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PATINATING BLACK BRONZES: TEXTS AND TESTS.

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Introduction.

Recent researches of one of the authors on black patinated objects of Cu-alloys containing small amounts of gold and inlaid with gold, from ancient Egypt and Palestine, dated to the early 2nd millennium BC (the earliest examples of *shakudo*-type alloys in the West) seemed to suggest a correlation between the patina nuances and the presence and quantity of other minor alloying elements in the metal (Giumlia-Mair 1996; 1997; Giumlia-Mair & Quirke 1997; Giumlia-Mair & Riederer in press.). The copper of the statuette of Amenemhat III from el-Faiyum (mid 19th c.BC) in the Ortiz´collection in Geneva (Ortiz 1994; 1996, N° 37) contains small amounts of gold, but also of other metals. The piece has been recently cleaned and shows a purple-black, iridescent and shiny patina, doubtless the best preserved seen up to now by the authors on ancient objects. The statuette is also the largest (H.:26.5 cm) ancient object of this patinated material discovered up to now. Other known examples are significantly smaller and most objects are of normal bronze and only show inlays of this obviously rare and precious material.
The recently cleaned bronze crocodile (19th c.BC, Ägyptische Sammlung Munich, 6080) has a deep black colour and contains gold and small amounts of other metals (Giumlia-Mair 1996; 1997). Most objects of this material identified up to now were found several decades ago and there is a strong possibility that in the past their surface had been variously treated, however on the surface of the Amenemhat III statuette and of the crocodile we have without doubt the best examples of what can be still called an original patina.
The broadly contemporary Syro-Palestinian sword from Balata Shechem (Ägyptische Sammlung Munich, 2907) is of particular interest, because of the clear differences in the composition of the blade of bronze (with around 12% Sn, no Au and only very low traces of other metals) and the blue-black midrib, with 0.5% Au and noticeable amounts of other metals (in particular around 3%As) (Giumlia-Mair 1997; Giumlia-Mair & Riederer in press). This suggested that the small amounts of metals present in the alloy were deliberate additions and induced to wonder wether the ancient artisans were able to control the patina nuances by adding small amounts of metals other than gold and silver to their alloys.
The important pioneering work of the Japanese scholar Denzo Uno (1929) on the patination of the Japanese alloy *shakudo* evidenced the role of gold in the formation of the patina. He produced a large number of test alloys, containing copper, around 5% Au and different amounts of other metals and treated them with several aqueous solutions containing different salts. His experiments showed that the presence of minor alloying elements influences the colour nuances of the patina. His work encouraged the authors to a docimastic approach to this matter. Later studies on *shakudo* and other *irogane*-alloys (Notis 1988, Murakami et al. 1988; Murakami 1993 with further bibl.) were carried out on Japanese alloys treated with the Japanese processes, however no experiments had been carried out before by applying the methods described in ancient texts. The authors reproduced 24 binary, ternary and polimetallic copper alloys containing small amounts of Au, Ag, As, Fe, Sn and Pb, similar to the ancient alloys and tried out the Japanese and other different working and patination processes, as they can be drawn or inferred from Egyptian, Greek, Latin and later sources on the production of black bronzes.

Experimental procedure.

24 copper-based alloys of different composition, some containing Au and Ag, some only containing non-precious metals, were produced in the workshop of the Gold-und Silberschmiedeklasse, Akademie der Bildenden Künste, Nürnberg (Tab.1). Binary specimens containing higher amounts of gold and pure copper samples were added for comparison, but will not be considered in this paper, as their composition does not correspond to that of known ancient alloys. Specimens of all different alloys were worked in different ways:cast only, hammered and laminated by rolling. The best patination results were achieved on hammered pieces. About 1/3 of the samples were polished as in antiquity by means of a smooth semiprecious stone, other were polished with modern instruments for goldsmiths. No differences in the patina growth were noticed by employing the 2 different polishing methods.

Different patination experiments were carried out:

1)Japanese process as described in modern literature (Notis 1988, 316,Table 28.2, solution Nr.1 and 3; Untracht 1982, 671, Rokusho 1 and 4; Murakami 1993, 86)

2)Greek process, as described by Pausanias (ΕΛΛΑΔΟΣ ΠΕΡΙΗΓΗΣΙΣ, 2,3,3), by quenching the red hot samples in aqueous solutions.

3) Chinese process, with 15 test persons, holding in their hands for several hours samples of composition Nr.10, 11,14,16, and pure Cu.

4) the recipe of the alchemist Zosimos as in Syriac Ms 6.29, Cambridge Univ. Library.

