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NEW INSIGHTS ON THE MECHANISM OF CARBIDE BANDING IN THERMOMECHANICALLY PROCESSED WOOTZ STEEL OBTAINED USING ELECTRON BACK SCATTERING DIFFRACTION

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Wootz blades have attracted considerable interest over the years and it seems that the quality and price of these swords were often dictated by the intricacy of the surface watering pattern. This indirectly hinted at superior mechanical properties and arises from the formation of bands of coarse carbides. The present paper employs Electron Back Scattering Diffraction (EBSD) technique, for the first time, to characterize these bands in a sword forged from wootz steel. The technique reveals the substructure of the carbides as well as their crystallographic orientation. The cracking of the carbides, their distinct internal structure of sub-grain boundaries and the similarity of orientation of nearby particles seem to suggest all points to the heavy working received by the particles. The formation of the structure of the present blade also appears to indicate the importance of a mechanism in which the bulky carbide structure persists through cycles of relatively low temperature forging.

Keywords: Carbide banding, Electron back scattered diffraction technique, Mechanism, Thermomechanical processing, Wootz steel.

INTRODUCTION

The history of scientific investigation into wootz-steel derived swords has been reviewed in many places[1,2]. Of considerable interest is the formation of the coarse carbide bands that produce the characteristic watered pattern, which could be visually noticed on the surface of blades and swords wrought out of wootz steel. The quality and price of these swords were often dictated by the intricacy of the watering pattern, which indirectly hinted at the good mechanical property (namely toughness) of the material.

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The intersection of the bulky carbide bands with the blade surface produces the well known pattern. This is much like the effect produced by the intersection of tree rings with the surface of a sawn plank. As for the mechanisms of carbide band formation, Wadsworth, Sherby and co-workers[3] emphasize the importance of the distribution of coarse cementite prior to forging and their thermomechanical processing at relatively lower temperatures (such that pearlite structure is converted to a spheroidized cementite in a ferritic matrix microstructure by the divorced eutectoid reaction). Verhoeven and co-workers[4] emphasize the importance of the distribution of segregating elements such as vanadium in the carbide in the original wootz, which help in "remembering" to precipitate the bulky carbides at the same location even if the temperatures are taken to a temperature above the Acm of the steel. Therefore the debate has centered on how the bulky carbide banding visible on the surface of the worked wootz objects develop. This on-going debate[5-7] between the two groups can be followed in the journal *Materials Characterization* and is of considerable interest because it brings to light, the range of issues involved in understanding the physical metallurgy of wootz steels.

The papers by Wadsworth, Sherby, Verhoeven and co-workers have relied largely on optical microscopy to gain insights on the physical metallurgy of wootz steel-derived worked objects and also on high carbon steels synthesized by these two groups. This technique has also been traditionally used in earlier investigations of banding of watered blades[1,8]. Optical microscopy relies on the contrast provided by the carbides in the microstructure. A big advantage of optical microscopy is the *in-situ* metallography that can be performed on historical objects[9]. Additional information about the structure can be obtained using scanning electron microscopy, which, surprisingly, has not been applied in a systematic manner in case of these wootz-steel derived objects. This would be particularly useful if one combines other modern characterization tools available in the SEM to gain additional insights on the nature of the microstructure. For example, compositional analysis can be performed either by energy dispersive spectroscopy or wavelength dispersive spectroscopy. Texturing can be usefully studied by orientation imaging microscopy in the SEM. The present study describes the technique known as Electron Back Scattering Diffraction (EBSD)[10-12] in an attempt to gain insights into the microstructures of wootz steel-derived objects. EBSD provides the crystallographic orientation so long as the crystal structure is known. Thus, it enables one to identify grain and phase boundaries without etching. It also permits local textures to be determined. The nature and type of carbides in an ancient forged wootz blade have been understood using this technique, the results of which will be published in detail elsewhere[13]. In the present communication, the technique is briefly described first. This is followed by characterization of one type of carbides, namely the coarse carbides, in an ancient blade using optical microscopy and EBSD. The work concludes by identifying how the technique might be employed to distinguish between the competing carbide formation theories for wootz steel forging.

