foundation, Haps, The Netherlands

- A few of the Roman bridge oak piles from the Maas river.
- Some of the pile-shoes are still attached.

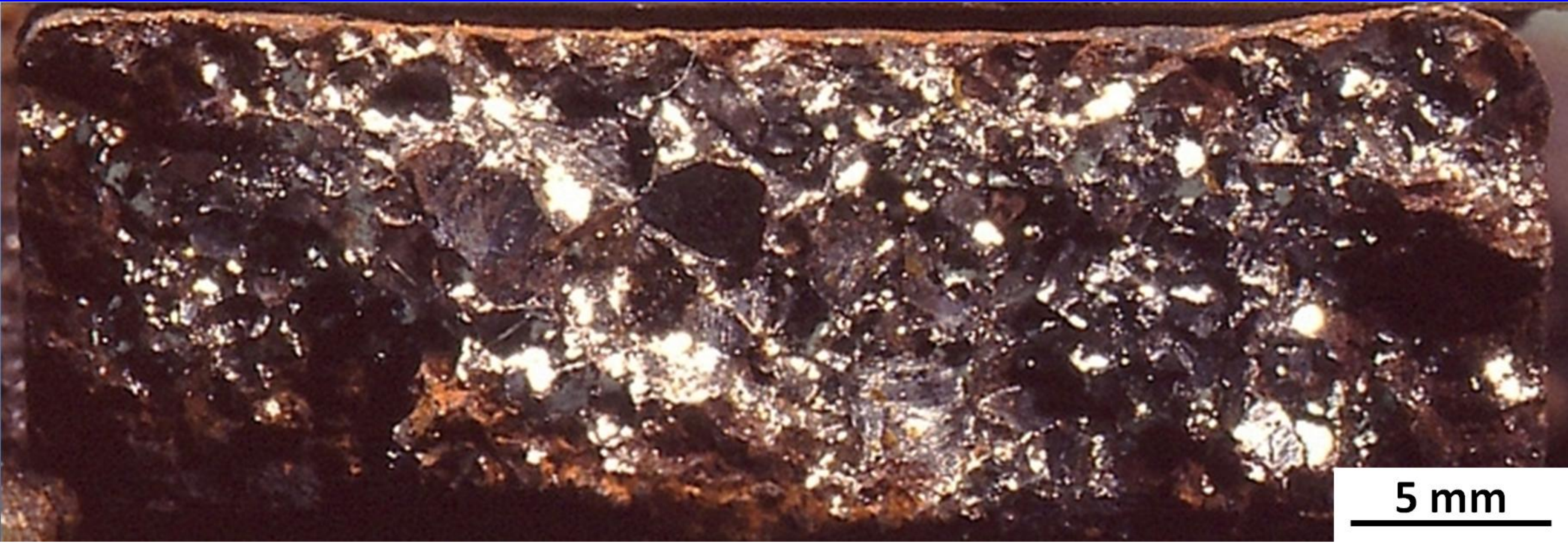
Microstructural embrittlement II: Roman Pile-shoe, 4th Century AD

