Medieval nanotechnology – FIB/SEM analysis of metal embroidery threads

K. Gherdán[1], T.G. Weiszburg[1], M. Járó[2], G. Varga[1], Gy. Szakmány[1]

with contribution of N. Zajzon[3], K. Ratter[1] , Zs. Bendő[1]

e-mail: gherdankata@hotmail.com ; 1. Eötvös L. University, H-1117, Budapest, Pázmány Péter sétány 1/C; 2. Hungarian National Museum, H-1088, Budapest, Múzeum körút 14–16; 3. University of Miskolc, H-3515, Miskolc, Egyetemváros

1 MEDIEVAL NANOTECHNOLOGY?!

When hearing the word *nanotechnology* one usually thinks of very recent if not futuristic things. However, there are much earlier applications: Theophilus at the turn of the 11th-12th centuries published recipes of metal gilding [1] which suggest the very early creation of nanoscale structures (for details see insert 7).
However, these early nanofilms could not be studied without the 21st century nanotechniques.

Drawing wire in the beginning of the 17th century [2].

16th century goldbeaters at work on a duplex plate of gold and silver [3].

3 CHALLENGES

Is it possible to identify Medieval nanotechnology?
Is it possible to reconstruct gilding techniques?

Trying to do so the following questions should be answered:

- What is the nanoscale texture of the threads like?
- What is the thickness of the surface gold layer?
- How does chemical composition change through the layers: is there an enrichment of any component (e.g. Cu, Hg) referring to the gilding technique?

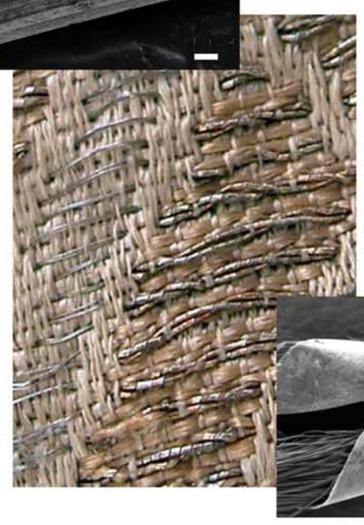
2 "ALL THAT GLISTERS IS NOT GOLD": MATERIALS

Metal threads are fine textile decorations, which have been used in embroideries and woven fabrics as well, for thousands of years.

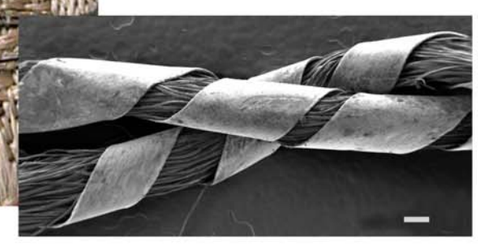
Silver wire.
Typical wire diameter 70 – 500 μm
(SE image, bar: 10 μm).

The **pure gold** and gold alloy threads of the Bible [5] were partly replaced by **gilt silver** etc. threads from the 13th century.

On that poster a metal thread from a **16th century woman's dress,** excavated in Sopron, Hungary is used for demonstration. (Silver strip gilt on one side; width: ~650 μm, thickness: ~20 μm).

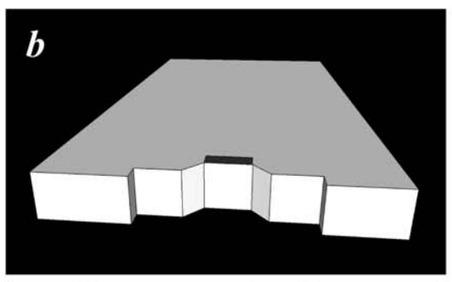


Gilt silver strip wound around a fibrous core. Typical strip width 150 – 1500 μm and strip thickness 7 – 40 μm (SE image, bar: 100 μm).

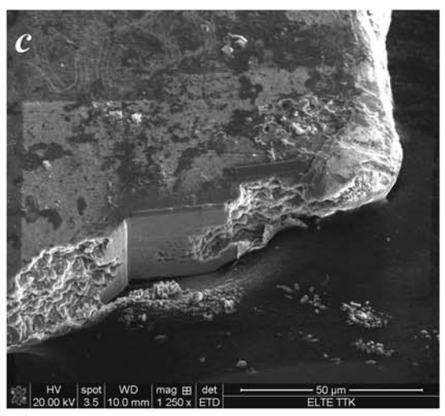


4 METHODS

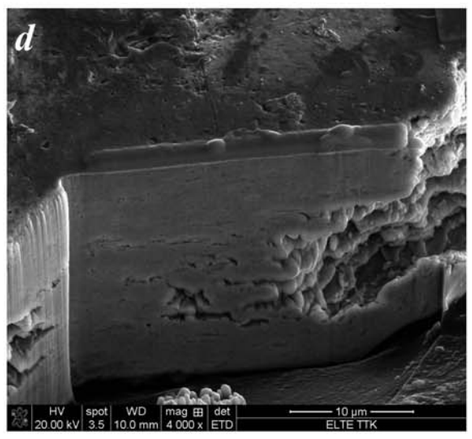
The threads were mounted on tilted (45) **sample holders**.
(Image of the FIB/SEM sample chamber with the tilted sample holder inside.)



