revista Matéria
ISSN 1517-7076

Revista Matéria, v. 16, n. 1, pp. 540 –559, 2011
http://www.materia.coppe.ufrj.br/sarra/artigos/artigo11439

Foil and leaf gilding on cultural artifacts; forming and adhesion

E. Darque-Ceretti[I], Eric Felder[I], Marc Aucouturier[II]

[I] MINES Paristech-CEMEF, Centre de Mise en Forme des Matériaux, CNRS UMR 7635, BP 207, F-06904 Sophia-Antipolis, France.
e-mails: Evelyne.darque-ceretti@mines-paristech.fr ; eric.felder@mines-paristech.fr
[II] Centre de Recherche et de Restauration des Musées de France, CNRS UMR 171, Palais du Louvre, porte des Lions, 14 quai François Mitterrand, F-75001 Paris France.
e-mail: Marc.aucouturier@culture.gouv.fr

ABSTRACT

The process used to obtain foils of more and more thin thickness and coat them on artefacts varied during centuries. It started from thick foils of the first ages mechanically assembled and evolved until the rolled and beaten leaves, a few hundred nanometres thick. This paper will develop, through examples taken from laboratory studies on museum objects, the main evolution steps of gold leaf forming. It will discuss the present knowledge about processes used by hand-workers of different origins and periods: antic Egypt, Roman Empire, western and oriental Middle-Age, South America, modern Europe. A recent mechanical modelling work about gold forming by beating will be exposed. Then will be described, still through recent examples, some of the non-destructive and destructive laboratory methods used to characterise ancient and modern gildings, their composition, thickness and adhesion modes. The different coating process will be discussed, owing to the presently available knowledge. These depend on the substrate nature and the possible necessity to treat its surface before and during the gilding process. Such treatment varies from the “white preparation” found on antic Egyptian artefacts and also on wooden decoration of baroque Brazilian churches, to “oil gilding” used for the recent restoration of the Invalides roof in Paris. It may also include a high temperature firing, as for gilding with powder issued from leaf grinding on Middle-Age Syria glass. The paper will end with a listing of the numerous research perspectives open for the presently poorly developed study of the adhesion mechanisms between gold leaf and its substrate, to understand fully the gilding process.

Keywords: Cultural heritage, Gilding, Surface, Adhesion, Forming

1 INTRODUCTION

Gold foil and leaf have been used by most human civilisations to decorate all kinds of artworks: bronze, stone, ceramic, wood, cartonnage of the Egyptian sarcophagi, glass objects, etc. The present paper is an attempt to draw a summarised story of the gold foil and leaf preparation and coating on various materials used in cultural heritage artefacts along the ages, starting from the thick gold foils mechanically fastened onto metal or ceramic pieces of ancient Egypt or Mesopotamia to reach the very thin gold leaves applied on the surface of precious wood sculptures during the Baroque period or on the metallic roof of the Invalid Church in Paris. That crucial question of the mode of thinning of the gold leaves will be discussed from the mechanical viewpoint and a model will be developed explaining how the exceptional mechanical properties of gold allow obtaining metal leaves of an extreme thinness, a specific process refined by generations of gold hand workers and still used at the present time.

But foil or leaf gilding is not only a question of obtaining good quality and colour gold films; it is also a process of coating which was applied to a very large number of substrate materials. This required from the artisans the invention of various kinds of recipes to obtain more or less liable adhesion results onto those substrates. That question will be discussed through the description of the gilding studied on cultural heritage material as different as metal, stone, ceramic, glass, wood or other organic artefacts. Some studies conducted in the laboratories of the present authors with modern investigation means will be described in that framework.

The question of the structure of the interface between the bulk object and its gold coating and of the adhesion mode leading to a reasonable strength of the assembly will be detailed and the necessary studies to be developed in order to better understand and better preserve that strength will be discussed.

Autor Responsável: E. DARQUE-CERETTI Data de envio: 13/05/11 Data de aceite: 07/06/11

2 A BRIEF HISTORY OF GILDING, DEFINITIONS

The base product used for gilding may be either pure gold or a gold-base alloy. The alloys were traditionally obtained by alloying gold with silver, copper or both metals. The content of alloying element is adjusted to obtain a desired colour, varying from the pure "gold" colour to "red gold" (mainly copper addition), "green gold" (limited silver addition) or "white gold" (larger silver addition) [1]. Modern goldsmiths are using other alloying elements, such as palladium, platinum, mercury, etc. but they are not commonly used for gilding. The gold content of a gold alloy is measured in carat; 100 % gold is 24 carat; so for instance 18 carat gold is a 75 % gold alloy.

The numerous authors who focused their writings on foil and leaf gilding agreed more or less to the following definitions for the description of the large range of gold film thickness applied to various substrates [2-3].

- A *gold sheet* is a thick plate of gold obtained by the first hammering or rolling of the gold or gold alloy ingot;

- *Gold foils* have an intermediate thickness, more than about 10 µm, obtained by hammering or rolling the sheets;

- *Gold leaves* are obtained by beating. Their thickness is smaller than 10 µm and can be as low as 0.1 µm. They are not able to support their own mass and must be handled with a special knife blade or brush.

The first gilding technique was carried out using foils. As foil can be handled without special precaution, it could be directly applied to the objects and mechanically fastened. A stone vase (fig. 1) found in south Egypt dating from the Nagada period (end of prehistory 4000-3100 BC) is kept in the Louvre museum. Its handles are decorated with thick gold foils mechanically fastened.

Figure 1: Stone vase with foil-gilded handles. South Egypt 4000-3100 BC, Louvre museum

The first application of gold foil onto metal is reported on the 3rd millenary BC [3,4]. The British museum holds a set of "nails" in silver from Syria (c. 3000 BC) whose heads are covered by gold foils folded on the back of the nail's head to fasten them [3]. That technique of foil mechanical fastening lasted for a long period of time. For instance the child's head of figure 2, from the treasure of Oxus dated of the 3rd century BC is covered with a gold foil assembled on its edges by burnishing [4]. Similarly, on the bronze statue of Karomama (850 BC) kept in the Louvre museum, one finds on the arms and legs engraved incisions where the edges of the gold foil, now lost, were forced to keep the foil in place.

Figure 2: Foil-gilded head with mechanical fastening of the foil. Ancient Iran, 500 BC, British museum

The most ancient document about gold foil or leaf mechanical forming was found in an Egyptian tomb of Saqqara, dated of 2500 BC (fig. 3) [6]. One sees a gold melting operation and a worker beating (or hammering?) gold with a round stone. Another Egyptian illustration, found on the funerary manuscript of Neferhonpet (14th century BC) describes him as the "chief of the makers of thin gold" which indicates he was probably a true goldbeater. The beating technique appears to have been brought to its perfection in ancient Egypt as some authors [5] report a leaf thickness of 0.2 µm already in Luxor during the 18th Dynasty (1550-1300 BC). This is not more than twice the ultimate thickness reached by the modern gold beaters (with pure 24 carat gold). Even if that value is not very safely attested, another value is given by Pliny the Elder at the beginning of the 1st century AD [6]. Starting from data given by that author on the weight of a stack of 1000 gold leafs, a simple calculation shows that the goldbeaters of that period were able to reach a thickness of 0.4 µm. One can then consider that leaf processing was completely mastered during antic civilisations, Greece and Rome, at least after the 1st millenary BC. It was applied on all kinds of materials until now.

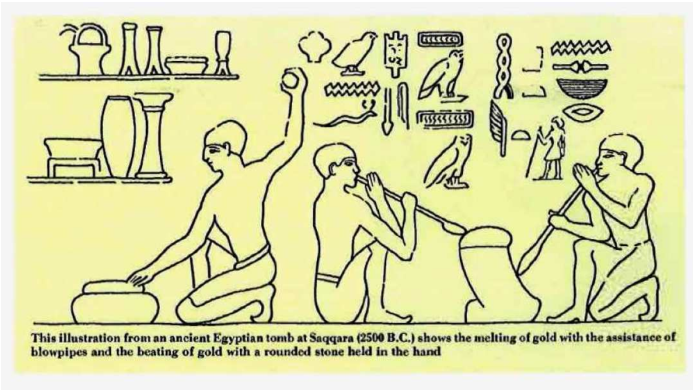


Figure 3: Illustration from an ancient Egyptian tomb at Saqqara (2500B.C.) showing the melting and beating of gold

At the end of the 1st millenary BC, probably around the 3rd century BC in China, appeared *mercury gilding* on metals. Pliny the Elder in its Encyclopaedia written during the 1st century AD [6] reports a special foil gilding technique on metals in which mercury is used as an adhesive. That technique is mentioned in the modern literature as *cold mercury gilding* in opposition with *amalgam gilding* for which gold powder or fragments are first mixed with liquid mercury to obtain an amalgam further applied on the metal surface and heated to a temperature high enough (about 400° C) to eliminate most of the mercury by evaporation [4].

