Discovery of Nanotubes in Ancient Damascus Steel

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Abstract. Using high-resolution electron microscopy, we have found in a sample of Damascus sabres from the 17[th] century both cementite nanowires and carbon nanotubes. These might be the missing link between the banding and ancient recipes to make that ultrahigh carbon steel. The sample considered belonged to the wootz-type of Damascus steel which is fundamentally different from welded Damast. The nanotubes have only been revealed after dissolution of the sample in hydrochloric acid. Some remnants showed not yet completely dissolved cementite nanowires, suggesting that these wires were encapsulated by carbon nanotubes. Only recently, considerable progress has been achieved in reproducing the process of making the characteristic pattern of wootz. We propose a connection between impurity segregation, nanotube formation, nanotube filling with cementite, cementite wire growth, and formation of large cementite particles. Needless to say that the presence of a nanostructure will have an impact upon the mechanical properties.

1. Introduction

Damascus blades featured two qualities not found in European steels at that time: an attractive wavy-like banding, known today as Damast, an extremely sharp edge (according to the legend a sword could slice through a silk handkerchief floating in the air) (cf., e.g., [1-4]). When talking about the damast pattern three kinds of technologies have to be distinguished carefully: (i) false damast, (ii) artificial or welded, (iii) genuine or wootz-based. False damast (i) is made by a treatment of the surface region of a steel blade only (for example by etching or scratching). It can easily be identified when looking at the cross section. Type (ii) is obtained when thin steel blades of different carbon content are welded by repeated forging and folding. This technology is widespread giving rise to spectacular patterns, the formation of which depends mainly on the flow of material during forging. In this sense it may be called artificial. In what follows we will restrict ourselves on the type (iii), whose Damast pattern appears after forging a cake-like piece of ultra-high carbon crucible steel. The formation of the pattern depends on the formation of cementite (Fe_3C) particles of a certain size, shape and spatial distribution. It is just this process of formation, obviously representing a complex combination of plastic deformation, diffusion and phase transitions, that still needs further exploration.

How was genuine Damascus steel done ? It is generally agreed that those ingots of crucible steel were made in ancient India (‘wootz’) and Central Asia (‘bulad’), then sold to the Near East and to Europe for forging. Details of the blade production were kept secret. At the end of the 18th century the ability to produce this type of steel got_lost. Numerous attempts have been made since that time to reproduce this quality. Thanks modern methods of analysis, progress has been achieved on a trial-and- error basis [5–6]. The processes behind pattern formation at nanoscale, however, are still subject of controversy.

2. Experimental Methods

Our analytical methods have been applied to samples of genuine Damascus sabres. We were lucky to get them from the Berne Historical Museum. There are a few earlier reports dealing with samples of the identical sabres [7–10]. They are documented as product of the famous blacksmith Assad Ullah (17th Century) [7, 11].

We have collected data for phase analysis using optical microscopy, high resolution transmission electron microscopy (HRTEM; Philips CM200FEG) and X-ray diffraction. Furthermore, elemental analysis with the aid of optical spectrometry and electron beam microanalysis as well as nanohardness measurements have been performed. For details of our methods and the results we refer to [12–16]. Though several metallographic studies of this material have been published by other authors, no HRTEM has been applied to historic specimens.

3. Results and Discussion

Focussing on the results of HRTEM, apart from the presence of microscopic particles of cementite already known from the early works of [17], a pronounced structuring of the material at nanoscale has been observed. One component of this

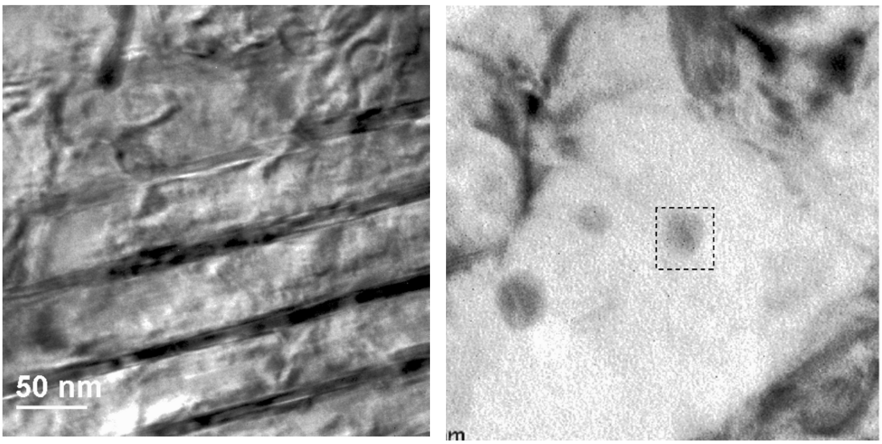

Fig. 1. TEM image of cementite nanowires in a Damascus sabre. Left panel: The dark stripes indicate wires of several hundreds nanometers in length. Right panel: View showing an almost circular cross section (dotted)

