

Letter

Nanowires in ancient Damascus steel

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Received 29 September 2003; accepted 10 October 2003

Abstract

The long-lasting search for the recipes of making the legendary Damascus swords may become a new direction by our finding that a genuine Damascus sabre contains a high density of cementite nanowires, which interact with dislocations and which might have influenced the nucleation of perlite. The nanohardness as measured separately for cementite and perlite indicated striking differences in the inelastic behaviour of those phases.

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Keywords: Interstitial alloys, Fullerenes; TEM, Transmission electron microscopy, X-ray diffraction

1. Introduction

Swords made from Damascus steels have become renowned because of (i) the uncontested retention of their cutting edge, (ii) the beauty of their characteristic surface patterns and (iii) fascinating legends concerning the way these materials were manufactured [1–7]. They were made from cakes originating in India (called ‘wootz’), the exact composition of which and the subsequent processing were crucial for the success and dealt with as top-secret. The recipe of blades of that type has been rediscovered several times, e.g. by Anozoff [1] in the nineteenth century and by Sherby and Wadsworth [8], recently. However, a number of key properties of the Damascus blades are still not yet understood. Here we show for the first time that nanowires in a real Damascus blade exist, which could be the missing link between the praised macroscopic properties of this material and some obscure recipes intuitively applied by ancient blacksmiths.

There have been various studies of genuine Damascus blades so far [3,9–11]. The present investigation proposed

by Kochmann [12] was inspired by fullerenes filled with lanthanides [13] and by nanowires formed catalytically under the action of nickel and cobalt [14].

2. Experimental

The specimens under investigation were part of one of those sabres which had been examined already by Zschokke [3] (Materials Testing Institution, Zurich) in 1924 benefiting from a donation of the Swiss collector Henri Moser. We refer to no.10 of his sabres which was kindly left to one of us (W.K.) by E.J. Kläy (Berne). It is well documented as product of the famous blacksmith Assad Ullah (seventeenth century) [3,9]. The surfaces of the blade exhibited a pronounced Damascus pattern. The cross section is an isosceles triangle of 26 mm height with curved sides and a base of 5 mm thickness. Two samples were taken from the middle part. They were sectioned using a spark erosion technique. Both samples of an area 6 mm × 6 mm parallel to the surface of the sabre covered the cutting edge.

The average composition of non-iron components as determined by optical emission spectrometry is (in wt.%) C 2.24, Si 0.04, Mn 0.02, P 0.11, S 0.04, Cr < 0.01, Ni 0.05, Mo < 0.01, Al 0.05, Co 0.05, Cu 0.17, Nb < 0.05, Ti <

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0.01, V 0.02, W < 0.01, Pb < 0.01, Sn < 0.01, Ca \ll 0.01, Ce \ll 0.01, B \ll 0.01, where the estimated uncertainty is 0.08 wt.% for C and 0.01 wt.% for the rest. Because, thanks to two other publications (Zschokke [3] {Z}, Verhoeven et al. [15] {V}), independent analyses of specimens of just the same sabre no.10 have become available, we compare our current results {K} with them: C 1.726 {Z}, 1.79 {V}, 2.24 {K}; Si 0.062 {Z}, 0.050 {V}, 0.04 {K}; Mn 0.028 {Z}, 0.030 {V}, 0.02 {K}; S 0.020 {Z}, 0.016 {V}, 0.04 {K}; P 0.172 {Z}, 0.133 {V}, 0.11 {K}. Presumably, the differences are rather reflecting compositional gradients than different uncertainties of measurement. This is supported by an analysis of the lateral elemental distribution along the surface of the blade near the cutting edge as well as in the central part using electron scanning microanalysis, which revealed inhomogeneities. Remarkably, fluctuations of certain elements were found to be strikingly correlated, like, e.g., iron and aluminium. Additionally, a sample thinned for transmission electron microscopy was analysed by energy dispersive X-ray analysis. Fe, C, B, Nd, Ce, Sm, and Th have been detected off the surface. Rare earths were anticipated by Kochmann after having observed weak γ radiation [16] emitted by a wootz of M. Sachse. He attributed this radioactivity to thorium as a constituent of the monazite group of minerals (RPO₄, which may contain ThO₂ and SiO₂, R being a rare earth metal [17,18]) which Indian metallurgists were presumably adding as source of phosphorus to the wootz. The presence of Ce has also been reported by Petersen et al. [10].