Focused ion beam (FIB) milling was used to make cross sections of threads perpendicular to the direction of elongation. Note the special trapezoid geometry.
(The black bar represents deposited platinum.)

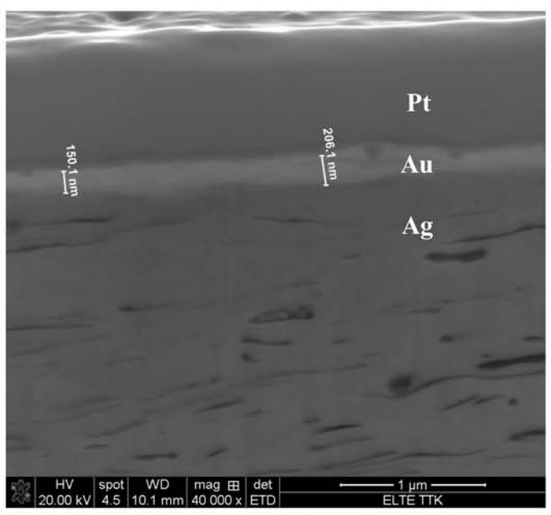


General view of FIB milled cross section on a broken edge of the sample (SE image).

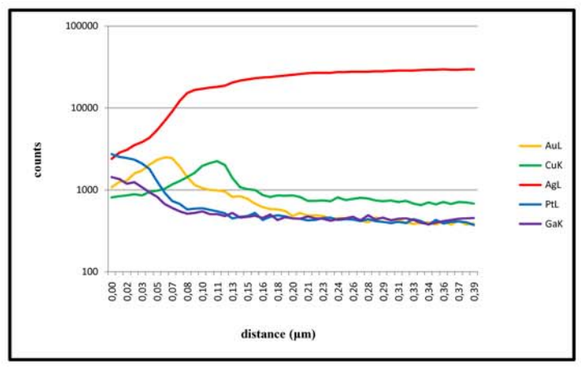


Close view of the **special trapezoid geometry** prepared for further **EDX, WDX** analysis (SE image).

5 RESULTS

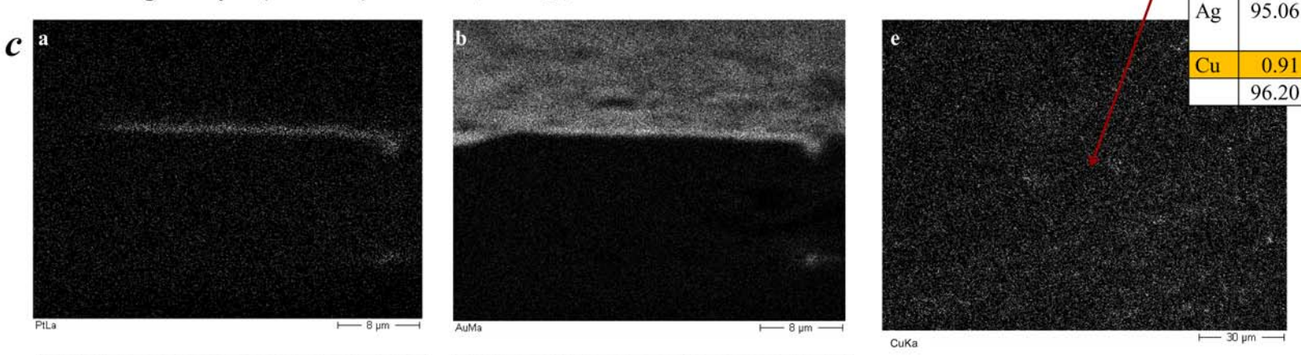


The perfect fitting between deposited platinum and gold made it possible to measure the **thickness of the surface gold layer** (<255 nm) on silver (SE image).



Copper enrichment at the gold/silver interface as a 50 – 100 nm thick layer.
(EDX line-scan through the layers.)

3	wt%	at%
Hg	0.13	0.07
Au	0.10	0.06
Ag	95.06	98.27
Cu	0.91	1.6
	96.20	



No copper enrichment on the non-gilt (back) side of the strip and the bottom of the cross section. (WDX mapping, back side of the strip (e).)

