MATERIALS

Carbon nanotubes in an ancient Damascus sabre

The steel of Damascus blades, which were first encountered by the Crusaders when fighting against Muslims, had features not found in European steels — a characteristic wavy banding pattern known as damask, extraordinary mechanical properties, and an exceptionally sharp cutting edge. Here we use high-resolution transmission electron microscopy to examine a sample of Damascus sabre steel from the seventeenth century and find that it contains carbon nanotubes as well as cementite nanowires. This microstructure may offer insight into the beautiful banding pattern of the ultrahigh-carbon steel created from an ancient recipe that was lost long ago.

It is believed that Damascus blades were forged directly from small cakes of steel (named '*wootz*') produced in ancient India. A sophisticated thermomechanical treatment of forging and annealing was applied to these cakes to refine the steel to its exceptional quality. However, European bladesmiths were unable to replicate the process, and its secret was lost at about the end of the eighteenth century. It was unclear how medieval blacksmiths would have overcome the inherent brittleness of the plates of cementite (Fe_3C, a mineral known as cohenite) that form in steel with a carbon content of 1–2 wt%, as well as how the steel's characteristic banding could have arisen from these plates.

Mechanical processing at the appropriate temperature can cause the steel's microstructure to become fine-grained, and superplastic behaviour is induced at higher temperatures[1]. Small additions of the elements vanadium, chromium, manganese, cobalt, nickel and others are known to facilitate the formation of cementite bands during thermal cycling at temperatures below the cementite formation temperature[2] (about 800 °C). Moreover, the Damascene steel contains rare-earth elements and shows evidence of cementite nanowires in its microstructure[3–5].

Using high-resolution transmission electron microscopy, we have now also detected carbon nanotubes in a specimen taken from a genuine Damascus sabre (sabre no.10 (ref. 6); sample kindly provided by E. J. Kläy of Berne Historical Museum, Switzerland) produced by the famous blacksmith Assad Ullah in the seventeenth century. Its microstructure has been investigated previously[4], but the nanotubes only become apparent (Fig. 1) after dissolution of the sample in hydrochloric acid (for methods, see supplementary information). Some remnants (Fig. 1c) show evidence of incompletely dissolved cementite nanowires[3], indicating that these wires could have been encapsulated and protected by the carbon nanotubes[7].

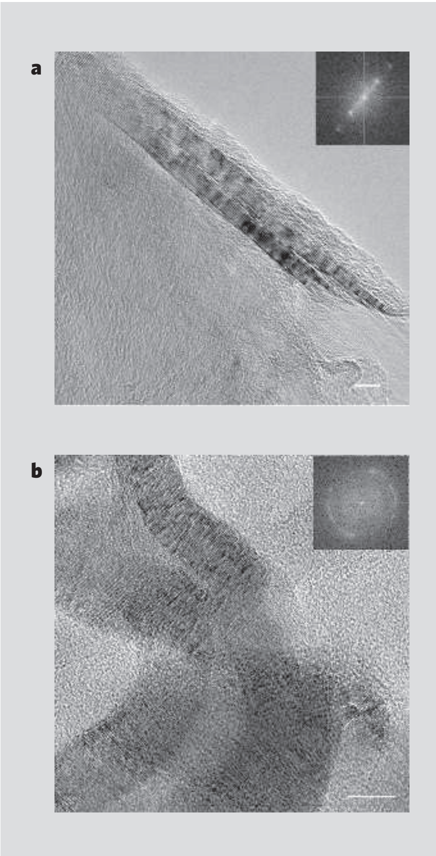

Figure 1 | High-resolution transmission electron microscopy images of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid. **a**, **b**, Multiwalled tubes with the characteristic layer distance $d \approx 0.34$ nm (ref. 12), as indicated by the Fourier transforms (see insets). Scale bars: 5 nm (**a**) and 10 nm (**b**). In **b**, the tubes are bent like a rope. **c**, Remnants of cementite nanowires encapsulated by carbon nanotubes, which prevent the wires from dissolving in acid. Scale bar, 5 nm. The fringe spacing of the wire is 0.635 nm, taken from the Fourier transform (inset), and is attributed to the (010) lattice planes of cementite.

Nanotubes can be formed catalytically[8], as well as from hydrocarbons inside micropores at reduced temperatures[9]. We suggest therefore that our finding could link the distinctive banding seen in Damascus blades with 'impurities' contained in the steel[2,4]. By empirically optimizing their blade-treatment procedure, craftsmen ended up making nanotubes more than 400 years ago.

According to an early report on Indian *wootz* production[10], particular ingredients were mandatory — such as wood from *Cassia auriculata* and leaves of *Calotropis gigantea*, and ores taken from particular mines in India. The diminishing supply of some of these ores during the eighteenth century may have prevented bladesmiths, who would not have been aware of the importance of these alloying elements, from practising their ancient recipes.

Thermal cycling and cyclic forging cause catalytic elements to segregate gradually into planar arrays parallel to the forging plane[11]. These elements may give rise to the growth of carbon nanotubes, which in turn initiate formation of cementite nanowires and coarse cementite particles. As the nanoscale structure of Damascus steel emerges, a refined interpretation of its remarkable mechanical properties should become possible.

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