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PAUL MARDIKIAN
CLAUDIA CHEMELLO
CHRISTOPHER WATTERS
PETER HULL

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HOT-TINNING OF LOW TIN BRONZES

Panagiota Manti*, David Watkinson

Department of Archaeology and Conservation
Cardiff University, Colum Drive
Cardiff, CF10 3EU, United Kingdom

Abstract

Identification of hot-tinning on corroded bronze is often a challenging task due to the various mechanisms by which shiny or grey surface finishes can be formed. The nature of intermetallic compounds formed during hot-tinning changes during use because of solid state diffusion of copper, or due to application of heat at temperatures above the melting point of tin. To identify their presence, a clear understanding of tinning microstructures must be combined with knowledge of their forms relative to corrosion structures developed from general corrosion of the underlying bronze. This study reports on the examination and identification of the intermetallic phases associated with tinning. Reported experimental work is designed to examine aspects of the formation and detection of intermetallic compounds that can be used to discuss the challenges associated with definitive identification of tinning on low-tin bronzes.

Keywords: Hot-tinning, low-tin bronzes, intermetallic phases, room temperature diffusion, X-ray diffraction

Introduction

Studies suggest that various tinning methods were used in antiquity to confer a silver color finish on copper alloys. Apart from work by Meeks (1986, 1993 a,b), there are only few published analyses of tinned archaeological bronzes in Europe. Scientific examinations focus on the presence of black or silver colored surfaces on high tin Chinese bronzes (Shoukang and Tangkun 1993), low and high tin Roman and Chinese mirrors (Meeks 1993b, 1993a), Bronze Age axes (Kinnes et al. 1979, Tylecote 1985) and various small objects reported to be dip-tinned (Oddy and Bimson 1985). Analysis often omits information on body composition and microstructure, or relies on scanning electron microscopy (SEM), backscattered electron (BSE) imaging and elemental mapping with little supporting diffraction analysis of phases. It may be significant that publications identifying hot tinning of bronze seem to report its occurrence on cast objects, yet tinning of worked bronzes is expected to have been extensively applied in antiquity. Is this because the production technology and the preservation mechanisms of tinning on worked bronzes influence the survival of evidence for tinning? More needs to be known about the preservation of tinning and its various corrosion paths.

While Meeks’s experimental work (1986) reports extensive microstructural evidence that could be employed to identify tinning methods, this now needs to be viewed in association with current knowledge of copper/tin (Cu/Sn) interactions to better understand what constitutes evidence of tinning. Consequently, this study reports examination and identification of the phases associated with tinning, and it forms part of an ongoing investigation to further understand the formation, preservation and detection of tinning layers. Experimental tinning is used to establish the phases present and determine the efficacy of detection methods. This data is then used to examine corroded archaeological bronze microstructures, followed by a brief discussion of current hypotheses and scientific evidence on their identification.

‘Tinned’ surfaces on low tin archaeological bronzes

How is tinning defined and identified? Silvery or grey surfaces on archaeological bronzes appear deceptively similar to tinning or silvering and occur either intentionally or unintentionally during manufacture or corrosion (Meeks 1986). ‘Tinned’ surfaces with high relative tin concentration can be achieved in various ways that produce different microstructural evidence (Meeks 1986, Meeks 1993b).