That technique of mercury gilding was the most common for metals (silver and bronze) gilding during the whole period between the 1st century AD up to 19th century. Magnificent examples of artworks may be mentioned as the Paradise door of the Baptistery of Florence (Italy), achieved in 1452.

Mercury gilding of metals, a health-hazardous process, was replaced by *electrolytic gilding* as soon as the electrical batteries were invented, i.e. in 1800 for the Volta battery, 1836 for the more efficient Daniell battery.

In fact, gilding by an electrochemical process was invented well before electrolytic gilding itself. It has been shown indeed [7] that the ancient pre-Columbian South American civilisations Vicus (300 BC-500 AD) and Mochica (100 BC-850 AD) used already the natural electrochemical potential difference between gold and copper to obtain thin gold deposits from gold solutions on their jewels or ritual objects. That technique, called *electroless gilding* is still used in the electronic industry.

Those same pre-Columbian civilisations apparently also invented a very ingenious technique of surface gilding, *depletion gilding* or *mise en couleurs* (the French term is used in all languages) in which a copper-gold alloy is oxidised and/or etched to eliminate the copper of the surface. A final polishing (*burnishing*) leaves a pure gilded surface. *Burnishing* is the technical term for mechanical surface flattening.

The 13th century treatise of Bartholomeus Angelicus *De Proprietatibus Rerum* mentions the possibility of joining gold and silver by simple hammering [8]. That practice of joining gold leaf to a metal substrate, not only silver but also bronze and iron, by simple mechanical pressing (eventually hammering), was used during the Middle Age in Europe and in the Middle East.

Another ancient gilding process is *powder gilding*. Less expensive than foil or leaf gilding and normally easier to process, it appeared as soon as it was possible to grind gold foils or leaves into a fine powder, which was then mixed with a binder, generally an organic binder, and appliedt as a paint on the surface to be gilded. The binder may be eliminated by heating. It can be applied on any kind of substrate and is reported as soon as the 1st millenary AD in China. A good example is the enamelled and gilded glass elaborated in Islamic Iran in the 12th century (fig. 4) [9].

Figure 4: Enamelled and gilded glass fragment [10]. Syria 12th -13th century. Louvre museum

To end that summarised history of gilding through the ages, one comes to the modern (20th century) gilding techniques. It was seen that *electrolytic* or *electroless gilding* are still practiced in industry and jewellery. Other processes are: gilding by thermal decomposition of an organometallic compound containing gold ("liquid gold"), physical deposition techniques as thermal evaporation or cathodic sputtering, etc. [15].

From now, this article will concentrate only on foil or leave gilding, ignoring the other processes.

3 THE MANUFACTURING PROCESS OF GOLD LEAVES, AN EXAMPLE OF MODERN PROCESS

For more than 4000 years man has been able of manufacturing very thin gold foils with a 0.2-0.3 µm thickness [5, 6]. This impressive technical know how is based on a very ingenious process, *the beating*, where one strikes with a hammer many thousand times a stack put on a flat anvil. That stack may be composed of up to 2000 elements with alternatively gold foils and thicker inserts made of paper or polymer.

The two main steps of the process are described in fig. 5. Figure 6 shows how a gold beater workshop at the 18th century was organised.

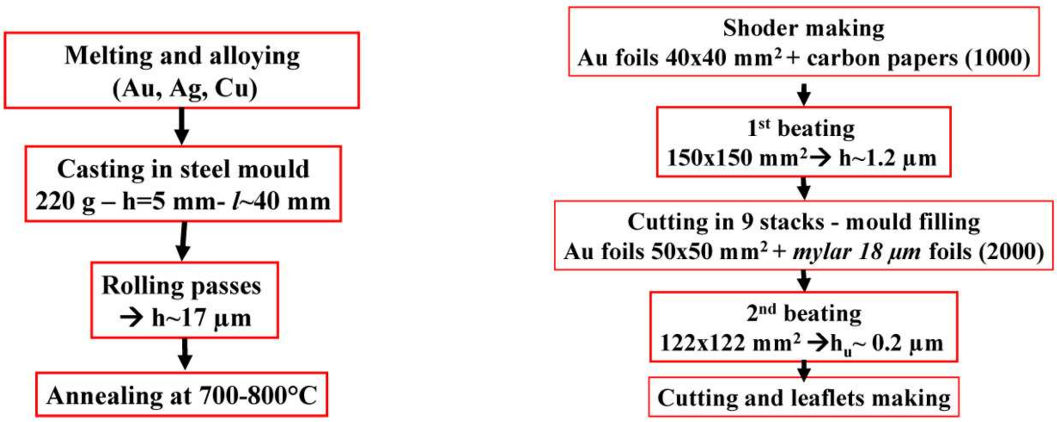


Figure 5: The successive steps of gold leaves manufacturing process

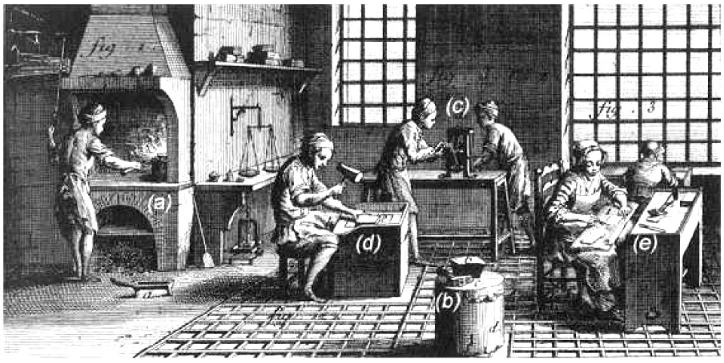


Figure 6: A goldbeater workshop at 18th century [from 10]

- After melting of gold in a furnace and alloy elements addition, an ingot with 220 g and about 5 mm thickness is casted. The thickness is reduced to about 17 µm by successive passes on a reversible rolling mill with mirror polished well lubricated surfaces. Before the invention of the rolling mill that operation was probably done by hammering (see fig.3). This step ends by an annealing in order to restore the gold ductility.

- The step of beating is much more complex and time consuming. It includes not only the two beatings, but also intermediate steps for treating the surfaces of the inserts, making the stacks and opening them for transferring and treating gold foils.

Some decades ago, four beatings were necessary. They were brought down to two by various improvements such as increase in the thinning by rolling, larger dimensions of the actual paper inserts with respect to those of the Montgolfier paper used previously, use of mechanical presses insuring about 4 strikes/s for performing the beatings and automation of nearly all operations.

During the first beating, the stack (shoder) is contained in a parchment sheath. The inserts of the shoder are made of paper covered with non electrostatic carbon black. The cutting after the first beating is performed by hand with a guillotine.

The mould used for the second beating is made of a stack of mylar films with dimensions much greater than the final dimensions of the gold leaves. Mylar is bi-stretched polyethylene terephtalate (PET). These polymeric films replace now the old and much more expensive “goldbeaters’ skins”. The films are surface treated with organic varnish and a fine powder of gypsum and soap to ensure an adapted friction with gold, as explained below.

Finally an operator opens the mould, cuts the leaves to the commercial dimensions (e. g 8 cm side square) and inserts them in a leaflet of silk films. The chemical composition and the final thickness are adapted to the destination of the leaves.

This process presents many exceptional aspects. It imposes a very high elongation, equal to 5/0.0002=25 000. The final product is very flexible, but the risks of wrinkling and tearing it are high. It is handled only with a special knife blade or brush. For manufacturing 100 g gold leaves, it is necessary to start with approximately 400 g gold.

