Surface analyses on modern and ancient copper based fakes

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Over the last two decades, together with the increasing prices in the antique market and the proliferation of private 'hobby collectors', the number of fakes in circulation among antique shops, auctions and even institutions and museums has noticeably increased. So called 'bronzes' seem to be the favourite objects for both fakers and inexperienced collectors. In some cases the fakes are well made, so that often the professional can be fooled by them also. In this paper some examples of modern and ancient fake objects will be discussed.

Keywords: Ancient fakes, Modern fakes, Noble patina, False patina, Artificial patina, Artificially patinated copper alloys, Imitations, Roman series production jewels, Special alloys, Fake coins, XRF, SEM/EDS, XRD, AAS, ICP

Introduction

The borderlines between fakes, imitations, replicas and facsimiles are a matter of intention, for instance, in the case of objects such as the many facsimile and reproductions that circulate in flea markets, trash shops and small 'antiques' shops. Many of them were indeed made with the intention of producing fakes and are sold as ancient objects mainly on the black market and without any documentation.

However, more and more such fakes end up in museums and other institutions, mostly as gifts of well intentioned private collectors and these have to be identified. In most cases, and mainly for diplomatic reasons, nondestructive methods are required by the people who are responsible at the various institutions in which the suspicious pieces have landed. The examination of the patina by surface analyses such as XRF and SEM/EDS can represent a good solution in various cases and an excellent approach to the problem in more complex situations.

Ancient fakes can be particularly important for the understanding of the value of the various materials and of finished objects in antiquity. Some examples of fake items, normally produced in valuable materials, are discussed in this paper.

Analytical procedure

For the determination of the composition of the different patinae and surface layers, various analytical methods were employed. All objects were first examined by different optical devices with different magnifications and by optical microscopy. X-ray fluorescence spectrometry was mainly employed as the first overall analysis method and in many cases it was also sufficient for the identification of clumsy fakes, such as painted fake patina or for the determination of 'wrong' elements present in both, surface layers and in the bulk metal. As a next step, when the pieces to be analysed were small enough to be introduced into the chamber of a scanning electron microscope (SEM) or when a sample could be taken, an SEM study of the microstructure and of the surface layers was carried out. Particular attention was given to the examination of the structures on sections and to the interface between the various layers. Further, energy dispersive X-ray analysis (EDX) was performed on the microstructural differences visible within the surface layers.

Backscattered electron images were generally very helpful for the determination of the micromorphology and for the identification of the layers on the sections or fractures. In many cases the elemental distribution, as revealed by backscattered electron images, allowed the quick identification of fake patinas.

X-ray diffraction (XRD) analyses were in some cases employed for the identification of crystalline compounds present on the surfaces of the examined pieces. Bulk analyses were performed by atomic absorption spectrometry (AAS) and/or by inductively coupled plasma spectrometry (ICP). For these analyses samples of clean metal were taken with a jeweller drill. Any surface layer and any corrosion visible in the sample were discarded and the clean turnings were weighed, dissolved in aqua regia and diluted as required for the common AAS or ICP procedure.

Noble patina, artificial patina and fake patina

Copper based alloys develop their patina in the soil, i.e. in a damp oxygenated environment. Copper dissolves first along grain boundaries and forms red cuprite (Cu_2O), which in the upper layers reacts again with the environment, forming carbonates (malachite, Cu (II) carbonate ($CuCO_3.Cu\ (OH)_2$) or, in drier soil, blue azurite, copper (II) carbonate ($2CuCO_3.Cu\ (OH)_2$).[1] Of