In Europe, hot-tinning of low-tin bronzes is documented in the literature since Roman times (Oddy 1980). The two common methods of hot-tinning flux the object with resin, followed by wiping tin over the surface over an open fire at a temperature above the melting point of tin (232°C), or immersion in a tin bath. The latter is unlikely to have been practiced on large objects, because of uneconomic use of tin and copper contamination of the tin bath (Meeks 1993b).
Tinning at elevated temperatures involves diffusion at the tin/bronze interface to produce intermetallic compounds (IMCs), typically with a $\text{Cu}_3\text{Sn}|\text{Cu}_6\text{Sn}_5|\text{Sn}$ profile according to the Cu/Sn equilibrium phase diagram. Compositional variations at the interfaces of the IMCs are reported (Lee and Duh 1999). At equilibrium conditions, epsilon ($\varepsilon$-$\text{Cu}_3\text{Sn}$, 37.74–39.50 wt%Sn) and the low temperature transformation of eta ($\eta$-$\text{Cu}_6\text{Sn}_5$, 61 wt%Sn) are stable at room temperature. However, the high temperature eta ($\eta'$-$\text{Cu}_6\text{Sn}_5$, 61 wt%Sn) is also reported at room temperature because cooling following tinning can be too quick for it to transform into eta' (Laurila et al. 2005). The presence of epsilon and/or eta (or eta') is considered evidence of hot-tinning on archaeological bronzes (Meeks 1986). Interestingly, research has shown that eta' can form and grow linearly at temperatures below 60°C due to solid state diffusion of copper atoms into tin at the Cu/Sn interface, whereas epsilon only starts appearing above 60°C (Tu 1973). Aging of eta at room temperature turns it into eta' (Wang et al. 2009). Using compositional analysis for the detection of epsilon and/or eta' can be problematic because similar composition ranges are found on surface corrosion of archaeological low-tin bronzes (Oddy 1980, Scott 1985, Robbiola et al. 1998). Also, visual errors can occur because corroded homogenised low-tin bronzes and corrosion of alpha-bronze in the alpha+delta eutectoid of cast low-tin bronzes can produce a metallic grey colour that looks deceptively like tinning (Oddy and Meeks 1982).

The following experimental work is designed to examine aspects of IMC formation and detection that can be used to discuss the challenges associated with definitive identification of tinning on low-tin bronzes.

**Experimental**

**Tinning replication and analysed archaeological objects**

Copper tokens (99.9 wt% Cu, 3.25mm thick) were tinned using a wiping procedure based on practical observation and an interview with a modern tinsmith (Mr Panagiotis). Following cleaning (50wt% hydrochloric acid, HCl), the tokens were individually heated over a Bunsen burner, then fluxed with rosin just before a tin wire (99.75 wt% Sn) was passed over the surface and wiped across it with cotton pads.

Thermal aging experiments above tin’s melting temperature (reflow experiments) were designed to examine the influence of temperature on the intermetallic compounds that formed from tinning. This offers insight into IMC microstructural changes as a result of heat treatment.
of applied heat during use in antiquity, such as cooking. Reflow temperatures of 250°C, 350°C, 450°C and 550°C were applied in an electric furnace on two different sample sets of tinned copper tokens for 5 minutes and 60 minutes.

Objects with visual and archaeological evidence of tinning were analysed for comparison. These included two Roman cast bronze skillets with evidence of a wrought microstructure in the bowl area, a cast, tinned, decorated bronze harness fitting, and a hammered Archaic Greek helmet (see Figure 1). Apart from the helmet, all objects contained small amounts of lead in the low-tin bronze alloy.

**Instrumental analyses**

All samples were examined using polarised light microscopy, SEM with secondary and backscattered electron imaging (SEM-SEI and SEM-BSE), in top view prior to mounting and in cross section after mounting in epoxy resin. Intermetallic phases on replica samples were revealed by dissolving excess surface tin using 5% aqueous HCl (Gagliano and Fine 2001). Compositional analysis employed a CamScan 2040 SEM (20 kV with 120x96µm spot area) with an Oxford Link Pentafet 5518 Dispersive X-ray spectrometer and Isis 300 software. The spectrometer’s super thin atmosphere window (ATW2) permits X-ray detection of light elements (Z>4). Calibration involved pure elements, mineral and bronze standards (No. 4629, Micro-Analysis Consultants Ltd). Oxygen calibration used wollastonite (CaSiO₃), and showed 1.85% mean relative error of accuracy and 1% relative precision. Accuracy and precision are reduced when analysing corroded surfaces as micro-roughness is inevitably encountered after polishing due to hardness differences and some loss of material. X-ray diffraction (XRD) was undertaken using an XPERT-PRO PANalytical diffractometer. Flat samples were analysed in situ on a fixed stage with divergent beam footprint of 100 or 200mm² for 20-60 minutes acquisition time depending on sample. Data was analysed with XPert HighScore V2.1.2 using the PDF-02 database.