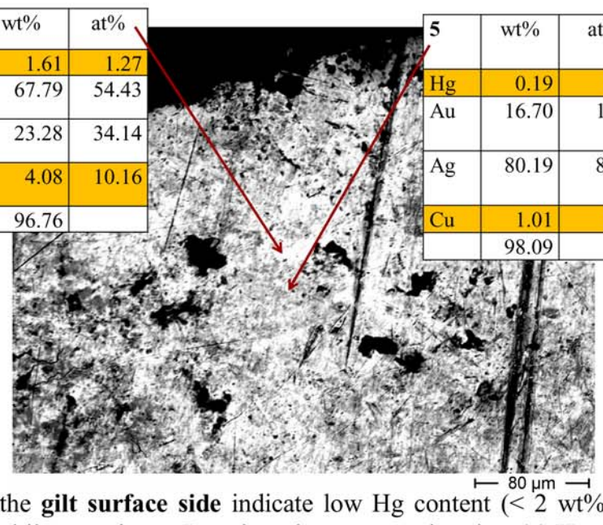
1	wt%	at%
Hg	0	0
Au	0	0
Ag	94.48	96.29
Cu	2.14	3.71
	96.62	

2	wt%	at%
Hg	0	0
Au	0	0
Ag	94.16	98.43
Cu	0.88	1.57
	95.1	

Starting from the gold layer on the cross section **copper is enriched** in a wider zone (~10 μm).
Neither gold nor mercury was found below the surface gold layer. That means not the technique described by Biringuccio [3] (for details see insert 7), respectively no fire gilding [4] was used while manufacturing the strip.
(WDX and EDX mapping of the FIB-milled cross sections (a-d).)

d

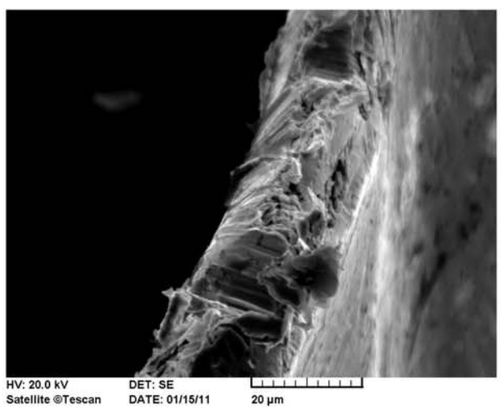
4	wt%	at%
Hg	1.61	1.27
Au	67.79	54.43
Ag	23.28	34.14
Cu	4.08	10.16
	96.76	



5	wt%	at%
Hg	0.19	0.11
Au	16.70	10.03
Ag	80.19	87.97
Cu	1.01	1.89
	98.09	

Data from the **gilt surface side** indicate low Hg content (< 2 wt%) in the analysed multilayer volume. Based on the cross section data (c) Hg connects only to the gold layer [4] (Results of comparative WDX analysis of the surface with thicker (4) and thinner (5) gold layers. BSE image of the gilt surface).

e



The **morphology of the edge** of the strip reflects the use of scissors for cutting the foil into strips (SE image).

6 DISCUSSION/CONCLUSIONS

a In case of the sample used for demonstration here results showed that a copper-based soldering material [1] was used to attach gold on the silver substrate (*5c*). Then the metal sandwich was most probably hammered *(see patterns on the gilt surface (5d) and fine texture of the cross section (5a))* and annealed when necessary. The gilt foil prepared this way was then cut into strips (*5e*). Fire gilding could be excluded.

b With focused ion beam (FIB) milling it was possible, for the first time, to reveal the layer structure of historical metal threads.
Combining FIB cross sectioning with SEM+EDX and EPMA made the direct observation of geometrical and chemical data possible, which proved to be much more efficient than surface analysis in distinguishing between the different gilding methods.

7 HISTORICAL DESCRIPTIONS

Engraving from c. 1450 showing the goldsmith's workshop.

The **first written** record of metal threads comes from the ***Bible*** [5].
Pliny in his ***Natural History*** [6] writes about the use of gold leaf, an extremely thin gold foil, which could be applied by burnishing the leaves on the silver surface and then heating on a flame for a few seconds, causing diffusion bonding.

Theophilus [1] published recipes of gilding by using a **copper-rich soldering** material. Another widely used gilding method was (and still is) **fire gilding** that was described for example by **Biringuccio [3]**. He describes also *"The method of preparing gold for spinning":* where after laying silver and gold together they should be soldered on a little furnace of charcoal, and then *"the bar is hammered on a flat anvil and elongated. It is doubled over in several folds, turning the gold sides against each other."*

REFERENCES:

[1] Theophilus, On Divers Arts, c. 1125; [2] Die Hausbücher, Landauer ***I***, 1635; [3] V. Biringuccio, The Pirotechnia, 1540; [4] K. Anhauser, JOM (1997); [5] Old Testament, Exodus, 39:2-3; [6] Pliny, Natural History 77 – 79 AD

ACKNOWLEDGEMENTS: The European Union and the European Social Fund have provided financial support to the project under the grant agreement no. TÁMOP 4.2.1./B-09/KMR-2010-0003.