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Gold Leaf Alloys Specifically Designed for Conservation

Dominique Robcis*

Centre de Recherche et de
Restauration des Musées de France
(C2RMF), Paris, France
dominique.robcis@culture.gouv.fr

Caroline Thomas

Centre de Recherche et de
Restauration des Musées de France
(C2RMF), Paris, France
caroline.thomas@culture.gouv.fr

Marc Aucouturier

Formerly CNRS research director
Paris, France
marc.aucouturier@wanadoo.fr

*Author for correspondence

Abstract

Modern conservation ethics requires that materials and products used for restoration should be reversible, identifiable and traceable. While great improvements have been made in most artistic fields, conservation of gilded objects has yet to develop better solutions to this problem. Leaf gilding restoration on museum objects is often performed with gold leaf substitutes like mica powders or watercolours, although the result can be unsatisfactory in terms of aesthetics and ageing. Gaps in the gilded surfaces are still frequently covered with new gold leaf, which is neither traceable nor reversible. This technique makes it difficult, if not impossible, to differentiate the restored gilding from the original, because the composition and thickness of the new leaf may be indistinguishable from the original authentic gilding or re-gilding. A research program has been developed by the Centre de Recherche et de Restauration des Musées de France (C2RMF) in collaboration with the Dauvet goldbeater society to elaborate on new gold alloys containing small amounts of chemical

markers, which could be easily detected by commonly available analytical techniques. This paper presents the development of such alloys, including choice of chemical markers, elaboration process and thermo-mechanical treatments to be applied during the fabrication of foil and leaf. The new leaf needs to have similar appearance in colour and thickness to the authentic gilding. The metal leaf was tested on various substrates and analysed with ion beam analyses using the C2RMF particle accelerator by particle induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS) to validate the pXRF analysis performed. This paper also addresses the implications of the proposed processes with respect to conservation-restoration ethics, practical beating and gilding workshop procedures.

Keywords

gilding conservation, gold leaf, gold beating, chemical marker, indium, palladium, XRF analysis, ion beam analysis

Introduction

Restoration involving precious metals (gold or silver) raises specific issues in terms of reintegration, both in the archaeological field as well as decorative arts. On archaeological objects, the choice is often made to reintegrate the area of loss with synthetic materials such as epoxy or acrylic compounds and to homogenize the surface with bronze paint, mica or metallic pigments. Results are often disappointing in terms of aesthetics as well as ageing, as seen in Figure 1.

Indeed, the metallic shine is difficult to reproduce especially on large surfaces, which is a major issue even if one does not aim at illusionism.

Concerning the decorative arts, furniture conservation was marked by its use as a functional object. This influences the interpretation of the pieces even when they are no longer in use and held in a museum collec-



Figure 1. Examples of ancient restorations on gilded objects: on the left, detail of a Roman gilded-silver vessel (Musée du Biterrois, Béziers, inv. 84.16.1); on the right, the leg of a gilded-wood chair (Musée National du Château de Malmaison, inv. MM40.47.7122). © C2RMF

tion. Therefore, the traditional restoration practice for gilded surfaces was to heavily re-gild damaged parts. Furthermore, applying new gold leaf is an irreversible practice that reactivates the original bole and glue and partly covers the old gilding. With the evolution of the practices of conservation, there is greater insistence on how to modulate the answers to these issues and to harmonize the surface with less intervention by using more reversible techniques. The trend is to avoid using new gold leaf whenever possible, selecting substitutes such as watercolor, mica powder, gold powder or shell-gold. These substitutes work very well on small surfaces and offer an interesting way to tone the damaged surface without applying new gold leaf. However, they are not completely satisfying in terms of visual effects, and in many cases one is forced to use traditional leaf gilding.

The main issue is that this practice of re-gilding with gold leaf does not match with modern conservation ethics. As reasserted by the ICOM Code of Ethics for Museums (ICOM 2013), it is necessary to be able to distinguish the original materials from the restoration products or techniques used. Despite the efforts made nowadays to document restorations, they cannot always be accurate enough to locate the restored areas precisely. It is often difficult to distinguish original gilding from a restoration because the replacement gold leaf is no different from the original in its composition and thickness. Since antiquity, objects have shown a composition and thickness similar to modern gold leaf (Oddy 1993, Darque-Ceretti 2012).