The patina of most samples of alloys containing Au was analysed by **XRD** at the Dept. of Materials Engineering and Applied Chemistry, University of Trieste, Italy, and resulted to be cuprite, in some cases with some metallic gold and copper. Sample Nr.16 also contained tenorite. In the patina of samples treated by the Chinese method some chlorides were present. The samples were then examined and analysed under the **SEM/EDX** at the University of Trieste. It should be noted that by this surface method no exact analysis of the elements present in the patina of the test pieces of known composition could be obtained: the Au results varied greatly and the values obtained with different measurements on the same sample were quite discordant, going from 0 to significantly **enhanced percentages** (cfr. also Notis 1988, 323; Craddock & La Niece 1995, 92). 5 of the samples containing gold and silver (10,11,14,15,18) were analysed by **AAS** at the University of Trieste. As expected, there was no variation in the composition of the alloy after the patination treatment. Samples taken from these alloys were examined under the metallographic microscope. The structures were typical of cast, hammered, hammered and annealed, and rolled copper alloys, without noticeable anomalies.

Because of the limited space only the colour nuances, which resulted from the Japanese treatment, are reported in the table (Tab.N°1). A detailed study will be published elsewhere, but some of the results obtained by other treatments will be discussed below.

General Observations.

According to Uno (1929) the addition of small amounts of gold to the copper allows the development of a stable patina, but more than 7 % of Au in the alloy renders difficult the patination. The experiences of the authors by applying different methods showed that the patina developes much easier with lower amounts of precious metals in the alloy. In general already a content of 3% of Au considerably slows down the process. Only in the case of the Greek treatment the samples containing 3% Au developed a good patina. Higher amounts of gold in the alloy result in increasingly longer patination times. Experiments conducted on specimens of *shakudo* with a gold content under 5% demonstrated that the addition of 1% and of 5% of other metals influence the colour of the patina, particularly if the alloy has been previously worked and its crystals are fine (cfr.Uno 1929). The experiments of the authors had similar results:

extensively worked objects with a homogeneous structure, (but also abrasively finished surfaces) are more easily patinated than annealed objects. The addition of small amounts of other metals, such as silver, tin, lead and arsenic to the alloy, improves the texture and speeds up the patination. However, according to Japanese experiments, higher amounts of these elements deteriorate the patination properties of the alloy (Uno 1929).

After the addition of 1% Ag, on some samples a change of the patina colour from black to purple could be observed. An addition of 0.5% As to an alloy containing gold and silver changed the colour to an iridescent blue-black, while the addition of 0.5% As to an alloy containing 1%Au became purple black. According to Uno an addition of 1% Fe changes the colour to blue, but the texture of the patina becomes rough. However the addition of 0.5% Fe to an alloy containing 1% Au and Ag resulted deep purple after the Greek treatment. In general the addition of 2% Sn blackens the patina, but Sn clearly hinders the patination if the Greek method is used. The addition of 5% Sn can produce a brownish patina, if the metal was annealed, but on an abrasively worked surface of the same alloy the patina becomes black. The addition of arsenic produces in general an iridescent patina, but iridescence can appear on other alloys too. Japanese experiments have shown that with higher percentages of the same elements there are further changes in the colour. The addition of 5% Ag turns the colour to brownish, while 5% As turns it to blue. Of course the addition of higher arsenic percentages renders the alloy fragile and difficult to work. This kind of tests were not carried out by the authors, as such high percentages of arsenic and silver, at least up to now, were never encountered in ancient objects.

As instances of ancient patinated objects containing only small amounts of arsenic, tin, iron, lead and no precious metals are known from earlier studies (Giumlia-Mair & Craddock 1993,18; 1993a, 14; Giumlia-Mair 1996, 320;1997, 4; 7) also the patination of such copper based alloys was attempted. All samples were hammered and annealed several times to obtain a homogeneous and finely recrystallized metallographic structure and better patination effects. The addition of 0.5%As to copper produced a dark reddish brown, but iridescent patina, while the addition of 1%As resulted in a darker brown colour of the patina, but also in a bluish iridescence. Copper containing 2% Pb became brownish red, while an addition of 0.5%Fe to copper gave a somewhat spotty, dark purple colour. Copper containing 2% Sn acquired a very pleasant dark orange-red colour and a homogeneous matt surface.

The additions of different alloying elements greatly influence the working properties of the alloys. The following characteristics were observed on samples of different composition, but all worked in the same way, for the same length of time and treated in the same solution. The addition of only one element, such as arsenic (0.5 and 1%), iron, lead and tin to the copper resulted in a low malleability of the alloy (except by addying 2% Sn). The malleability became significantly lower, if the amount of gold was increased to 3%. For example it should be mentioned that the copper-based alloy with 1% Au, 1% Ag and 0.5% Fe had fairly good working properties and could be easily cast and hammered, while the alloy containing 3% Au, 1% Ag and 0.5% Fe resulted to be absolutely unworkable. Alloys containing 6 or 7 alloying elements had a good malleability and good working properties (cfr.Tab.1).

