

January 2005

News and Views

Materials witness: Old masters

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doi: 10.1038/nmat1304

Once again ancient technology has provided inspiration to the modern materials scientist. Jonah Erlebacher and his coworkers at Johns Hopkins University have prepared nanoporous gold films, with potential applications in membrane technology and catalysis, by adapting the ancient technique of depletion gilding, used both in the Incan civilization and in medieval Europe (*Adv. Mat.* **16**, 1897; 2004).

The goal of the historical artisans was to give a gold-copper or gold-silver alloy the surface appearance of pure gold, cutting costs without any apparent reduction in product quality. Typically this was achieved by acid etching of the alloy to remove the less precious (and less inert) metal from the surface layer, followed by burnishing (polishing with a smooth stone) to consolidate the spongy gold film that resulted.

In Europe, nitric acid, discovered by Arabic alchemists, was the usual etchant. The etching process is complex and dynamic, involving more than the mere excavation of microscopic silver or copper islands in the alloy. As these metals are removed, the gold atoms diffuse to form a continuous, porous nanostructure, exposing ever deeper portions of the material. So the pore size changes over time, rather than being defined by the microstructure of the initial alloy.

Erlebacher and colleagues have found that commercial 12-carat white-gold leaf, with a 1:1 ratio of gold to silver, can be treated in this way to make porous gold films 100 nm thick, with an average pore width that increases gradually the longer the film is immersed in nitric acid – from about 8 nm for etching times of a few minutes to around 50 nm after several days of acid treatment.

What is truly humbling here is that the metallurgy involves nothing more, in terms of materials or techniques, than was known to pre-Columbian Central Americans and to medieval monks. The invitation is then to marvel at what, without any fundamental scientific understanding, these technologists were able to achieve. But it is all too easy to make both more and less of this than is warranted.

It is tempting but ahistorical, for example, to couch such discussions in modern terms, so that medieval blacksmiths become engaged in defect engineering, or (mea culpa) Renaissance potters who created glazes of finely divided metals become nanotechnologists (see Pérez-Arantequi *et al.*, *J. Am. Ceram. Soc.* **84**, 442; 2001). On the other hand, some purists insist that, because of the lack of a conceptual basis, there is no connection between these manipulations of matter and true ‘science’.

The fact is that historical technologies, while almost always ungrounded in valid theory, could be extremely inventive, precisely formulated and exhaustively tested (in the marketplace). Materials scientist Ian Freestone has said of the writings of the twelfth-century monk Theophilus on stained glass that “the most remarkable aspect... is just how frequently and in what detail they prove accurate.” And theory isn’t everything. Nineteenth-century French scientists knew a lot more chemistry than Chinese potters of the Song dynasty (960-1279), but they were unable to reproduce the ancient artisans’ marvellous opalescent blue-white glazes.