Confronted with these issues, C2RMF decided to launch a project for the development of specific precious metal alloys for cultural heritage restoration. The idea is to incorporate chemical markers into the leaf alloys which could be used to differentiate the restored parts from the original with simple non-destructive analytical tools such as portable X-ray fluorescence (pXRF). To reconcile the traditional approach of gilding with the specifics of modern conservation ethics, the constraints are to preserve the know-how and obtain optimal aesthetic effects similar to traditional techniques. In order to gain professional knowledge regarding the production of gilding leaf, a partnership was established with Dauvet¹, the last goldbeating company in France (Dauvet Society 2016). The professional conservators who are specialised in gilded-wood at C2RMF² performed gilding tests to validate the implementation.

Two different metals were chosen as chemical markers: indium and palladium. The present paper describes the approach adopted such as choice of the markers, analysis and composition of the new alloys, manufacture and properties of gilding leaf, and validation of the success of differentiating the new gilding leaf from the original substrate through instrumental analysis.

Selection of markers for the new alloys

As a starting reference, we chose our partner Dauvet's most popular alloy, *or supérieur* (Superior Gold). It is a 23.52 karat gold (980 thousandth) containing small additions of silver and copper (1 wt percent each) to improve its mechanical properties. The new alloys proposed for conservation need to:

- Present optical, mechanical and physical properties similar to the traditional leaf in terms of colour, thickness and application.
- Contain marker(s) easily detectable by current analytical tools such as portable XRF, with no interference from elements present in the equipment such as the X-ray tube, shutter and filters.
- Contain chemical marker(s) that did not exist in similar proportions in ancient gilding alloys or in the underlying preparation layers.
- Be soluble in solid gold in high enough concentrations without affecting mechanical properties of the alloy and interfering with cold rolling and beating; a very delicate operation from the metallurgical viewpoint (Darque-Ceretti 2012, Felder 2010).
- Be commercially available at a reasonable cost and be non-toxic once alloyed.

After a rigorous selection process two elemental markers fulfilling these criteria were chosen: indium and palladium. These white metals were both intended to replace silver in the alloy. They were to be added at a concentration low enough in theory not to significantly change the colour and remain in solid solution (ASM Alloy Phase Diagrams Database 2006).

It needs to be emphasized that palladium may exist either as a natural or as an intentional alloying element in gold alloys, but its concentration is much higher (5-10 wt percent palladium) in goldsmith recipes or much lower (0.1 wt percent) for the known "Brazilian gold" (Guerra 2004) than the amount used here.

Gold leaf manufacture for the new alloys

Small ingots of each alloy were smelted in the C2RMF laboratory furnace at a temperature high enough and an annealing time long enough to ensure complete melting and mixing of all components. Optimal annealing conditions such as a reducing environment and cooling rate were utilized to obtain proper surface and mechanical behaviour for leaf manufacture. Indium is a surfactant known to favour surface segregation in alloys that contain it (Dowben 1987); the annealing conditions were adapted to avoid this effect.

Analyses was done by SEM-EDS³, by PIXE on the C2RMF Accelérateur Grand Louvre d'Analyse Elementaire (AGLAE)⁴ (Calligaro 2004) and by pXRF⁵ to assess the homogeneity of the alloys produced. Mechanical properties were controlled by micro-hardness measurements. The results of these tests were recorded to optimise the smelting and annealing conditions to be used by the goldbeater Dauvet for leaf production.

The manufacturing procedure is summarised in Figure 2 and described in detail in other publications (Darque-Ceretti 2012, Felder 2010).

