

CHEMICAL EXAMINATION OF AN ANCIENT SHEET OF METAL OF UNIQUE COMPOSITION FOUND IN GREECE¹

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Several years ago a native found in the bed of the Alpheus River in Greece a roughly rectangular sheet of metal which was evidently the flattened side of a cylindrical vessel, possibly a bucket or similar container. A repoussé design in Greek style of considerable artistic merit had been formed in the metal. This sheet of metal was brought to the attention of an archaeologist who purchased it because of its artistic value.² Since the object was uniformly covered with a green patina, it was first believed to be composed of bronze or copper, but, in the course of cleaning it for the purposes of study and exhibition, the surface of the bare metal was seen to have the appearance of silver, which was puzzling in view of the color of the patina. Because of this discrepancy the writer was asked to make a chemical examination.

Visual inspection of cleaned places on the edge of the sheet showed that it was composite in structure. The sheet consisted of a layer of a reddish metal sandwiched between two layers of a white metal, and the three were firmly bonded

TABLE 1

Quantitative analysis and probable original composition of the white alloy

Elements Present	Analytical Figures, %	Probable Original Composition, %
Copper	52.0	52.8
Tin	32.5	33.0
Lead	13.6	13.8
Iron	0.4	0.4
Oxygen and other non-metallic impurities	1.5	none
	100.0	100.0

together. The reddish metal was ductile, but the white metal was slightly brittle and had a noticeably crystalline structure. In addition to the thin layer of patina on its outer surface, a slight amount of intercrystalline corrosion was evident in the white metal. Qualitative tests on minute samples of the two metals showed that the reddish metal was essentially pure copper and that the white metal was an alloy of copper, tin, and lead. For a quantitative analysis of the white metal a total sample of 100 milligrams of filings was collected from various parts of the edge of the sheet. The results of this analysis are shown in table 1 along with the corresponding figures for the probable composition of the unoxidized alloy. These data are given only through the first decimal place because of the small size of the sample and the uncertainty inherent in the method of sampling. The oxygen and other nonmetallic impurities were estimated by difference. It seems reasonable to conclude that the intended composition of the alloy was about one-half copper, one-third tin, and one-sixth lead, and that the iron is an accidental impurity.

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The composition of this white alloy is of considerable interest, as there appears to be no experimental evidence that any ancient or modern alloy of exactly this composition has ever been used in the fabrication of any other object. Of the ancient objects that have been analyzed only one other approaches this one in form and composition. This was a fragment of sheet metal, reported as apparently being tin plated on one side, which was found in the Crimea under circumstances that indicated an ancient Greek origin. The results of the analysis² are shown in table 2.

From these analytical figures and the description it is somewhat probable that this fragment of sheet metal may have been very similar in structure and composition to the object found in Greece. Possibly the sample that was taken for analysis included material from an underlying or intermediate layer of copper. This would account for the higher percentage of copper and the lower percentages of tin and lead as compared with those in the white alloy of the sheet of metal found in Greece. What was reported to be a coating of tin on the fragment of sheet metal from the Crimea may in fact have been an alloy very similar in composition to this white alloy. However, a close similarity of the two objects in structure and composition is by no means certain.

TABLE 2
Analysis of a fragment of sheet metal found in the Crimea

Elements Present	Analytical figures, %
Copper	66.80
Tin	21.70
Lead	11.36
Iron	0.09
Cobalt	0.05

The excellent state of preservation of the thin sheet of metal found in the river bed in Greece is explained by its chemical composition. Though pure copper itself is resistant to natural agents of corrosion, copper alloys containing a high proportion of tin, such as the white alloy of this object, are much more resistant. This is known from a detailed study made by Fink and Polushkin (1936) of the mechanism of corrosion in ancient bronze. They found that copper-tin alloys containing upwards of 25 percent of tin, or the components of an ordinary bronze that contain high percentages of tin, are much more resistant to corrosion than copper-tin alloys that contain lower percentages. They found that an alloy containing 25 to 26 percent of tin, the so-called eutectoid, survived in an isolated form in the mass of corrosion products resulting from the complete mineralization of the remainder of an ordinary bronze. The same high resistance to corrosion holds for copper-tin alloys that contain still higher proportions of tin; in these the alloy is composed of eutectoid and delta bronze. This high resistance to corrosion of copper-tin alloys containing high proportions of tin is also shown by the usual excellent state of preservation of Greek, Roman, or Chinese mirrors, many of which have been found with much of their original lustrous surface still intact.