Original image: Ronny Meijers, Museum Het Valkhof, Nijmegen, The Netherlands



Microstructural embrittlement III: Roman Pile-shoe, 4th Century AD

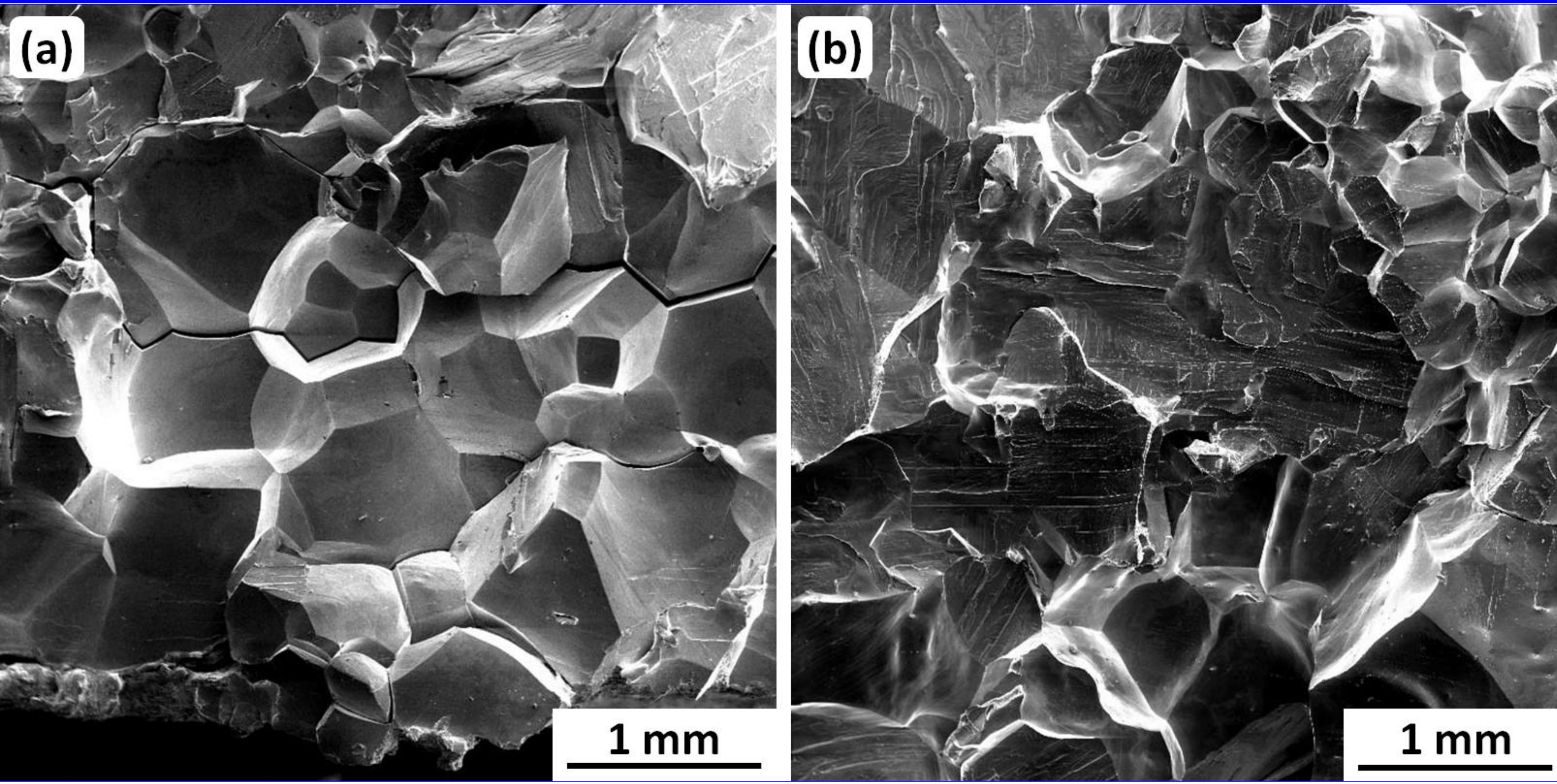
Original image: Ronny Meijers, Museum Het Valkhof, Nijmegen, The Netherlands



- **Macrofractograph of a 'recent' impact fracture of one of the pile-shoe iron bars. Note (i) the brittleness, with internal fracture consisting of shiny uncorroded facets, some nearly 3 mm in diameter, and (ii) the non-uniform corroded surface layer mainly less than 0.5 mm thick.**

Microstructural embrittlement IV: Roman Pile-shoe, 4^{th} Century AD

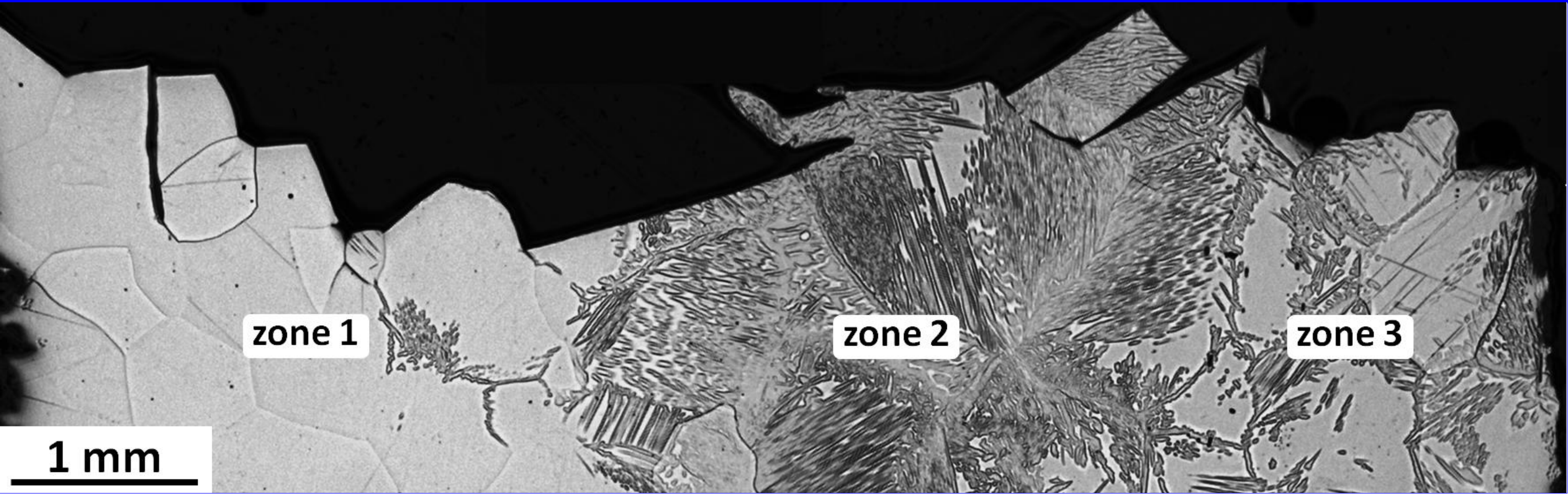
Original image: NLR, Marknesse, The Netherlands



- Brittle fracture: (a) Near-surface: intergranular; (b) interior: intergranular + cleavage.