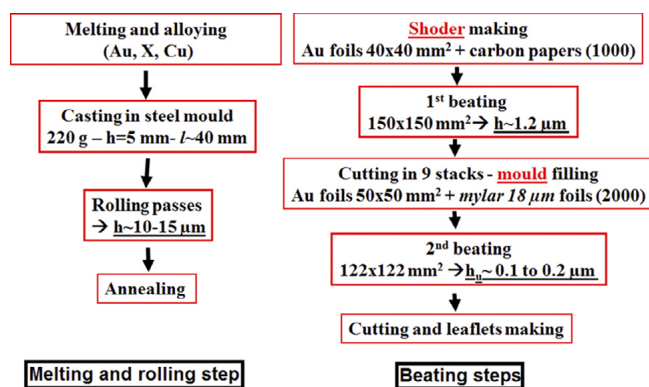


Figure 2. The successive steps of the gold leaf manufacturing process. © C2RMF

Samples were taken at each stage in manufacture to check the composition and microstructure of the alloy foil (more than 10 µm thick) or the leaf (1 µm thick or less). The final gold leaf thickness was between 0.1 and 0.3 µm.

Control of mechanical properties, thickness and composition of alloys and leaf

It was observed that even for a low content (< 1 wt percent), indium significantly increases the yield strength of the gold alloy. A new annealing procedure was devised to overcome this problem. Table 1 shows the results of Vickers

micro-hardness measurements on a gold-copper-indium-silver alloy used for the preliminary test, showing the beneficial effect of the adapted annealing conditions.

Table 1. Influence of the annealing conditions on Vickers hardness and yield strength of an Au-Cu-In alloy

Alloy	Annealing	Hardness HV	Yield strength (MPa)
Au-Cu-Ag commercial (Dauvet)	usual	79	227
Au-Cu-Ag-In preliminary test alloy	usual	84.6	240
Au-Cu-In test alloy	modified	67	221

The new manufacturing process was performed by the goldbeater Dauvet in the light of the analytical results. Several hundred leaves were thus obtained and again tested at C2RMF.

To measure the thickness of the final leaves, Rutherford Backscattering spectrometry (RBS) was used under bombardment by protons of 3 MeV energy on the C2RMF particle accelerator AGLAE (Calligaro 2004). This method allows for non-destructive in-depth analysis from the surface and an estimation of the leaf thickness. In this experiment, a glass substrate was coated with gold leaves. Figure 3 shows an example of RBS spectra taken from a gold-copper-indium leaf. A simulation of the RBS spectra led to an estimation of the gold leaf thickness, found to be of $0.1 \pm 0.02 \mu\text{m}$ for both gold-copper-indium and gold-copper-palladium alloys.

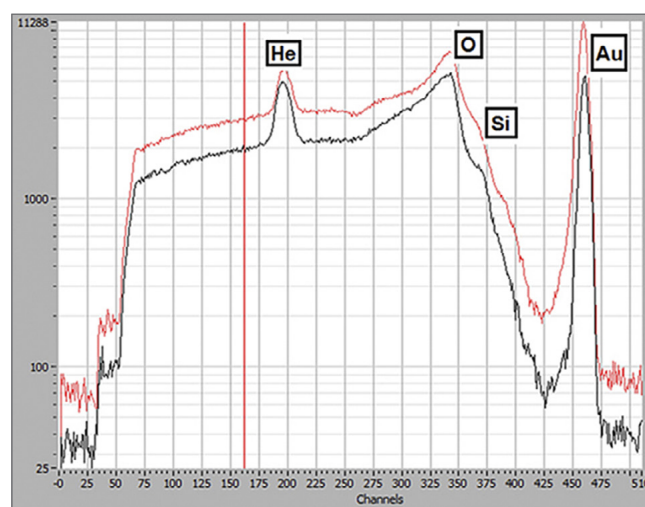


Figure 3. RBS spectra (two different areas, 3 MeV protons) of an Au-Cu-In on glass coated with the new alloy leaf. The channel number is representative of the backscattered proton energy (channel 512 = 3 MeV). © C2RMF

PIXE analyses was performed on a glass substrate coated with the gold leaf. Figure 4 presents examples of PIXE spectra obtained under 3 MeV protons for both alloys.