3.1 The minimal thickness obtained by rolling

The problem of the minimal thickness is well known in rolling shops. A natural idea for displacing this limit is to roll several sheets together. It is used for instance for manufacturing packaging aluminium foils [11]. It cannot be applied to gold, because, as a consequence of their high oxidation resistance, pure gold foils weld to themselves when pressed together.

In fact, the friction and the rolls elasticity impose a minimal thickness in rolling. Below some thickness h_f, the foil passes through the roll gap without plastic strain by elastically flattening the rolls.

Figure 7 shows the simplified set up used to calculate the limit thickness. The two rolls of radius R_c, elastic modulus E_c and a Poisson ratio υ_c are replaced by a single roll of radius $R^* = R_c/2$ and elastic modulus $E^* = E_c/[2(1-\upsilon_c^2)]$ on a rigid plane. The foil has the flow stress σ_0.while p is the pressure induced by the combination of friction and strain in the rolling process.

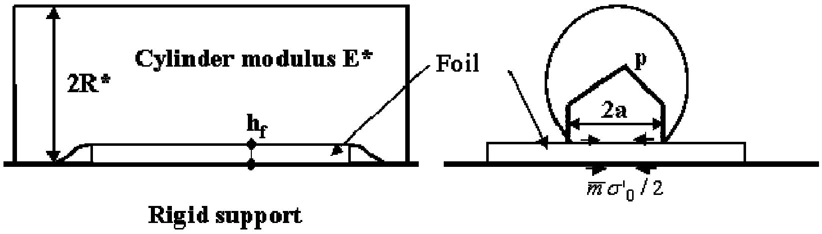


Figure 7: Minimal thickness in rolling (curvatures and elasticity reported to top roll)

A complete calculation [12] gives the value of the minimum thickness:

$$h_f = R^*\left(\frac{\sqrt{2+\pi\overline{m}E^*/\sigma'_0}-\sqrt{2}}{2\overline{m}}\right)^{-2} \quad \text{and} \quad \sigma'_0 = \frac{2\sigma_0}{\sqrt{3}} \tag{1}$$

Where $\overline{m}$ is the Tresca friction coefficient at the gold-roll interface.

By assuming that: (a) the Vickers hardness of hard drawn gold [13] is three times the flow stress of rolled gold foil, (b) σ_0~0.2 GPa, and (c) for steel rolls (E^*=115 GPa) with radius R^* = 100 mm , then the equation (1) gives $\boldsymbol{h_f}$ **= 17 µm** for $\overline{m}$ =0.05 and $\boldsymbol{h_f}$**~32 µm** for $\overline{m}$ = 0.1 (fig. 8).

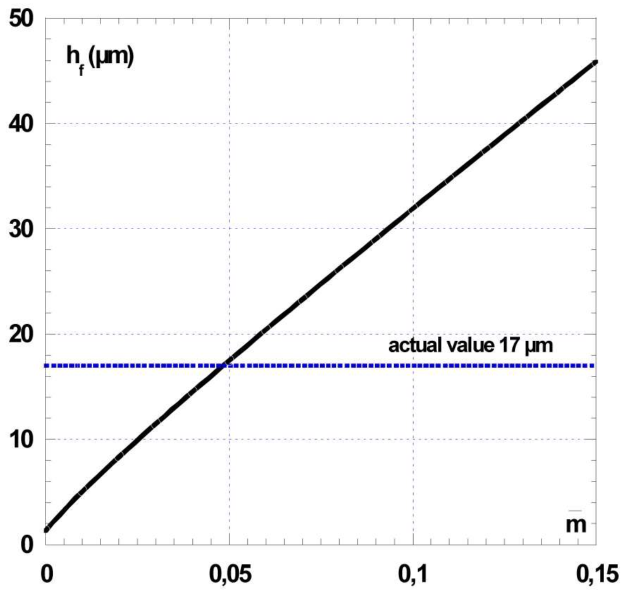


Figure 8: Evolution with the friction coefficient of the minimal thickness h_f in rolling gold foils (σ_0 = 0.2 GPa) with steel rolls (E*=115 GPa- R*=100 mm) [12].

The minimal thickness increases strongly with friction. It is thus important to use mirror polished well lubricated rolls in order to minimise that minimal thickness.

A minimum thickness limitation was evidently also true for hammering of single foils practiced by the antic artisans. It is the reason why they had to invent composite stack beating, which will now be analysed.

3.2 Mechanical analysis of beating

The basic facts to consider in the mechanical analysis of a beater blow on a composite stack containing alternatively plastic gold leaves and much thicker polymer foil inserts are:

- Each blow induces only a small plastic strain increment to the gold foils and deforms only elastically the inserts.

- The elastic energy stored in the inserts would ensure their recovery between two blows without damaging the gold leaves.

One considers the case of the second beating with a mould, because one knows an order of magnitude of the mylar inserts mechanical properties. The phenomena during the beating of the shoder are probably similar.

The full calculation is developed in another publication [12], so here it is only summarised the main principles and conclusions of that calculation. Figure 9 shows a simplified sketch of the part under the hammer of a polymeric foil inserted between two gold leaves.

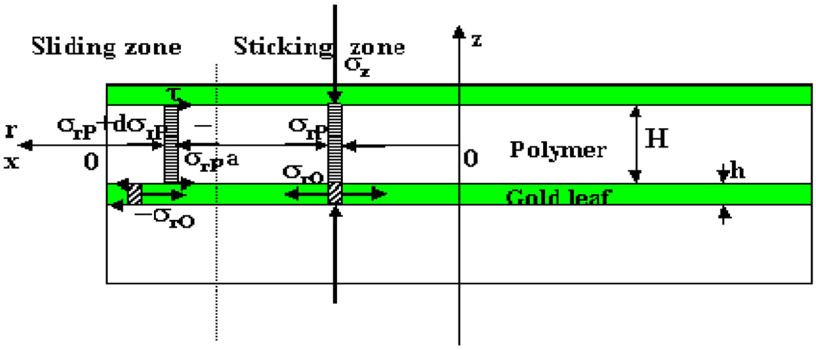


Figure 9: Stress state in two foils of the mould during the beating [12]

The penetration of the hammer provokes an elastic thinning of the polymer foils which are stretched at the impact boundary. Thanks to gold/polymer friction this induces bi-tensile stresses on the gold leaves. These bi-tensile stresses induce the thinning of the gold leaves. After release of the hammer the elastic energy stored in the polymer foils promotes their separation from gold by peeling. The coating of interlayers is designed to favour that separation without damaging the gold leaves. The system is then ready for the next blow.

Evidently, the successive blows are distributed on the surface of the mould to level evenly the deformation. Moreover, the mould is turned over periodically to compensate the fact that both the hammer is not flat as the anvil and straining is not uniform from the bottom to the top.

Because the Young's modulus of gold E_{Au} is much larger than the Young's modulus of the polymer E_p and the gold thickness *h* is much smaller than the polymer thickness *H*, the deformation of the polymer is exclusively elastic and gold can be considered as rigid. The mechanical system of figure 9 can then be solved quite simply [12].

A numerical application may be done, using the following estimations:

- Polymer: Young's modulus E_p = 4 GPa; Poisson' s ratio $\upsilon = 0.35$; thickness of one foil H = 17 µm
- Gold: Flow stress $\sigma_0 = 0.2$ GPa; thickness $h = 1$ µm
- Friction coefficient: $\mu = 0.05$.

After a first small step where the gold leaves remain rigid, they thin rapidly whereas the sliding zone width decreases (fig. 10). The gold strain ε_{z0} increases initially very sharply, much more quickly than the polymer contraction ε_{zP}. So thinning of the gold leaves is almost complete after the first quarter of the beating. During almost the whole process the gold foil is strained under an in-plane isotropic tensile stress. Because the metallic leaves stress state is mainly in-plane bi-tensile stress, one understands well that this process can be applied only to very tough alloys. This stress state explains why the gold leaves contain always pinholes which do not degrade the aesthetic aspect, but confirm that the ductility limit is locally reached.