3. Results

Then the microstructure of the blade was examined with ion beam processing and scanning electron microscopy. By ion beam slope cutting with 7 keV Kr⁺ ions an oblique section of several millimetres including the cutting edge was obtained free of mechanical damage [19]. This area was selectively etched by short-time bombardment with 7 keV Ar⁺ ions. The ion beam processing steps were carried out with the Gatan precision etching and coating system. Fig. 1 shows the microstructure revealed with a field emission scanning electron microscope (FESEM). It is characterized by the following features: (i) large (sometimes elongated) grains of cementite from 2 to 10 μm in diameter similar in size from the cutting edge to the back, arranged in almost linear (i.e. planar) arrays with an average spacing of 100–150 μm , (ii) a homogeneous fine-grained matrix with globular particle sizes down to ~ 100 nm, (iii) mostly spherical voids from 0.5 to 1 μm diameter. An example is shown in Fig. 1. Comparison with the microstructural observations of Verhoeven et al. [15] indicates at least qualitative agreement.

The surface of the sabre has been screened using X-ray diffraction (Cu K β radiation, Bragg-Brentano geometry) spatially resolved across seven zones of 2 mm width each parallel to the cutting edge and including the latter. While ferrite and tetragonal martensite was found in all parts, cementite could be detected only in some of them in agreement with the microstructure of Fig. 1. Also orthorhombic

