Contribution ID: **37** Type: **Oral**

Detection of Cu-Sn intermetallic compounds on tinned archaeological bronzes using diffraction methods: an evaluation of XRD and TOF-ND methods

Wednesday 11 September 2013 15:00 (20 minutes)

This paper reports results of our systematic investigation of detection of tinning on low tin copper alloy using diffraction methods. Many ancient bronzes are likely to have been tinned in antiquity for their protection or aesthetics. Corrosion of low tin bronze can result in grey, tin-rich surfaces that are deceptively similar to tinning, which makes tinning difficult to identify on archaeological bronzes. During tinning, silver-colour Cu-Sn intermetallic compounds of characteristic composition are formed; their presence on low tin bronzes is evidence of tinning. Current methodology relies strongly on examination of cross-sectioned sampled using scanning electron microscopy and composition analyses. Corrosion can change the characteristic composition of intermetallics; taking a representative sample from an archaeological object is equally challenging. XRD and time-of-flight neutron diffraction offer the opportunity for non-destructive identification of tinned archaeological bronzes. To further understanding of how best to identify tinning on corroded bronzes using diffraction methods, model tinned copper analogues were prepared to establish limitations of detection of Cu-Sn intermetallics. Results showed that XRD as a surface technique has an advantage over TOF-ND. Rietveld analysis of the TOF-ND data showed a great sensitivity of TOF-ND to detect the δ-phase and ε-Cu3Sn depending on the thickness of the metal coating and its volume fraction but was unsuccessful in detecting η-Cu6Sn5. Considering these limitations, neutron diffraction can be a useful non-destructive diffraction method for analysis of archaeological tinned bronzes.

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Session Classification: Scattering Methods II

Track Classification: NINMACH