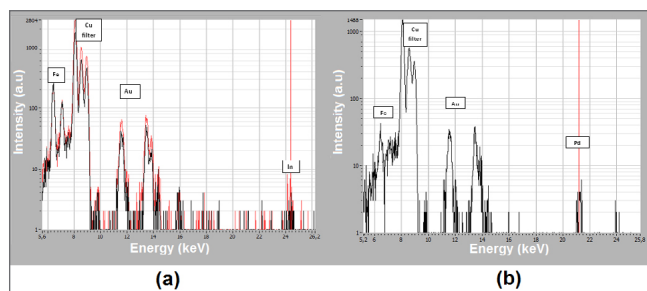


Figure 4. PIXE spectra (3 MeV protons, 25 μm Cu filter) on glass coated with the final new leaf; (a) Au-Cu-In and (b) Au-Cu-Pd alloys. © C2RMF

Gilding tests with the new alloys

After completing the analytical tests, C2RMF gilders tested the mechanical properties of the new gold leaf compared to traditional gold leaf. In the first test, wood was chosen as substrate and covered with a primer made of calcium carbonate (CaCO_3) in proteinaceous rabbit skin glue, followed by a yellow ochre layer and finally red bole. Alloys containing indium and palladium were tested on the prepared wood specimens (Figure 5). The mechanical properties proved satisfactory and the gilders did not discern a noticeable difference when comparing the application of the new leaf with the traditional gilding leaf.

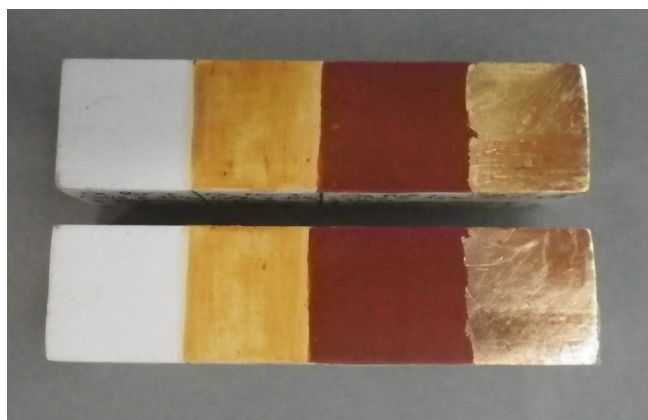


Figure 5. Wood specimens successively covered (from left to right) with the calcium carbonate primer, the yellow size, the red bole and the two new types of gold leaf (top: Au-Cu-In, bottom: Au-Cu-Pd). © C2RMF

At this stage it was important to check the detectability of the markers on the specimens. This was done by PIXE and portable XRF. Quantitative analysis is difficult to interpret in such multi-layered material and was not the goal. Instead, the priority was to detect the trace elements in the elemental spectra. Indeed, all the elements present in the wood and in the preparation layers appear in the spectra, and the challenge is to detect the very small quantity of indium or palladium contained in the leaf.

Figure 6 presents the spectra obtained by PIXE in high-energy range for gold-copper-indium and gold-copper-palladium leaf applied on the specimens.

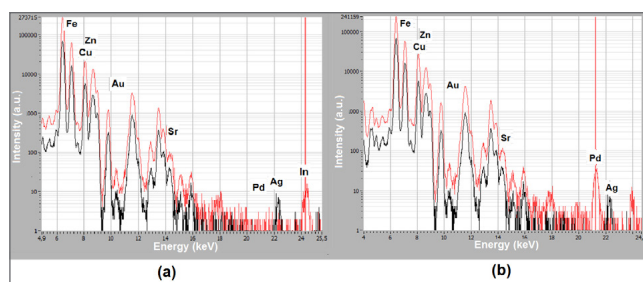


Figure 6. PIXE spectra in high energy range for the traditional Au-Cu-Ag (in black) and (in red) for (a) Au-Cu-In and (b) Au-Cu-Pd leaf applied to the specimens. © C2RMF

For PIXE analysis, the best results were obtained in high-energy range with a 25 μm copper filter. For XRF analysis, the best results were obtained in the low energy range. On high energy, the Compton Effect makes the identification difficult.

