Use Case

The Corrosion-Resistance Bronze Bowls of Urartu

A Microscopic Investigation

Seeing beyond

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This article is an overview of our research into the unusual corrosion-resistance of the bronze bowls of Urartu. These bowls, from the collection at the State Hermitage Museum, have been on display there for 70 years. Although buried underground for some 2,700 years prior to excavation, they bear almost no traces of corrosion. Environmental conditions excluded any inhibitors, electrochemical corrosion protection or other external causes. The measurements of the composition of the bronze eliminated any additives to the alloy. And even an Auger spectrometer could not confirm the presence of any coating or passivation film on the surface. In fact, it appears that ordinary bronze, the surface of which is only slightly enriched with tin, has simply resisted corrosion for 28 centuries.

Archaeological discovery

In 1949 the bowls were discovered by archaeologist Boris Piotrovsky during the excavations of the Teishebaini Urartu Fortress (7th century BC) on the Karmir-Blur hill in Armenia. Boris Piotrovsky (1908 – 1990), a director of the Hermitage for nearly 40 years, was himself a well-known authority on Urartu.

"97 bronze bowls with cuneiform inscriptions of the Urartu kings: Menua, Argishti, Sarduri and Rusa were stacked in the karas (No. 5) in the northern part of the eastern half of room 25, the furthest from the door ... The stack of bowls was covered with wooden planks, apparently to disguise them. These bowls were ceremonial no doubt. Some of them have retained their original shine and traces of thorough cleansing in antiquity, apparently with sand. There are scratches with a knife on some specimens, both random and intentional, conveying a simple schematic drawing – fish in one case, standard in the other. There is no doubt that during the siege of the fortress, an empty karas in the storeroom was used to hide valuable bronze bowls from enemies."

Boris Piotrovsky, excavation report, 1950, p. 20

Eighty-two large clay vessels (karas) for wine had been dug into the ground in a large storeroom with just one entrance and no windows. All except five vessels were empty. Of the others, three held grain (wheat, barley and millet), one held flour and the bronze bowls lay in the last one. Although a fire had raged during the storming of the fortress, the grain, flour and the planks that covered the bowls did not burn. Inscriptions in the bowls indicated various kings and times (Table 1).

It is doubtful that one king would have claimed a bowl as the inventory of a long-dead predecessor. It is more logical to assume that the bowls were made during the reign of the king referred to on each bowl. Therefore, the minimum number of years between the manufacturing times of the bowls would be 51, 93 or 143 years. This hints that we should look for the cause of corrosion-resistance in the conditions that prevailed during of the bowls' existence rather than in tricks of manufacture.

Figure 1 *Bronze bowl decorated with cuneiform name of King Sarduri and two hieroglyphic symbols of Urartu, 8th century BC. © The State Hermitage Museum*

King	Years, BC
Sarduri I	844 – 828
Menua	810 – 786
Argishti I	786 – 764
Sarduri II	764 – 735
Rusa I	735 – 714
Rusa II	685 – 639
6 kings	**844 – 639**

Table 1 *The kings and the reign period*

In the 7th century BC, Teishebaini was a new administrative center built to control the northern regions of Urartu.
It gained the status of being the actual capital of Urartu only when the state began to decline. Thus it seems obvious that all the bowls would have been collected in Teishebaini from other cities when those cities became unusable, lost their strategic importance or were close to destruction. In the end, Teishebaini itself was captured and destroyed in the 7th century BC.

Macro research

The bowls (Figure 2) entered The State Hermitage collection in 1950. In 2018 they were taken from the permanent exhibition to the Laboratory for Scientific Restoration of Precious Metals for further research. One had been preserved in

Figure 2 *The bowls showed different conditions of preservation. © The State Hermitage Museum*

perfect condition: it was pale brown but looked gray at some angles, with a glossy surface and no visible patina areas. The second bowl (left, L) was preserved in a worse state than the other: it was pale brown, smooth and matte in places, and with a rough, darker surface in other places. It had small defects (holes), but was also without patina.

Both bowls are irregular ellipsoids (Figure 3), but differ in shape. They have no common patterns. This, of course, does not mean that there will not be at least two bowls out of all 97 that are the same shape.

There are small black and green formations in the left in the photo. If judging by color, they are most likely copper oxide and copper carbonate. However, should the patina be removed, the surface would remain as smooth and uncorded as the rest of the fragment.