**Results and Discussion**

*Experimental tinning*

Thickness of the tin layers varied according to the amount of tin used and the dexterity and skill of the person applying it, which directly affected the type and thickness of microstructures observed in cross section (see Figure 2 a,b). SEM-BSE imaging of polished cross section profiles shows the presence of Cu/Cu₆Sn₅/Sn for as-tinned samples (see Figure 2d). XRD confirms the presence of Sn and η-Cu₆Sn₅ (PDF 65-2303) as well as a small amount of ε invisible to microscopic observation (see Figure 2d). During tinning, Cu₆Sn₅ is the first phase to form (Tu 1973). The Cu₆Sn₅ is initially granular (see Figure 2c) but becomes elongated and angular in later stages of annealing (Gagliano and Fine 2001), which can be seen in this experiment at higher annealing temperatures (see Figure 3; S11).
With increasing annealing temperature or time, diffusion phenomena result in further morphological change and growth of Cu₆Sn₅, accompanied with the growth of planar shaped ε-Cu₃Sn at the expense of Cu₅Sn, at the Cu/Cu₅Sn interface (Prakash and Sritharan 2001). Consequently, the presence of ε is cited as evidence for tinning at relatively higher temperatures (Meeks 1993b). An increased amount of ε is visible using BSE imaging for annealing between one hour at 250°C and five minutes at 550°C, and is readily detectable by XRD (PDF 03-065-4653) (see Figure 3, S7, S11-S17). Growth of ε is reported to be parabolic with time and exhibits variable growth rates at different temperatures (Laurila et al. 2005).

Similar phase formation of Cu₅Sn and Cu₃Sn is reported for Sn/Pb alloys, with Cu₅Sn being observed at higher temperatures (290-310°C) for a 27Sn73Pb alloy (Prakash and Sritharan 2001). Therefore, if a Sn/Pb alloy coating applied in antiquity has been lost due to polishing or corrosion, it would leave the same IMCs as those left behind after loss of a pure tin coating; this further complicates interpretation of tinning microstructures.

A small amount of δ-Cu₆Sn₅ (PDF 03-065-7047) is detectable only by XRD after annealing at one hour at 450°C (or 5 min at 550°C) (see Figure 3; S15, S17), with δ in a tin matrix being the only phase at temperatures above that detected with both XRD and BSE imaging (see Figure 3; S19).

Porous tin layers were formed at low aging temperatures/short time period due to the large amount of flux used (see Figure 3 S5, S7). Samples S11-S19 (see Figure 3) show Kirkendall porosity at the Cu₃Sn/Sn interface. Kirkendall porosity is associated with atomic vacancy diffusion phenomena at the Cu/Sn diffusion couple because the diffusion rates of the two species are different (Nakajima 1997). Their nucleation depends on activation temperature and the addition of other elements (Laurila et al. 2005). Although these voids are generally observed at the Cu/Sn interface or in the CuSn-matrix, their formation at the Cu₃Sn/Sn is likely due to the elevated aging temperatures used here or impurities in the flux that increase this effect (Yu and Kim 2008). Kirkendall voids are detrimental to IMC mechanical properties and this causes reliability problems in the electronic industry (Lee and Chen 2002, Yu and Kim 2008). The voids could provide an additional explanation for the mechanical loss of tinning layers, alongside the current hypothesis of wear due to polishing (Meeks 1986). Crude polishing could perhaps lead to loss of the Cu₅Sn, (and Sn) leaving a firm and thin Cu₅Sn layer (1-2µm) on the substrate. Unfortunately, this will resemble compositions observed on corroded surfaces of low tin bronzes (Robbiola et al. 1998). A thin ε-Cu₃Sn layer is very easily missed in SEM-BSE observation unless it is still un-corroded metal, which could be detected by XRD. For example, a substantial ε layer found under an Cu₅Sn layer was identified on mercury tinned samples (Qinglin and Scott, 2003).

Archaeological bronzes

XRD and SEM-BSE detected η-Cu₃Sn on the Brecon Gaer harness fitting (see Figure 4b), whereas Cu₃Sn scallops were visible with BSE on the surface of the Ceredigion skillet (CER) (Figure 4a). No ε-Cu₃Sn was detected in either sample. Energy dispersive X-ray spectroscopy (EDX) elemental mapping of the Brecon Gaer cross section sample showed a complex core microstructure and a lead compound deposited locally on the surface rather than in association with the η (see Figure 4a).