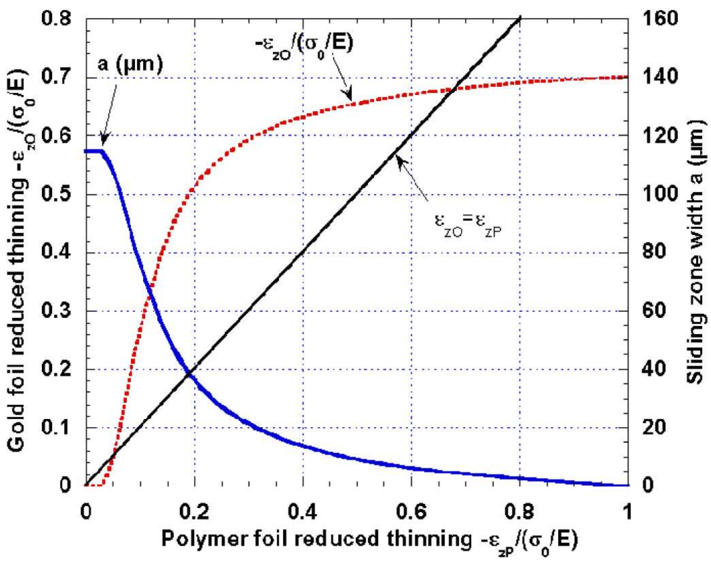


Figure 10: Evolution with the reduced polymer thinning of the width a of the sliding zone and the reduced thinning of the gold foil in the centre zone (E is the polymer Young's modulus) [12]

The strain for a thickness change of 1.2 to 0.2 µm is ln(6)~1.79. Because for one blow the maximum thickness stress is 3.5%, the minimum number of blows necessary for performing it is: 1.79/0.035~51. One deduces from the previous values that about 3200 blows are necessary for extending a gold foil to a square surface with 120 mm side, in rather good agreement with industrial practice.

The elastic energy for a blow on an area *S*=15x15 mm^2 is:

$$W_P \sim 2.10^3.15^2.17.10^{-6}.(200)^2.(2.4000)^{-1} = 38\ J \tag{2}$$

This is within the order of magnitude of the available energy on a 9 kg hammer for a 0.5 m drop height, which corresponds approximately to the old process performed by hand.

An important problem needs also consideration. What happens between two blows? After each blow the inserts must recover their initial size. The elastic energy stored in the inserts is available for this recovery by peeling the gold/polymer interfaces. The available energy release rate at the end of the blow is:

$$G = H\frac{\sigma_0^2}{2E} \sim 85\ J.m^{-2} \tag{3}$$

This value seems high enough for insuring the separation of the polymer inserts from the gold leaves. The surface treatment of the inserts is probably the determinant factor of the process. It controls the friction level between gold and polymer foils and above all the critical value of the energy release rate G_c of the peeling process insert/gold leave.

To our knowledge, this model, developed for the first time is a good demonstration of the ability of ancient artisans to overpass technical difficulties for their artistic purpose, through sophisticated hand processing.

4 SOME LABORATORY TOOLS FOR THE STUDY OF LEAF GILDING ON CULTURAL ARTEFACTS

Laboratory studies of cultural heritage objects gold coatings are aimed to answer three kinds of questions:

- The first concerns the composition, possibly the origin of the gold leaf;

- The second is the thickness, if possible the microstructure and consequently the processing mode of the leaf itself;

- The third is to try to identify the mode of adhesion of the leaf onto the substrate, and hence the recipe used by the craftsman to apply it.

As always when cultural heritage items are concerned, the important question is: does the study have to be totally conducted with non-destructive/non-invasive methods or is it possible to obtain samples taken from the object for a more comprehensive examination and analysis?

The choice of the used laboratory means depends fundamentally on the answer to that question and the short inventory given here will follow that logic.

4.1 Non-destructive characterisation

If the gilded artefact has to be examined without possible sampling of a part, which is often the case, specially for museum items, it remains possible to conduct a series of analysis with the available modern tools [14,15].

-*X-ray fluorescence*. The well-known method of X-ray fluorescence under X-ray excitation allows elemental analysis to be obtained from the surface. Modern equipments and computer codes [16] are now able to perform a quantitative precise exploitation of the X-ray spectra. Portable equipments are available, which bring a reasonable quantitative precision for *in situ* analyses. For an analysis of very small areas it is possible to perform microfluorescence measurements by using the beam of the synchrotron radiation sources. Depending on the synchrotron source, the diameter of the incident X-ray beam may be as small as less than 1 µm.

- *X-ray diffraction* may be useful to characterise the metallurgical state of the gold leafs, particularly its possible crystallographic texture [17], but eventually also to identify the crystallised compounds contained in the adhesive or supporting layer of the leaf. A considerable improvement has been brought to the X-ray diffraction equipments quite recently, thanks to the use of X-ray focusing devices (multilayer mirrors, multicapillary devices) and of 2D acquisition of the patterns (imaging plates). It is now possible to acquire X-ray diffraction patterns in a short time, on very small areas, a few tens µm in laboratory practice, about 1 µm on a synchrotron radiation source. Portable X-ray diffraction equipments, coupled with X-ray fluorescence, have been recently worked out [18], allowing crystallographic characterisation on large pieces in their usual environment).

- *Raman microspectroscopy* is a very efficient tool for identification of inorganic compounds contained for instance in the sublayers supporting the gold leaf. Because Raman effect is an inelastic light diffusion phenomenon, it can be measured with a microscope, on an analysed area of the order of a few μm^2; and it is contactless. Portable Raman microspectrometres were developed, using glass fibres to drive the incident laser light to the specimen and collect the Raman-diffused light.

- *Optical measurements*, specially photospectrometry, may also be used to characterize the properties of coloured ceramics. Portable spectrophotometers exist.

- A *particle accelerator* may be a very powerful tool for a set of measurements. It is all contactless and possible to be used on large objects when the particle beam is extracted to the atmosphere as for the AGLAE accelerator of the C2RMF [19].

Local chemical analysis is done by *PIXE* (particle-induced X-ray emission) and PIGE (particle-induced gamma emission) with high precision and very low detection limits for a great number of elements;

Depth profiling of the elements from the surface down to a few µm into the object is obtained by *RBS* (Rutherford backscattering spectrometry) with a rather good depth resolution. RBS allows to obtain a reliable value of the gold leaf thickness with an essential procedure without any sampling. RBS allows it.

4.2 Destructive characterisation

If one is allowed to sample a mall part of gilding, possibly still attached to a part of its substrate, supplementary tools may be used:

- *Optical metallography* (OM) or *scanning electron micrography* (SEM), both on polished cross-sections, give interesting information. One must however be conscious that polishing a cross section including a gold layer and a much harder substrate is a difficult operation, as the difference in hardness may induce an uncontrolled spreading of gold onto the neighbouring substrate. The consequence is an overestimation of the leaf thickness or of possible gold diffusion phenomena into the substrate. On the other hand, microanalysis using EDS (energy dispersive spectrometry) in the SEM is often the only way to have information on the composition of the materials laying under the gold leaf.

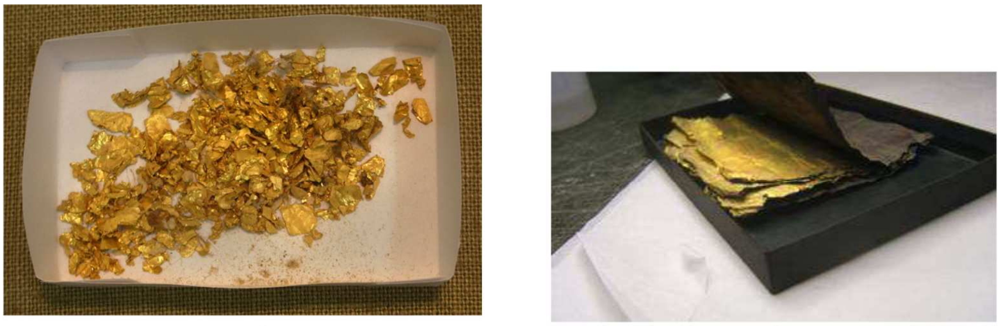
- Chemical analysis by usual chemical tools may be necessary to identify the underlayers between gold and the bulk substrate. This is especially true if these layers contain organic compounds (glue, oil, gum arabic, etc.). The analysis means are various, from liquid phase analysis and infrared absorption spectrometry to gas chromatography eventually coupled to mass spectrometry, etc.

- Evidently, X-ray diffraction on small samples (now existing X-ray microdiffractometre allows to work with very small samples) is essential to identify the crystalline compounds.

