The Aging of Solder Joints over 1,600 Years: Evidence from Nubian Bronze Artifacts

Heather Galli, Robert Knopf, and Robert Gordon

Solder joints and coatings found in bronze artifacts recovered from the Nubian Desert in Egypt show evidence of the decomposition of the lead-tin eutectic structure and solid-state growth of the ε and η intermetallic phases at the solder–bronze interface at ambient temperature. Accelerated aging experiments reproduced the structures observed in the artifacts. The data show that the growth of the intermetallic compounds is diffusion-controlled at low as well as high temperature with an activation energy of 20 kcal/mol.

INTRODUCTION

Soldering with lead-tin alloys was a technique well known and widely used by metalsmiths making bronze and silver products in the ancient world. These artisans also used tinning to decorate bronze and iron objects. In addition, they used it to cover the insides of bronze vessels used as tableware or in the kitchen to protect users from the bad taste that results from direct contact between bronze and food.[1–5] Aging of tin-based solders is of particular interest today due to concern about the long-term reliability of soldered connections in electronic devices. This article reports on evidence of microstructural changes in the solder used in bronze artifacts retrieved from the Nubian Desert in Egypt. The solder has aged at ambient desert temperatures for at least 1,600 years.

Table I. Artifacts Studied

	Peabody Museum Catalog	Dimensions (mm)	Features
A	265,791	178 dia.	Mirror with handle soldered on
B	265,790	125 dia.	Thin-wall bowl, tinned, with solder repair
C	262,230	145 dia.	Thin-wall bowl, tinned
D	262,485	48 dia., 305 long	Ladle

The artifacts were recovered by the Pennsylvania–Yale Expedition to Egypt at the sites of two communities in Lower Nubia, Arminna West, and Toshka West, located on the west bank of the Nile between the major archaeological sites of Abu Simbel to the south and Karanog to the north.[6,7] The cemeteries at these sites contained more than 250 grave complexes that held iron and bronze artifacts from the Meroitic (300 B.C to A.D. 370) and X-Group (A.D. 370–550) periods.[8]

The excavators determined the ages of the artifacts from their knowledge of the burial characteristics and the associated grave goods. Since the only bronze smelting known to have been carried out in Lower Nubia was about 2500 B.C.,[9] long before the Meroitic Period, the bronze artifacts are identified as trade goods manufactured within the Roman Empire and traded into Lower Nubia.[10] It is possible that Nubian artisans undertook some repairs or modifications before the artifacts were finally placed in graves.

SOLDER IN THE BRONZE ARTIFACTS

Examples of solder and of tinning were found on a mirror, a ladle, and two bronze bowls in the course of laboratory examination. These artifacts are in the collections of the Peabody Museum at Yale University, and are identified by

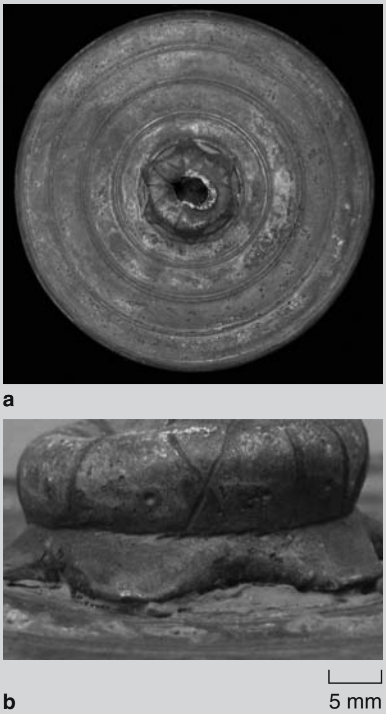

Figure 1. (a) The backside of mirror A showing a handle attached with solder. The decorative rings were cast into the bronze mirror plate. (b) Detail of the solder joint on the back of the mirror showing the abundant use of solder in the attachment of the handle.

