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NEW LEAF GILDING ALLOYS: PHYSICO-CHEMISTRY, COLOUR, MECHANICAL BEHAVIOR

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Abstract

In the frame of a systematic investigation on leaf gilding history and processes, in a research program intending to propose gold leaf alloys specially devoted to restoration, new gold alloys containing low concentration additions of In or Pd were designed and leaves were elaborated in collaboration with the goldbeater Dauvet. The influence of those elements on the colour change induced by alloying was obtained by colorimetry. The microstructural and metallurgical properties of the alloys were studied by scanning electron microscopy (SEM). The foils and leaves were characterized at the different manufacturing steps by EBSD (Backscattered Electron Diffraction), in order to evaluate the effect of the fabrication process on the microstructure and crystallographic texture. Surface segregation of the alloying element, influencing surface colour, was sometimes evidenced and discussed. The mechanical properties of the foils or leaves were measured by micro- and nano-indentation. The obtained properties and behaviour of the new alloys were compared with those of the leaves currently used for leaf gilding. The results conducted the beating company to consider developing new gold leaves production range(s) devoted specially for restoration application. As a result of the present investigation, new manufacturing and gilding procedures have been proposed.

Keywords: Gold alloys; Leaf gilding; Colour; Mechanical properties; Texture

Introduction

Leaf gilding is the most ancient gilding decoration applied on all kind of artistic, funeral and worship objects [1-3]. Because ancient gilded objects may have been deteriorated through the ages, or because the known difficulty to perform that kind of decoration with a necessary perfect and perennial quality, it is common to detect during archaeological investigations the presence of additional surface gold leaves which may be or not authentic, belonging or not either to an ancient local repair done by the artisan himself or to a restoration performed later at an unknown period and not documented. Some examples of gilding repair may be often found in published archaeometric studies. As those repairs have generally the same composition as the authentic gilding, it is impossible to draw any conclusion about them in terms of dating, authentication or restoration history.

In the frame of its research and conservation activity devoted to gilding knowledge and conservation, the Centre de Recherche et de Restauration des Musées de France (C2RMF)

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developed a program aiming to propose an answer to that question. The idea is to propose the elaboration of gilding leaves used specifically for restoration, which could be identified by future conservators when compared to the authentic or older gilding. That program, performed with the help of the French goldbeater Dauvet [4], was named Alienor. The chief decision is to elaborate leaves with alloys containing chemical markers easily identifiable and measurable with current analysis means, and not existing in ancient gildings.

The present article discusses the choice of two elements added to gold to elaborate two specific alloys, and describes a metallurgical characterization of the leaves obtained with the alloys, as well as the problems encountered and the solutions proposed to overcome these problems. A brief description of the leaves elaboration by the goldbeater is first recalled to set the bases of the process, and the results of microstructural, mechanical, crystallographic and micro-analytical characterization are presented.

Various laboratory facilities are used for that study: optical (OM) and scanning electron microscopies (SEM); XRF (X-ray fluorescence) and ion beam (IBA) microanalyses; microtexture measurements using EBSD (BackScattered Electron Diffraction); micro-hardness; nano-indentation.

Materials and Methods

**Gold alloys. The choice of the alloying markers**

The highest quality gold commercially sold by the goldbeater as leaves (Or supérieur) is a 23.42 karat gold (980 thousands) containing small additions of silver and copper to improve its mechanical properties. The new alloys proposed for restoration should be:
- Easy to thin down by beating
- Of the same colour as the commercial one
- With chemical tracer(s) as “exotic” as possible
- With tracer(s) easily analysed with current analysing tools, as, for instance portable XRF

The present study shows the tests done with two alloys, both of 23.42 karat gold:
- A gold-copper-indium alloy
- A gold-copper-palladium alloy

Indium and Palladium are both white metals and replace silver of the commercial alloy. They are added at a concentration low enough to not significantly change the colour, and remain in solid solution.

A remark should be emphasized: palladium may exist either as a natural or an intentional alloying element of gold, but its concentration is much higher (5-10 wt.% Pd) for natural porpezite [5] and for goldsmith alloy (more than 10 wt.%), or much lower (0.1 wt.%) for the known “Brazilian gold” [6], than the addition done here.

