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GILDING FOR MATTER DECORATION AND SUBLIMATION. A BRIEF HISTORY OF THE ARTISANAL TECHNICAL KNOW-HOW

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Abstract

The process used to decorate art objects with thinner and thinner gold coatings varied during centuries. Foil or leaf metal gilding technology was complemented around the beginning of the Christian era by mercury gilding. Simultaneously was developed in some geographic areas the surface depletion process for gilded copper/silver alloys. This paper is motivated by the recent publication by the authors of a didactic opus devoted to the description and the discussion of the technical history of the various gilding procedures, based on the study by modern investigation techniques of a number of gilded museum objects. Through examples from laboratory studies on museum objects, the main evolution steps of gold application are described. A recent mechanical modelling work about gold leaf forming by beating is reported. The different coating processes are discussed, depending on the substrate nature and surface treatment before gilding. It includes high temperature firing for mercury gilding, or powder gilding, e.g. on Middle-Age Syria glass. The paper ends with a listing of the research perspectives open for the presently poorly developed study of the adhesion mechanisms between gold leaf and its substrate. It discusses the important issue of gold-metal interdiffusion during metal gilding processes involving a high temperature step.

Keywords: *Antic gilding; Modern gilding; Leaf gilding; Fire gilding; Powder gilding; Leaf adhesion; Gold-metal diffusion; Surface preparation.*

Introduction

Gold foil and leaf have been used by most human civilisations since very early times to decorate all kinds of artwork materials: metal, stone, ceramic, wood, cartonnage of the Egyptian sarcophagi, glass [1]. Most of the progresses done throughout centuries by the artisans are linked to two parameters: one is the evolution of the thickness of the gold film, starting from simple hammered foils with a thickness of several micrometres and progressively improved until obtaining very thin leaves of some tenth of micrometre [1-4]. The second one is the continuous research on good adhesive material suitable for the various substrates to be gilded, as it is known that, thanks to its high natural surface energy, pure gold is one of the most difficult materials to apply on low surface energy substrates [1, 5]. Another way to insure a long-time conservation of a gilding film without the help of an adhesive "third material", especially on metals, is to use thermal treatment, mercury amalgamation or a combination of both to obtain a structural interface between the substrate and the gold film [1, 2]. Foil or leaf

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gilding technology was more or less complemented for metal gilding around the beginning of the Christian era by mercury (amalgam) gilding, a technology which involves a completely different know-how than leaf gilding. Both gilding procedures were simultaneously used until the middle of nineteenth century, when electrolytic deposition and electrotyping techniques appeared. Simultaneously was developed in some geographic areas the surface depletion process to obtain gilded objects from copper-gold or silver-gold alloys. That overview must be completed with the widespread procedure of using gold powder and a binder.

This paper is motivated by the recent publication by the authors of a didactic opus [**1**] devoted to the description and the discussion of the technical history of the various gilding procedures, based on the study by modern investigation techniques of a number of gilded museum objects. The paper will first develop, through examples taken from laboratory studies on museum objects, the main evolution steps of gold coating during centuries. It will discuss the present knowledge about the various processes used by hand-workers of different origins and periods: antic Egypt, Roman Empire, western and oriental Middle-Age, Latin America and modern Europe. A recent mechanical modelling work about gold leaf forming by beating will be reported. We shall describe, still with 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 processes will be discussed, owing to the presently available knowledge. Those depend on the substrate nature and the possible necessity to treat its surface before and during the process.

The paper ends with a listing of the numerous research perspectives open for the presently poorly developed study of the adhesion mechanisms between the gold surface coating and its substrate, to understand fully the gilding process whatever it may be, leaf application, fire gilding, powder gilding, etc. It will in particular discuss the important issue of gold-metal interdiffusion during gilding processes involving a step of high temperature treatment.