is the appearance of wire-like objects of cementite structure (Figs. 1–4). They are locally ordered in colonies of parallel wires, changing orientation in neighboured regions. Their spacing is of the order of 100nm. From earlier work on conventional steels cementite plates or laths have become known already, however, on a much larger microscopic scale. The spacing of lattice planes in high-resolution mode has been used to identify the structure (see, e.g., Fig. 2).

The mechanical effect of wire-like obstacles may be anticipated from Fig. 4, where dislocations are tangled between them.

To check a previous proposal made by Kochmann (cf. [13]) presuming carbon nanotubes in this Damascus steel, a small remnant (ca. 2 × 3 × 4 mm) of the sample, also investigated by [12–14], was dissolved completely in HCl (20%) for one week in a glass evaporating dish. Unlike iron and iron carbide, carbon should

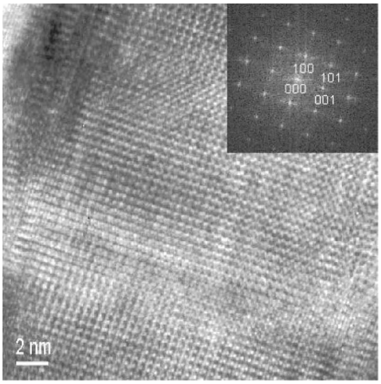

Fig. 2. Nanowire of Fig. 1 in high-resolution mode Inset : Fourier transform. Reflections (d = 0.4434 nm 0.3342 nm and 0.4900 nm) are indexed as Fe_3C 001, 101 and 100, respectively

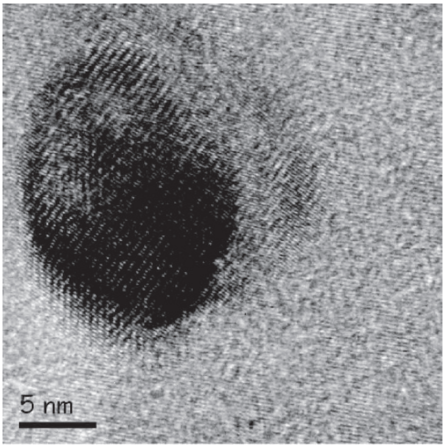

Fig. 3. Same as Fig. 2 for cross section of a cementite nanowire piercing the image plane

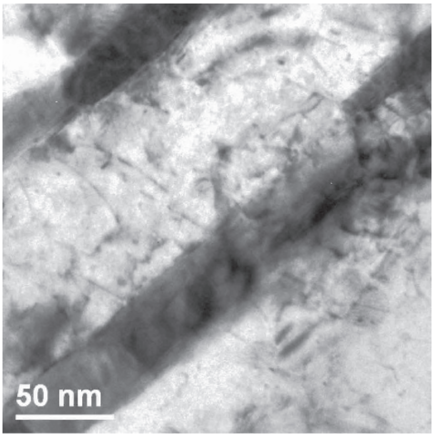

Fig. 4. Dislocation lines tangled at nanowires in a sample prior to annealing. Two samples are marked by arrows. No. 1 shows a straight section between the wires and No. 2 is bent around a wire

be retained. With the aid of a copper grid covered by an amorphous carbon layer the remnants were picked up from the acid and investigated by HRTEM (Figs. 5–7). This experiment has been repeated about one year later dissolving a second sample. Cylindrical remnants found this way were of two types: (i) straight (Fig. 5) and bent (Fig. 6) homogeneous particles and (ii) embedded particles (Fig. 7). Determination of the lattice spacings and consideration of the chemical processing let us conclude that the particles found are carbon nanotubes occasionally filled with cementite. This mode of nanostructuring is also suggested looking at Fig. 8, which was obtained from our most recent sample not yet dissolved in HCl. The formation of carbon nanotubes and nanowires in steel