Normalised (Cu+Sn+O=100wt%) EDX multiple spot analyses of Cu₅Sn shows generally reduced Sn wt% and Cu wt% concentration relative to their expected concentrations due to the presence of oxygen (see Table 1). It is likely that composition reflects some oxidation of tin combined with copper dissolution from the η-phase due to corrosion. Corrosion behaviour of the IMCs is unknown. It is often deciphered by comparison to other high-tin phases, such as the preservation of δ in the α+δ eutectoid bronzes (Tylecote 1985). However, localised anodes can be formed and copper depletion from the copper-rich center of δ dendrites is reported (Scott 2002). Tin is theoretically anodic to copper and low tin bronze
due to electrode potential differences (Wranglén 1972). Preservation of IMCs can be due to either the Sn/Cu bimetallic corrosion couple, where IMCs are reported to be cathodic to both copper and tin (Hedges 1960), or to the formation of thermodynamically stable tin compounds that delay corrosion rates of the underlying layers (Britton 1952, Turgoose 1985). Published analyses of corroded tin solder report its complete conversion to tin oxides (Piccardo et al. 2007), but with no reference to the presence or corrosion of IMCs. Overall, more work is required to understand the corrosion behaviour of IMCs.

Conventional XRD of a sample from the Manorbier skillet and the helmet comprised mostly malachite deposits and ε or η were not detected. On the helmet sample, the surface microstructures can be characterised as a Type I corrosion structure (Robbiola et al. 1998). The surface of the helmet sample retains polishing marks and is rich in oxygen (30-50wt%) with increased tin (30-60wt%) and reduced copper concentration, fitting a Type I corrosion pattern. Similar composition ranges are detected at the surface of the Manorbier skillet, where surface colour is due to corrosion. In contrast to the Brecon Gaer harness fitting and the Ceredigion skillet where η-Cu₆Sn₅ was detected, the Manorbier and helmet samples exhibited a wrought and annealed microstructure in the core metal. Substrate texture is important for the growth of Cu₆Sn₅ (Wang et al. 2009) during tinning, so it could perhaps be significant for its preservation. Analysis of more samples is underway to examine whether cast or wrought microstructures can somehow influence the preservation of IMCs on low tin bronzes.

<table>
<thead>
<tr>
<th>Object</th>
<th>Position/Phase</th>
<th>Normalised Cu/Sn=O=100 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu₆Sn₅</td>
<td>η Cu Sn</td>
</tr>
<tr>
<td>Ceredigion skillet</td>
<td>Cu₆Sn₅</td>
<td>19.7 31.3 49.1</td>
</tr>
<tr>
<td>Ceredigion skillet</td>
<td>Cu₆Sn₅</td>
<td>8.6 39.8 51.7</td>
</tr>
<tr>
<td>Ceredigion skillet</td>
<td>Cu₆Sn₅</td>
<td>26.6 14.3 59.1</td>
</tr>
<tr>
<td>Ceredigion skillet</td>
<td>Cu₆Sn₅</td>
<td>23.1 18.8 58.1</td>
</tr>
<tr>
<td>Brecon Gear fitting</td>
<td>Cu rich</td>
<td>35.7 55.6 8.7</td>
</tr>
<tr>
<td>Brecon Gear fitting</td>
<td>Deposit</td>
<td>33.3 7.6 59.1</td>
</tr>
<tr>
<td>Brecon Gear fitting</td>
<td>Pb rich inclusion</td>
<td>56.4 11.1 32.5</td>
</tr>
<tr>
<td>Brecon Gear fitting</td>
<td>Cu₆Sn₅</td>
<td>17.0 28.0 55.0</td>
</tr>
<tr>
<td>Manor Bier skillet</td>
<td>Inclusion</td>
<td>2.5 87.8 9.7</td>
</tr>
<tr>
<td>Manor Bier skillet</td>
<td>Outer surface</td>
<td>36.1 31.6 32.3</td>
</tr>
<tr>
<td>Manor Bier skillet</td>
<td>Outer surface</td>
<td>17.1 35.7 47.2</td>
</tr>
<tr>
<td>Manor Bier skillet</td>
<td>Below outer surface</td>
<td>33.7 36.0 30.4</td>
</tr>
<tr>
<td>Helmet</td>
<td>Inner layer</td>
<td>20.5 56.8 22.7</td>
</tr>
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<td>Helmet</td>
<td>Outer surface</td>
<td>30.5 23.3 46.3</td>
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<tr>
<td>Helmet</td>
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<td>25.0 45.9 29.0</td>
</tr>
<tr>
<td>Helmet</td>
<td>Outer surface</td>
<td>19.4 64.0 16.6</td>
</tr>
</tbody>
</table>