History and definitions

Gold foil and leaf, the first gilding process

Gold thinning for being applied for decoration to art, funeral or cultic objects appeared as soon as more than 6000 years ago. One knows for instance an Egyptian ceramic vase displayed in the Louvre museum, dating from approximately 4000 A.C. (Nagada period) whose handles are decorated with two pieces of a quite thick gold foil (Fig. 1). Since that the technology of gold thinning did not cease to improve during the centuries. One considers that the oldest drawn representation of the gold melting and thinning process has been found in an Egyptian tomb of Saqqara dated from ca 2500 A.C. (Fig. 2). That illustration shows the action of workers using a round stone to hammer (or beat, see below) a gold foil issued from an ingot melted on the right part of the drawing.

Fig. 1. Vase from Nagada (Egypt), 4000-3100 A.C.. Louvre museum (inv. E 23206)

Fig. 2. Illustration from an Egyptian tomb in Saqqara. Ca 2500 A.C. [6]

At this stage, it is necessary to precise the definition given by the scientific specialists [2, 3] to differentiate precisely the different kinds of gold films used for decoration:

- The term *sheet* is used for the thick (several tens of µm) plates;
- Gold *foils* describe thinner foils which can still be handled easily, i.e. several µm thick;
- When the foil is so thin that it cannot sustain its own weight, i.e. less than 1 µm, it is recommended to use the term *leaf*.

Those terms may also be used, in fact with somewhat different thickness ranges, to differentiate the two fundamental steps of gold thinning: *hammering* (ancient process) or *rolling* (modern process) to obtain foils, *beating* to obtain leaves. The next section of this paper shall justify that classification.

The decoration of objects with surface gilding started indeed with gold foil application. The foils were initially fastened mechanically. For instance the foil could be assembled around the object by mechanically burnishing the edges together; in the case of a metal object the surface might be notched and the edges of the foils were hammered into the grooves to maintain the foil stretched over the surface. But rapidly, as the thickness of the foil was decreasing, mostly because of cost considerations, the mechanical application methods became unworkable. Decoration of sarcophagi's by gold leaf less than 1 micrometre thick is attested already in antic Egypt during the 3rd millenary A.C. [4]. Pliny the Elder, in one of the first encyclopaedias ever published [**7**], mentions that the gold artisans were able to obtain very thin gold leaves whose thickness could be evaluated, through the weights and areas given by the author, to less than 0.4 µm. That important information means that the thickness of the gold coating decoration cannot be used a dating criterion of antic or ancient objects.

Figure 3 show examples of leaf gilding on different substrates, with their dating and thickness when available.

Fig. 3. Some examples of leaf gilding on ancient objects. The leaf thickness is indicated when measured in authors' laboratory or (?) when approximated by the literature: (a) Syria, 8th cent. A.C., on ivory; (b) Meroe empire, ca 300 A.C., 7 µm, on bronze; (c) Egypt ca 200 A.C., 6 µm ?, on cartonage; (d) Arles, France, 1st cent. A.C., 1.5-2.5 µm, on bronze; (e) Lillebonne, France, ca 1.5 µm, on bronze; (f) Rio de Janeiro, Brazil, 0.2 µm ?, on wood; (g) Paris, France, 0.3 µm ?, on lead.

Mercury gilding

When mercury (called intially *quicksilver*) became available, the metal art workers found rapidly a way to avoid the delicate problem of gold leaf elaboration and application, especially on metals (copper alloys, silver, iron). It seems that the process of mercury gilding appeared in China, and perhaps in Greece, around the 3rd century A.C. [3, 10]. The general development of the technique in the western (Greco-Roman) world was effective during the Ist century A.C. [2, 8]. There is some confusion about the definition of the process, due to difficulties of interpretation of its mention in Pliny the Elder's encyclopaedia [7, 9]. Indeed Pliny mentions a process based on the use of mercury as an adhesive to apply gold leaves on metals, and the process is usually referred in modern publications as *cold mercury gilding*, different from the *fire gilding* or *amalgam gilding* process. In that latter process gold fragments are first dissolved into liquid mercury at a moderate temperature to obtain an amalgam, and that amalgam is applied on the metal object which is then heated to a temperature higher than the mercury boiling point (356.5°C) to eliminate it. As discussed below in the present paper and underlined by some authors [1, 9], the so-called *cold gilding* cannot be effective without a final heat treatment, which Pliny probably omits to mention.