These spectra also show the presence of elements not belonging to the gilding, such as iron, zinc and strontium. These elements are clearly contained in the underlying layers: strontium is associated with the calcium of natural calcium carbonate primer, iron belongs to yellow ochre and red bole, and zinc may be contained in the wood but also in the sizing.

Discussion and perspectives

These analyses show that the new alloys were successfully executed. Colour and leaf manufacturing adaptability were satisfactory enough for use in gilding restoration. This study also provides important information on adapting the beating procedure in order to obtain good quality leaf. The results have been validated for wood gilding, which presents a very difficult case study. In fact, the various elements contained in the underlying layers do not help in understanding the analysis in some cases. For other substrates such as glass, enamel and metal, the detection is much more straightforward. Figure 7 shows an example of gilded-copper with traditional gold alloy (in black) and gold-indium alloy (in red). Similar results were obtained with the gold-palladium alloy in terms of detectability, although a small hue variation was observed compared to the traditional gold alloy.

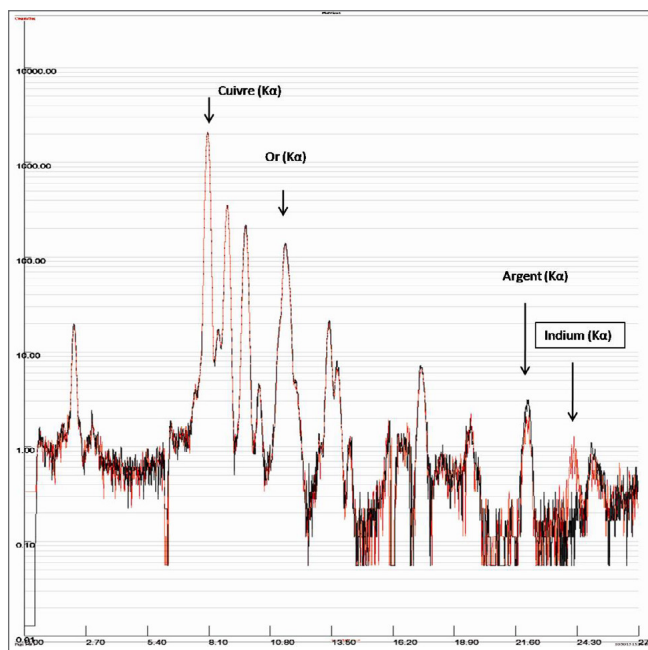


Figure 7. XRF spectra in high energy range of a gilded-copper specimen, coated with a traditional Au-Cu-Ag alloy (in black) and Au-Cu-In alloy (in red). © C2RMF

In order to overcome this potential difficulty, we have extended this traceable principle to the primer used for wood gilding. Some preliminary experiments have already been done by introducing small quantities of chemically pure titanium dioxide (TiO_2 , titanium white) in the calcium carbonate (CaCO_3) powder. This ingredient is never present in ancient primers. Wood specimens with this primer have been prepared by conservators (Figure 8). One half was gilded with a traditional gold alloy and the other with gold-copper-indium alloy.

In the XRF spectra (Figure 9) we can easily detect the titanium present in the substrate and the indium in the gold alloy.



Figure 8. Specimen with the primer marked with TiO_2 and gilded half with traditional gold (left) and half with Au-Cu-In leaf (right). © C2RMF