Microstructural embrittlement V: Roman Pile-shoe, 4th Century AD

Original image: NLR, Marknesse, The Netherlands



- Metallograph, nital etch, of a cross-section of the pile-shoe bar, including the opposite fracture surface to that shown in slide 25. The three zones are from strips of iron welded together. The microstructure consists of large ferrite grains, some deformation twinning close to the outside surfaces (zones 1 and 3), and an unusual etching effect especially in zone 2. This effect is due to phosphorus segregation and occurs in ancient phosphoric iron.

Microstructural embrittlement VI: Roman Pile-shoe, 4th Century AD

- **Chemical analyses of broken bar**
  - phosphoric iron (0.25–0.52 wt.% P) with very low Si, Mn and S content, and extremely low C content (0.0033 wt.%) at the breakage location
  - corroded layer was akaganeite formed after recovery of the pile-shoe
  - composition suggests bloomery iron, obtained from smelting local bog iron ores containing P

- **Damage assessment**
  - large grain sizes suggest low C content was due to final decarburisation
  - low C content enabled high-temperature intergranular segregation of P, resulting in an ambient temperature susceptibility to impact fracture

NOTE: Brittleness obviously not manifested during pile-shoe fabrication and attachment to the pile. The most probable reason is that impact forces were not applied directly to the pile-shoe, since it was attached via iron nails. Also there would not be a possible notch effect due to corrosion.

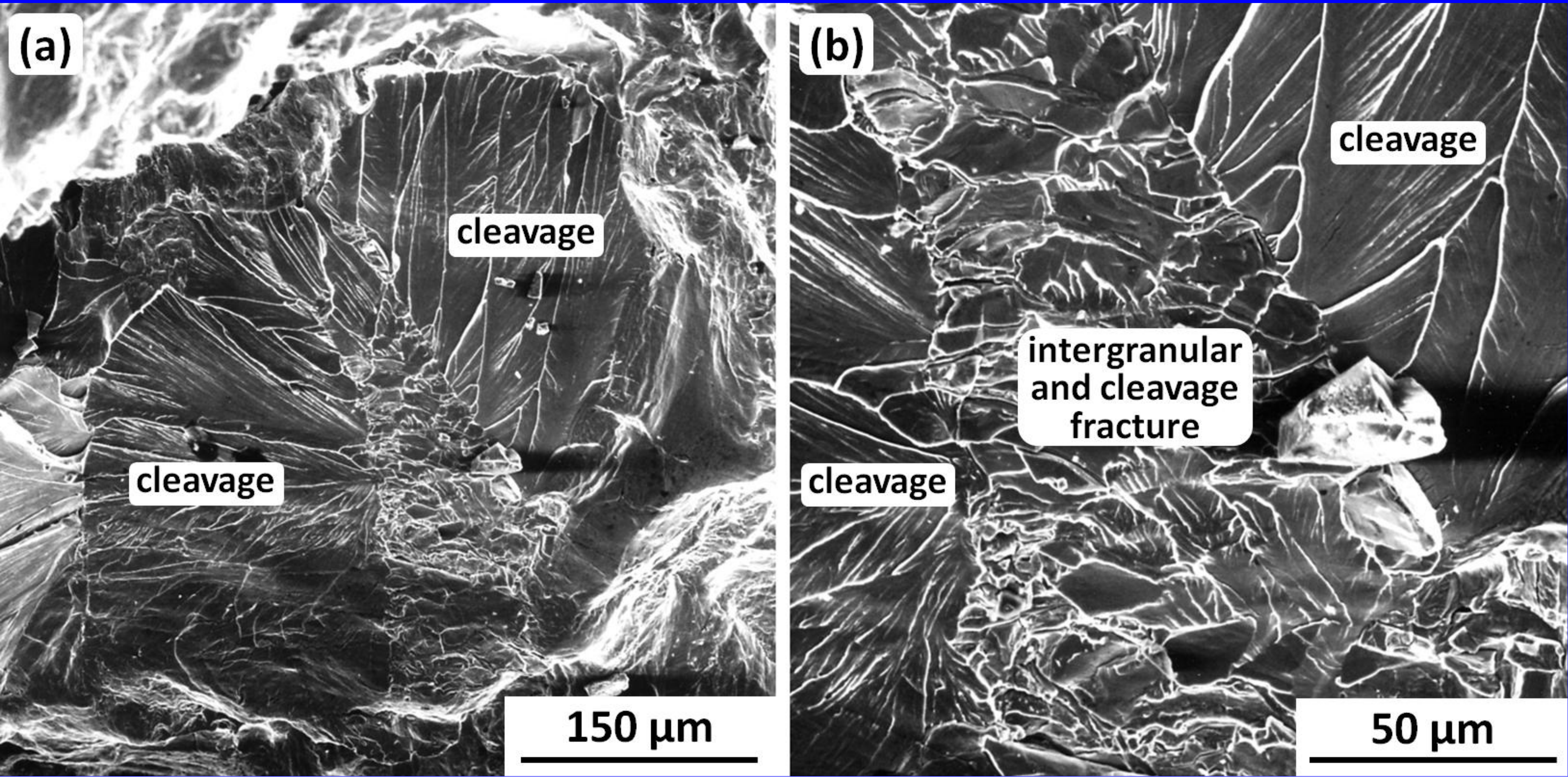
Brittle fracture I: Japanese Zunari Kabuto, 17th Century AD

Original image: George Vander Voort, Wadsworth, IL 60083-9293, USA

- This is a five-plate Samurai helmet.
- The arrow shows a damaged area on the brim plate.