Figure 4 gives some examples of mercury (amalgam) gildings.

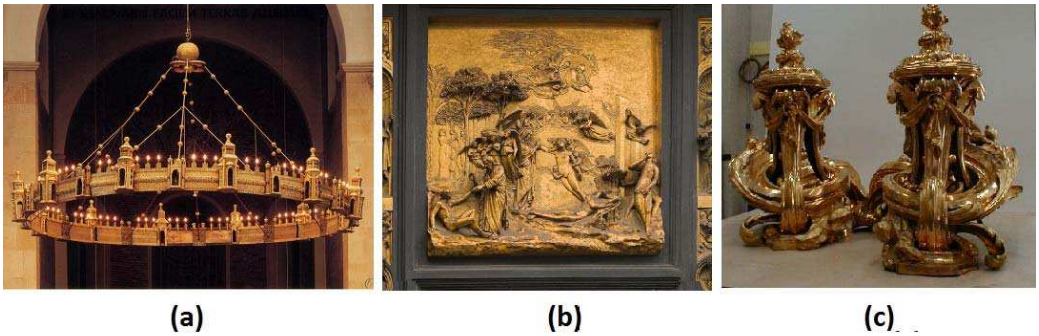

Fig. 4. Fire-gilded art objects: (a) the Hildesheim cathedral(Germany) Hezilo Leuchter, 11th cent., gilded copper, 2-5 µm [11]; (b) a panel of the Lorenzo Ghiberti's Door of Paradise in Firenze [12], 1452 CE, a few µm ?; (c) Firedogs executed by François Thomas-Germain, sculptor of King Louis the XVth (18th cent.), fire gilding on cast brass, Louvre museum, remaining thickness 0.1 µm + important diffusion (10 µm) into the substrate.

Fire gilding, was used for gilding of more or less small metal pieces (silver, bronze and copper alloys, sometimes iron). It was practised simultaneously with less expensive leaf gilding, for the entire period between the beginnings of Christian Era to the middle of the 19th century. It was then replaced, both for safety and cost reason, by electrolytic or electroless gilding (see below section 2.5).

Depletion gilding

A way to obtain a gold-looking surface at a lower cost was discovered at a neighbouring period in Central and South America, and perhaps also more confidentially in the Roman Empire around the first centuries of the Christian Era. It is called *depletion gilding* or *mise en couleur* and the Latin America process is referenced as *Tumbaga* and *Guamin* [1, 13]. A gold-copper or gold-silver alloy is oxidised to eliminate the alloying element on a limited depth and the oxidation product is eliminated to leave a gold-enriched layer at the surface. The process is renewed several times to obtain a nearly pure gold coloured surface (Fig. 5). The object is subsequently burnished to obtain a shining surface as the chemical etching has left a porous surface.

Fig. 5. Tumbaga pectoral from Quimbaya culture, 300-1600 CE.
Copper-depleted Cu-Au alloy.

Powder gilding

Another way to apply a gilt decoration is to use a gold powder dispersed in a binder, through a technique approaching colour painting. The oldest way to obtain a fine gold powder is to grind gold foils or gold leaves. It seems that the process was already used in China around 1000 years A.C. [14]. A recent study on the characterisation of enamelled and gilded Syrian glass artefacts produced at the 13th-14th centuries [15] has shown that the leaf ground to prepare the gold powder was about 200 nm thick. As the process implied a final firing to ensure the adhesion of the powder to the glass substrate, the binder used for the application, probably organic, has disappeared and could not be identified (Fig. 6).

Fig. 6. Gilded and enameled glass shards, Egypt or Syria 13th or 14th cent.
Louvre museum; right: steps of the elaboration process

Nowadays, the powder is fabricated either by leaf grinding or by chemical precipitation from a gold compound. The latter process gives a finer and homogenous granulometry. The use of gold decoration “painting” allows to multiply the kind of substrates (fabric wires, silk, leather, etc.) and simplifies the use of industrial serial production.

