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The Use of Sulphur in Hollow Ancient Gold Objects

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Archaeologists interpreted residues inside hollow gold rings found in Roman burials of girls in the Rhineland as a "cement for chasing". The aim of this study was to analyse this material and to compare it with Mediaeval and modern specimens made from pitch with inorganic filler and organic additives. The cement inside the Roman rings was identified as crystalline sulphur, which has occasionally been reported in the analytical literature as a filler in hollow gold objects from Hellenistic to Merovingian times. As was shown by practical experiments, the consistency of solidified sulphur can easily be adjusted to allow embossing and chasing of filled objects. Therefore, sulphur might act not only as a filler in such items, as was sometimes suggested, but also play a decisive role in the manufacturing of them.

Keywords: SULPHUR, GOLD OBJECTS, FILLER, CEMENT FOR CHASING.

Introduction

During all periods gold has been a very expensive material which people tried to save. The ancient goldsmiths were masters in producing hollow objects from thin gold sheet. Because of the ductile character of gold such items must contain a filling material to prevent them from deformation during use.

The occurence of sulphur in hollow ancient gold objects has so far not been studied systematically. An on-line search for the words "sulphur" (or "sulfur") and "gold" occurring together in titles, keywords, and texts of the abstracts of the Conservation Information Network (CIN, including, among others, the Art & Archaeology Technical Abstracts, AATA) produced no relevant hit. By manual browsing through the literature on ancient gold objects only a few passages, which mention sulphur could be found, starting with Henkel's (1913: 278) book on Roman finger-rings. Deppert-Lippitz (1985: 5) reports sulphur in addition to gypsum, clay, and wax in the gold jewellery of the Römisch-Germanisches Zentralmuseum in Mainz. By employing EDX-analysis, virtually pure sulphur was found in a Roman armring from Eauze la Gars (Eluère & Raub, 1991). According to Ogden's (1982) discussion of filling materials, sulphur occurs in the majority of Roman objects and can even be found in some Hellenistic pieces. Noll (1984, 1988) detected it in the so-called golden Hercules clubs of the 3rd and 4th century AD. Gold objects from the Thetford Treasure contain sulphur as a filler and a cement for gemstones (Cowell, La Niece & Meeks, 1983). There is even an interesting passage in classical literature. In his *Interpretation of Dreams*, Artemidorus (2nd century AD (trans., 1975) says (Book II, chapter 5), while discussing dreams of golden finger-rings:

> "For those that are hollow and filled with brimstone signify deceit and treachery, since they contain something that is hidden. They also signify expectations that exceed the actual benefits, since their mass is greater than their weight."

This entry in an ancient encyclopaedia of dreams and their supposed meaning proves that sulphur was at that time commonly known to people as a filler in gold jewellery.

The use of sulphur did not end with the Roman period. Merovingian garnet jewellery (Arrhenius, 1985), the great gold buckle from a 7th century Anglo-Saxon ship burial (Cowell, La Niece & Meeks, 1983), the head of a 4th century Early Alamannic needle (Raub, 1981), and the 6/7th century lions' heads terminals and their connection of a Byzantine torc in the

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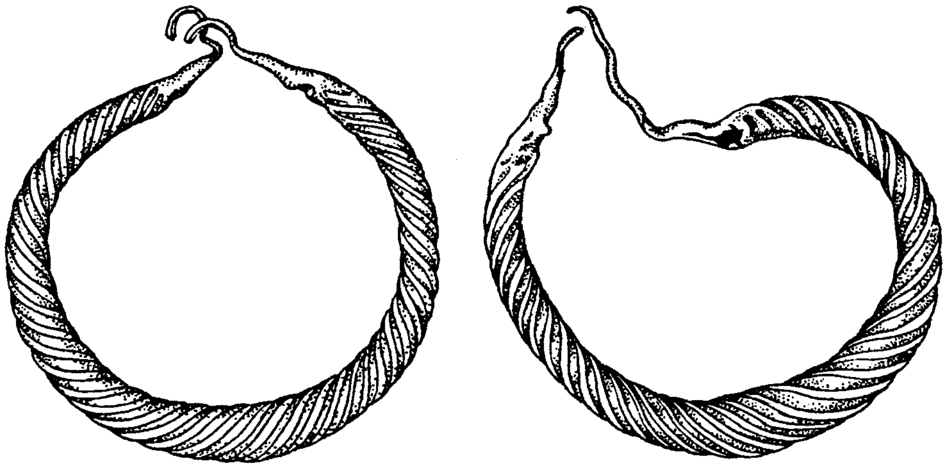

Figure 1. The pair of gold rings from Bonn, Josefstraße (Haberey, 1961). Scale 1:1.