The thin greenish layer of corrosion products on the surface of the object was probably formed in large part from the corrosion of the white alloy, as the copper content of this alloy is high enough to yield a sufficient proportion of copper compounds to mask the white compounds formed from the corrosion of the tin and lead

²Analyzed by Fellenberg and cited by Bibra (1869).

in the alloy. However, numerous isolated specks of the corrosion products of tin and lead were plainly visible in various areas on the surface. Some of the greenish patina may have been a result of the corrosion of the underlying layer of copper, for it seems entirely possible that corrosion products of copper could have diffused up between the crystals of the white alloy.

Both the composite structure of this sheet of metal and the physical properties of the component metals indicate that only one method could have been used in its fabrication. Casting seems clearly impossible, either for the thin central layer of copper or for the object as a whole. The formation of the sheet by hammering out metal of this composite structure also seems impossible because the white alloy is so brittle that such treatment would have cracked it. There are at least two indications that the central layer of pure copper was formed from a plain sheet of copper by hammering, probably by hammering it against a form bearing the design in relief. The variable thickness of the layer of copper indicates this technique. The use of pure copper rather than the more usual bronze is also an indication, since pure copper is much more suitable for such repoussé work than bronze because of its greater softness and malleability. After the design had been formed in the copper sheet by this method, the sheet was probably then coated with the white alloy by dipping the cleaned and cold copper into the molten alloy and withdrawing it. Since the melting point of this white alloy is about 300° C below that of pure copper no distortion of the copper from softening or fusion could have occurred. The white alloy probably solidified rapidly on removal from the fused alloy, and the result was a thick, uniform coating that adhered firmly to the copper. The intimate bond observed between the layer of copper and the layers of white metal indicates that this alloy was applied in a molten condition. It seems rather likely that the side and bottom were coated separately and then united in making a vessel of such composite metal, but it is by no means improbable that the copper parts were first united before coating. Regardless of the exact procedure, the coated surfaces were probably finished by tooling and polishing. In its completed state such a vessel must have closely resembled one of polished silver.

This sheet of metal is of considerable historical interest as an example of a large plated ancient object. Many plated ancient coins have been found, especially coins with a silver plate on a copper core (Campbell, 1933), but very few large plated objects have been found, or at least very few have been identified as such. That the art of plating large objects was known and practiced in Roman times, at least, is evident from some remarks of Pliny. In one place³ he states, "A method has been devised in Gaul for plating copper objects with tin, so skillfully that they can scarcely be distinguished from silver; these are called *incocilia*." In another place⁴ he states, "When copper vessels are plated with *stagnum* they have a less disagreeable taste, and the onset of verdigris is checked." From his remarks in a preceding passage it would appear that *stagnum* was ordinarily an alloy of silver and lead. He then goes on to say, "A counterfeit *stagnum* is now made from pale bronze and tin in the proportion of two to one, and another, now called *argentarium*, from tin and lead in equal amounts." Since Roman bronze was an alloy of copper, tin, and lead, usually with a considerably higher proportion of lead than tin, the first kind of counterfeit *stagnum* was evidently an alloy containing a little more than one-third tin, about one-half copper, and the remainder lead, or in other words an alloy very similar in composition to the white alloy of this sheet of metal found in Greece. As a matter of fact, this object found in Greece may very well have been made in Roman times, for the conditions under which it was found gave no clue as to its date of manufacture or date of deposition. At any rate, the rather

³*Natural History*, Book XXXIV, par. 162.

⁴Book XXXIV, par. 160.

close correlation between the composition of the one kind of alloy mentioned by Pliny as being used to plate copper objects and the actual composition of the plating on this object is both interesting and significant.

It seems quite possible that various large Greek and Roman metal objects, especially vessels of sheet metal, now on exhibition in our museums, and which are now regarded as being composed of bronze or copper, may in fact be plated objects of various sorts. At least this possibility seems worthy of some investigation.

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