Brittle fracture II: Japanese Zunari Kabuto, 17th Century AD

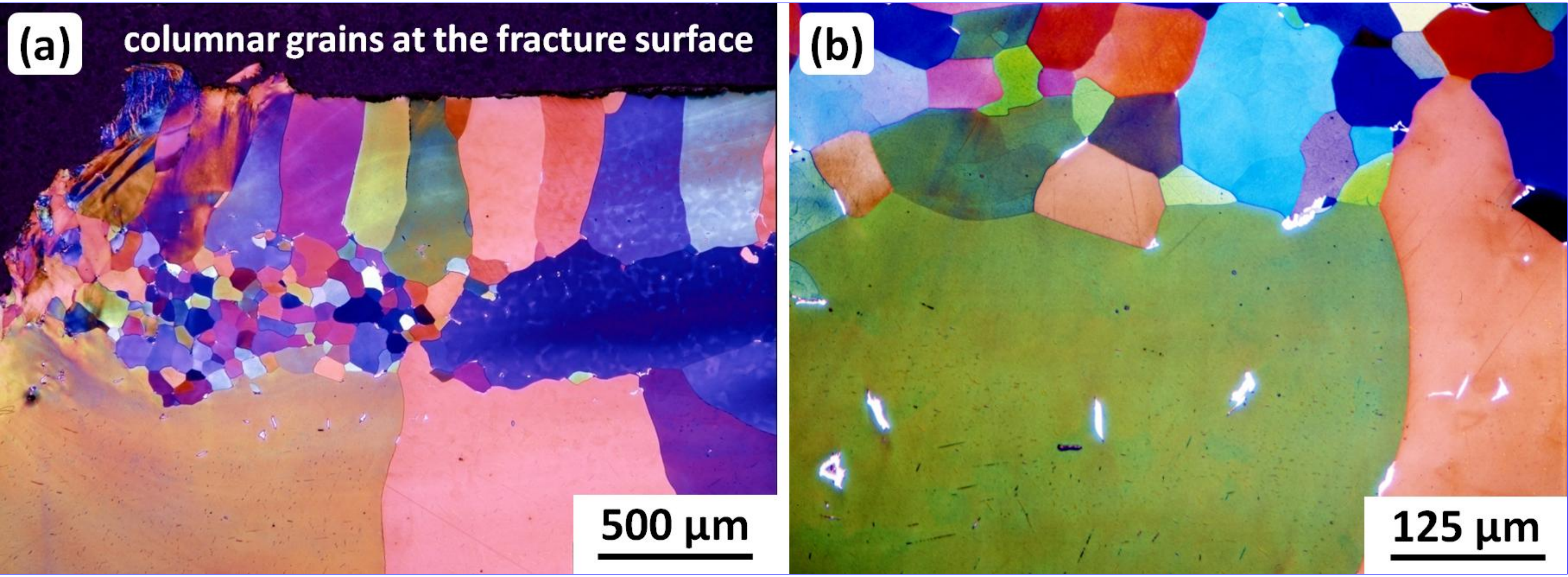
Original images: George Vander Voort, Wadsworth, IL 60083-9293, USA



- **Brittle fracture: cleavage of coarse grains and intergranular + cleavage fracture of fine grains.**