Table 1. EDX wt% composition analyses of archaeological samples. Each analysis is the averaged value of 3 spot analyses.

Conclusions

Laboratory experiments showed that η-Cu₆Sn₅ is the major phase formed during hot-tinning, and because of its granular nature it is easy to detect by SEM. Kirkendall voids formed on some samples, and it is suggested that these may contribute to future mechanical detachment of the tinning layers as a whole, or detachment of the Cu₆Sn₅ layer, leaving only planar ε-Cu₆Sn₅ on the surface. Identification of thin ε layers using SEM-BSE or EDX is challenging, even for modern samples, and on corroded archaeological samples it will be very difficult to detect. This study has shown how useful XRD can be to identify evidence of tinning, while SEM analysis is of limited use.

A literature review revealed that the same IMCs are developed during application of Sn/Pb alloy coatings on bronzes. Therefore, where metal layers have been lost, it may be difficult to conclusively link occurrence of η to either tinning or a Sn/Pb coating. This can be further confusing, as analysis of archaeological samples in this paper showed that lead compounds on their surface were due to corrosion of the bulk alloy, rather than application of Sn/Pb coating.

Experimental work confirmed that heating following tinning changes IMC evidence, which means the life use of an object would influence evidence of tinning, with high temperatures eventually diffusing the tin layer into the copper alloy. Additionally, published work demonstrates occurrence of solid state diffusion at the Cu/IMCs/Sn interface at room temperature. Consequently, even prolonged exposure to hot sunlight could potentially change IMC morphology.

The overall lack of evidence for tinning on wrought low tin bronze in the literature is of concern, as it may be a result of detection limitations or corrosion processes.
For instance, our analyses of tinned archaeological samples show that some loss of copper and tin oxidation is possible in Cu$_6$Sn$_5$, but greater understanding of the mechanisms is required. Definitive identification of tinning can be very easy where an uncorroded metal layer remains intact, but will be challenging on heavily corroded bronzes.

**Acknowledgements**

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**Materials**

Elements and mineral standards Block No. 4629
Micro-Analysis Consultants Ltd
19 Edison Road, St. Ives Industrial Estate
St. Ives, Cambridgeshire, PE27 3LF, UK
Tel: (44) 1480 462626 Fax: (44) 1480 462901.
Email: standards@dial.pipex.com
Website: www.macstandards.co.uk

Tin metal 99.75wt%
Copper 99.9 wt% 3.25mm thick, half hard
Goodfellow Ltd
Ermine Business Park
Huntingdon, PE29 6WR, UK
Tel: (44) 1480 424 800 Fax: (44) 1480 424 900
Email: info@goodfellow.com
Web site: www.goodfellow.com

Hydrochloric acid
Rosin (or colophony)
Fisher Scientific UK Ltd,
Bishop Meadow Road
Loughborough, Leicestershire, LE11 5RG, UK
Tel: (44) 1509 231166 Fax: (44) 01509 231893
Email: fsuk.sales@thermofisher.com
Website: www.fisher.co.uk

Epofix Epoxy Resin
Struers Ltd.
Unit 11 Evolution @ the AMP, Whittle Way
Catcliffe, Rotherham, S60 5BL, UK
Tel: (44) 845 604 6664, Fax: (44) 845 604 6651
Email: info@struers.co.uk
Website: www.struers.co.uk

CamScan 2040 Scanning Electron Microscope,
Housed at the Conservation Section, Cardiff University
Obducat CamScan Ltd
CamScan House
Pembroke Avenue, Waterbeach
Cambridgeshire, CB5 9PY, UK
Tel: (44) 1223 861066 Fax: (44)1223 861077
Email: info@camscan.com
Website: www.camscan.com

**References**


Mr Panagiotis, professional tinker, Thessaloniki, Greece, personal communication (March 2007).