5 EXAMPLES OF FOIL AND LEAF COATINGS

5.1 Egyptian gold leaves

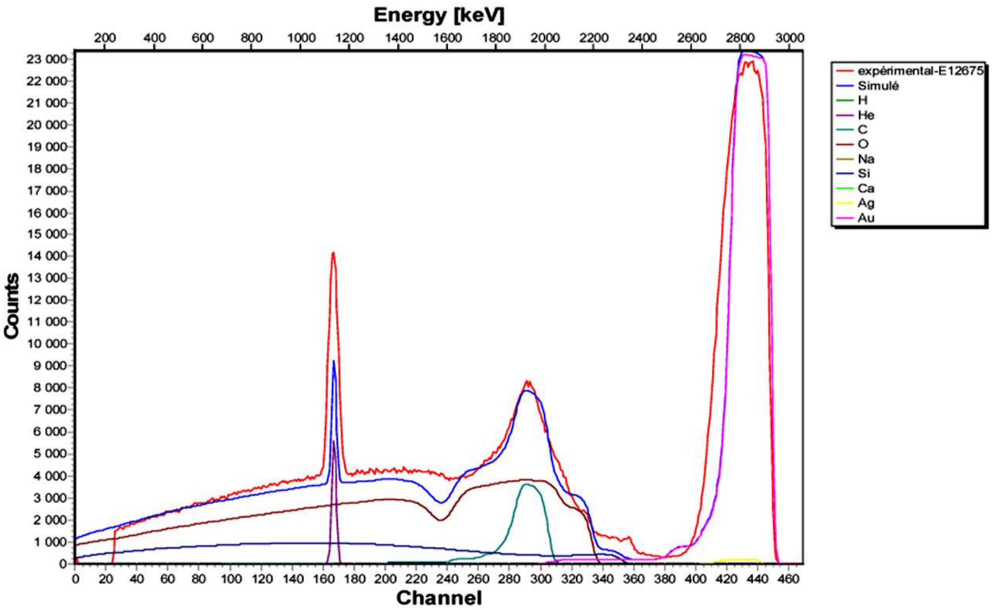
The Egyptian antiquities department of the Louvre museum holds many gilded objects of different kinds and various origins and ages. The most well-known are numerous sarcophagi for which wood or cartonnage substrate is covered with gold foils. Here it is discussed two interesting items also kept in that department: a set of small gold leaves fragments (fig. 11a) found in a tomb of battering ram in Elephantine island, dated from the Late Period, and a set of large gold leaves assembled as in a gilder book (fig. 11b) whose origin is uncertain and the age probably that of the Late Period [20]. The “book” is in fact not what it appears, but only an assembly of 8 leaves protected by a folded copper sheet, something like a gilder stock.



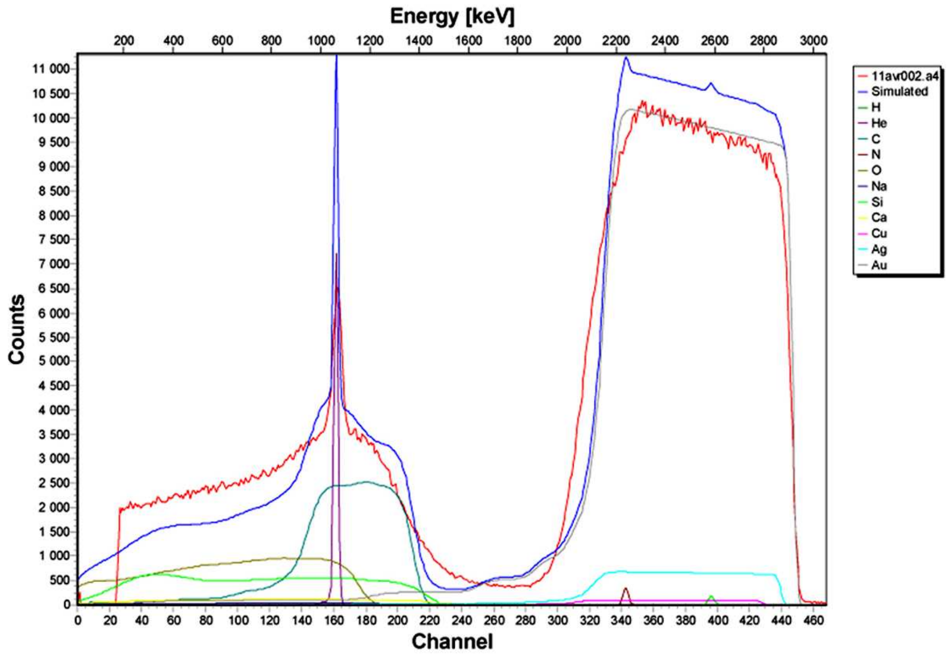
a b

Figure 11: (a): Gold fragmets found in a ram tomb in Elephantine Island, Egypt, about 4th century BC, Louvre museum; (b): “Gilder book”, Egypt, date unknown, Louvre museum

The composition and thickness of these objects have been measured by PIXE, RBS, and SEM. Figure 12 shows the RBS spectra of each object. The Elephantine leaves are of a quite pure gold (1.3 wt% Ag, 0.3 wt% Cu) and rather thin (about 1.2 µm). The “book” leaves are of an Au - 8 wt % Ag alloy, and much thicker (about 5 µm).



(a)



(b)

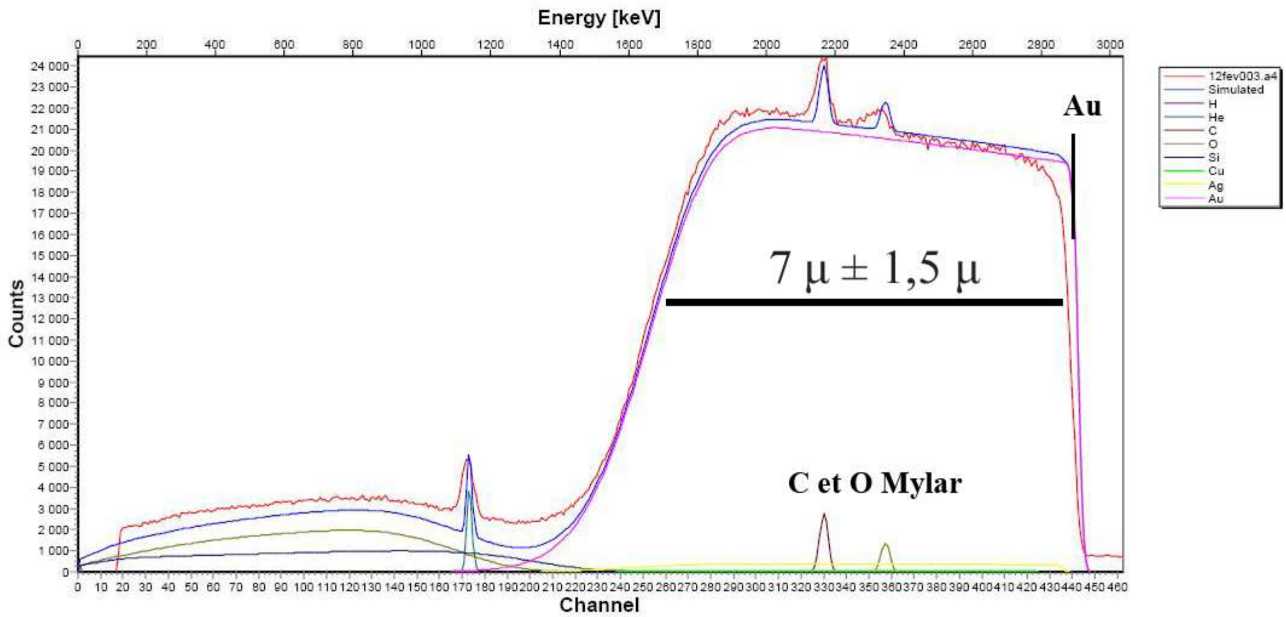
Figure 12: RBS spectra of a gold fragment of fig 11a (a) and of a piece of the "gilder book" of figure 11b (b)

This confirms a number of data about Egyptian gilding, which report that the composition and thickness of the leaves have a very broad range whatever the age and location of the items. Composition may vary from white gold (> 25 wt % Ag) or Au-Cu-Ag alloys to very pure gold (> 99.8 wt % Au) and thicknesses are between 1 µm and 10 µm. Thicknesses of 1 µm or less were already reached at the beginning of the second millenary BC [21].