Brittle fracture III: Japanese Zunari Kabuto, 17th Century AD

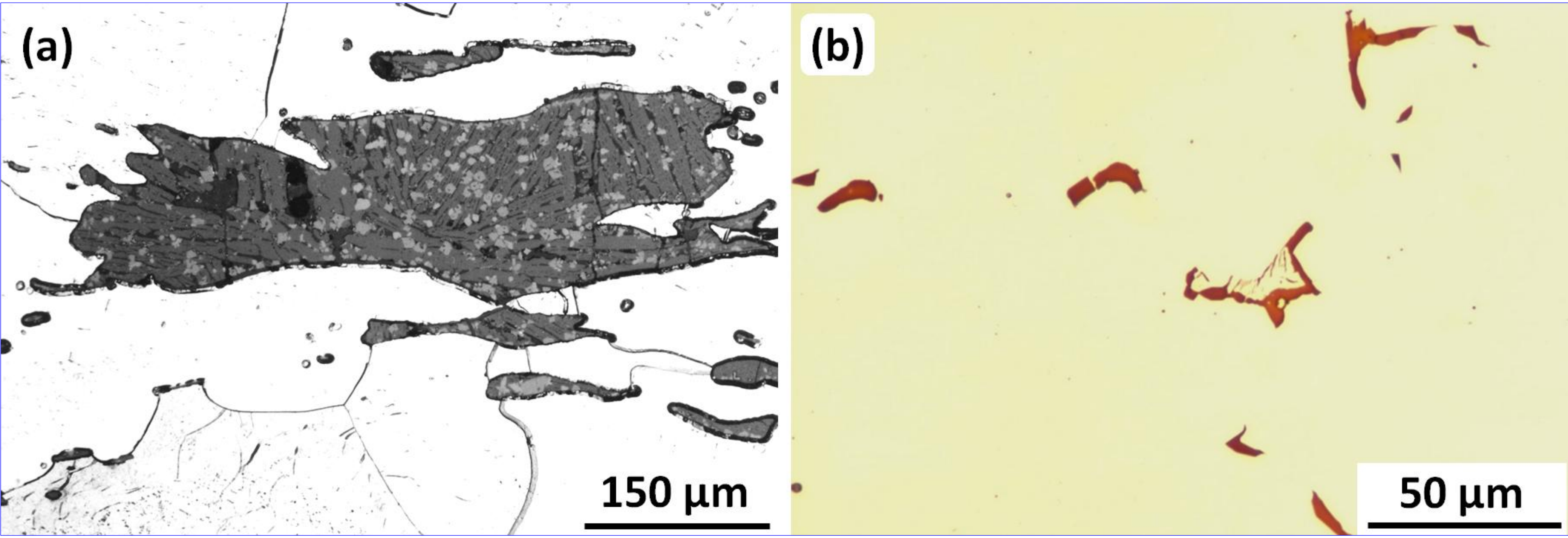
Original images: George Vander Voort, Wadsworth, IL 60083-9293, USA



- **Metallographs, Klemm's etch, showing (a) columnar grains at the fracture surface and a duplex grain structure; and (b) carbide precipitates at grain boundaries and also within some of the grains. Note: (b) is a detail of (a).**

Brittle fracture IV: Japanese Zunari Kabuto, 17th Century AD

Original images: George Vander Voort, Wadsworth, IL 60083-9293, USA



- Metallographs showing (a) coarse slag, nital etch; and (b) grain boundary cementite (Fe_3C) films, alkaline sodium picrate etch.

Brittle fracture V: Japanese Zunari Kabuto, 17th Century AD

Original images: George Vander Voort, Wadsworth, IL 60083-9293, USA

- **Chemical analyses of Kabuto :** ***not available***
- **Damage assessment**
  - **evident that at least part of the helmet is susceptible to brittle fracture**
  - **no further conclusions are possible without the chemical analyses**

Restoration and Conservation of Corroded and Embrittled Artifacts

Introduction: ethical and technical considerations

- Restorations and conservation are concerned with both ethical and technical aspects
  - an artifact's integrity, meaning *veracity*, should be respected
  - remedial measures should be *reversible* (as much as possible)
- 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 and must be carefully considered for each artifact
- Detailed technical guidelines differ, depending on
  - the classes of metals and alloys
  - a particular artifact's condition

Ancient Gold Alloys

Original images: Mikkel Storch-Christiansen, Copenhagen, Denmark; Fries Museum, Leeuwarden, The Netherlands

- **High-karat gold requires no treatment for corrosion. But an *easily* removable coating could be applied to stabilize wide cracks and fractures of microstructurally-embrittled artifacts, e.g. the gold ring.**

- **Low-to-medium karat gold, if embrittled by SCC, could have removable coatings for long-term conservation, e.g. the Runic coin.**