Over the last 40 years, there has been a discernible increase in the number of scholars who have focused their research on early industrial organizations, a field of study that has come to be known as Archaeotechnology. Archaeologists have conducted fieldwork geared to the study of ancient technologies in a cultural context and have drawn on the laboratory analyses developed by materials scientists as one portion of their interpretive program. Papers for this department are solicited and/or reviewed by Michael Notis, a professor and director of the Archaeometallurgy Laboratory (www.Lehigh.edu/~inarcmet) *at Lehigh University.*

their numbers in the museum catalog (Table I). The bronze mirror (Figure 1) is from the X-Group Period and is similar to the high-tin bronze mirrors widely used in Etruscan and Roman times, and also in India and China.[11–13] A small piece of the solder used to attach the handle was taken for analysis without damaging the artifact.

Two thin-walled bronze bowls (B and C in Table I), have remains of tinning on both interior and exterior surfaces, and bowl B (Figure 2) has an accumulation of solder in the bottom, perhaps from an attempt to repair damage. A sample of this accumulated material was extracted for analysis. The lining material was examined on cross sections taken from the bowl rims.

The ladle, D (Figure 3), was made from one piece of 2 mm thick bronze sheet by a complex metal-forming operation that shaped a bowl at the end of a handle that terminates in the figure of a serpent's head. A sample was taken from the solder present in the bottom of the bowl that appears to have been used in an attempt at a repair.

Metallographic samples were prepared by standard methods. For optical microscopy the lead-tin alloys were etched with a glycerin-acetic acid-nitric acid (84:8:8, respectively) mixture when needed. The specimens were examined in the as-polished condition for microprobe analysis. A JEOL Superprobe 733 operating at 15 kV with a beam current of 20 nA to 50 nA, depending on the element analyzed, was used with wavelength-dispersive spectrometry (WDS) to determine alloy compositions. Energy-dispersive spectrometry (EDS) was used to analyze the coating on bowl PM 262,230. Overall compositions, reported as weight percent in Table II, were determined from the compositions of the individual phases present and the volume fraction of each constituent as found by image analysis.

Figure 3. The bronze ladle D was fabricated from one piece of sheet bronze. Remnants of tinning remain on the handle, whose top is decorated with a representation of a serpent's head. The insert shows the solder present in the bottom of the bowl.

Microstructures Observed

A solder joint made with 60/40 weight percent lead-tin alloy (Figure 4) has primary lead dendrites dispersed in a matrix of lead-tin eutectic.[14] A layer of intermetallic compound ε (Cu_3Sn) forms at the interface between the solder and a substrate of copper or copper-based alloy and is followed by the compound η (Cu_6Sn_5) between the ε phase and the solder alloy (Figure 5). The thickness of the layer of ε and η layer shown in Figure 5 has been enhanced by aging for better visibility. This layer is only about 1 µm thick in a joint made by a conventional soldering technique at about 300°C. The structures found in the Nubian artifacts differ significantly from those in a freshly made solder joint.

The solder from the mirror (Figure 6) consists of continuous lead solid solution containing regions of tin solid solution, and a layer of intermetallic compound originally in contact with the mirror surface. Dispersed particles of the intermetallic compound η phase are present within the tin phase. Compositions of the constituents are shown in Table II. There is no trace of a eutectic structure in the solder. The composition of the dark constituent in the intermetallic layer is 60% copper and 40% tin, identifying it as the ε phase, and the lighter gray constituent has 38% copper and 62% tin, corresponding to the η phase. The average thickness of the ε phase is 4 µm, and of the η phase, 12 µm. Since the solder separated from the bronze substrate by fracture through the ε phase, the total thickness of the intermetallic compound layer may have been greater than 16 µm.

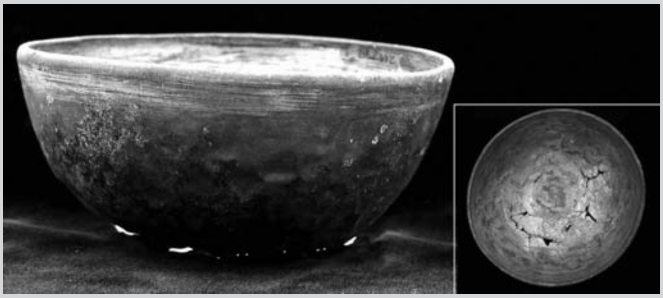

Figure 2. The thin-walled bowl B was made by spinning or raising bronze sheet. The inner and outer surfaces were subsequently tinned, and remnants of the tinning remain in place.