In a preliminary testing process, an alloy, still 23.42 karat, in which silver was only partially replaced by indium, has been tested but abandoned because the indium amount was not high enough. Some results on that test alloy are nevertheless mentioned in the present paper.

**A few indications about the leaf elaboration technical procedure**

As mentioned in the introduction, the leaf elaboration was performed in the workshop of Dauvet goldbeater society [4]. In previous publications [1,3,7,8] a mechanical analysis of the whole beating process is described in detail. For a better understanding of the present study it is necessary to recall just a few important points. Figure 1 summarises the whole process, starting by alloy melting followed by a cold rolling step and two beating steps.

Mechanical modelling shows that cold rolling (or hammering on a single foil) cannot produce a gold foil thinner than 10-15 µm thickness. That limitation led to the invention of the process of beating which is based on the constitution of multi-foil stacks by piling large
numbers of gold foils cut from the rolled ribbon (called *quartiers*), separated by polymer thicker spacers. In the modern process, two beating steps are done. The first multiple stack is called *shoder*, it contains less than 1000 *quartiers* separated by black (carbon containing) paper sheets, and the final gold thickness attained is about 1 to 2 µm. The second stack, called *mould*, may contain 2 to 3 thousand gold leaves separated by mylar® sheets (a PET polymer). The final gold leaf thickness is between 0.1 and 0.3 µm.

**Observations**

After optical observation, the specimens are observed in the scanning electron microscope on secondary electron mode (SE): direct surface observation for thick foils, surface observation for thin leaves coated on a wood substrate.

**Physico-chemical analyses. Leaf thickness measurements**

Three kinds of tools have been used for composition analysis of the alloys at different steps of leaf manufacturing:

- SEM-EDS (Scanning electron microscopy coupled with Energy Dispersive Spectrometry); sometimes the electron acceleration voltage was varied in order to detect in-depth variations of element concentrations;
- Portable X-Ray Fluorescence (XRF);
- Ion Beam Analyses (IBA) with the AGLAE particle accelerator, situated in the C2RMF laboratory.

That last facility [9] is working with a particle beam (here 3 MeV protons) extracted to the atmosphere and allows:

- PIXE (Particle-Induced X-ray Emission) elemental analysis. In the case of gold analysis, a filter of copper (25 or 50 µm) is used in front of the X-ray detector to “kill” the very large X-ray Lα emission of the gold matrix in order to optimise the sensibility (decrease the detection limit) for the minor elements [6], here Indium or Palladium.
- RBS (Rutherford Backscattering Spectrometry) in depth non-destructive investigation. That method, based on the spectrometry of the backscattered particles, allows a precise determination of surface film thickness by using a simulation code (SIMNRA) to quantify the spectra [10].

As a particle accelerator is not easily available for restorers, a comparative investigation of the results between portable XRF and the more precise IBA means is currently running.
**Colour measurements**

Colour measurements are done with a spectro-colorimeter Konica, using a standard illuminant D65, at an angle of 10 degrees. The results are given in the CIE L*a*b* system [11]. With that system, the $a$ and $b$ orthogonal axes represent respectively the colour ranges from green to red and from blue to yellow and $L$ represents the luminance (from black to white). It has the advantage of showing quantitatively the colour difference between two measurements as the Euclidian distance between the two points representing them.

**Micro-hardness and nano-indentation**

Vickers hardness of the alloys was evaluated using micro-hardness common laboratory equipment. Measurement of the dimension of the indent obtained with a pyramidal indenter (here under a load of 0.25 N), gives the Vickers hardness $HV$. That number may be converted into an approximate value of the yield strength $\sigma_y$ by the formula $\sigma_y \sim 3HV$.

Nanoindentation measurements were done using an Agilent 5500-LS AFM (Atomic Force Microscope) with Hysitron device. From the force-indentation depth data during loading and unloading cycle, it is possible to obtain values of the contact reduced modulus $E^*$ and an evaluation of the hardness, at a nanometric scale.

The modulus writes $E^* = \((1-\nu^2)/E+8.7.10^{-4})^{-1}$, in which:
- $E$ is the Young’s modulus of the indented material = slope of the stress-longitudinal strain curve in the elastic tensile testing;
- $\nu$ is the Poisson’s ratio of the indented material (ratio between lateral contraction and longitudinal strain);
- $8.7.10^{-4}$ is the contribution of the indenter material (diamond).

