Evaluation of corrosion potential measurements as a means to monitor the storage and stabilization processes of archaeological copper-based artifacts

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overview

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• aim
• strategy
• results and discussion
copper-tin alloy
copper-tin-lead alloy
• conclusions
• future work
introduction

archaeological copper artefacts recovered from wet saline environments corrode at accelerated rate in oxygen-rich air

storage in a solution:
- tap water or sodium sesquicarbonate

however, results often show a certain instability of the artefacts (e.g. Chemical transformation or development of active corrosion)

monitoring the treatment remains necessary
present monitoring method:

• analysis of the chloride concentration in solution
  – change of solution when predetermined value is exceeded
  – repetition until value low enough

• disadvantages
  – indirect monitoring method
  – which chloride concentration is “low enough”?
  – no idea of potential side reactions
aim of this work

- investigate the use of **corrosion potential measurements** \( (E_{corr}) \) to monitor the behaviour of copper based alloys during their storage and stabilization processes

- benefits
  - simple tool
  - inexpensive to conservators
  - direct monitoring method of the metal surface
  - more complete reaction profile when combined with the analysis of the solution
$E_{\text{corr}}$ measurements

- measure the corrosion potential of the metal object against a stable reference electrode using a potentiostat

- potential depends on:
  - the solution (known)
  - the metal (composition)
  - interface metal - solution
    - corrosion products
    - coatings
strategy

1. corrosion simulation
   - artificial preparation of different corrosion products,
     single as well as multilayer patinas
   - pure copper, bronze, leaded bronze

2. surface characterization
   - visual, voltammetry, synchrotron radiation X-ray diffraction

3. corrosion potential measurements
   - 1% sodium sesquicarbonate solution (Na$_2$CO$_3$.NaHCO$_3$)

4. surface characterization
   - visual, voltammetry, synchrotron radiation X-ray diffraction
strategy

• **electrodes:**
  - reference materials with known and uniform composition †
    - copper
    - **copper-tin alloy**
    - **copper-tin-lead alloy**

• **corrosion protocols**

  [Images of various corrosion products]
  
  cuprite *  
  Cu$_2$O

  nantokite °  
  CuCl

  atacamite °  
  Cu$_2$(OH)$_3$Cl

  atacamite and paratacamite °  
  Cu$_2$(OH)$_3$Cl

  chalcocite °  
  Cu$_2$S

  brochantite  
  Cu$_4$(SO$_4$)(OH)$_6$


results and discussion

• main corrosion product = desired corrosion product

• $E_{\text{corr}}$ depends on:
  
  – the substrate:

  $E_{\text{corr}}$ copper-tin-lead alloy = 20 mV lower than $E_{\text{corr}}$ copper-tin alloy

  – the corrosion products:

  **four types of behaviour**

• SR-XRD after fourteen days immersion
results and discussion

Type 1
- steep rise at the beginning of the immersion, more or less stable potential after a few hours
- uncorroded, cuprite coverage
- XRD: no change in the composition of the corrosion products
- unalloyed copper: same behaviour
results and discussion

Type 2
- similar behavior as type 1, but at higher potentials and the potential slowly descends
- atacamite, chalcocite
- XRD: formation of cuprite, cassiterite and lead carbonates
- unalloyed copper: slow increase in stead of slow descend
results and discussion

Type 3
- steep rise at the beginning of the immersion, through a maximum after 1 to 4 days, progresses to behaviour of cuprite (type 1) afterwards
- nantokite, mixture of atacamite and paratacamite
- XRD: nantokite and atacamite transform into cuprite and malachite
- unalloyed copper: in case of nantokite increase after 6-7 days
results and discussion

Type 4
- strong descend at the beginning of the immersion, more steady descent afterwards (resembles type 2)
- brochantite
- XRD: no change
- unalloyed copper: same behaviour
conclusions

variations of the corrosion potential as function of time mainly depend on the composition of the corrosion layer present

promising and simple technique to monitor variations of the corrosion layers
further research

- use of an in-situ cell for simultaneous performing SR-XRD and electrochemical measurements

- layered corrosion structures