The bad working properties and the longer patination times of alloys with slightly higher gold percentages, as well as the problems encountered in determining the right amount of alloying elements in samples of known composition by superficial analysis, awakened the suspicion that analysis data over around 3%, reported in papers on ancient black bronzes were the result of similar enhanced measurements. Indeed a check of the available data confirmed that higher percentages had been determined by using different kinds of surface analyses, while data obtained by analysing the bulk of the metal by AAS or ICP never exceeded 3%.

Ancient texts and test results.

The writer Pausanias visited Corinth in 165 AD and in his "Description of Greece" he states : "*...also they say that Corinthian bronze, made red-hot and incandescent is dyed by means of its water (of the spring Peirene)....*". The authors tried out this patination method by making the samples red hot and dipping them into different solutions. Among the alloys, which very quickly developed a patina were those containing iron (0.5%) and the alloys N°10 and 12, while alloys without iron were not much affected by this treatment. The small amounts of iron present in most of the ancient patinated objects were previously thought to be impurities coming from the copper ore, but could be due to the use of the Greek process. Apparently the presence of small amounts of iron improves the colour and speeds up the patination. The addition of iron to black alloys is actually mentioned in ancient texts. In the 2nd c.AD, the Greek author *Clemens Alexandrinus (Protr.4,43P)* described the statue of the god Serapis in Alexandria (Egypt) and stated that the artist Bryaxis employed an alloy containing gold filings, silver, copper, iron, lead and tin and that "*..after the polishing and assembling of all parts he dyed it with kyanos and, for this reason, the colour of the statue is almost black.*"(authors transl. Cfr.Giumlia-Mair 1997,12). The medieval scholar Bar Bahlul, who collected alchemistic texts and wrote a Syriac Lexicon, listing metals, alloys and other substances with explanations (Berthelot,1893,II,XVI,123), gives more definitions of Corinthian bronze (the name of these alloys in Roman times). One states that it is an "*alloy of iron and other kinds (of metals)*", a second one that it is "*a mixture of gold, silver, iron and other things*" (I, *Kings*, VII, 45). It is important to note that with the Greek method no patination was achieved on samples containing tin, even when 1% Au and 1% Ag were present. However a fairly good patina developed on samples containing tin, when more gold (3% Au) was present in the alloy.

The Chinese patination method, carried out just by holding the objects in the hands (Giumlia-Mair & Craddock 1993a) works perfectly well and surprisingly fast. Also pieces patinated by other methods, when scratched, redeveloped very quickly a fine patina just by handling. Latin texts mention that collectors of Corinthian statuettes used to carry them around (Pl., N.H., 34, 48) and spent most of their days with their "rusty metal sheets" (*in aeruginosis lamellis*) (Seneca, brev.vit., 12,2). The emperor Nero carried about an Amazon statuette and G.Cestius had his statuette with him even in battle (Pl., N.H., 34, 48). Handling the statuettes was surely a good idea: it enhanced the beauty of the patina and restored it, when scratched.

About 10 years ago one of the authors came by chance across the Syriac translation of the by now repeatedly published and discussed recipe of the Egyptian alchemist Zosimos (Berthelot 1893, II, 223) for preparing "*Corinthian bronze or black metal stripes*". This is the only text, which states that Corinthian bronze was black and gives in weight the exact recipe (1 mina of Cu, 8 drachmas of Au and 8 drachmas of Ag = 82,6% Cu, 6.9% Au, 6.9% Ag) for the preparation of the copper "*which is used for the process of colouring*". Earlier interpretations of the text should now be corrected as follows. The text specifies "*the primary dyes are ripened from gold, silver and copper*" and are used, depending on the quantity, for the doublement, the multiplying, the softening and stretching of gold, silver and copper. This is clearly the description of the substance called by alchemists "the ferment of gold". One of the most important principles of alchemy is "what has been dyed will dye"(Berthelot, 1888, 3, 160; III, XIX, 1, 170). This means that the alchemist prepared an alloy of particular composition, which had to be treated in different ways to become "the preparation" for dyeing. It is clear that an alchemistic "preparation" is meant, because the first stage of the process involves the blackening or "*melanosis*", by breaking down the copper with sulphur, then reverting it to metal, as some sort of rebirth and purification of the material. For the patinating solution 2 half setias of vinegar and