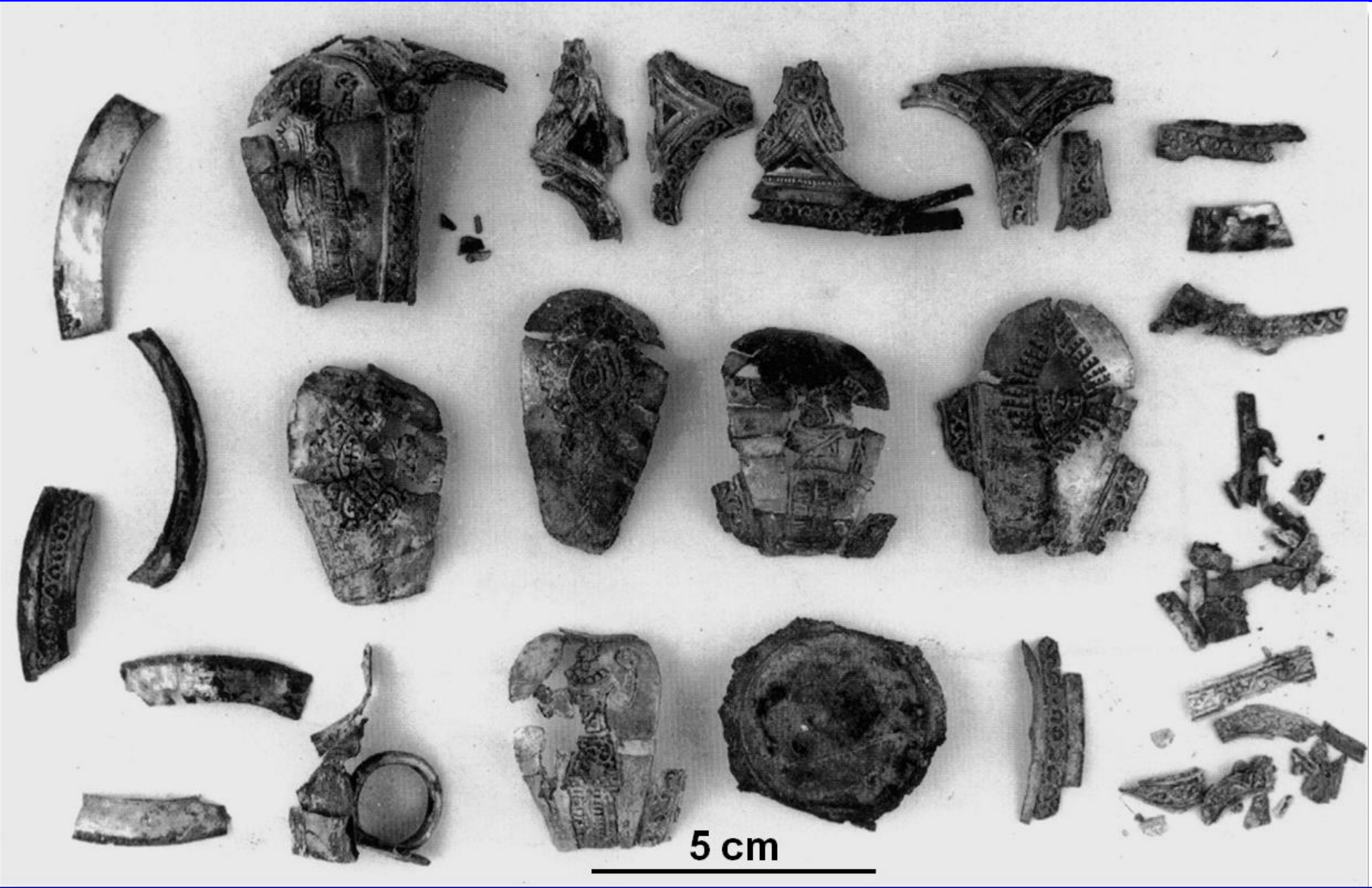
Ancient Silver Alloys I:

- **High-silver alloy embrittled artifacts present a number of issues**
  - **they can be very fragile**
  - **cause(s) of embrittlement should be determined**
  - **coatings should be considered for conservation**
  - **the best or only treatments may be nonreversible**

- **An outstanding example of restoration, making *some* treatment stages reversible is the famous Khan Cup, shown before and after restoration in the next two slides. Restoration enabled the Cup's aesthetic appreciation and showed how it had been made**

Ancient Silver Alloys II: Khan Cup before restoration

Original image: Gerhard Stawinoga, Archaeological Landesmuseum, Schleswig, Germany



Ancient Silver Alloys III: Khan Cup after restoration

Original image: Gerhard Stawinoga, Archaeological Landesmuseum, Schleswig, Germany

Ancient Silver Alloys IV: Khan Cup restoration

- 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
  - *partial assembly*: the fragments were fixed using strips of adhesive tape (Tesapack)
  - *full assembly*: joining under stress using wooden clamps: this required 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 B72, a clear non-yellowing lacquer removable with acetone and toluene
- Final coating of the restored Cup with Paraloid B72 dissolved in toluene

Ancient Bronze Alloys I:

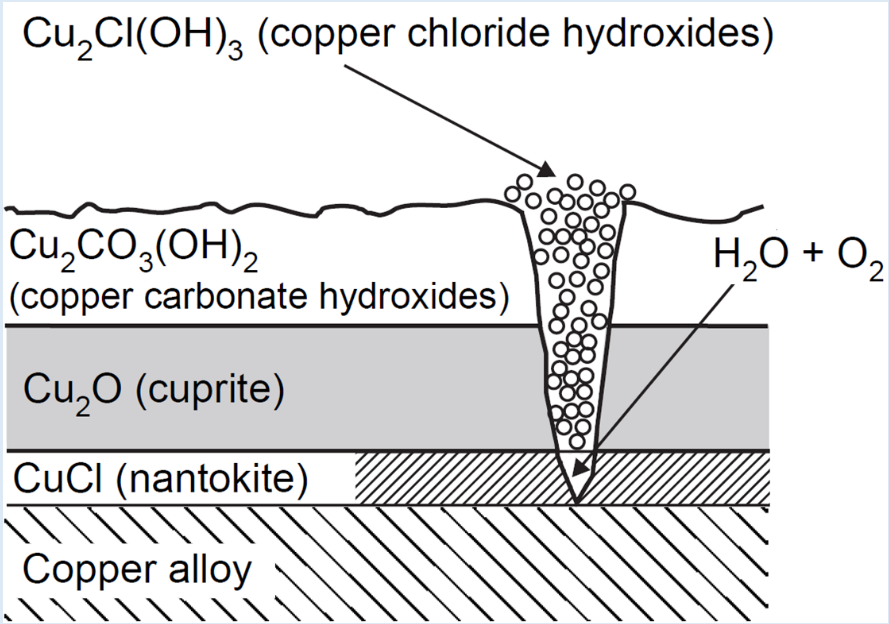
- The major problem for ancient bronzes and other copper-based alloys is corrosion, which can result in fragility, breakages and even complete destruction of artifacts
  - a particularly damaging type of corrosion is ‘Bronze Disease’
  - note that corrosion destroys evidence of SCC, see slide 18
- A large variety of corrosion products occur, some of which form attractive patinas that will have to be preserved by conservators
- The conservation procedures for the short- and long-terms are summarised in the next two slides