The microstructure of the solder taken from the bottom of bowl B (Figure 7) has a nearly continuous lead phase containing regions of tin phase, and a layer of intermetallic compound that was in contact with the bronze bowl surface. The x-ray maps define the layer of intermetallic compound, showing that the η phase is 6 µm thick and that particles of

Table II. Compositions of Solders and Constituents (Wt. %)

Specimen	Sn	Pb	Cu
A Mirror	32	68	—
Pb-Phase	2	98	—
Sn-Phase	99	0.7	—
B Bowl			
Bottom	48	52	—
Pb-Phase	2	98	—
Sn-Phase	99	0.7	—
Exterior Coating	47	—	53
Interior Coating	38	4.7	47
C Bowl			
Exterior Coating	61	0.8	38
Interior Coating	58	—	42
D Ladle	13	87	—
Pb-Phase	2	98	—
Sn-Phase	99	0.7	—

η are dispersed in the solder. There is no trace of eutectic structure.

The microstructure of the solder retrieved from ladle D (Figure 8) consists of a continuous lead solid solution (dark in the micrograph), islands of tin solid solution dispersed in the lead constituent, and a few particles of η intermetallic compound. No layer of intermetallic compound detached from the substrate was present in this sample, and there is no trace of eutectic structure.

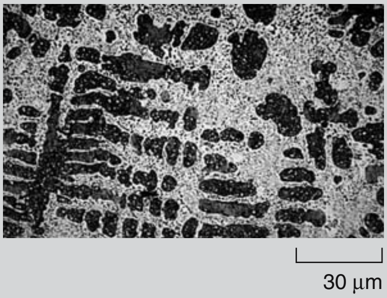

Figure 4. The microstructure of solder in a joint between two pieces of copper. The solder alloy was 44% tin and 56% lead. The structure consists of dendrites of primary lead phase in a matrix or eutectic. No etch; optical micrograph; original magnification 920×.

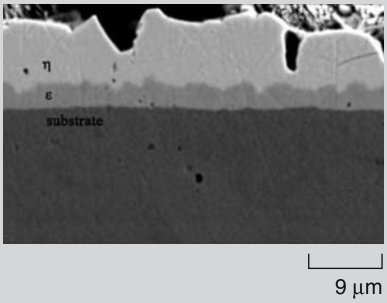

Figure 5. A backscattered-electron–scanning-electron image (BESEI) of the intermetallic layer formed on a copper substrate after aging for 192 hours at 170°C. In this image the copper substrate is dark. The intermetallic layer is composed of ε (gray) and η (light gray).

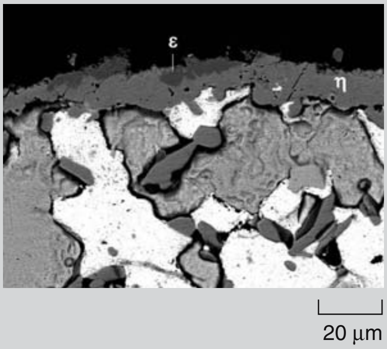

Figure 6. A BEI image of the solder from mirror A showing the layer of intermetallic compound containing the ε phase (dark) at the former interface with the bronze and the η phase formed adjacent to the solder consisting of lead (bright) and tin (darker) phases. Particles of the η intermetallic compound are dispersed in the solder.