For indentation of pure gold, the specific value is $E^* = 98$ GPa.

As discussed further, the roughness of the specimens provoked a large uncertainty and a strong dispersion of the results. In addition, the tip defect of the indenter induces measurement errors for small indentation depths. General trends could nevertheless be proposed.

**Diffraction of backscattered electron (EBSD, Electron Backscatter Diffraction)**

That technique [12] is used with a SEM instrument (FEI Philips XL30 ESEM) equipped with a camera to record the backscattered electrons diffraction Kikuchi lines. The diffraction pattern is recorded for each position of the electron beam and treated with a devoted computation code (OIM™). An image of the surface at the SEM scale is obtained with a colour code for each region, depending of the crystallographic orientation. The grains and their boundaries are therefore evidenced.

**Results and discussion**

**Mechanical behaviour of the new alloys**

During the first tests of cold rolling, it was found that the new alloys appeared harder than the usual commercial Au-Cu-Ag product. A new annealing procedure was then decided, and tested by micro-hardness measurements. Table 1 gives the results of those tests on mm-thick specimens. It shows that the hardness and yield strength have been successfully drawn back to those of the usual manufacturing alloy.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Annealing</th>
<th>Hardness $HV$</th>
<th>Yield strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Cu-Ag commercial (Dauvet)</td>
<td>usual</td>
<td>79</td>
<td>227</td>
</tr>
<tr>
<td>Au-Cu-Ag-In preliminary test alloy</td>
<td>usual</td>
<td>84.6</td>
<td>240</td>
</tr>
<tr>
<td>Au-Cu-In Test alloy</td>
<td>modified</td>
<td>67</td>
<td>221</td>
</tr>
</tbody>
</table>

Table 1. influence of the annealing conditions on hardness and yield strength of Au-Cu-In alloy
The nanoindentation results, giving the reduced modulus \( E^* \), as defined above, appear very scattered (for example fig. 2). That scattering must be attributed to the roughness of the tested specimens, which is not compatible with the size of the testing indenter. It was evidently not possible to submit the specimens to a mechanical polishing which would destroy the intrinsic mechanical properties.

A statistical treatment of the results was nevertheless used to make apparent a possible trend amongst those results. Figure 3 shows that trend computed from the results obtained on the commercial Au-Ag-Cu and on the Au-In-Cu alloys. The comparison between the two curves indicates a slight influence of the indium addition to increase the reduced modulus, i.e. to make the alloy stiffer. This confirms a trend qualitatively observed during rolling operation.

![Fig. 2. Example of experimental nanoindentation reduced modulus \( E^* \) results obtained on a quartier specimen (rolled and annealed, just before beating, thickness \( \sim 15 \mu m \)) of the commercial Au-Cu-Ag alloy.](image)

For comparison, the reduced Young’s modulus of pure gold is 98 GPa. All alloys are stiffer than pure gold, which is known to intentionally adapt the material to the beating process.

![Fig. 3. Statistical trend lines for the reduced modulus \( E^* \) obtained from the experimental nanoindentation on quartier specimens (rolled and annealed, just before beating, thickness \( \sim 15 \mu m \)) of the Au-Ag-Cu and Au-In-Cu alloys.](image)
Microstructure

Figure 4 shows some SEM images of the alloys surfaces at different steps of leaf manufacturing: end of the cold rolling and end of the first beating (*shoder* leaf). Traces of the rolls are visible, they disappear during beating but the surface remains tormented.

![SEM micrographs of the alloys. (a) Au-Cu-Pd at the end of cold rolling; (b) Au-Cu-In at the end of cold rolling; (c) Au-Cu-Ag-In after the first beating (*shoder*); (d) Au-Cu-In after the first beating (*shoder*)](image)

Fig. 4. SEM micrographs of the alloys. (a) Au-Cu-Pd at the end of cold rolling; (b) Au-Cu-In at the end of cold rolling; (c) Au-Cu-Ag-In after the first beating (*shoder*); (d) Au-Cu-In after the first beating (*shoder*)

In order to appreciate the degree of crystallisation and possible crystallographic textures, **EBSD images** were obtained. They are shown in figures 5, 6 and 7.