ELECTRON BACK SCATTERING DIFFRACTION (EBSD)

Electron Back Scattering Diffraction (EBSD) involves the generation, collection and indexing of Kikuchi diffraction patterns in a scanning electron microscope[10-12]. The technique provides the crystallographic orientation of the crystal under investigation. A simple schematic of the technique is provided in Fig. 1. The electron beam interacts with a small volume (~20-50 nanometers in diameter) of the sample and backscattered electrons are produced. These electrons leave the sample in diffraction cones as determined by the Bragg condition. The impingement of these cones on a phosphor screen produces a distinctive diffraction pattern (Fig. 1b) unique to the crystal orientation in relation to the microscope reference frame. These patterns are collected by a digital camera behind the phosphor screen. The electronic images thus produced are subjected to transformation and the pattern is indexed by comparing it to patterns expected for the material in question, the crystallographic structure of which needs to be known beforehand.

Typically, measurements are taken over a raster, the spacing of which can be as low as tens of nanometers. The result is a map of crystallographic orientation that is often presented by assigning colours to regions of orientation space. It is also possible to plot the boundaries between neighbouring crystallites. As will be shown further below, valuable information is provided by the contrast evident in the Kikuchi diffraction lines. The less perfect the crystal producing the diffraction pattern, the "fuzzier" the pattern. The contrast of the diffraction pattern can be quantified in a single parameter and converted to a grey level. When the result is plotted as a map, important microstructural features can often be discerned.