Ancient Bronze Alloys II:
Summary of Short-term Conservation Procedures

- **Initial cleaning**
  - **patina preservation: use extended washing in water or sodium sesquicarbonate, $Na_3H(CO_3)_2$**
  - ***careful* mechanical cleaning, rinsing in water: *or* chemical solution immersion to remove all encrustations**
- **Treatments for 'Bronze Disease' when artifacts are contaminated by chlorides: nantokite is the active culprit. The favoured method(s) are to treat with an ethanol solution of benzotriazole (BTA), either in an ambient air environment or under vacuum, followed by drying using acetone or an alcohol**
- **Coating with an acrylic lacquer (e.g. B48 or B72): use microcrystalline wax as a popular alternative**

N.B: Repairs can be made with acrylic-based adhesives, since these are removable

'Bronze Disease'



Ancient Bronze Alloys III:
Summary of Long-term Conservation Procedures

- **Establish relative humidity (R.H.) recording systems for the artifact storage rooms and also museum environments**
- **Install portable dehumidifier equipment in storage rooms, with temperature and humidity controls to keep the R.H. below 50% over a wide range of ambient temperatures. *This will prevent active corrosion***
- **Use desiccants, e.g. silica gel, in display cases, since the display areas do not usually have controlled environments**
- **Organise and set up periodic monitoring systems for the collections in order to check on the artifacts' conditions**

Ancient Ferrous Alloys (Mainly Wrought Irons) I:

- **The major problem for ancient ferrous alloys is corrosion, of which two kinds are very destructive and involve chlorides**
  - **akaganeite formation: this red-brown solid iron hydroxide oxide forms on exposed metal surfaces and indicates *active* corrosion**
  - **'weeping': an acid regeneration cycle resulting in (i) formation of solid iron hydroxide oxides, also including akaganeite, within or below the surface corrosion layer; (ii) cracks and spalling and easier access for oxygen and moisture to continue the corrosion**
- **The conservation procedures for the short- and long-terms are summarised in the next two slides**

NOTE: **The surface layer on the broken Roman pile-shoe was akaganeite.**

Ancient Ferrous Alloys (Mainly Wrought Irons) II:
Summary of Short-term Conservation Procedures

- **Cleaning**
  - **mechanical cleaning with small hand tools or power tools; rinsing in water**
  - **removal of chloride contamination (*very important*) using (i) several baths of hot (60°C) alkaline solutions, e.g. sodium hydroxide and sodium sulphite; (ii) rinsing in distilled water; (ii) a final soaking in aqueous barium hydroxide**
  - **drying with the aid of a water-miscible solvent such as acetone or ethanol**
- **Coating with an acrylic lacquer (e.g. B48 or B72) or microcrystalline wax**

N.B: Repairs can be made with acrylic-based adhesives, since they are removable

Ancient Ferrous Alloys (Mainly Wrought Irons) III:
Summary of Long-term Conservation Procedures

- **Establish relative humidity (R.H.) recording systems for the artifact storage rooms and also museum environments**
- **Install portable dehumidifier equipment in storage rooms, with temperature and humidity controls to keep the R.H. below 50% over a wide range of ambient temperatures.** ***This will prevent active corrosion***
- **Use desiccants, e.g. silica gel, in display cases, since the display areas do not usually have controlled environments**
- **Organise and set up periodic monitoring systems for the collections in order to check on the artifacts' conditions**

Coatings for Preservation and Conservation I:
Requirements and Available Types

- **Coating requirements (ideal)**
  - 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

- **Coating types**
  - acrylic resins
  - aliphatic polyurethanes
  - cellulose nitrate

  } liquid phase application

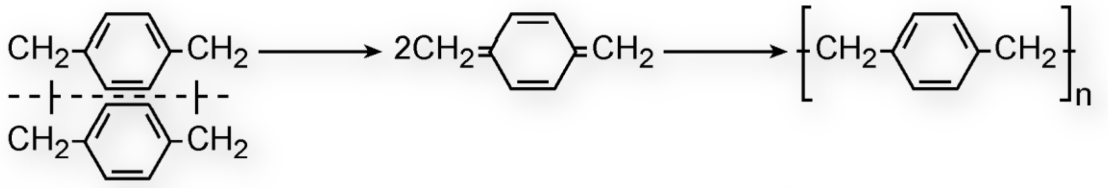
  - parylenes — vapour phase application
  - microcrystalline wax — solid phase application