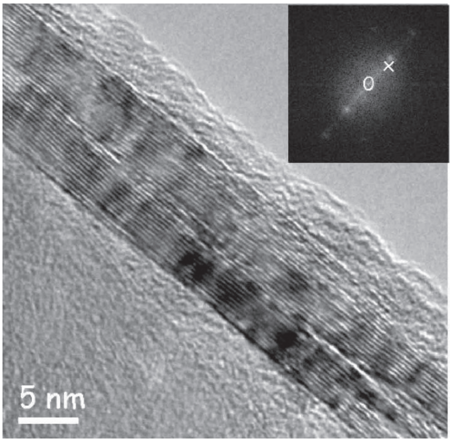

Fig. 5. Straight homogeneous remnant with a fringe spacing of 0.342 nm, which is characteristic of carbon nanotubes, in this case multiwalled

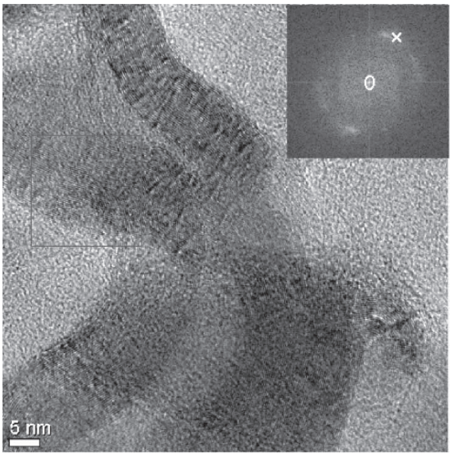

Fig. 6. Bent homogeneous remnants with a fringe spacing of 0.349 nm, which is characteristic of carbon nanotubes

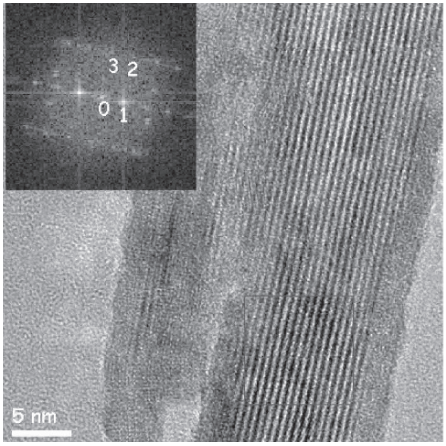

Fig. 7. Embedded remnant with a fringe spacing of 0.63 nm, which is characteristic of cementite. It is embedded in an almost structureless surrounding, which prevented dissolution

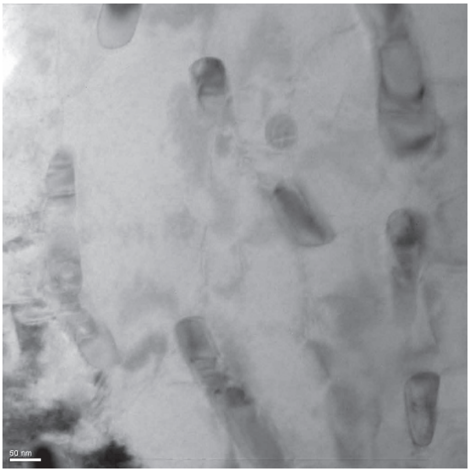

Fig. 8. Wire-like particles consisting of an outer wall partly filled with a dense material. TEM image of a preliminary study of sabre No. 9 (according to Zschokke [7]) showing similar nanostructuring like sabre No. 10

during a thermomechanical treatment has not yet been observed. Taking ancient recipes of wootz-technology into account, we have speculated that organic additions with the aid of metallic catalysts might have given rise to this carbon nanotube formation [15, 19]. Recent results of wood research (group of Barry Goodell) seem to support this route[18].

4. Conclusions

The nanostructure of an ancient steel sample opens a new view upon the formation of the Damast pattern. The formation of carbon nanotubes could be a missing link between the role of impurities and the existence of cementite particles. Moreover, the effect on the special mechanical properties of Damascus steel deserves further investigation.

Acknowledgements

Authors thank the Historical Museum Berne for supply of the samples and Ms. Heide Müller for help with the TEM-preparation.

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