![EBSD image on a specimen of the commercial Au-Cu-Ag alloy at an intermediate state of cold rolling (not annealed). The rolling direction and the colour code of crystal orientation are shown beside](image)

Fig. 5. EBSD image on a specimen of the commercial Au-Cu-Ag alloy at an intermediate state of cold rolling (not annealed). The rolling direction and the colour code of crystal orientation are shown beside

![EBSD image on a specimen of the Au-Cu-In alloy after annealing at the end of cold rolling (*quartier*). The rolling direction and the colour code of crystal orientation are shown beside](image)

Fig. 6. EBSD image on a specimen of the Au-Cu-In alloy after annealing at the end of cold rolling (*quartier*). The rolling direction and the colour code of crystal orientation are shown beside
Figure 5 points out that, although heavily strained by rolling and not annealed, the alloy shows a beginning of recrystallization: grains sometimes very small (less than 1 µm diameter) are visible, oriented in the rolling direction with a preferential crystallographic orientation. Figure 6 shows the success of the annealing operation, with development of large grains (diameter > 50 µm); the black lines are either due to the rolling roughness (see fig. 4a and b), or imperfect crystallization.

The two images of figure 7 show that, in spite of the important strain imposed by the beating process, ancient grains resulting from the annealing are still visible. Moreover, the interior of the grains exhibits colour progressive variations due to small deformations resulting from beating. It is worth recalling that the mechanical modelling has shown [7] that the deformation during beating is a planar 2D stretching provoked by the friction of the polymer sheets inserted in-between the gold leaves.

**Colorimetry**

The results of the colorimetry measurements are summarised in figure 8 in the CIE a*b* representation. That figure shows that the colour difference between the leaves of the commercial reference Au-Cu-Ag alloy and those of the two new alloys is quite small.

The Au-Cu-In leaf is slightly less red than the reference; the Au-Cu-Pd leaf is slightly more red and less yellow than the reference.
Analytical characterisations. Evidence of indium surface segregation

At this step of the research program the aim of the elemental analyses was to demonstrate the possibility of detecting the added markers - indium or palladium - even in the very thin leaves. Among the different analytical tools used, only results from SEM-EDS and PIXE on the particle accelerator are shown, as the optimisation of XRF analyses is still under progress. Results of PIXE measurements are shown in figure 9 in the form of X-ray emission spectra on fully manufactured leaves, using, as discussed in the above “methods” part, a copper filter on the X-ray detector to attenuate the Au Lα radiation. The small quantity of indium or palladium is clearly detected without problem (detection time < 3 minutes).

Fig. 9. PIXE spectra on final leaves of both Au-Cu-In and Au-Cu-Pd alloys.
3 MeV protons, 25 µm copper filter on the detector.

SEM-EDS measurements are summarised in table 2. Acquisition was performed for different annealing conditions and under two different electron accelerating voltages.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Annealing</th>
<th>Acceleration voltage</th>
<th>Au</th>
<th>Cu</th>
<th>Ag</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Cu-Ag-In (preliminary test alloy). Thickness &gt; 100 µm</td>
<td>usual</td>
<td>20 kV</td>
<td>97.3</td>
<td>1.1</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Au-Cu-Ag-In (preliminary test alloy), beated</td>
<td>usual</td>
<td>20 kV</td>
<td>97.7</td>
<td>0.9</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Au-Cu-In-Ag (preliminary test alloy). Thickness &gt; 100 µm</td>
<td>usual</td>
<td>10 kV</td>
<td>91.9</td>
<td>1.0</td>
<td>0.3</td>
<td><strong>3.8</strong></td>
</tr>
<tr>
<td>Au-Cu-Ag-In (preliminary test alloy). Thickness &gt; 100 µm</td>
<td>modified</td>
<td>20 kV</td>
<td>97.6</td>
<td>1.1</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Au-Cu-Ag-In (preliminary test alloy). Beated</td>
<td>usual</td>
<td>10 kV</td>
<td>96.5</td>
<td>1.6</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Au-Cu-In 20 µm thick</td>
<td>modified</td>
<td>20 kV</td>
<td>97.9</td>
<td>1.0</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Au-Cu-In 20 µm thick</td>
<td>modified</td>
<td>12 kV</td>
<td>96.6</td>
<td>0.9</td>
<td>-</td>
<td><strong>2.6</strong></td>
</tr>
<tr>
<td>Au-Cu-In beated</td>
<td>modified</td>
<td>20 kV</td>
<td>97.5</td>
<td>1.6</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Au-Cu-In beated</td>
<td>modified</td>
<td>12 kV</td>
<td>98.7</td>
<td>0.9</td>
<td>-</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The comparison of the results obtained for different acceleration voltage shows that indium concentration looks much higher when measured under lower acceleration voltage, at least for specimens annealed with the current usual conditions of the beater workshop. This is a proof of a surface segregation of indium, because lower acceleration voltage favours analysis of the near-surface region. Indium is known as a surfactant agent, known to favour its surface segregation in metallic alloys which contain it [13]. In order to avoid that segregation, the annealing conditions were modified. Thus, table 2 shows that surface segregation is somewhat inhibited by these new annealing conditions. Further experiments have shown that annealing can be optimised to avoid completely the effect.