If any source of corrosion is formed, it is only local and won't spread further. Preliminary measurements have already shown that the elemental composition of the bowls is heterogeneous (as in almost all ancient alloys) and it is impossible to say anything definite about the composition of any bowl as a whole. Therefore, we divided all the measurements into three parts: bowl R, bowl L (light) – light parts and bowl R (dark) – dark parts. We then tried to find any regularity in the composition of the elements. Except for copper and tin, all elements that were revealed can be considered random metal dust. The only result that can reasonably be taken into account is the ratio of the mass content of Cu / Sn. Therefore, the elemental composition of bowl R and bowl L (light) is Cu 90 – Sn 10 wt% or Cu94Sn6, which we will consider further as the composition of bronze bulk. We got the exact same result later using an SEM EDS. The tin content is higher in the dark areas of bowl L.

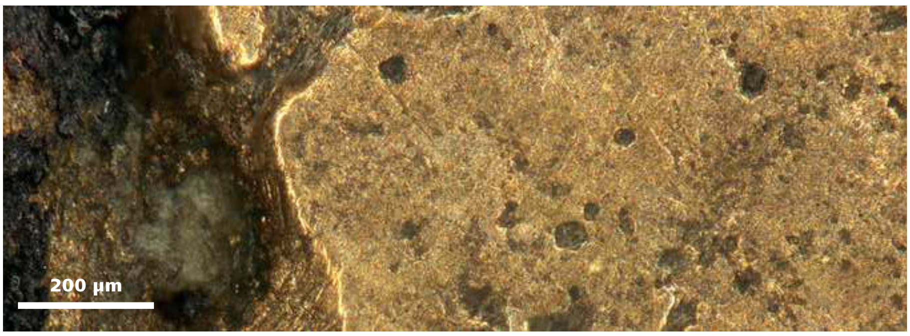

Figure 3 *Typical fragment of the surface of the right bowl under a light microscope. © The State Hermitage Museum*

Possible causes for non-corrosion

Corrosion of copper and its alloys in the earth's atmosphere is a spontaneous process that proceeds with a decrease in the Gibbs energy of the system. Pure copper corrodes at a rate of not less than 0.4 µm/a in the rural atmosphere, and corrosion-resistant, copper-based alloys are even slower, down to 0.08 µm/a. So, as copper does not corrode in the air or at least corrodes abnormally slowly (<0.08 µm/a), this phenomenon will require a specific cause and/or some special conditions.

Theoretical causes:

- v1 alloying additive
- v2 organic or inorganic coating
- v3 surface or environmental inhibitor
- v4 a thin (10 – 100 nm) film of oxidation products preventing further corrosion
- v5 electrochemical corrosion protection
- v6 pure O_2-free water (Hedin 2018)
- v7 smooth surface (Toloei, et al. 2015)
- v8 amorphous alloy
- v9 passive film
- v10 something else

For 2,700 years, these bowls were buried, stacked one inside another in an earthen vessel, and for 70 years after excavation they have been on display at the museum, protected only by glass. There has been no contact with other metals so version v5 can be excluded. As with version v3, since the bowls' environment changed after excavation, version v6 is not applicable. Consequently, we must look for our specific cause of the phenomenon either in the composition of the alloy or in the surface layer – or in "something else". Moreover, the version of the composition v1 is the most unlikely because of the great age of 2,800 years:

2800 years * [even if] 0.01 µm/a = 28 µm

It would be noticeable. As for version v7, unfortunately we could not find any works that have studied the dependence of the bronze or copper corrosion rate on surface roughness.

Nevertheless, it is also impossible to discard such a version completely, at least in theory.

Searching the scientific literature as well as in the public catalogs of museums, we managed to find one single example of ancient corrosion-resistance in bronze (and copper) artifacts: Chinese black mirrors produced during the Chou and Han periods. Corrosion-resistant bronze mirrors are coated with a layer of an amorphous silicate or mixed oxide-containing SiO_2 enriched in tin (→ black), 30 µm thick. The thickness of the entire surface layer, both the non-metallic layer and the "altered zone", is ca. 250 µm. In our list of versions this would be v2, i.e. a coating.

Check with electron microscopes

A thin and very smooth film similar to glass (figure a), paper (figure b) or cardboard (figure c) was found on the smooth surface of bowl R. The film thickness is 200 – 300 nm. In some cases, there are 5 to 6 films by 200 – 300 nm each (figure c).