Electrochemical gilding

Nearly immediately after the invention of electricity generators, the Volta and Daniell electric cells, on the middle of the 19th century, the use of electrical power for electrolytic deposition of gold on metals was proposed [16]. Indeed that process was a long expected alternative to replace the very health-hazardous mercury gilding. The latter was rapidly prohibited, except for ancient object restoration.

In fact, metal gilding through an electrochemical process *stricto sensu* was discovered much earlier than that. The ancient Latin American civilisations (as the Mochica kingdom in Peru during the seven first centuries of our Era) were already using the fact that gold is the noblest metal from the electrochemical potential viewpoint to provoke its deposition on a less noble metal as copper or silver [17]. The process used aqueous gold salt solutions containing for instance natural salts as NaCl, KNO_3 and $KAl(SO_4)_2{\cdot}12H_2O$. That kind of process, called *electroless gilding*, is still used nowadays, for instance in electronic industry but also in jewellery. Evidently, the deposition should stop as soon as the surface is entirely covered by a compact gold film, because the electric contact with the less noble substrate does no more exist. In the modern process, oxidising species are added to the deposition solution to ensure the electrochemical reduction of the gold ionised species.

Concerning *electrolysis gilding*, using an electrical power source, it developed with a great success as soon as powerful DC electrical cells were available (Fig. 7), and even more when the other power generators as dynamos and hydroelectric generators became available from the end of the 19th century. The Hildesheim *Hezilo lustre* shown in figure 4a, although originally fire-gilded in the 11th century, has been repaired at the beginning of the 20th century with electrolysis-gilded pieces [11]. The thickness of the gold film may be very small (some tenths of µm) because it is very homogeneous and not porous, on the contrary to the mercury gilding film. That thickness may also be as large as required, eventually several micrometres.

The main drawback of the electrolysis process is the high toxicity of the gold solutions, often constituted of cyanide compounds. The modern processes tend to promote new solutions, as sulphite ($Na_3Au(SO_3)_2$) or thiosulfate ($Na_3Au(S_2O_3)_2$).

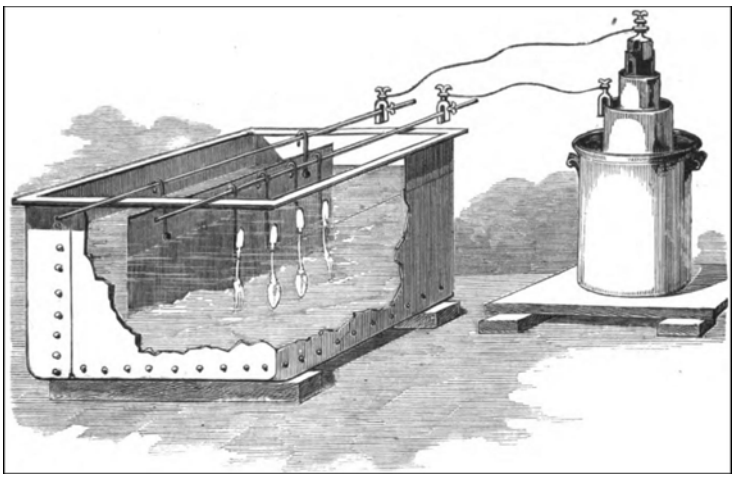

Fig. 7. Gold deposition tank and electrochemical cell power supply used in the Christofle Company, Paris, during the 1800's years.

Modern gilding processes: liquid gold, physical deposition.

Since mercury gilding is prohibited except for artwork restoration, gilding for decoration or industrial applications (electric contacts, electronic devices, etc.) is done nowadays by gold leaf, powder or modern processes as *liquid gold* or physical deposition.

Liquid gold [18] was developed after the 1920's and applied on table ware items for instance but also for industrial use. It uses a mixture containing gold organometallic compounds (e.g. sulforesinates, mercaptides, carboxylates, etc.) mixed in paste with a resin and a number of additives. That paste is displayed on the object, for instance by screen-printing. The item is then fired to decompose the mixture and lead to the precipitation of metallic gold as a thin film, whose thickness does not exceed 0.2 to 0.5µm.