British Museum (Hockey, 1989) were all filled with brimstone.

Although sulphur occurs quite frequently in volcanic areas and is associated with gypsum deposits, it must have gone out of use at some time. No further objects could be found in the analytical literature. Theophilus's detailed 12th century treatise on goldsmithing and later works do not mention this use of sulphur; modern goldsmiths are seemingly unaware of it.

It should be noted that because of the reactivity of molten sulphur, its use in metal objects is restricted to the noble metal gold (and, theoretically, platinum and iridium) and its not too debased alloys (Ogden, 1993). Silver and copper alloys would be destroyed by the exothermic reactions to the corresponding sulphides.

The Material Inside Three Roman Gold Rings

This study started with the analysis of the material inside three gold rings in the Rheinisches Landesmuseum Bonn (RLMB) which were found in the graves of Roman girls in the Rhineland. Two were excavated in Bonn, Josefstraße, in a girl's grave of the second half of the 3rd century (Figure 1). They were each made from two thin (0·2 mm) sheets of gold, which were rolled into tubes and soldered. The two tubes were then bent into semi-circles which were soldered together to create the full ring. This soldered joint is not visible even under the microscope and could only be detected by X-ray radiography (RLMB 4193, B. v. Zelewski). Finally, the torsion grooves had to be chased with punches.

The rings were possibly worn in the ear, although the catch does not look well-suited for this purpose. There is visible wear on one side only. Haberey (1961) noticed, through the holes near the catches, loose pieces of a light brown crystalline material inside, which he interpreted as cement for chasing. Using X-ray diffraction, we found plain (orthorhombic) sulphur (JCPDS 8–247) in both cases (Ring i: RLMB Lab. 8905; Ring h: RLMB Lab. 8906). In a micro-test-tube the material could be easily melted and evaporated without residue condensing at colder parts of the glass, so there is no hint of the presence of any other material except sulphur.

The sulphur sample taken from Ring h had a sooty black material on top. After extraction of the sulphur with carbon disulphide, copper (II) sulphide (Covellite, JCPDS 6–464) and some copper sulphate pentahydrate (Chalcanthite, JCPDS 11–646) were identified. Chalcanthite is known as an oxidation product in the oxidation zone of covellite ores. The covellite must have formed by the reaction of copper out of the gold alloy with the sulphur. There were even some green particles inside the ring which contain copper (tested microchemically), but could not be identified by XRD. The loose, powdery, and sooty appearance of the black material resembles that of the copper sulphide occuring sometimes in black spots on copper alloys (Hjelm-Hansen, 1984; Eggert & Sobottka-Braun, 1999). Ogden's (1982: 40) observation that "Sometimes there is a noticeable admixture of charcoal [in the sulphur filling of gold items, G.E.], but there seems no reason why this should have been deliberate", might very well be a misinterpretation of the appearance of such copper sulphides in one case or another.

Sulphur was also found by XRD (RLMB Lab. 8555) in an armring of the 4th century from Zülpich-Enzen (Follmann-Schulz, 1989). The sample was totally soluble in carbon sulphide (no long chain sulphur molecules present). Other rings of the Rheinisches Landesmuseum Bonn could not be sampled, because the opening for pouring in the filling material is covered by gemstones *in situ*.

Typically, in all three cases much of the now brittle sulphur is obviously missing. Only loose, rustling sulphur particles are left, which might easily get lost (or sampled) through the openings. Further loss of elemental sulphur may not only be due to chemical reaction with alloying metals, which may end in water soluble products like chalcanthite, but also to bacterial action forming either SO_2 or H_2S gas depending on the (an)aerobic situation. In the course of the millennia, even the low vapour pressure of orthorhombic sulphur ($2{\cdot}3 \times 10^{-6}$ hPa at 23°C) must be taken into consideration. There might be cases of now empty gold items where the original sulphur has totally disappeared today.

Sulphur—A Cement for Chasing?

When chasing was the last step in the manufacture of a gold object, is it reasonable to assume that the cement for chasing was then exchanged with sulphur as a filler? Is sulphur, which can even be produced in a plastic variety, suitable for chasing, as was postulated by Hockey (1989), Ogden (1993), Haberey (1961) and Follmann-Schulz (1989); the latter two not knowing the chemical nature of the material inside? To answer this question, one has to look for the required properties of such a material and then perform experiments.