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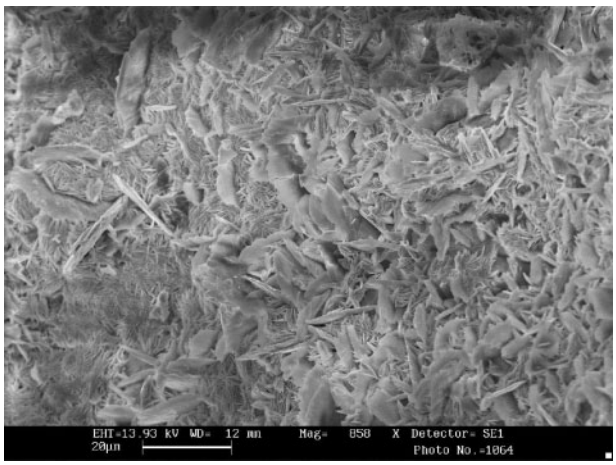
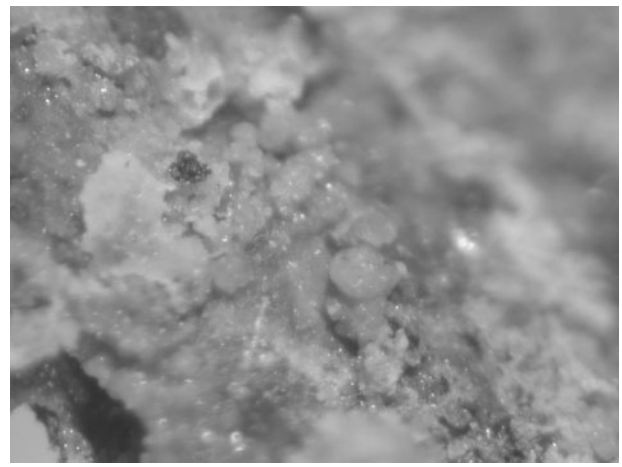


1 SEM micrograph of the loose patina on the surface of a fake 'early Italic' statuette, produced by treatment with acids. (Photo: A.Giumlia-Mair)



2 Ground malachite and other substances, applied with glue on the surface of a fake, seen under the microscope. (Photo: A. Giumlia-Mair)

course, if the soil is acidic, the dangerous and very active chlorides (atacamite and paratacamite) can form and these have to be promptly treated. However, the natural patina, which develops on copper alloys and mainly shows in section as an internal thin red layer of cuprite, covered by the well known green surface of carbonates, is the so called noble patina, a stabile and attractive protective layer. The noble patina grows between the surface crystals and often, particularly on hammered pieces, also inside the crystals, as intergranular and infragranular corrosion, a natural phenomenon, which is very difficult to imitate.[2]

Several elements, notably zinc and iron, which do not belong to the original composition of the metal, but are absorbed during burial from the environment, are often present in the corrosion layers, while some of the elements, which originally belonged to the composition of the alloy, can completely disappear from the upper levels and also from the regions immediately under the patina. Therefore, surface analyses of patinated or corroded copper based objects are always to be considered as semi quantitative only, but can be perfectly suited for preliminary examinations and for spotting out fakes. Particularly high zinc percentages, present in the patina, but not in the bulk metal, might also be the consequence of electrochemical cleaning, carried out in the past, by using a zinc plate or foil in an acidic solution.

It is further important to note, that in antiquity, in different periods and in different regions of the ancient world, several artificially patinated copper based alloys, mostly containing low amounts of precious metals (around 0·5–1%) were employed. However these beautiful blue-black, purple-black or silvery-beige surfaces, mostly inlaid with precious metals, are very different from the layers found on modern fakes.[3,4]

There is in circulation, in flea markets and small antique shops all over Europe, quite a number of statuettes made of copper alloys, which try to imitate ancient objects with a surface layer of fake patina. A whole series of different treatments employed to achieve a credible surface is by now well known. A few examples are listed below.

The loose patina on the surface of a fake 'early Italic' statuette, seen on a SEM micrograph (Fig. 1), is produced by treating the metal with acids. Several of these statuettes are made of common leaded brass or of gunmetal and the surface layer looks thin and powdery.

In other cases (Fig. 2) the patina is simply ground malachite, applied on the surface with glue, on the same type of modern copper based alloys.

Other methods, which are quite easily detected by surface analyses, are the (relatively clumsy) use of paint or lacquer in different greenish hues and the application of mixtures of glue, lacquer and even gypsum, mixed with ground up copper carbonates, green paint and dirt, often also partially stained with rust to make the piece look 'ancient' (Fig. 3).

A natural looking patina develops very quickly on copper based alloys by exposing the finished objects to rain, wind and polluted air for some months or by covering them with dung. The copper compounds, which develop on the surface are however different from those found in a patina, developed during burial.[5,6] Some fakes of this kind are also easy to recognise because of the typical 'runny' features of the corrosion.