Authors

Panagiota (or Yiota) Manti is a lecturer in Conservation Science at Cardiff University. She trained as a conservator and archaeological scientist at Cardiff and Oxford University. Her PhD investigates surface finishes and patination of bronzes, focusing on 6th c. BC Greek helmets. Yiota is interested in scientific methodology in heritage materials’ studies, decay and manufacture of archaeological material, non-destructive analysis and pedagogy in conservation.

David Watkinson graduated in Archaeological Conservation from University College London and Cardiff University, where he is now a Reader coordinating conservation teaching and research. His main research activity lies in metal corrosion and, with
emphasis on iron. Research into desiccated storage of unstable iron underpinned the conservation strategy devised for Brunel’s iconic steamship SS Great Britain, which won the Gulbenkian Museum prize in 2006. He has served widely on committees and grant-awarding bodies and is currently a Council Member of the International Institute for Conservation.

Email: Watkinson@cf.ac.uk

Q & A SESSION

Aaron Shugar: Thank you for an excellent presentation, I’m glad to see your future work will include micro-structure investigation. I think that there is a program called LISPIX from NIST, it’s free software and it is a quantitative mapping program. So it takes your pictures you showed of the maps – they are average maps, showing you what is above average and below average in color. This will actually take that data set and make it quantitative. So it is a free software package that you can download from NIST, and you can actually get data off it instead of just showing averaging maps.

Panagiota Manti: Excellent, thank you.

Peter Northover: I only look at these things through cross-section, and the epsilon-phase layers are often only very very thin. When you are detecting it with X-ray diffraction, you can usually see it in the cross-section optically with good enough sample preparation. But it can be very very thin. Another thought is that the tin dioxide corrosion layers can very often be nanocrystalline or amorphous. I think the last section, from what I could see with my poor eye sight from where I was sitting, looked like a very thick layer of tin dioxide corrosion, which was not particularly crystalline and was perhaps from excess tin. And it looked like a very thin layer of epsilon right up against the metal surface. It would be unusual to have a whole solid layer of epsilon as you might imagine. So I think [the thick layer] is mainly tin-rich corrosion products and there is a very thin layer of epsilon at the interface with the substrate. To me that would suggest it is tin-rich corrosion, or do you think that is corroded epsilon?

Panagiota Manti: I would expect to see epsilon here [points to thicker layer on slide]. Because this is inwards and so is unlikely to be just tin corrosion products.

Peter Northover: Yes, but there is always eta and tin on the outside of the epsilon and there can be a lot of tin and I would not expect to see epsilon as the outside layer.

Panagiota Manti: Well you can see here [points to slide] that this is a corrosion profile. Therefore this is the patina layer, this is the marker of the original surface.

Peter Northover: But that original surface might have been tin.

Panagiota Manti: Yes it could have been.

Peter Northover: What puzzles me also is that epsilon tends to be reasonably corrosion resistant.

Panagiota Manti: Is it more corrosion resistant than eta?

Peter Northover: Well delta tends to be the most corrosion resistant but epsilon is nearly as corrosion resistant as delta.

Panagiota Manti: So what about eta?

Peter Northover: Eta does corrode. If the tin corrodes, then the eta corrodes and then quite often – because there is a granular interface between the epsilon and the eta, the outside surface of the epsilon could be the first sound metal you see. I had a Master student do a dissertation on this in 1992 and you are very welcome to a copy of the thesis.

Panagiota Manti: Thank you. Can I just reply as well that you say about the epsilon and the eta phase but I think there is more that we need to know and we need to understand about the corrosion of these phases. Because we can see the eta-phase in several artifacts, but the epsilon – I just tried to point out how tricky it is to identify this phase, and especially if it is corroded. Now bearing in mind that during tinning we only have the eta phase, or we mainly have the eta phase present and a tiny little bit, a very thin layer perhaps of epsilon, which is planar in shape, it is extremely difficult to identify this phase. But that is why I think that if you have uncorroded epsilon, the best chance [of identifying it] is by x-ray diffraction. Because it just looks very very similar to corrosion of the metal.