5.2 Gilding on bronze in the Meroe Kingdom

The Meroe Kingdom was established in the region of present Soudan, in the high valley of the Nil river (old Nubia), during a period lasting from the end of the 3rd century BC to the Roman period (4th century AD). A bronze statuette called Bowman King is a major object, dated from the golden age of that civilisation, between the 3rd and the 2nd century BC, and kept in the museum of Khartoum. The statuette is gilded (fig. 13) and one gold leaf fragment temporarily separated from the object could be analysed by PIXE and RBS (fig. 13b). It is a rather pure gold (2.6 wt % Ag, < 0.1 wt % Cu) and the thickness is 7 µm ± 1.5 µm. That relatively thick gold leaf was not applied directly on the bronze body, but an intermediate thick layer of stucco, a mixture of quartz, calcite and an organic binder, lies in between the bronze and the gold film. That stucco layer is itself engraved with decorations followed by the overlaying gold.

(a)



(b)

Figure 13: (a): The Bowman King of Meroe 2nd - 3rd century: Khartoum museum; (b): RBS spectrum of a fragment of gold leaf from the Bowman King

This example confirms that the gilding thickness is not limited by the technological skilfulness of the hand workers but adapted to the shape and value of the object. The technique of inserting a mineral layer, often called “white preparation” between the substrate and the gold leaf for bronze artefacts from Egypt and related civilisations, is frequent. That “white preparation” was usually made of calcite or plaster (gypsum). One does not know if it contained additionally an organic binder or a glue to ensure gold adhesion, or if it was covered with a layer of glue for that purpose.

5.3 Gilding on bronze in the Roman Empire

The example chosen here is the statue called “Apollon de Lillebonne” shown in the Louvre museum. This is a statue larger than natural height (1.92 m), dated of the 1^{st} or 2^{nd} century AD, entirely leaf gilded on a bronze substrate (fig. 14). A careful examination of the surface reveals straight bands which are the places were the gold leave squares were overlaid on their edges. The visibility of these bands comes from the fact that gilding is wear by multiple cleaning operations. The object was much too heavy to be brought in front of the AGLAE particle accelerator, and a portable X-ray fluorescence and X-ray diffraction equipment had to be used to characterise the gilding leaf. The x-ray fluorescence spectrum, quantified with the computation code PyMCA [16], shows not only the gold and silver lines due to the gilding film but also a signal of copper which may be a combination of the copper contained in the leave and of copper from the substrate. It is thus impossible to know the copper content of the gold. Only the ratio Ag/Au could be estimated as equal to 0.05, i.e.5 wt %. The gold of the leave contains less than 5 wt % silver and an unknown content of copper. A quantitative application of the same computation code in a multilayer configuration allows an estimation of the gold leaf thickness. It was found to be about 1.5 µm.

Figure 14: The “Lillebonne Apollo” 1^{st} 2^{nd} century BC, Louvre museum

It has not been possible to obtain information on the possible existence of an adhesive between the gold film and the substrate. So the question of the recipe used for gilding the Roman gilded statues and related items remains open.

5.4 Summary on metal leaf gilding

Trying to gather what is known about metal leaf gilding recipes established through actual quantitative measurements, one is drawn to the following conclusions.

In ancient Egypt gilding could be done either by mechanical fastening of foils or by applying thin leaves of various thickness (between 1 and 10 µm) on an intermediate “white preparation” containing calcite, gypsum and perhaps an organic adhesive. Another possibility could the use of a specific organic adhesive on the top of the “white preparation” before applying the gold leave.

During western antiquity (Greece and Rome), no intermediate layer of a reasonable thickness exist between the substrate and the gold leave. If an adhesive was used to fix the leaves, it was probably organic and its composition is not known. Pliny the Elder reports another possibility: using mercury as an adhesive.

By western Middle Age, the preceding recipe was probably applied. Bartholomeus Angelicus mentions also the possibility of mechanical adhesion gilding at least on silver [8].

At the present time, the recipe commonly applied is “oil gilding”. An oily varnish is applied onto the metal and let dry to a precise stage before applying the leaf. For instance the lead and copper roof of the Invalides church in Paris was restored with that recipe.

5.5 Gilding on stone

Figure 15 depicts the "Golden Rock", Kyaik-Hti-Yo belonging to a sanctuary in Burma which is supposed to be dated more than 2400 years old. This figure shows that permanent gilding on stone is possible and was an ancient practice. Gilding the walls for external decoration is observed on numerous monuments around the world. The known recipes mention the preparation of gilding by application of a *gesso,* an Italian word designating a coating often made with plaster (gypsum) but sometimes more complex. An adhesive to fasten the gold foil is either incorporated into the *gesso* or coated on the top of it.

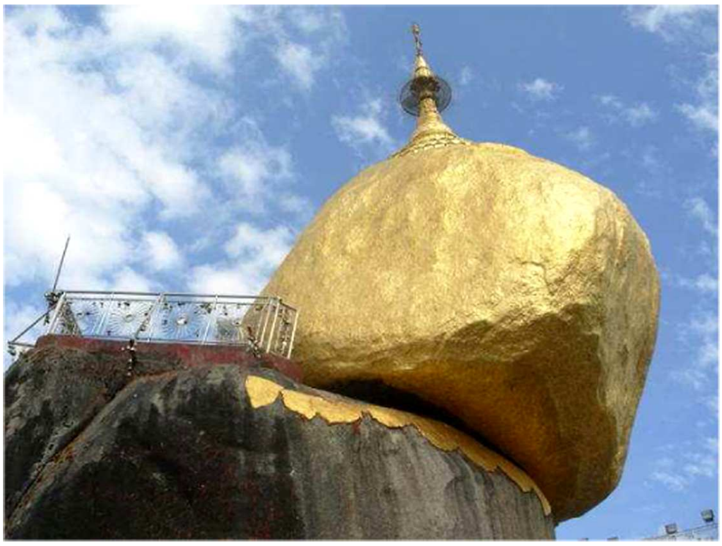


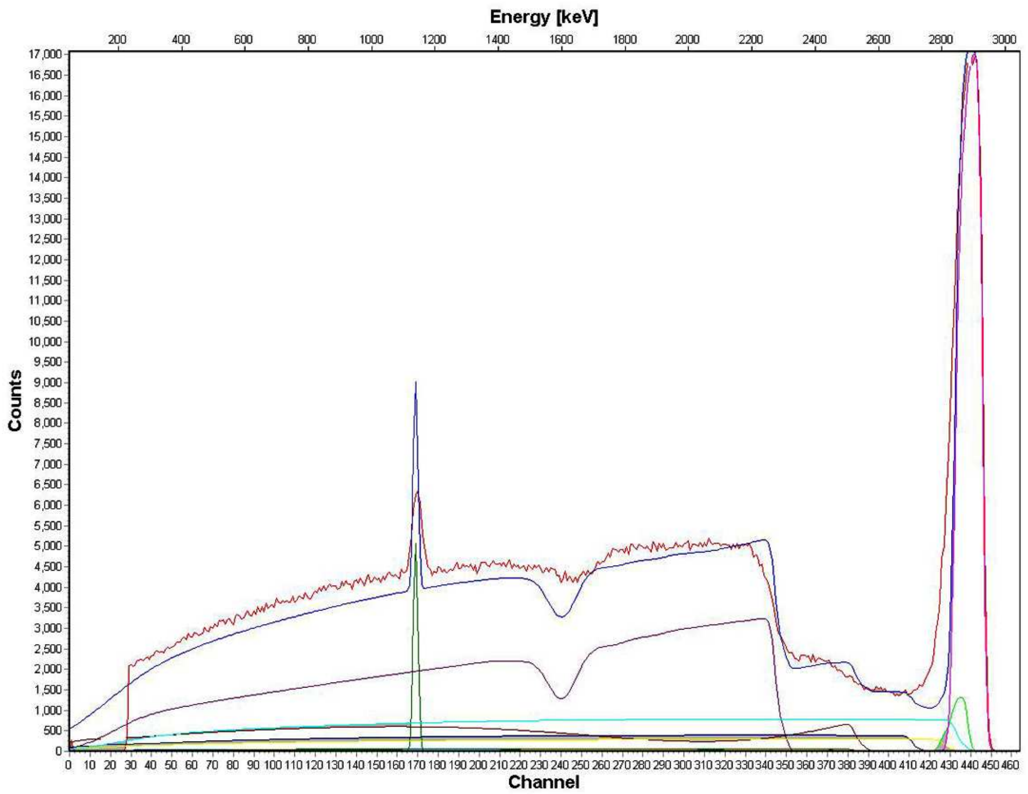
Figure 15: "Golden Rock", Kyaik-Hti-Yo, Burma

On stone objects, as statues for instance, inserting *gesso* is not always necessary. Recipes mention only a careful cleaning of the stone surface followed by application of an adhesives mixture like "oil", i.e. an oily varnish or the well-known *Armenian bole,* a clay containing iron oxide and organic additives.