A further relatively common type of fake patina, most probably coming from Eastern workshops producing fakes, shows a characteristic very dark brown or blackish double layer, containing, among other elements, zinc, lead, sulphur and chlorine. Often there are visible blue-whitish spots on the upper level. In all these cases no visible corrosion penetrates the metal.

Different workshops, which use various techniques, are active in different places and countries. The different patina layers and the various compositions of the bulk metal can, at least in some cases, give an idea of the larger regions in which the fakes might have been produced.

False patinations were also fashionable in the last centuries and were achieved mainly by using chemicals. Handbooks for metal artisans give a variety of recipes for the production of real looking *patinae*, which can however be easily detected by examination and with simple analyses, especially because of the presence of indicative elements.[7,8]

Ancient fakes and imitations of costly objects

Fakes of valuable objects are not a modern invention. A fairly large number of ancient fakes have been known for a long time, from the famous Shabaka Stone, which

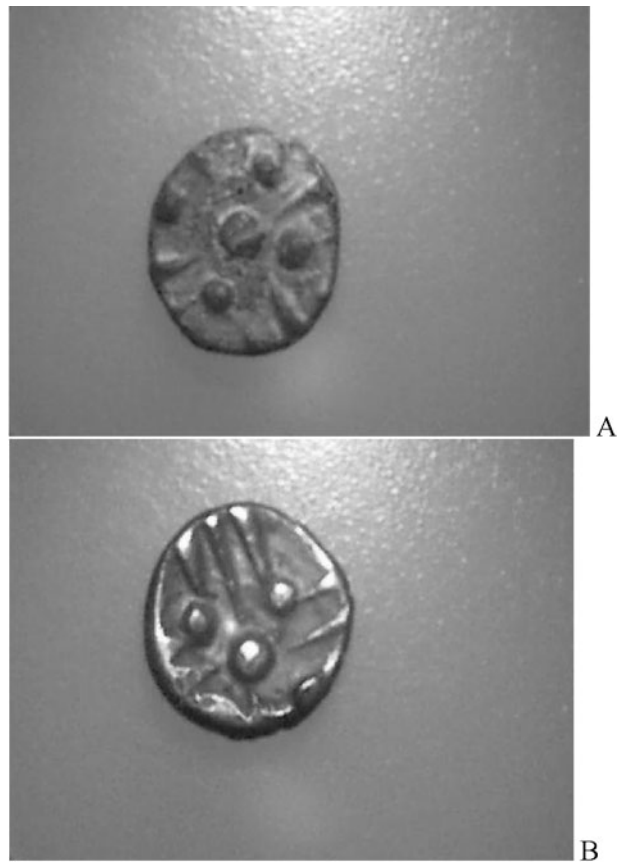
3 Fake statuette of a satyr. The 'patina' is a mixture of organic lacquer, gypsum, ground up copper carbonates and dirt, partially stained with rust. (Photo: A. Giumlia-Mair)

pretends to report a much older text, but is dated to the time of the 25th Dynasty, 716–702 BC, when the text was carved,[9] to the many gold and silver imitations used in particular by Egyptian and Roman alchemists, but still known and employed in the Middle Ages.

The most common fakes, both in antiquity and in modern times, are coins. The example in Fig. 4 is an ancient fake of a Celtic silver *drachma,* which shows, compared to other similar *drachmae*, a particularly rough and dark surface. The XRF analysis revealed it to be made of a tin–copper alloy (65% Sn, 24% Cu) with only 1·5% silver and 3·5% lead, while authentic Celtic coins are made of silver with only ca. 2–6% of copper. The high tin alloy is much harder than unalloyed tin and looked convincingly silvery to the eyes of ancient people who did not see silver coins very often.