One more thing: the Cu94Sn6 bronze should be reddish. And if we assume that it is the surface film of 200 nm that changes color to pale brown / gray (at a certain angle), it possible to calculate the refractive index of the film. There were similar smooth films on the micro sample from the edge of the hole in bowl L. Surprisingly, the micro holes of this film melted quickly under

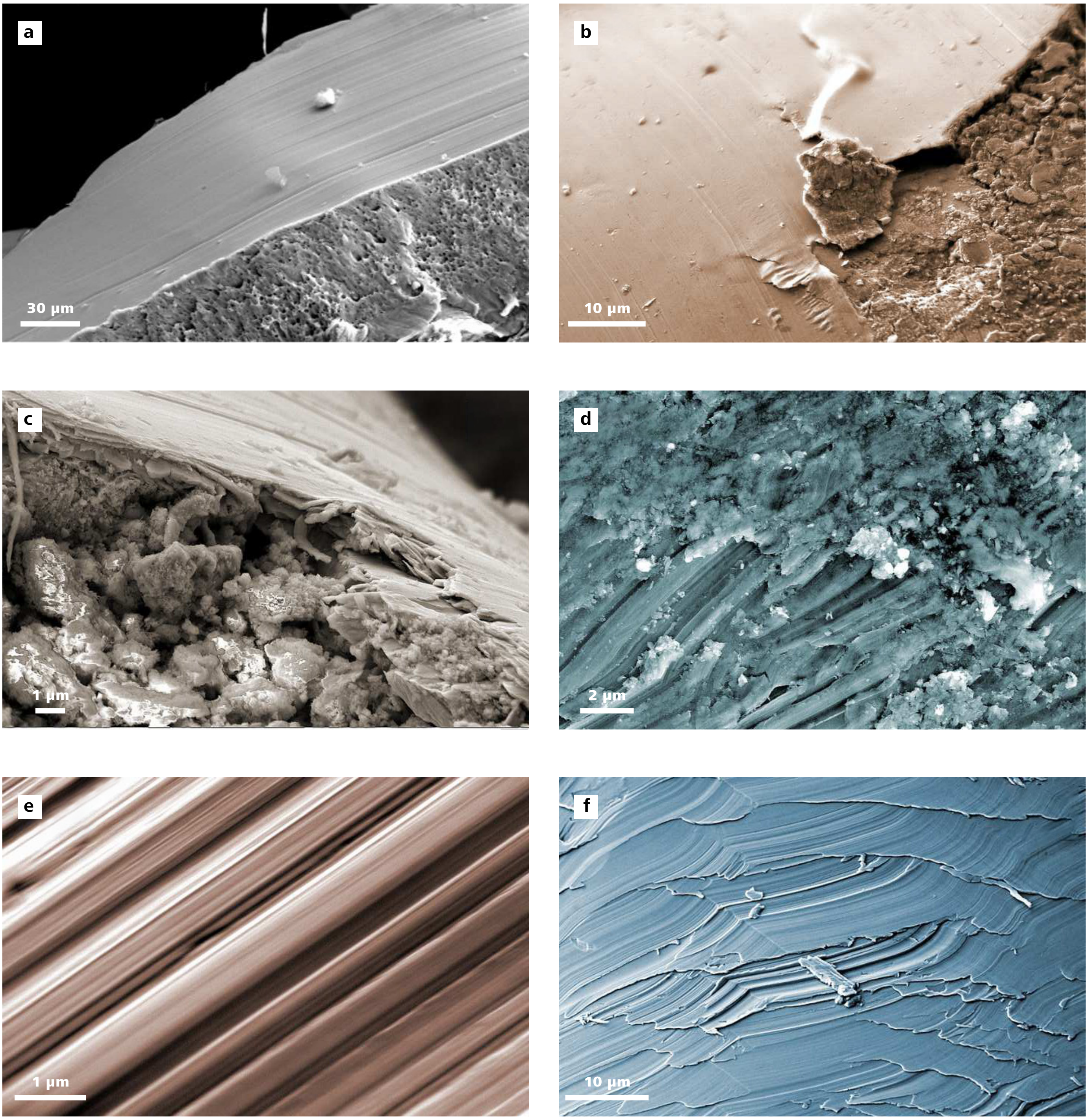

Figure 4 *SEM images of the smooth film (tinted). © The State Hermitage Museum*

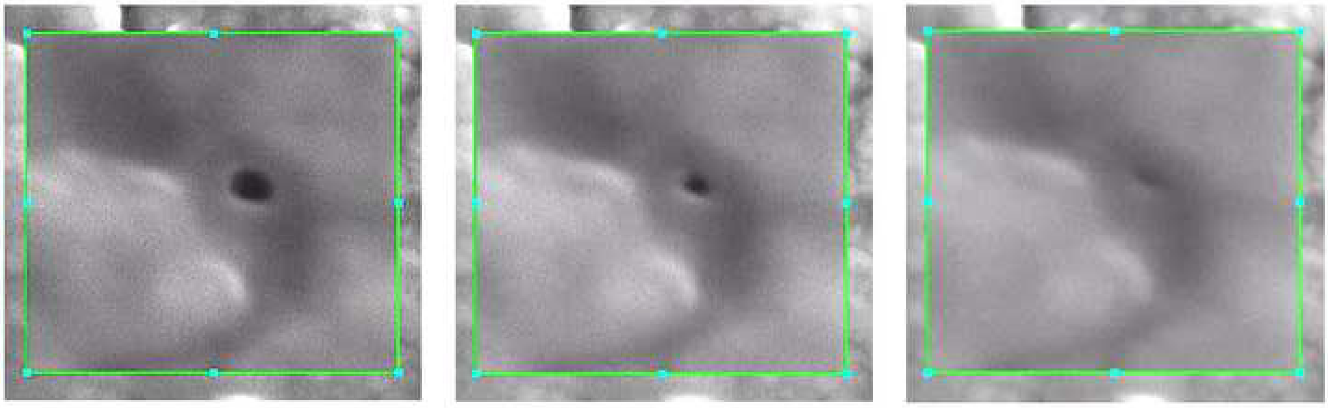

Figure 5 *The melting of the edges of the micro holes on a film under the influence of an electron beam (3 keV, I probe = 283 pA, scan area size = 240 nm).*

the influence of an electron beam with an energy of only 3 keV (figure 5). The effect resembles the electron beam-induced crystallization of amorphous metal, but only the energy must be higher by an order of magnitude. This effect was not found on micro samples from the surface of bowl R.

Composition and structure of the smooth surface

A smooth film's micro sample (bowl R) was also investigated using an Auger spectrometer. The most interesting result of the Auger spectra was that no coatings and no passive film are visible with the spectrometer (aside from a very thin carbon film). Only a smooth film $Cu_{92}Sn_8$ exists which, for some unknown reason, does not corrode.

Historical-technical hypothesis

The method used for bowl-making was no different from making any other similar bronze objects. The bowls appear to have had special meaning since they were cleaned with sand (chalk, coal), which explains the pattern on the surface. Then there came a day when Urartu went into decline and everything was at risk, including these bowls that had become covered with a thin layer of corrosion. When the enemy began the siege of the fortress, someone must have hidden the bowls in an empty vessel in the basement in the most unventilated corner of the building. A fire started, the wooden floors burst into flame and the smoldering charcoal completely covered the bowls in the vessel. The temperature in the vessel was suitable for the reaction of copper reduction from oxides with carbon monoxide CO. Temperature and other conditions were also suitable for depositing carbon in a film on copper.

Conclusion