The microstructures of the solders in the artifacts differ from that of a freshly made solder joint in the absence of eutectic structure, the greater thickness of the layer of ε and η intermetallic compounds, the presence of η-phase particles within the solder, and the absence of dendritic form in the primary lead constituent. The composition of the lead and tin phases (Table II) correspond to the equilibrium compositions of the alloy phases at about 50ºC. Since in a freshly made solder joint the lead phase contains 3.3% tin in solution and the tin phase, 1.6% lead, it is evident that composition changes in both constituents have occurred in the 1,600-year interval since soldering was done. It is also evident that whatever eutectic structure was present in the solder at the time the joints were made has vanished in the intervening 1,600 years. Recent research has shown that the eutectic structure formed upon cooling; lead-tin solder is not completely stable at room temperature. Coarsening of the eutectic structure can be observed within five years at room temperature, and can be accelerated by creep deformation or stresses induced by temperature changes.[15,16] Growth of copper-tin intermetallic compounds at the interface between solder and a copper substrate at room temperature has also been observed.[17]

If solder aging and growth of the intermetallic compounds are thermally activated processes, it should be possible to reproduce the structures observed in the Nubian artifacts in laboratory aging trials at elevated temperature. Data on the rate of growth of intermetallic layers in solder joints has been reported previously.[18–20] Those trials were carried out on solder drops less than 0.1 mm in diameter, where edge effects could be important. The authors conducted trials on surfaces comparable in size to those in the artifacts. Also studied was the effect of substrate composition on the structure of the solder joints.

LABORATORY SOLDERING TRIALS

Solder consisting of 44% tin and 56% lead (approximating that used in the

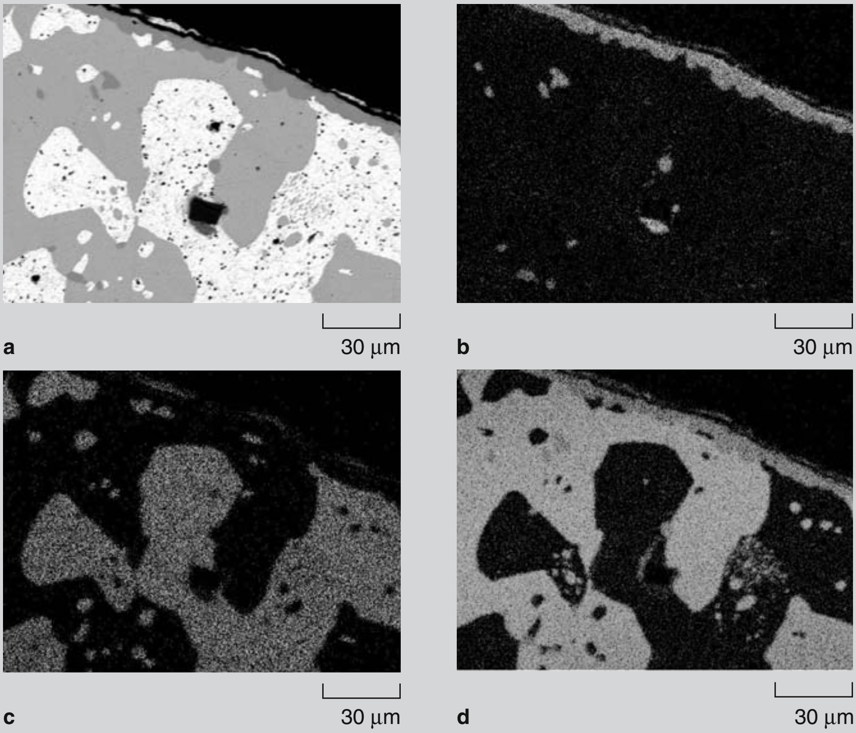

Figure 7. (a) A BEI image of solder from bowl PM 265,790 showing the layer of η intermetallic compound (dark) formed at contact with the bronze substrate. (b) Copper x-ray map showing the layer of η phase and particles of η within the solder. The intermetallic layer measures 6 µm thick. (c) Tin x-ray map showing small islands of tin within the lead. (d) Lead x-ray map showing that some lead particles are incorporated within the tin. No trace of the original eutectic structure survives.