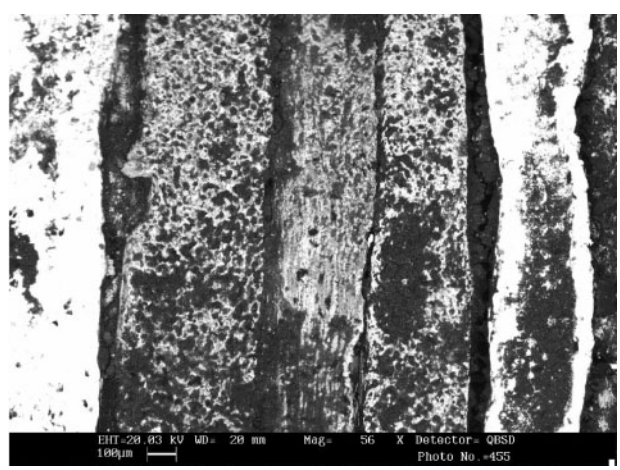
The artificially patinated objects, as previously mentioned, were luxury items for the rich[3,4] and as such, very interesting for fakers. Analyses of ancient items, but also information from ancient Egyptian, Greek and Latin sources[10] indicate, that there were fakes (or imitations?) of patinated and inlaid items, produced with alloys that did not contain precious metals.

Recent experiments showed that copper alloys containing small amounts of As and Fe also develop a patina, but the dark layer is not as deep blue- or purple-black as the real *Corinthium aes* alloys and the patina is friable and not compact.[11]

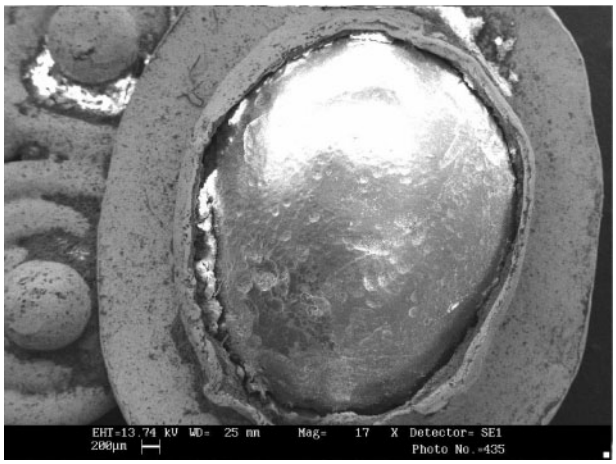


4 *a* Ancient fake of a Celtic silver *drachma*, made of 65% tin, 24% copper, 1·5% silver and 3·5% lead. *b* Authentic Celtic *drachma.* Celtic *drachmae* are made of silver with only ca. 2–6% copper. (Photo: A. Giumlia-Mair)

A good example is a Roman medical instrument from a physician's grave at Cologne (Römisch-Germanisches Museum Köln, inv. No. 8675), inlaid with silvery and reddish, dark spotted, wires. The EDS analysis (Fig. 5) showed that the body metal was brass with around 20% zinc, the silvery wire was made of a good silver with only



5 SEM detail of Roman medical instrument, Römisch-Germanisches Museum Köln, inv. No. 8675. The body metal is brass with ca. 20% of zinc, inlaid with a silvery wire, made of silver and a reddish wire of copper with ca. 3% of arsenic, which was originally artificially patinated as cheaper imitation of Corinthian bronze. (Photo: A. Giumlia-Mair)



6 SEM micrograph of the green central stone of a Roman earring of the type *crotalium*, first century AD. The bubbles in the stone show that it is a simple green glass and not prase or plasma (stones of the quartz group). The jewel is a series product, but made with good quality gold and real pearls. (Photo: A. Giumlia-Mair)

around 3% copper, and the reddish wire was copper containing around 3% arsenic (a deliberate addition). Patination experiments demonstrated that, after a chemical bath, copper containing 0·5–1% of arsenic, becomes dark brown with a bluish iridescence. This was most probably the original colour of the inlaid wire.

The question if the studied object was a fake or simply a cheap imitation of a more precious version does not always have a simple answer. In several cases the borderline is extremely difficult to establish, however, finding out more about such ancient fakes or imitations is always worth the effort, because the knowledge about these items can give us more than just the facts and the data about the composition of the various materials. Fakes and, perhaps even more, imitations of costly objects allow us a glimpse into everyday life of ancient man, into the taste of the period and into the value of worked materials and can sometimes tell us more than the discovery of extremely precious and rare exceptional finds, which could only belong to a few persons in a restricted society.