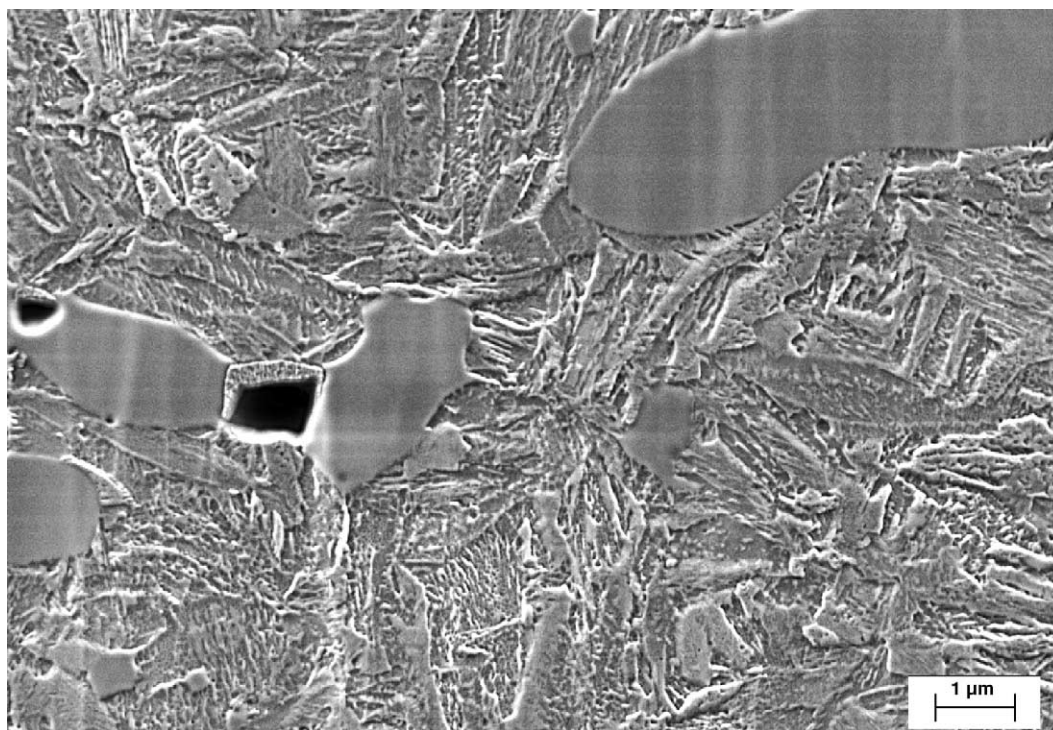


Fig. 1. Microstructure of a seventeenth century Damascus sabre. Oblique section through the blade prepared by ion beam slope cutting and selectively etched by Ar⁺ ions. The micrograph shows large cementite grains embedded in a fine grained pearlitic matrix and two voids. For the FESEM image the authors thank S. Menzel (IFW Dresden).

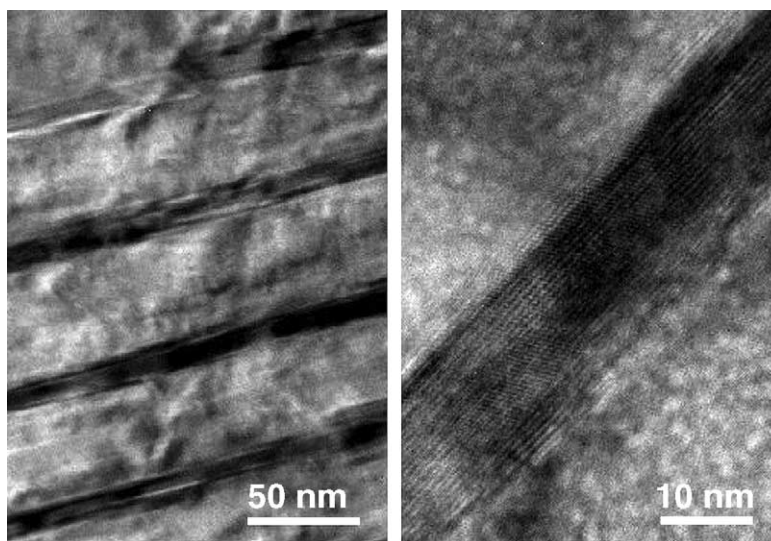


Fig. 2. Detection of nanowires in Damascus steel. The dark stripes indicate nanowires of several hundreds nanometers in length. Imaging was done using the transmission mode (a) and the high-resolution mode (b) of a Philips CM200 FEG microscope at 200 kV acceleration voltage. The image (b) is rotated with respect to that of (a). The fringes along the wire and those inclined to it in (b) correspond to lattice planes. The section shown in (b) lies slightly outside the area shown in (a).

and hexagonal phases of tridymite cannot be excluded. The results of a detailed phase analysis will be dealt with elsewhere [20].

Thin foils were prepared for transmission electron microscopy parallel to the surface of the blade by a standard technique involving mechanical grinding, mechanical dimpling and ion milling to perforation. The samples were examined in a Philips CM200 FEG microscope. A rather high density of nanowires has been identified in samples taken from different places. Some of them were straight,

others were curved. Fig. 2a gives an example. They were observed outside the cementite particles and were found oriented mainly parallel to each other with a fairly constant spacing of about 50 nm. Also, we succeeded in high resolution imaging of lattice planes of these wires (Fig. 2b). From Fourier transformation the structure has been identified as orthorhombic cementite. Details of the structure will be dealt with in Ref. [20].

Moreover, dislocations have been detected between the nanowires being tangled there (Fig. 3).