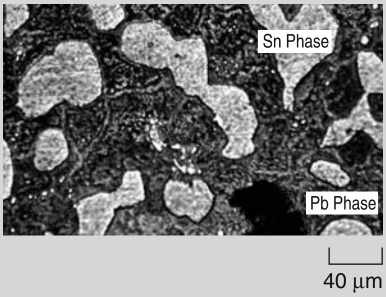

Figure 8. A microstructure of solder taken from the ladle D showing islands of tin (bright) in a matrix of lead. A few particles of the η intermetallic compound are dispersed within the solder. Glycerin-acid etch; original magnification 735×.

solder found in the bowl PM 265,790) was fused at 300ºC between parallel plates of substrate metal held fixed 4 mm apart in a graphite block. Four substrate metals were used: pure copper, a 5% tin bronze, a 20% tin bronze, and a leaded bronze containing 10% tin and 13% lead. After melting the solder was kept at the fusion temperature for three minutes. The assembly was then removed from the furnace and air cooled. Sections cut from the soldered plates were aged for successive times at 170ºC and then air cooled.

The as-made solder structure (Figure 9a) consists of primary lead containing a few islands of included tin, and eutectic with lead particles approaching plate form. Coarsening of the eutectic is evident after aging for 24 hours at 170ºC (Figure 9b) and was nearly complete by 92 hours (Figure 9c). After aging for 334 hours the eutectic structure had completely decomposed, leaving islands of lead phase in a matrix of tin solid solution (Figure 9d). This aging process was found to proceed in the same way in the solder on all the substrates tested.

A layer of the η intermetallic compound about 1 µm thick formed at the substrate surface in the un-aged solder joints. The interface between the η and solder had the scalloped form that arises from growth by a non-conservative ripening mechanism.[21] During aging of the solder at 170ºC for 336 hours the layers of both ε and η intermetallic phases grew continuously. The backscattered-electron–scanning-electron imaging image (Figure 5) shows that the interface between the copper substrate and the ε phase is sharp and smooth while that between the ε and η is rough. The interface between the η and the solder is deeply indented. However, no release of η into the solder is detected. The ε phase makes up about 30% of the intermetallic layer.

The same sequence of phases is found on all the substrates tested, but here the ε phase makes up nearly 50% of the total intermetallic layer thickness, as shown in Figure 10. On the 5% tin bronze the interface layer structure is similar to that formed on the copper substrate. The microstructure of the 20% tin bronze substrate used consists of approximately equal proportions of α phase and β martensite. The ε intermetallic phase grew to equal thickness on both bronze constituents (Figure 10b). Particles of lead in the leaded bronze substrate are exposed to the solder at the interface. These particles dissolved in the liquid solder, which then reacted with the exposed bronze surface to fill the resulting cavities with the ε and η intermetallic compounds (Figure 10c). Where the filling was incomplete residual lead was retained within the intermetallic layers. In all of these specimens the solder adjacent to the intermetallic layer is depleted in tin to a depth of about 10 µm.

The rate of growth of the ε and η intermetallic layers on the bronze substrates (Figure 11a) decreases with time following the $t^{1/2}$ law expected for a diffusion-controlled process.[20] The growth rate of the total thickness of the intermetallic layer is faster on the bronze substrates than on pure copper (Figure 11b) since less copper diffusion is required to achieve the same amount of intermetallic compound on the bronze substrates.

No release of particles of the η phase intermetallic compound into the solder is observed in soldering substrates held in a fixed relation to one another. When two pieces of 22% tin bronze not clamped to each other were soldered by hand with a torch rather than in a furnace, the layer of intermetallic compound formed at the solder to bronze interface released particles of η phase into the solder (Figure 12). The attached intermetallic layer is about 3 µm thick and particles of η phase are found in a zone about 10 µm thick adjacent to the interface.