There is still a third possibility of interpretation for the use of cheap substitute materials in the production of ornaments, which should not be forgotten. In periods of richness and general abundance the requirement for jewels increases and this leads to the accelerated production of decorative items, which in different times might have been finished with more accuracy and by using better quality materials. This was for example the case with a small Roman earring, a *crotalium*, found in Aquileia and dated to the first century AD.[12]

The jewel consists of a central green stone mounted in gold, decorated with tiny spirals and granules and with two pendants, hanging from two lateral loops and each ending with a pearl. SEM/EDS analyses have shown that the central stone bezel and its spiral and granules decorations were all cast in one piece, i.e. that they were directly reproduced as casting from an original jewel for which thin gold sheets and real filigree and granulation had been employed. The examination of the stone showed that it is simple green glass, but the pearls are

7 Modern fake of a silver stater from Metaponto, *Magna Graecia*, made of simple tin with an addition of 4% of copper. The original coins are dated to third century BC (Photo: A. Giumlia-Mair)

real and the gold is very pure and of good quality (Fig. 6). These data suggest that the *crotalium* was quickly reproduced by casting, most probably by producing several copies from an already existing, properly worked example, with the aim of speeding up the production of a particularly fashionable and therefore much requested piece of jewellery.

The piece is not a fake and also not a cheap imitation, because the materials used are of good quality, with the only exception being the green glass stone. However it is well known from the ancient literature, notably from Pliny,[13] that emeralds were highly appreciated in Roman times and that among precious stones they ranked third in value, after diamonds and pearls, but it is quite clear that not many real examples of these rare stones, which came all the way from India, were in circulation. Indeed many Roman jewels are decorated with green stones, but most of them are stones belonging to the quartz group (for example prase or plasma) or are made of glass as in this case. Imitations of emerald were therefore common practice, even for ornaments for which good gold alloys and real pearls were used. In this case these are not fakes or imitations, but series production.

Modern fakes of ancient coins

Fakes of ancient coins are countless and the variety of the materials employed, from gunmetal to debased silver alloys with nickel, to aluminium bronze, show the inventiveness of the fakers. In the present paper only a few examples can be given.

A fake of a silver stater from Metaponto in *Magna Graecia*, the original of which is dated to the third century BC,[14] is for example made of simple tin with an addition of 4% of copper (Fig. 7). The low copper content does not darken the white colour of the metal, but it stabilises the corrosion resistance of tin, which if not alloyed would transform into a whitish powder at 13°C, and hardens the metal enough to imitate the characteristics of silver to the eye of inexperienced buyers, but a simple examination by XRF would immediately reveal the deception.

However, not all fake coins now in circulation were made to deceive. An instance of simple imitation, without any intention of fraud, is the 'silver' tetradrachm with the owl and the head of the goddess Athena on the reverse (Fig. 8), produced as a token for his clients by an olive oil merchant in the last century and made of a common copper, tin, lead alloy. This is the imitation of a real silver coin, minted in Athens from the mid sixth century BC (*see* pp. 31–35 of Ref. 14).

The idea was that of advertising the olive oil company, however, now and again, some of these coins

8 Nineteenth century AD imitation (facsimile) of a real coin, minted in Athens from the mid sixth century BC, for advertising an olive oil company, now sold as antiquity (Photo: A. Giumlia-Mair)

are sold to inexperienced collectors as antiquities. Of course an examination by any surface analysis would easily show, that they are not made of the silver alloy employed in ancient times.

Conclusions

In this paper, some examples of modern fake surface layers were presented and compared with the common types of patina found on ancient objects. The instances presented have shown that the identification of fake *patinae* can be relatively easily carried out by employing common analysis methods, such as XRF, SEM/EDX and, in the case of more sophisticated fakes, by analysing the compounds by XRD.

It is however important to note, that the strange composition of surface layers often do not correspond to the composition of the bulk metal of the objects and that this can be due to conservation treatments carried out in the past.

Ancient fakes can be distinguished from 'real' ancient pieces by the same methods. In these cases the composition of the alloys (i.e. bulk analyses, such as AAS and ICP) are mostly necessary for an accurate identification.

Coins are certainly the most common fakes in circulation and a huge variety of imitations of mainly precious alloys have been recognised in the last decades. A comparison with the composition of certain ancient examples is, of course, the easiest way of recognising various types of modern fakes.

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