The results show moreover that the beating operation provokes a total vanishing of the segregation effect. This is due to the strain induced by beating, which provokes an accelerated
atomic diffusion and a re-homogenisation of the alloy, taking into account the small individual volume of the leaves.

*Leaf thickness measurement.*

Measurement of gold leaf thickness is a difficult problem. Estimation of the average leaf thickness is usually performed by weighing the booklet containing 25 leaves and assuming that the density of the material has the theoretical value.

Most of the values given in literature are obtained by SEM observation on cross sections. But it is known that during the preparation of such cross sections by mechanical polishing, an apparent unintended enlarging of the gold leaf section may be induced by the difference in hardness between the very ductile gold and the harder neighbouring phases. This often leads to an overestimation of the leaf thickness [1].

In the present case the leaf thickness after full beating has been evaluated by Rutherford backscattering spectrometry done with the AGLAE particle accelerator, i.e. on a fully non-destructive manner. That technique is based on the measurement of the energy of the backscattered particles under a particle beam bombardment, here 3 MeV protons [9]. Figure 10 is an example of the RBS spectrum obtained on an Au-Cu-In leaf deposited on a glass plate.

![RBS spectra under 3 MeV protons of an Au-Cu-In alloy coated on a glass plate.](http://www.ijcs.uaic.ro)

Fig. 10. RBS spectra under 3 MeV protons of an Au-Cu-In alloy coated on a glass plate.

The channel number is representative of the backscattered proton energy (channel 512 = 3 MeV)

A simulation of the RBS spectrum by using the devoted simulation calculation code SIMNRA [14] leads to an estimation of the gold leaf thickness, which has been found to be of $0.1 \pm 0.02 \mu m$ for both Au-Cu-In and Au-Cu-Pd alloys. That value is in the lowest range of the leaf thickness values commonly used for gilding.

**Conclusion and perspectives**

The manufacturing of leaves of two new 23.42 karat (980 thousands) gold alloys specially devoted to gilding restoration has been performed with success. A detailed metallurgical and physico-chemical investigation shows that those alloys containing respectively Indium or Palladium as chemical markers may be recommended for gilding restoration provided the manufacturing of the leaves is modified following a specific adapted procedure.

Colorimetry measurements are satisfactory enough to consider that the colour difference induced by the added alloying elements as compared to classical gilding alloy is acceptable.

The Dauvet society is now in the process of proposing a commercial version of those modified leaves. The possibility to detect the presence of the markers by using easily available analysis tool as portable XRF has been checked and it is presently under confirmation: it
remains necessary to control the influence of the gilding substrate elements (bole, preparation, support) on the analysis parameters to be recommended.

This will be the aim of the further research project, as well as an investigation on the adaptation of the same concept to other gilding alloys.

Acknowledgments

That study could not have been completed without the active collaboration of the Dauvet goldbeater society, in the names of its director Antonin Beurrier and its former director Bernard Dauvet, with the invaluable technical assistance of Nadine Acqueberge. EBSD and colorimetry measurements were done respectively by Suzanne Jacomet and Françoise Giulieri. The help of the team of the particle accelerator, Claire Pacheco, Laurent Pichon, Brice Moignard and Quentin Lemasson is gratefully acknowledged. We also acknowledge the contributions of the C2RMF gilders Stéphanie Courtier, Roland Février, Marie-Jeanne Dubois and Loïc Loussouan.

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