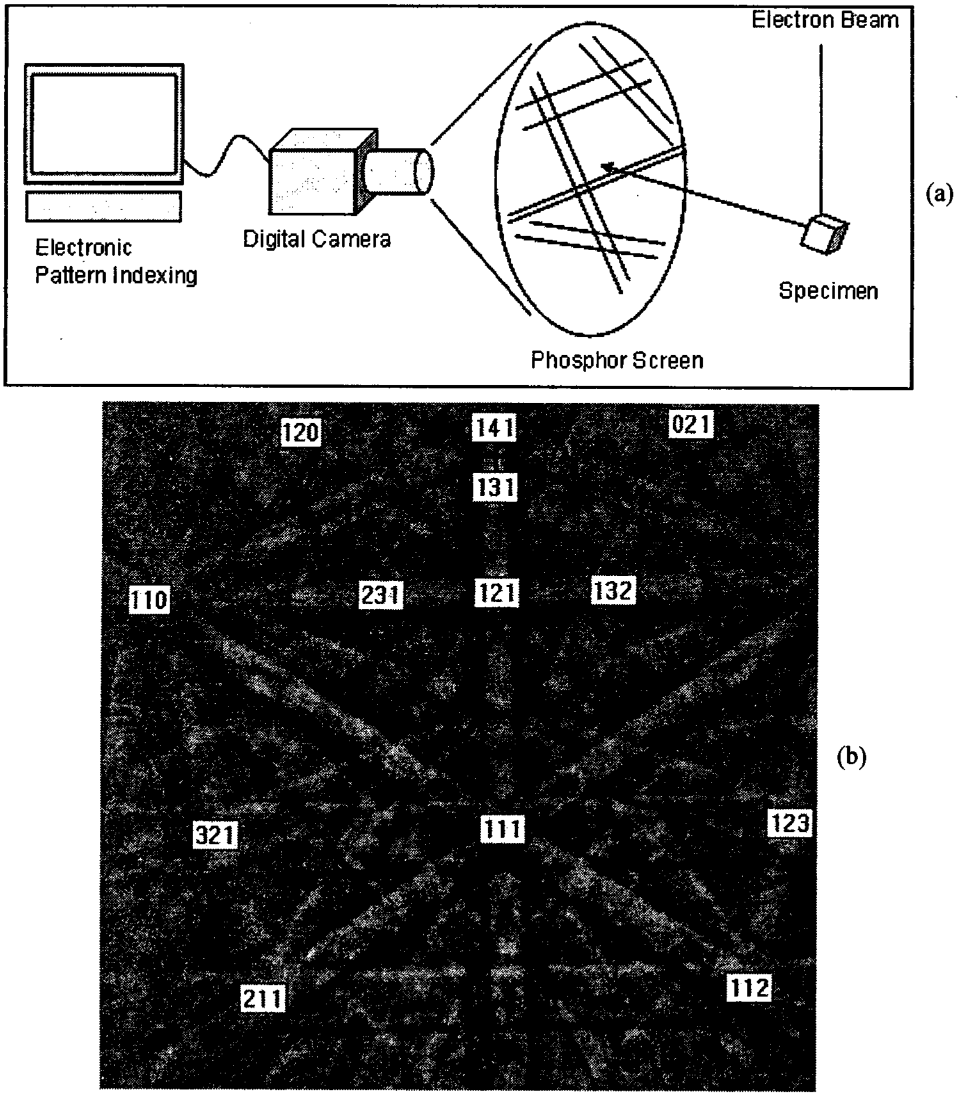

Fig. 1. (a) Diagram illustrating the main components of an EBSD system in a scanning electron microscope. (b) Example of an indexed Kikuchi pattern collected on a Phosphor screen.

In the present instance, the technique is employed to reveal carbides in a forged wootz implement without applying an acid etchant to the surface. The proximity of the orientations of neighbouring carbides is also considered. This is done by applying a shading to all orientations within a fixed angular deviation of a "central" orientation.

EXPERIMENTAL PROCEDURE

An ancient broken sword was obtained from an antique dealer in Sravanabelagola in Karnataka state. This region was traditionally very famous for making wootz steel and a large production of wootz steel was recorded by Buchanan[14,15] during his visit to this area in 1807. Buchanan has also described one typical wootz steel making furnace from this region apart from noting the people involved in the manufacture of wootz steel. The date of the sword is uncertain. However, based on the loss of wootz production know-how in the 1860s in the local area and the condition of the specimen, it can be surmised that it dates from, at youngest, the mid 1800's. The specimen is shown in Fig. 2a, where the sample removed for use in the present work can be seen on the left. The sample was sectioned and prepared for metallography, electron microscopy and Glow Discharge Optical Emission Spectrometry (GDOES) in the standard manner. This entailed rough grinding down to 1200 grit, followed by polishing in diamond paste to 1 μm. No etching was employed for the EBSD study but a 10% ferric chloride solution was used to reveal the structure for optical microscopy. The location from where images were obtained in the current study is shown in Fig. 2b. The detailed structures from the other locations in the same sample are available in Ref. 13.

EBSD analysis was performed on a LEO 1530 Schottky filament field emission gun scanning electron microscope. The EBSD system used was the HKL system, with a Nordys detector. A working distance of 35 mm and an aperture of 60 mm were employed. Maps were produced using a raster of approximately ~700,000 points which were 0.2-0.3 μm apart.

RESULTS AND DISCUSSIONS

Overall Structure

The focus of the discussion will be on the appearance and nature of the coarse carbides that are ubiquitous in forged wootz implements in optical microscopy. However, it is useful to first provide an overview of the structure of the ancient blade[13]. The worked blade possessed a microstructure that showed variations depending on the location where the observations were made. The main strengthening phase in the material is cementite, which is