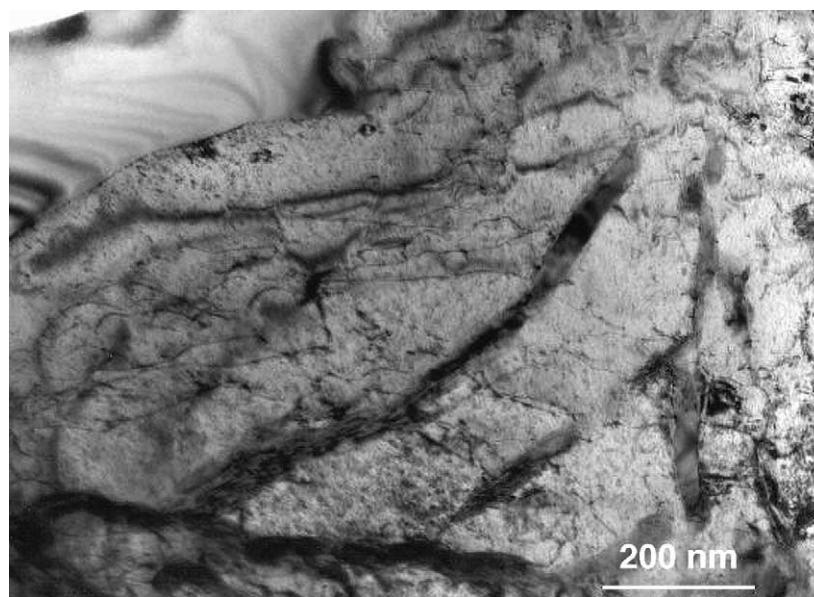


Fig. 3. Dislocations between nanowires in a Damascene blade. Dark band-like contrast corresponds to nanowires which appear slightly distorted in this part of the grain. Thin dark straight or bent lines between them indicate dislocations.