Coatings for preservation and conservation II: Choices and Pros and Cons

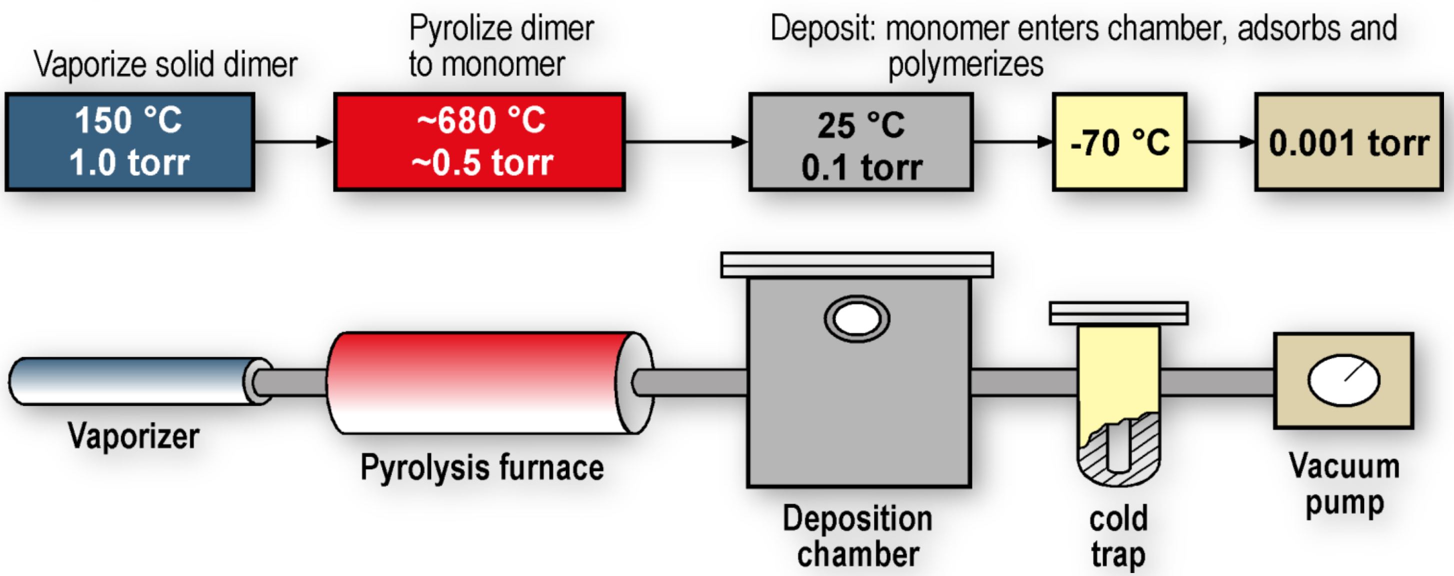
Coating type	Application conditions	Pros	Cons
• acrylics • polyurethanes • cellulose nitrate • wax	• liquid phase except wax and • normal air environment	• removable with some difficulty (most probably unfeasible for severely cracked objects)	• thickness variations, possible pinholes • poor crevice/crack 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, *next slide*

N.B: Coatings research continues, and several types are suitable. These include Poligen, Incralac (acrylic polymer + corrosion inhibitor), carboxylates, nanostructured films, and eco-friendly and non-hazardous coatings based on silanes and fluoropolymers.

Coatings for preservation and conservation III:
Parylene Deposition Process and Equipment



Di-para-xylylene (Dimer) | **para-xylylene** (Monomer) | **Poly-(para-xylylene)** (Polymer)



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

Summary

- Fractography is a useful *adjunct* to Metallography for damage assessment
  - enables distinguishing between microstructurally-induced, corrosion-induced, and SCC embrittlement in gold alloys and high-silver alloys
  - can assist in identifying the source of embrittlement in wrought irons
- Fractography can improve the approaches to restoration and conservation
  - restoration procedures, including any repairs and choices of coatings
  - an example is the Roman Kantharos, see slide 11, which was probably better impregnated with a parylene than an epoxy resin, since this did not appear able to seal many of the internal cracks

Acknowledgements

We thank many colleagues and institutions for information and assistance:

Pavel Bartuška, Co Dalemans, Jiří Děd, Ata Hasanpour, Tim Hattenberg, Roel Jansen, Ineke Joosten, Ron Leenheer, Ronny Meijers, Reza Naseri, Arjan Rijkenberg, Peter Seinen, Atefeh Shekofteh, Gerhard Stawinoga, Mikkel Storch-Christiansen, George Vander Voort, Jarka Vaníčková; Corus Research and Technology, The Fries Museum, Mergor in Mosam, Museum het Valkhof, National Museum of Iran, Falak-ol-Aflak Museum of Khorramabad, Royal Netherlands Aerospace Centre.