Physical deposition is done either by cathodic sputtering or evaporation under vacuum, largely used in the electronic industry [19]. That process allows obtaining very thin and well controlled homogeneous films, down to a few atomic layers. Incidentally, one may recall (see above) that electroless gilding described above is also used presently in electronic industry.

Gold leaf forming, a sophisticated traditional process

For more than 4000 years man has been able of manufacturing very thin gold foils with a 0.2-0.3µm thickness. This impressive technical know-how is based on a very ingenious process, *beating*, where one strikes with a hammer many thousand times a stack put on a flat anvil. That stack is 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 figure 8. Figure 9 shows how a gold beater workshop of the 18th century was organised.

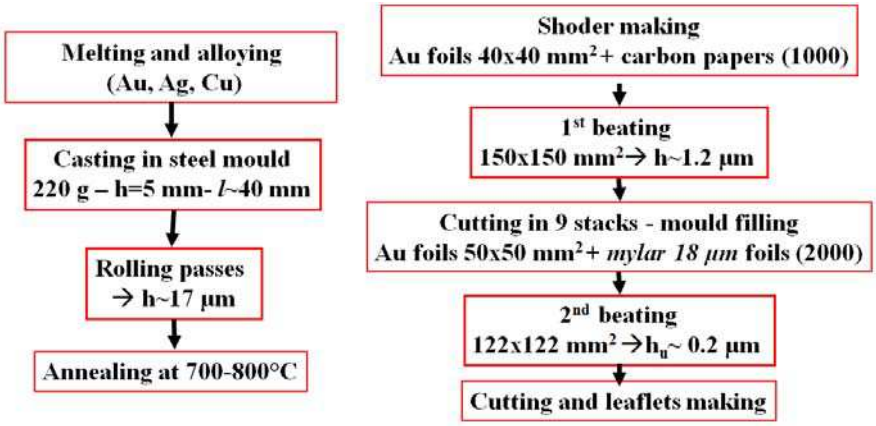

Fig. 8. The successive steps of gold leaves manufacturing process

Fig. 9. A goldbeater workshop at 18th century [from **20**]; (a) ingot melting; (b) cooling ingot; (c) rolling; (d) beating; (e) mould emptying and booklet packing

- After gold melting in a furnace and alloy elements addition, an ingot is casted with ~ 220g mass and about 5mm thickness. The thickness is reduced to about 17µm 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. 2). This step is punctuated and ends by intermediate annealings to restore the gold ductility.

- The step of beating is much more complex and time consuming. It includes 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 to two by various improvements as the use of mechanical hammers insuring about 4 strikes/s for performing the beating [21].

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 *mould* used for the second beating is made of a stack of intermediate mylar (PET polymer) films with dimensions much greater than the final dimensions of the gold leaves. These polymeric films replace now the old and much more expensive "goldbeaters' skins". They 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. 8cm side square) and inserts them in a leaflet of silk paper. This process presents many exceptional aspects. It imposes a very high elongation, equal to /0.0002=25 000!. The final product is very flexible, and the risks of wrinkling and tearing are high. For manufacturing 100g gold leaves, approximately 400g gold is necessary to start with.

The minimal thickness obtained by rolling

The problem of the minimal thickness is well known in rolling shops. It is called the *friction hill effect*. In fact, the friction and the rolls elasticity impose a minimal thickness. A natural idea for displacing this limit is to roll several sheets together. It is used for instance for manufacturing packaging aluminium foils; it cannot be applied to gold, because gold foils will weld to themselves. Below some thickness h_f, the foil passes through the roll gap without plastic strain by elastically flattening the rolls. That limit thickness can be calculated by mechanical modelling [22, 23], and, in a simplified model considering steel rolls of 50mm diameter, with a reduced Young's modulus of 115GPa, and a Tresca friction coefficient with gold of 0.05, the minimum attainable thickness is found to be about 17µm. It increases very strongly with the friction coefficient: mirror polished well lubricated rolling rolls must be used. To obtain micrometer-thick leaves, it is thus mandatory to use another process, *beating*.