8 drachmas of *šhahira* should be used. Several Japanese solutions containing vinegar are reported (Notis 1988, 316; Untracht 1982, 671), while the Lexicographie of Duval (1893, 336) gives for the word *šhahira* the meaning verdigris or copperas, not vitriol, as in Berthelot's translation (1893, 223). The ingredients of the solution listed in the Syriac recipe are therefore similar to those used in the Japanese process. Only a portion of this treated alloy had to be mixed with copper, thus the percentages given above would result much lower, being diluted with copper. In a passage Zosimos seems to recommend the double amount of copper (f.33r.,1.17). This reduces the percentage of precious metals to about 3%. Elsewhere (f.34r.1.2) one part of ten of the "preparation" is prescribed, i.e. about 0.7% of Au and Ag would be present in the alloy. The analysis of several ancient objects gave as result similar percentages.
It should also be mentioned that another entry on Corinthian bronze in the Lexicon of Bar Bahlul (Berthelot, 1893, II, 123) describes it as "*copper, alloyed with gold and silver and with copper*", referring clearly to ist use as a dyeing substance for copper.
In the Syriac text there are many more recipes for alloys containing gold and silver but also different amounts of other metals, such as lead, arsenic (also in form of realgar or orpiment) some iron compound and tin. Apparently the procedure was to prepare a larger amount of a treated alloy, which was then divided into the portions necessary to obtain the best patination results and, changing the ingredients, different hues. Of course in the eyes of the alchemists it was the complicated treatment, used to obtain the "preparation", which made all the difference.

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Nr.	Composition	Colour and iridescence	Workability
1	Cu 99,0 % Au 1 %	Black purple, blue irid.	cracks and casting faults
2	Cu 97,0 % Au 3 %	greyish brown, blue irid.	good malleability
3	Cu 99,0 % Ag 1 %	brown, purple irid.	fairly good mall.
4	Cu 97,0 % Ag 3 %	dark grey-green, purple irid.	good malleability
5	Cu 99,5 % As 0,5 %	brownish red, bluish irid.	brittle with cracks, patchy
6	Cu 99,0 % As 1 %	dark brown, slight blue irid.	porous, patchy, cracks
7	Cu 98,0 % Sn 2 %	dark orange-red	good malleability
8	Cu 98,0 % Pb 2 %	brownish-red	porous, patchy
9	Cu 99,5 % Fe 0,5 %	red-purple	fair malleability, casting faults
10	Cu 98,0 % Au 1 % Ag 1 %	purple-black	fair malleability, some cracks
11	Cu 96,0 % Au 3 % Ag 1 %	blue-black	low malleability, cracks, casting faults
12	Cu 98,5 % Au 1 % As 0,5 %	purplish-black, bluish irid.	fair malleability, some cracks
13	Cu 98,5 % Ag 1 % As 0,5 %	dark-blue, silvery irid.	fair malleability, cracks
14	Cu 96,0 % Au 1 % Ag 1 % Sn 2 %	shiny, black-purple	excellent malleability
15	Cu 94,0 % Au 3 % Ag 1 % Sn 2 %	inhomogeneous purple-black	very low malleability, brittle
16	Cu 95,0 % Au 1 % Ag 1 % Sn 3 %	greyish, greenish irid.	good malleability
17	Cu 94,0 % Au 1 % Ag 1 % Sn 4 %	dark purple-grey, blue irid.	good malleability
18	Cu 97,5 % Au 1 % Ag 1 % Fe 0,5 %	irregular purple-red	fair malleability, casting faults
19	Cu 95,5 % Au 3 % Ag 1 % Fe 0,5 %	dark brown-black	brittle, fragile, not workable
20	Cu 95,5 % Au 1 % Ag 1 % Sn 2 % As 0,5 %	dark purple, blue irid.	high malleability
21	Cu 96,0 % Ag 1 % Sn 1 % As 1 % Pb 1 %	purple-grey, purple-blue irid.	fair malleability
22	Cu 96,0 % Ag 1 % Sn 1 % Fe 1 % Pb 1 %	shiny, yellowish-green	low malleability, cracks, casting faults
23	Cu 95,0 % Au 1 % Ag 1 % Sn 2 % As 0,5 % Fe 0,5 %	purplish, silvery-blue ir.	good malleability
24	Cu 93,5 % Au 1 % Ag 1 % Sn 2 % As 0,5 % Pb 2 %	purplish, blue irid.	high malleability

Table N° 1

The picture used as background pattern for table N° 1 is a photo (by A.Giumlia-Mair) of the Amenemhat III statuette in Geneva (Ortiz 1994 and rev.ed. 1996), discussed in the text.