INTERPRETATION OF THE ARTIFACTS

The 2% tin content of the lead phase and the 0.7% lead content of the tin phase in the Nubian artifacts are those in equilibrium in this alloy at a temperature of about 45ºC. In a new solder joint these compositions are 3.3% lead in the tin phase and 1.6% lead in the tin phase, corresponding to a freezing-in temperature of about 90ºC. Thus, there is suf-

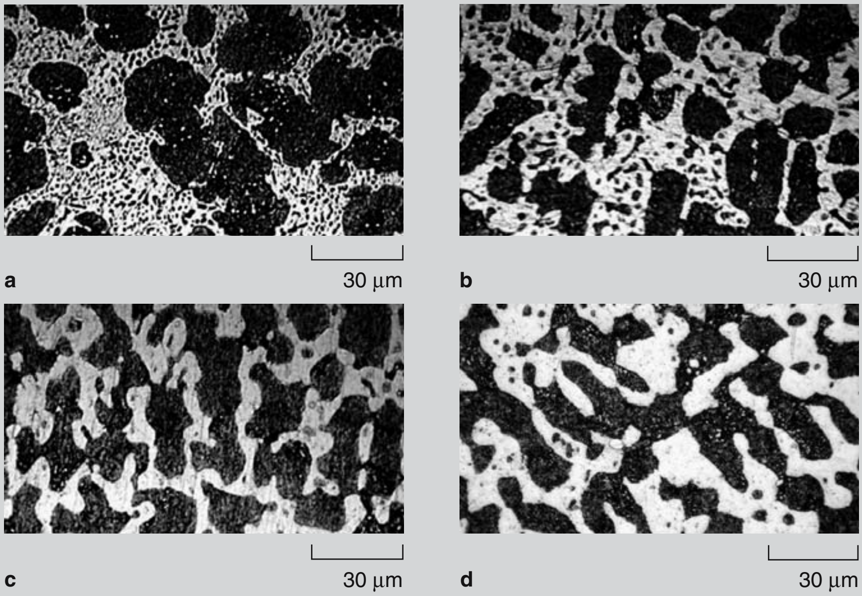

Figure 9. A microstructure of solder (a) as-cast and as-aged at 170ºC for (b) 24 h, (c) 92 h, and (d) 334 h. The eutectic consisting of lead particles (dark) approaching plate shape in a matrix of tin (bright) present in the original solder decomposed during aging. No etch; original magnification 920×.

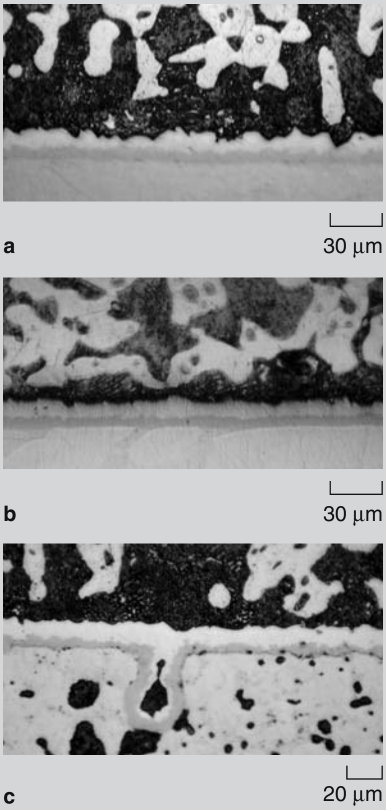

Figure 10. Optical micrographs showing the development of the ε and η intermetallic compounds by solid-state aging on substrates of (a) 5% tin bronze, (b) 20% tin bronze, and (c) leaded bronze (10% tin, 15% lead). The dark areas within the bronze in (c) are lead. No etch; original magnification 920×.

ficient atomic mobility in these alloys to allow composition readjustment at the ambient temperature of the Nubian Desert over a time interval of 1,600 years. This leads to the conclusion that the solder structure observed in the Nubian artifacts is the result of aging at desert temperature, about 30ºC for objects in a burial. The eutectic decomposed with redistribution of its lead constituent into the primary lead present, leaving a matrix of tin solid solution.