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 polymer 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 mechanical properties of the mylar inserts. The phenomena during the beating of the shoder are probably similar. The full calculation is developed in another publication [23]. Here are summarised the main principles and conclusions of that calculation. Figure 10 shows a simplified sketch of the part under the hammer of a polymeric foil inserted between two gold leaves.

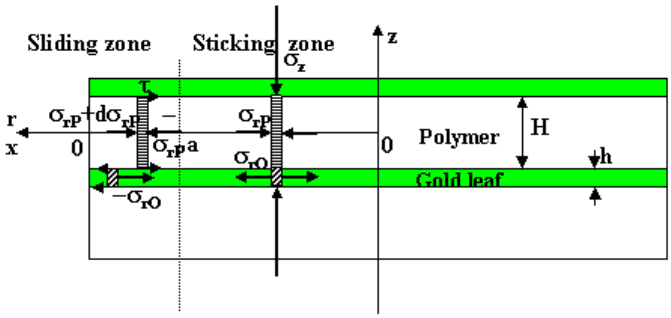

Fig. 10. Stress state in two foils of the mould during the beating

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 which ensure thinning of the gold leaves. After release of the hammer the elastic energy stored in the polymer promotes its separation from gold by peeling during its elastic recovery. The coating of interlayers is designed to favour that separation without damaging the gold leaves. The system is then ready for the next blow. Because the Young's modulus of gold 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 polymer deformation is exclusively elastic and gold can be considered as rigid. The mechanical system of figure 10 can then be solved quite simply by the slab method. Using reasonable values for the mechanical parameters (polymer Young's modulus of 4GPa, polymer Poisson ration 0.35, polymer thickness 17 µm; gold flow stress 0.2GPa, gold thickness 1 µm; friction coefficient 0.05), one obtains the following results. The strain for a thickness change 1.2 to 0.2µm is ln(6)~1.79. Because for one blow the maximal thickness stress is 3.5%, the minimal blows number 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 120mm side, in rather good agreement with actual practice.

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

Some laboratory tools for the study of gilding on cultural artefacts

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

- The composition, possibly the origin of the gold;
- The thickness of the gilding film, if possible the microstructure and consequently the processing mode;
- The mode of adhesion of gold onto the substrate.

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

Non-destructive characterisation

If the gilded artefact has to be examined without possible sampling it remains possible to conduct a series of analysis with the available modern tools:

-*X-ray fluorescence* under X-ray excitation allows elemental analyse from the surface. Modern equipments and computer codes 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.

- *X-ray diffraction* may be useful to characterise the metallurgical state of the gold leaf, particularly its possible crystallographic texture, but eventually also to identify the crystallised compounds contained in the adhesive or supporting layer of the leaf. Portable X-ray diffraction equipments, coupled with X-ray fluorescence, have been recently worked out, allowing crystallographic characterisation on large pieces in their usual environment.

- *Raman microspectroscopy* is, for identification of inorganic compounds contained for instance in the sublayers supporting the gold leaf, a very efficient tool. Raman shift data 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.

- *Optical measurements*, specially photospectrometry, may also be used. Portable spectrophotometers exist.

- A *particle accelerator* may be a very powerful tool for a set of measurements, all contactless and possible on large objects when the particle beam is extracted to atmosphere as for the AGLAE accelerator of the C2RMF [24]. Local chemical analysis is done by *PIXE* (particle-induced X-ray emission) and *PIGE* (particle-induced gamma emission) with a 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. It is essential to obtain a reliable value of the gold coating thickness without any sampling. RBS allows it.

Destructive characterisation

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

- *Optical metallography or scanning electron micrography* (SEM), both on polished cross-sections. One must however be conscious that polishing a cross section including a gold layer and a much harder substrate is a difficult operation, which may induce an uncontrolled spreading of gold onto the neighbouring substrate. The consequence is an overestimation of the coating thickness and of the possible gold diffusion 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 lying under the gold leaf.