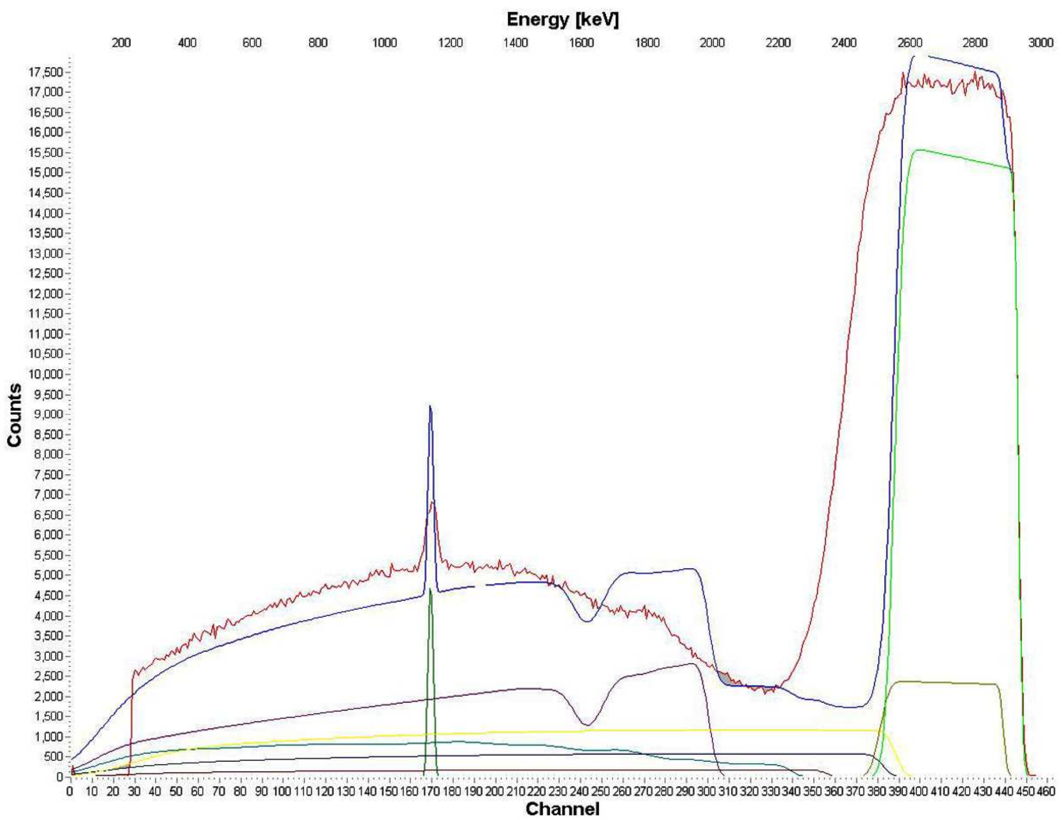
5.6 Gilding on ceramics. Example of Islamic gilded ceramics

In a recent study [17] a complete characterisation of Islamic gilded ceramics dating from the 12th – 13th century in Iran (Mongol period) and from the 14th - 15th century in Uzbekistan (Tamerlan period) has been made. In both cases, the ceramic pieces were covered with gold leaf decoration in a complex operation after the primary glazing. It was generally a decoration to enrich architectural pieces but also vases or table-ware (fig. 16).

(a) **(b)**



(c)



(d)

Figure 16: Islamic gilded ceramic shards. (a): Uzbekistan; (b): Iran. (c) and (d) RBS spectra of gildings [17]

The metal used was only pure (99 %) gold. The thickness of the leaves could vary between a few hundred nanometres (in Iran) up to more than 1 µm (in Uzbekistan). Often, specially during the Tamerlan period, the gold leaf was applied before adding other enamelled decorations made with pigmented glazes. The ceramic was fired again after those applications. One understand then why it is quite impossible to know if an adhesive was applied to fasten the gold leaf on its substrate. This is because that adhesive, if it existed contained probably organic compounds which were decomposed during firing. The only detected fact is that the gold leaf and the interface between it and the underlying glaze is highly rough, indicating a strong interaction during firing.

5.7 Gilding on glass, tesserae

Apart from the above mentioned powder gilding in Islamic Syria still practiced for modern glass art objects and the *liquid gold* gilding presently done on dinking and table ware, the occurrence of actual gilding on glass is rare.

An exception is the technique of tessera, in which a gold leaf is incorporated between two glass layers. The process is known since the 3rd century BC (fig. 17a) and was fully developed after the 6th century AD to give mosaics (fig. 17b). Byzantine mosaics are evidently well-known and the technique is still presently applied in Murano (Italy) workshops, for the decoration of pavements or swimming-pool bottoms. A gold leaf less than 1 µm thick is placed on the surface of a transparent glass sheet, cut into small squares of 1 or 2 cm side. A powder glass is coated on it and the pieces are fired to melt the over layer and ensure adhesion. Egg yolk is sometimes mentioned as an adhesive applied under the gold leaf. A detailed study of tessera forming process [22] shows that a diffusion of gold into the underlying glass occurs during the final firing and is responsible for the good adhesion.

(a) **(b)**

Figure 17: Gilded glass by the tessera technique. (a): Canosa bowl, 3rd century BC; (b): mosaic from Ravenne, 6th century AD

5.8 Gilding on wood

Gilding on wood is one of the most widespread decoration processes. It has been used on Egyptian sarcophagi, as a background on paintings, later on statues, on furniture, etc. (fig. 18). A very spectacular and magnificent application is found in the Brazilian churches of the colonial Baroque, often entirely decorated with gilded wood. A comprehensive physico-chemical description of the results of that art may be found in the thesis of Luiz Souza [23].

(a) (b)

Figure 18: Leaf gilding on wood. (a): painting of Fra Angelico 1440, Louvre museum; (b): Igreja da Ordem Terceira de São Francisco da Penintência in Rio de Janeiro.

The gold leaves composition and thickness and the gilding process varied along the ages, but the principles remained quite constant. The following description gives a summary of the gilding process used presently in a gilder's workshop completed with some historical comments.

There are two kinds of recipe: one is "bole gilding" where adhesion is ensured by a layer rich in collagen glue; the other is "water gilding" where the leaf, always very thin, is applied directly without intermediate layer other than a tin water film.

The preparation of the substrate is very important. After surface cleaning of the wood, a first layer of a collagen-rich glue (animal glue) mixture is applied to smoothen the surface and fill the porosity. Several layers of calcium carbonate solution with decreasing additions of animal collagen glue are then coated and individually dried. The surface is equalized to be ready for the next steps. In ancient recipes, that preliminary layer, the *white preparation*, could be gypsum or a calcite-gypsum mixture, or even a stucco.

Gilding itself begins by humidification of the surface and application of "gluing yellow" only in the bottoms. A clay containing iron oxide and a small content of collagen glue is laid down and gently smoothed with a brush in order to eliminate large grains. In ancient recipes, that clay containing iron oxide could be Armenian bole, but it is now replaced by a clay more easy to handle with controlled additions. Sometimes curious additives are proposed , as garlic juice. But if one knows that garlic juice contains sulphide salts and that sulphide ions are recognised to have a strong interaction with gold metal, one understand better these empirical recommendations.

The gold leaf is then applied. The non adherent excess gold is eliminated by a gentle brushing. Burnishing follows, as a mechanical operation which equalizes the surface, fills the pores and gaps and gives a bright polish. As a final operation, "mating" may be done; it consists of a thin film of very diluted glue.