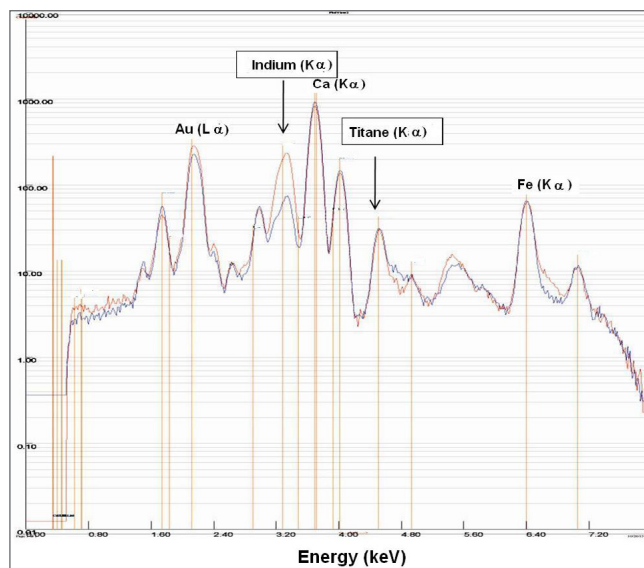


Figure 9. XRF spectra in low energy range for the traditional Au-Cu-Ag (in blue) and for Au-Cu-In (in red) leaf applied to the specimens using the primer marked with TiO_2 . © C2RMF

This complementary option gave good results and could be useful for difficult situations such as wood that contains small amounts of potassium. These issues will be studied in detail in a forthcoming publication.

Conclusion

Modern conservation ethics requires that materials and products used for restoration and conservation should be reversible, identifiable and traceable. This study initiated by C2RMF offers an alternative to the traditional practice of gilding restoration by proposing new gold leaf that contains chemical markers. Two gold alloys containing indium or palladium were successfully created by C2RMF and the goldbeater Dauvet, through an adapted process for leaf manufacturing, leading to conclusive tests and analyses. Gold leaf with these markers was applied on wood specimens by traditional methods and successfully analyzed to assess their detectability. Leaf production has already begun and products are available from the Dauvet society under the name “Patrimoine” (Dauvet 2016).

In an effort to improve the precise identification of conservation materials, the primer has also been marked so that its composition can form another detectable restoration criterion.

The issue of other substrates is currently explored to ensure the detectability of indium and palladium on various materials such as metal, enamel, ceramic, stone, etc. The success of the first stage of the project also encourages its extension to gold powder and other

precious metals such as silver, with promising experiments in progress.

It is essential to emphasize that these new materials have not been designed to promote widely re-gilded areas in conservation projects, but to offer an alternative when the application of new gold leaf is required. In cases where substitutes such as mica or watercolours are unsatisfactory, these new tools enable gold leaf to become a suitable material for conservation purposes.

Notes

1 The fabrication of the gold leaf was done in collaboration with the French goldbeater society Dauvet. The fruitful and efficient contributions of Antonin Beurrier, Director, Bernard Dauvet, former Director, Hugues de Lisle, Managing Director and Nadine Hacqueberge, smelter, are gratefully acknowledged.

2 All the gilding on chosen substrates was done by C2RMF conservator gilders Marie-Jeanne Dubois, Roland Février, Stéphanie Courtier and Loïc Lousouarn.

3 SEM analyses of Au-Cu-In were done in the CEMEF laboratory (CNRS UMR 7635), MINES Paristech, PSL – Research University, Sophia-Antipolis, France, by Evelyne Darque-Ceretti.

4 Ion beam analysis on AGLAE accelerator at C2RMF was conducted by the team of Claire Pacheco, Laurent Pichon, Quentin Lemasson and Brice Moignard.

5 XRF analyses were done at C2RMF by Dominique Robcis and Marc Aucouturier with a Niton XL3t 900 equipment, with a Ag Ka X-ray tube and a commercial software.

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Authors

Dominique Robcis is a conservator at C2RMF, Conservation Department. He is in charge of archaeological and ethnological metal restoration, portable XRF and 3D microscopy. He has developed studies on metal surface treatments (intentional patinas and gilding) since 2002.

Caroline Thomas is a curator at C2RMF, Conservation Department. She works in the decorative arts section with in-house and freelance conservators on woodwork, gilding, metal, textile and ceramics. She acts as an adviser for museums in conservation-restoration.

Marc Aucouturier is a metallurgist, formerly in CNRS (French national research centre) Directeur de Recherche (senior scientist). He is presently research advisor to C2RMF, concerning metal intentional patinas, surface analysis and gilding.