Theophilus (trans. 1979) gives the following recipe for "The Composition Called Chaser's Pitch" (Book III, chapter 59): "Grind a piece of brick or tile very small and melt some pitch in an earthenware dish and add a little wax." As opposed to recipes for other materials, he gives no definite amounts for the components ("some" pitch, a "little" wax). A compositional adaptibility is characteristic for such a material. Cellini (trans., 1967: 15), the 16th century artist and craftsman, used the same recipe and said that the composition has to vary with the season. Even today chaser's pitches are composed similarly and during winter more oil or fat is used to make the mixture softer, while during the hot summer more inorganic filler is used to make it more rigid. Resin, turpentine, and tallow are now in use as a modifier, and grinding bricks can be avoided by the use of gypsum powder as an inorganic filler. Every workshop has its own recipe and the consistency must be adjusted to the material and the form which is to be chased. The chaser's pitch must not be too hard (it must give way during punching) and not too soft (otherwise it will result in indistinct indentations instead of a sharp relief). The chaser can easily test the right consistency with a hammer after the mixture has cooled (Brepohl, 1987: 222).

Sulphur melts easily and can then be filled into hollow items without problem. The consistency of the solidified melt can vary considerably depending on temperature and time (Hollemann & Wiberg, 1985). At a temperature marginally above the melting point of 119·6°C, the melt (called S_λ) consists mainly of eight-membered rings of S-atoms, as in the solid phase (orthorhombic S_α below and monoclinic S_β above 95·6°C). S_λ is transparent, light yellow and fluid. Above 159°C the viscosity increases rapidly, owing mainly to the formation of long sulphur chains with 10^3–10^6 atoms (S_μ). Above the viscosity maximum, at 187°C, the average chain length in the dark red brown viscous melt decreases again. If such a melt is quenched in cold water, a plastic and rubber elastic modification is formed ("plastic sulphur"). The transformation of S_μ into crystalline S_α is extremely low at room temperature in pure sulphur, but can be catalysed by impurities. Therefore, one cannot conclude from the absence of S_μ (full solubility in carbon disulphide, proven for the ring from Enzen) in objects today that this modification was never formed during production.

To check if the right consistency for chasing is achievable practically, the forming of the torsion grooves of the rings from the Josefstraße by punches was taken as an example. A smooth ring with open ends was manufactured from a gold sheet using wooden models. Filling in S_λ-melt yielded a much too brittle crystalline material inside. On the other hand, plastic sulphur formed *in situ* in the ring is much too soft and elastic for use as a cement for chasing. If the melt is heated still higher and filled into the ring, the sulphur tends to fracture after cooling like cracknel during punching. The best results were obtained when the red brown melt was slowly cooled in the air, until it became fluid again. This was filled into the gold ring, which was cooled by water. Because of the volume shrinkage on solidifying, sulphur was poured in as long as possible to prevent the formation of cavities in the interior, which would collapse during chasing. If the sulphur stands overnight, it becomes too brittle again because the S_8-rings, which act as plasticizer in the polymer S_μ, recrystallize. In that case the sulphur could be removed from the ring by reheating: the molten sulphur gushes out of the ring and residues burn away with a blue flame. Removal of the sulphur was also necessary if the metal had to be heated red-hot and quenched to restore its flexibility. On the other hand, the later hardening of the rubbery sulphur makes this material better suited as a firm filling material (Ogden, 1993).

When worked directly after filling in the sulphur, good results which replicate the original rings were obtained. The preparation method uses easily observable properties of the melt (colour and viscosity) and, therefore, requires no measurements of time and temperature and no high degree of skill.

Conclusion

As in the three Roman girls' rings from the Rhineland discussed here, sulphur is frequently found in hollow ancient gold objects (and only in golden ones!). It can easily be melted and used to fill the insides of the objects to protect the thin walls from damage. As was shown by reproduction experiments, sulphur can be adjusted by simple means to the right consistency to allow the chasing of filled gold objects. Such a function seems reasonable, because the exchange of another chaser's pitch for sulphur as a filler does not make sense for the sake of parsimony.

Because of the frequent occurence of elemental sulphur in nature and the possible contamination during its ancient use and the long time of burial, trace element analysis of sulphur for provenancing does not seem very promising. Nevertheless, measuring the isotopic ratio of the sulphur might lead to a distinction between different kinds of geological sulphur deposits (Hoefs, 1980).

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