As a result of a series of studies, we managed to find out that the shiny surfaces of bronze bowls are protected from corrosion by carbon (mainly) film stuffed with copper and tin particles.

Exhibition at the State Hermitage Museum

Over 150 valuable items of the collection are exhibited at the Hermitage Museum. They are well preserved and need little restoration. The exhibition features Urartian bronze belts of various width with characteristic images – scenes of feast and gift-giving, scenes of hunting and fantastic creatures, as well as details of equine equipment decorated with inscriptions and images, votive plates, bracelets, pins and breastplates. One of the collection highlights is a bronze helmet with a fulgurous symbol on a forehead piece. It is believed to represent Teisheba, the Urartian god of war. Urartian belts are particularly interesting and prior to acquiring the new collection, the Hermitage had only one belt of this kind. The exhibition is supplemented by a selection of ceramic items – large vessels bright with painting. The exhibition is dedicated to the 90th anniversary of the Hermitage Oriental Department, which was established by Hovsep Orbeli – the academician who was a director of the museum for many years. The exhibition curator is Natalia Kozlova, head of the Oriental Department of the State Hermitage Museum.

The role of museums and microscope equipment

“Museums are reserves. Museums are not galleries for display. Museums are for taking objects of memory, storing them [and] studying them, because without study, to present a thing is nothing. A treasure is only recognized as such after it is studied and properly explained. Then it can be displayed.”

Prof. Dr. Mikhail Piotrovsky, director of the world-famous State Hermitage Museum of Saint Petersburg for almost three decades

Figure 6 *The State Hermitage Museum in St. Petersburg, Russia is one of the largest and oldest art galleries and museums of human history and culture in the world. (https://simple.wikipedia.org/wiki/Hermitage_Museum)*

Light microscope: inspection of surface

Electron microscope with EDS: elemental analysis of bowls

Figure 7 *The Urartu Room at the State Hermitage Museum, https://www.hermitagemuseum.org/*

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Acknowledgments

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