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

- Evidently, *X-ray diffraction* on small samples (X-ray microdiffractometers allow very small samples) is essential to identify the crystalline compounds.

The gold-substrate interface: an open research field

Depending of the gilding process chosen by the artisan or artist, the question of the adhesion mechanism of the coating onto the substrate is an essential question.

The leaf adhesion

As, on the contrary to gold foils, mechanical fastening of the gold leaves to the objects is impossible, it has been necessary to find a way to stick the leaf onto the surface through an intermediate product. That intermediate product is in fact a stack of several layers whose functions are: (i) to prepare a smooth and even surface in order to avoid a transmission of the eventual substrate roughness to the gold film; (ii) to provide adhesion of the leaf sufficiently efficient for the decoration to be preserved against environmental degradation.

The application of a surface preparation on the object to be decorated is, with the discovery of beating described in the previous section, the most important historical progress in the leaf gilding process. Evidently, that surface preparation depends entirely on the nature of the substrate, and a large number of recipes were used, already in antic Egypt for wood or cartonage sarcophagi [25] and in all civilisations. The very various recipes have been described in written manuscripts, especially during the medieval period. The thesis of I. Bonaduce [5] gives a compilation of a large number of those recipes with their written origin; those are summarised and discussed in [1]. An interesting point is that, whatever the substrate, the principles of preparation remained the same through the centuries even if the used products themselves were very various. Two processes were used and are still applied presently, for instance in the wood gilding workshops or for metallic gates or roofs gilding:

- In the first process (*Tempera gilding*) the substrate surface is first covered by a primer, sometimes called *preparation* or *gesso* (the Italian word for gypsum), a powdered compound, either gypsum of calcite, to which is added an adhesive agent (for instance animal glue) applied as several layers with thinner and thinner granulometry and less and less adhesive. On that primer is painted just before application of the gold a thin layer of an adhesive mixture, e.g. Armenian bole (Al_2O_3, SiO_2 + Fe_2O_3) containing animal glue. The gold foil or leaf may be burnished after application and/or surface-treated to adjust its appearance and colour;
- In the second process (*mixtion gilding*), the adhesive mixture (the *mixtion*, e.g. *oil mixtion* or *egg white mixtion*, etc.) is painted directly on the substrate before application of the gold foil or leaf.

But the choice of a given adhesive has always remained more or less empirical or based on immemorial traditions, without having a real scientific justification. For the moment one just states a rough classification between i) proteinic glues as rabbit skin glue or fish glue, ii) glucidic compounds as honey, polysaccharides, starch, etc., iii) lipid compounds as linseed oil or other oils, sometimes containing siccative additives as lead compounds. Each of those kinds finds its use for given application.

The gold substrate interface in absence of adhesive

In the case of gilding on metals, gold may be applied directly as a leaf and heated and/or hammered (gilding *à l'haché*) to ensure its perennial adhesion. In fire-gilding, a mercury gold amalgam is applied and subsequently heated to eliminate most of mercury (boiling point 359° C). Here, the interface between the gold coating and the substrate is structural and adhesion is ensured thanks to the high temperature interdiffusion between them.

In order to avoid fanciful interpretations of the thickness involved in that phenomenon, it is useful to comply with quantitative data. For instance, gold-silver interdiffusion coefficients have been quantitatively measured [26]. The diffusion coefficient D obeys to an Arrhenius equation : $D = 0{,}82\ cm^2s^{-1}*\exp(-202\ kJ/mol/RT)$, where T is the absolute temperature and R the perfect gas constant (8.31 $mol^{-1}K^{-1}$). A good approximation of the diffusion distance into the substrate during a time t is the quantity 2.sqr(D.t). At 600K (about 330°C), a firing temperature commonly practiced by the professional metalworkers to evaporate mercury, that quantity is less than 1.0µm for several hours duration. In fact the actual diffusion distance may be larger because short-circuit accelerated diffusion can occur along the metal defects as grain boundaries. But this means that the diffusion distance cannot be as large (several µm) as announced by most affirmations in literature. The reason of that overestimation, generally obtained through BSE SEM observation may be found in two origins: (i) one is the experimental artefact due to spreading of the soft gold on the harder substrate during mechanical polishing of the cross-section specimen; (ii) the second is the existence of an important roughness of the substrate induced by the pickling of that substrate done before the amalgam application to eliminate de pollution and oxide layers.