Since the layer of ε and η intermetallic compound is only about 1 μm thick in a solder joint made by heating with a torch, one can conclude that the relatively thick intermetallic layers observed in solder from the mirror and bowl arose through subsequent aging, unless the Roman or Nubian artisans held their solder molten for a prolonged time. The mirror solder has a liquidus temperature of 275ºC. Data by J.O.G. Parent and others[22] indicate that at least an hour exposure to liquid solder would have been needed to duplicate the structure found in the mirror solder unless the soldering temperature were as high as 350ºC. As shown in Figure 11, growth of the intermetallic layer can occur at elevated temperature with all constituents solid. At a temperature of 170ºC it takes 440 hours to grow an intermetallic layer to the 16 μm thickness of the mirror solder. This is a diffusion-controlled process. To attain the 16 μm thickness in the 1,600-year age of the mirror, the activation energy of the process would be 20 kcal/mol. Within the accuracy of the authors' data, this is in agreement with the activation energy of 21.8 kcal/mol reported for this process by K.N. Tu and others.[19]

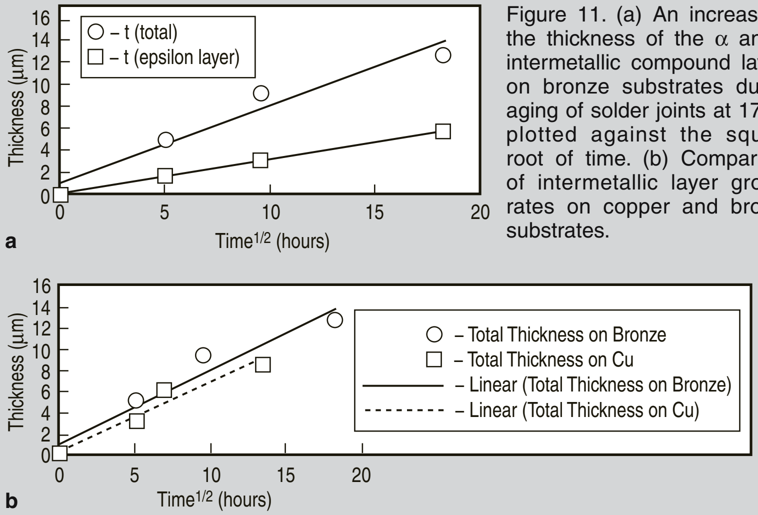

Figure 11. (a) An increase in the thickness of the α and β intermetallic compound layers on bronze substrates during aging of solder joints at 170ºC plotted against the square root of time. (b) Comparison of intermetallic layer growth rates on copper and bronze substrates.

Figure 12. An optical micrograph of the interface between solder and substrate in a joint made by heating plates of high-tin bronze with a torch. The bronze plates were not clamped to each other. Particles of η phase formed at the interface have been detached and are released into the solder. No etch; original magnification 1,375×.

In the aging trials a layer of solder adjacent to the bronze is depleted in tin phase to an average depth of about 8 μm. The depletion layer has been ascribed to tin consumption by the growing intermetallic layer.[20] The depletion layer is not present in the solder from the artifacts. Since the activation energy for diffusion of tin in lead, 23,750 kcal/mol,[23] is larger than that for the growth of the intermetallic layer, the decrease in its diffusion rate between 170ºC and 30ºC is eight times greater than that of the intermetallic layer. This would eliminate tin as an active part of the growth process at the lower temperature.

CONCLUSIONS

Solder recovered from the Nubian artifacts differs from that in a freshly made solder joint in the absence of eutectic structure in the solder and the large thickness of the layers of the ε and η intermetallic compounds at the interface with the bronze substrate. These structures were reproduced by accelerated aging experiments. Hence, the processes of controlling the decomposition of the lead-tin eutectic structure and the growth of the intermetallic layers active at 170ºC also proceed at temperatures as low as 30ºC fast enough to generate equivalent structural changes over an interval of 1,600 years.

Growth of the ε and η intermetallic compounds at the solder-substrate interface is accelerated by the presence of tin in the substrate alloy. The interface roughness is increased in leaded bronze due to reaction between lead particles exposed at the surface and the solder.

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