It is worth emphasising that leaf gilding on wood is one of the oldest gilding processes. Only gilding on metal can be considered, at least to our knowledge, as historically older (see above). Its mastering has been improved and reproduced quite faithfully through the ages, with logical evolution linked to the technological progress. Moreover, it is not difficult to notice that many leaf gilding processes on other substrates than wood are adapted from the basic process on wood [6].

5.9 Gilding on other organic substrates

Leaf gilding has been applied to many kinds of organic substrates: paper, cardboard, ivory, etc. The gold leaves are very thin to be easily adapted to the object shape.

The recipes, when they are known, mention different types of adhesives, often diluted collagen glue, without any preparation layer [24].

An interesting operation is gilt-edging practiced by bookbinders on the edge high quality books (fig. 19). The gold leaf, of minimum thickness is applied on the whole edge of the compressed book, generally only after a light humidification, sometimes with addition of egg white to the water. After drying, the leaf remains pasted on each page edge. On linen and other kinds of woven fabric material, powder gilding is preferred for evident reasons [24].

Figure 19: Books with gilt-edge

6 CONCLUSION

This summarised and rather restricted review of the history and different applications of foil and leaf gilding brings nevertheless interesting information on that ancestral cultural artistic practice, one of the first prestigious decoration technique invented by the first civilisations:

Foil and leaf gilding is used since the birth of metallurgy, thanks to the exceptional ductility of gold and, indeed, its high decorative and symbolic power.

The fabrication of gold leaves can only be done by beating, i.e. straining a large number of gold films separated by polymer films. The process was discovered at very early times. It is a very ingenious way to overpass the thickness limitation imposed by mechanical rules in normal hammering or cold rolling. It implies a sophisticated mechanical mechanism for which a model has been developed for the first time by the authors of the present work.

Gold leaves have been coated onto a great variety of substrates: metal, stone, ceramic, glass, wood, paper, ivory, etc.

The study of the interface between the gold leaf and its substrate is still an open problem, especially on ancient cultural heritage artefacts

That study of the interfaces is critical to understand the mechanism of adhesion of the gilding decoration, and to build a conservation policy for gilded cultural heritage items.

7 ACKNOWLEDGMENTS

Some results mentioned have been obtained in the frame of the program DORAI, financed by the French Agence Nationale de Recherche (ANR), and published in the thesis of Claire Pacheco, quoted in the following reference list.

Maison Dauvet-Bernard represents the fifth generation of the Dauvet goldbeaters. Mr Dauvet kindly provided all information on the beating procedure and specimens from his workshop.

The following Louvre museum curators kindly brought their objects for physico-chemical studies:

- Mrs Guillemette Andreu-Lanoe, head of the Egyptian Antiquities department
- Mrs Elisabeth Delange, from the Egyptian Antiquities department
- Mrs Sophie Descamps, from the Greek, Etruscan and Roman Antiquities department
- Mrs Sophie Makariou, head of the Islam Arts department

8 BIBLIOGRAPHY

[1] CRETU, C.,VAN DER LINGEN, E., “Coloured Gold Alloys”, *Gold Bulletin* , v. 32, n. 4, pp 115-126, 1999.

[2] ODDY, W.A., “Gilding of metals in the old world”, In: *Metal Plating and Patination*, ed. S La Niece, P. Craddock, Butterworth, London, 1993.

[3] CRADDOCK, P., “The Composition of the Copper Alloys used by the Greek, Etruscan and Roman Civilisations 2. The Archaic, Classical and Hellenistic Greeks”, *Journal of Archaeological Science*, v. 4, n. 2, pp. 103- 123, 1977.

[4] ODDY, W.A., "Gilding through the ages", *Gold Bulletin*, v. 14, n. 2, pp 75-79, 1981.

[5] NICHOLSON, E.D., "The ancient craft of gold beating", *Gold Bulletin*, v. 12, n. 4, pp 161-166, 1979.

[6] PLINY THE ELDER, Naturalis Historiae, XXXIII, xx et xxxii.

[7] LECHTMAN, H. "Pre-Columbian surface metallurgy", *Scientific American*, v. 250, n. 6, pp. 38-45, 1984.

[8] HUNT, L.B., "Bartholomaeus Anglicus on Gold", *Gold Bulletin*, v 8, n. 1, pp 22-27, 1975.

[9] GUEIT, E., DARQUE-CERETTI, E., AUCOUTURIER, M., "Glass gilding process in medieval Syria and Egypt (13th–14th century)", *Journal of Archaeological Science*, v. 37, n. 7, pp. 1742–1752, 2010.

[10] DIDEROT, D., D'ALEMBERT, J. L. R. *Encyclopédie, ou Dictionnaire Raisonné des Sciences, des Arts et des Métiers*, Paris, 1751-1772. Texts available on: http://portail.atilf.fr/encyclopedie/index.htm., acessado em 10 de junho de 2011.

[11] FEPPON, J.M., CHENAT,B. "Grain size and mechanical properties of aluminium foils used in packaging applications," *Matériaux et Techniques*, n. 5-6, pp 59-65, 2002.

[12] FELDER, E.,C "Mechanical analysis of the gold leaves beating", In: *Proceedings of the conference ICTMP 2010, Nice, E. Felder & P. Montmitonnet (Editors), Presses de l'Ecole des Mines de Paris*, pp. 528-538, 2010.

[13] TABOR, D., *The Hardness of Metals*, Oxford, Clarendon Press, 1951.

[14] JANSSENS, K., VAN GRIEKEN, R., *Non destructive microanalysis of cultural heritage materials*, Comprehensive analytical chemistry, Vol. XLII, Elsevier, Amsterdam, 2004.

[15] DARQUE-CERETTI, E., AUCOUTURIER, M., "The surface of cultural heritage artefacts physicochemical investigations for their knowledge and their conservation", *Chemical Society Reviews*, v.36, pp 1605-1621, 2007.

[16] SOLÉ, V.A., PAPILLON, E., COTTE, M., WALTER, Ph., SUSINI, J., "A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra", *Spectrochem. Acta*, Part B, v. 62, pp. 63-68, 2007. website: http://pymca.sourceforge.net/.

[17] PACHECO, C., *Etude de films d'or sur matière vitreuse . Application à la céramique glaçurée islamique médiévale Asie centrale XIVe-XVe- Iran XIIe-XIIIe Siècles*, Thesis, Université Michel de Montaigne, Bordeaux 3, 2007.

[18] GIANONCELLI, A., CASTAING, J.. ORTEGA, L., DOORHYEE, E., SALOMON, J., WALTER, P., HODEAU, J.-L., BORDET, P., "A portable instrument for *in situ* determination of the chemical and phase composition of cultural heritage objects", *X-Ray Spectrometry*, v. 37, pp. 418-423, 2008.

[19] CALLIGARO, T., DRAN, J-C., SALOMON, J., "Ion beam analyses", In: *Non destructive microanalysis of cultural heritage materials*, ed. K. Janssens, R. Van Grieken, *Comprehensive analytical chemistry*, Vol. XLII, Elsevier, Amsterdam, pp. 227-276, 2004.

[20] PERRAULT,G. "Le battage de l'or", *L'estampille, l'objet d'art*, n. 226, pp.44-51, juin, 1989.

[21] BERTHELOT, M., *Archéologie et Histoire des Sciences*, Steinheil, Paris, Mémoires de l'Académie des Sciences de l'Institut de France, tome 49, Gauthier-Villars, 1906.

[22] HELARY,D., *Etude de couches dorées sur matières vitreuses. Application aux tesselles à feuille d'or et aux céramiques glaçurées à décors de lustres dorés*, Thesis, Mines-Paristech, CEMEF, Paris, 2003.

[23] SOUZA, L.A.C., *Evolução da Tecnologia de Policromia nas Esculturas em Minas Gerais no Século XVIII: O interior inacabado da Igreja Matriz de Nossa Senhora da Conceição, em Catas Altas do*

Mato Dentro, um monumento exemplar, Tese de D. Sc, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil, 1996.

[24] WATIN, M., *L’art du peintre, doreur et vernisseur*, 9 ed., Paris, Belin-Leprieur, Paris, 1823.