Another interesting point is that the interdiffusion induces an alloying of the gold layer by mercury. Indeed, mercury is soluble in the solid state into gold. Figure 11 is for instance the Au-Hg equilibrium diagram, with the temperature range possibly used for mercury elimination [**27**]. It shows that at 300-400°C the gold layer may contain more than 10wt% of mercury in solid solution; which could be eliminated only by slow solid state diffusion.

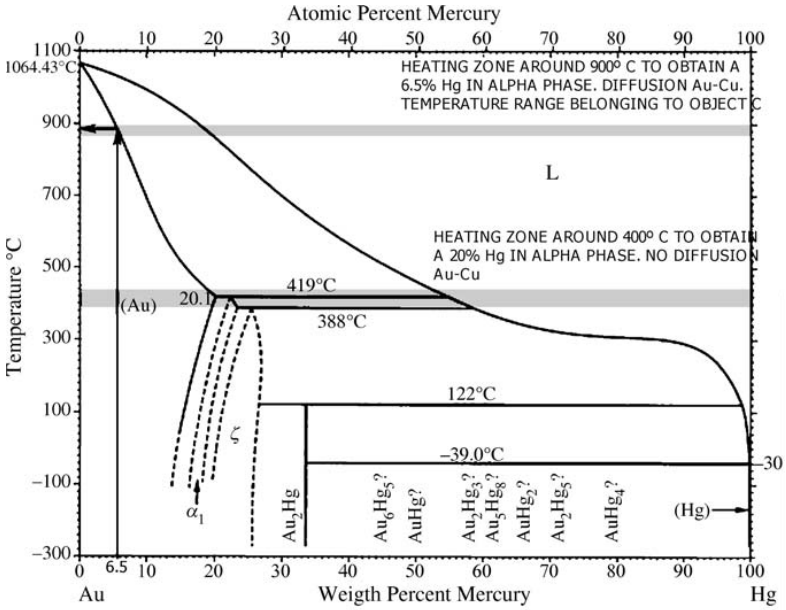

Fig. 11. Au-Hg equilibrium diagram, with typical behaviour during fire-gilding [**27**]

That fact has two consequences:

i) As already underlined by Oddy [2], when one analyses an ancient gilded object, the absence of mercury in the gilded layer is a definitive proof that it is *not* a mercury gilding; its presence is a clear indication of the use of the amalgam process;

ii) That presence of noticeable quantities of mercury in the gold film explains why Pliny the Elder states that the gilding is paler than the natural gold colour [7], especially because that author is describing the method of very thin leaf gilding using mercury as an adhesive.

Another case of gilding without using an adhesive is the *liquid gold* process described above, applied for instance to glass table ware. A detailed study [18] has shown that the mechanism of the gold adhesion is a diffusion of gold into the glass substrate over a very small distance, smaller than 100nm, during the firing at a temperature around 600°C. It seems that the diffusion mechanism is not entirely temperature-controlled; and the additives added to the liquid gold paste play an important role on the efficiency and resistance of adhesion, through a modification of the microstructure of the glass substrate first layers.

Conclusions

Gilding has been a fascinating and magnificent process of decoration for nearly all kind of artworks since nearly the beginning of humanity. The technical know-how developed by the artisans along the centuries has been in constant evolution and is still improving. Some of the most important methods has been described and discussed in the present article.

The laboratory study of gilded artistic or archaeological artworks remains a rich scientific issue. The development of non-destructive investigation means has open a wide field for a better knowledge of the ancient gilding processes. In particular, the physico-chemical

mechanisms of gold layer adhesion and of its degradation by aging and environmental action are still not well explained. Further research on those subjects will be of great help for the conservation and restoration procedures of the ancient gilded artworks.

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