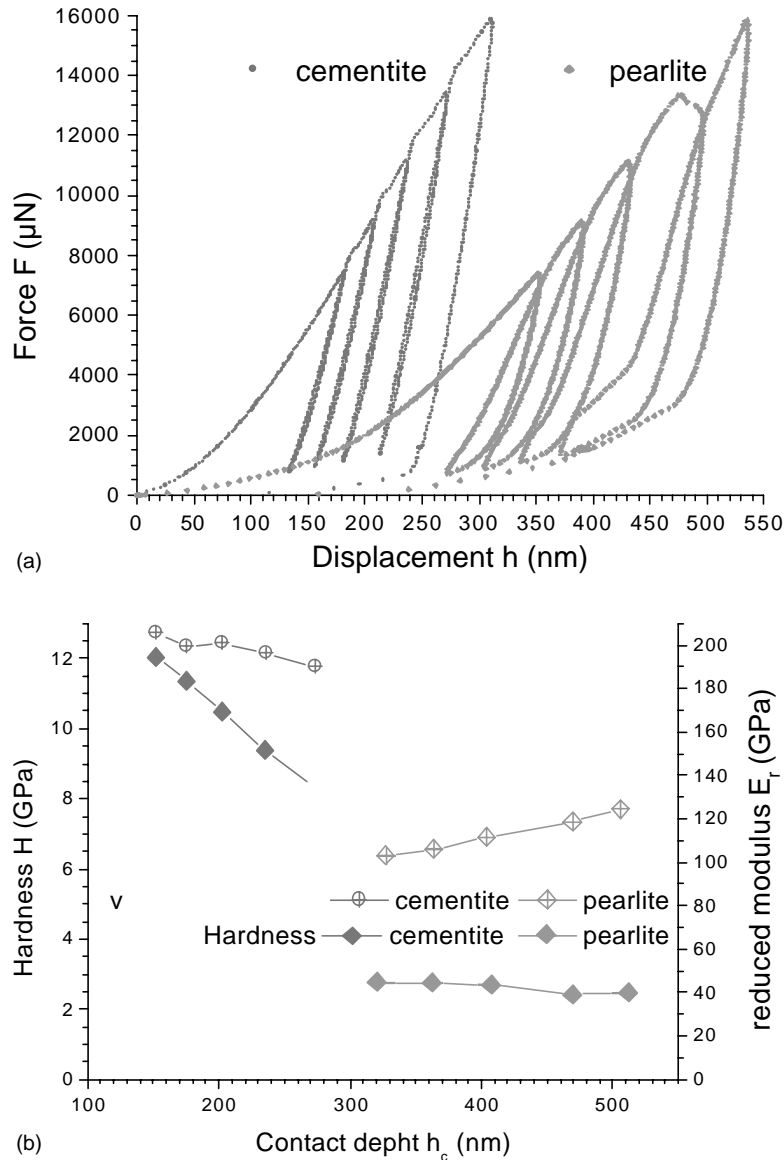


Fig. 4. Nanoindentation of cementite and pearlite. (a) Force–displacement curves measured separately for cementite and pearlite. Five loading–unloading cycles show a pronounced hysteresis in pearlite and none in cementite. (b) Hardness H and Young's modulus E_r as derived from (a) plotted versus the penetration depth h_c . The increase of H with decreasing h_c is known as indentation size effect. There is also a striking difference in E_r between cementite and pearlite.

Finally, using a nanoindenter (Hysitron TriboScope), we measured the indentation–displacement curves [21] in loading–unloading experiments separately both in the cementite grains and in the matrix (Fig. 4). The former were characterized by high Meyer hardness ($H = 12$ GPa at maximum) and no hysteresis, whereas the latter showed lower hardness (down to $H = 2.5$ GPa) and considerable hysteresis resembling a phase transition (cf. Fig. 4). Using a Brinell hardness test (indents done with a sphere of 9.5 mm diameter), Zschokke [3] found for sabre no. 10 the Meyer hardness $H = 2.43$ GPa as an average across all phases which is close to our results for the dominant pearlitic phase.

4. Discussion

Looking more closely at the exceptional mechanical properties which made Damascus steel famous reveals that they may be described by a high yield stress (for the onset of plastic flow) and a large ultimate strain. Both parameters together characterise high fracture toughness. Early reports indicated that a dagger-blade of good damascene steel cannot be broken by bending. When bent in the usual fashion, the blade retains its original shape. When bent, say, to a right angle, it does not lose its original elasticity after straightening again [1,2]. There are at least two requirements necessary for that. (i) High yield strength (and hardness) of iron which may be

obtained by adding carbon in particular when particles of the compound Fe_3C (cementite) are formed. A high stress is needed to initiate plastic flow of the latter, the elongation at fracture is, however, insufficiently small in ultrahigh carbon steels. When the carbon content exceeds 0.8 wt.%, steel becomes brittle at ambient temperature. (ii) To facilitate large strains without fracture those high-shear stress particles must be embedded in a ductile matrix. (iii) Normally, ultrahigh carbon content and ductility are disjunctive parameters. The key concept to overcome this problem was superplasticity. Wadsworth and Sherby [4] have shown that under an elaborate thermo-mechanical treatment (like forging) firstly the dangerous cementite networks can be broken up and secondly extremely fine grains of iron and iron carbide could be formed in ultrahigh carbon steels, i.e. from 1.3 to 2.1% C, enabling large deformations along the grain boundaries at elevated temperatures and pertaining toughness at room temperature.

Nanowires observed in the present blade might have influenced the growth kinetics of the microstructure. Verhoeven and Pendray [11] proposed submicroscopic particles acting as preferred nucleating sites for the cementite formation, but they were not able to reveal their nature. Moreover, as Fig. 3 is suggesting, the nanowires act as effective obstacles for dislocation as well as crack propagation, thus improving the toughness of this steel. The formation of these wires could in turn be facilitated by third elements as anticipated by Kochmann [12] and proposed for V and Mo by Verhoeven et al. [15].

Based on the present finding research aimed at disclosing the secret of Damascus steel will certainly be directed from the micro towards the nanoscale. Interesting questions remain to be solved as, e.g. how does the composition of wootz and/or the processing of Damascus blades lead to the formation of those nanowires and what are the consequences for their exceptional properties?

Acknowledgements

We thank Nora Paetzke and Siegfried Menzel for their collaboration.

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