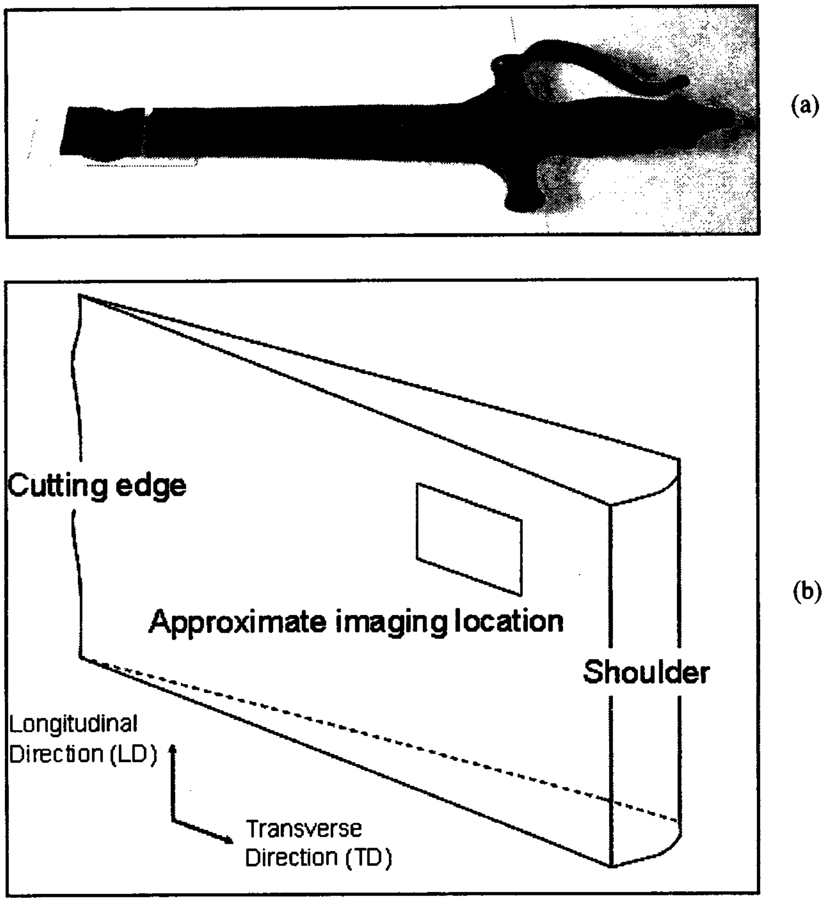

Fig. 2. (a) Sword and the sectioned sample examined in the present study and (b) region where imaging, reported in this paper, was carried out.

a hard and brittle phase. Therefore the distribution of carbides in the microstructure was critical in obtaining the required toughness from the blade. The three forms in which cementite is present in the original wootz steel microstructure is bulky carbides, proeuctectoid carbide along the prior austenite boundaries and cementite in pearlite. A typical microstructure from the blade showing these three characteristic features is shown in Fig. 3.

These carbides are affected by the thermomechanical processing of the blade while converting the wootz steel cake to the worked object. In this process of working wootz steel, the large bulky carbides are dispersed such that their dispersion provides the watering pattern on the surface. The grain

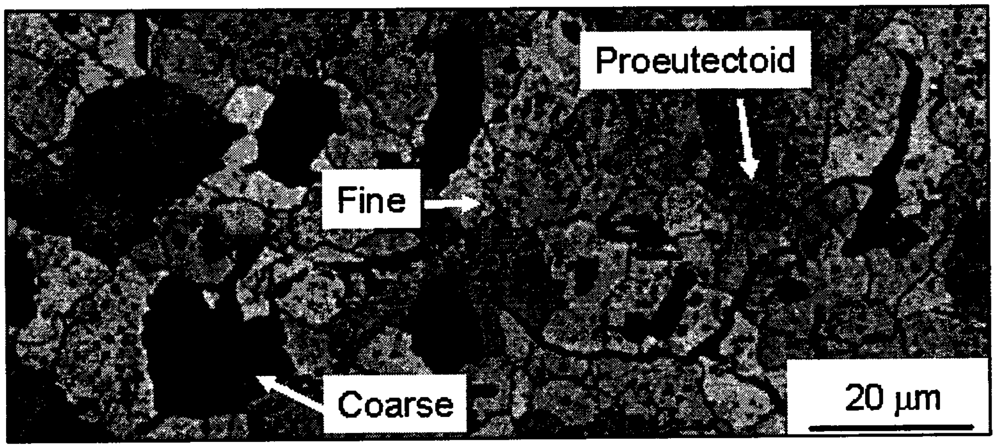

Fig. 3. Image generated by assigning a grey scale to the contrast values calculated for the Kikuchi patterns obtained during the EBSD scan. Darker shades correspond to poorer band contrast. The image reveals three morphologies of cementite in a ferrite matrix: I – large blocky carbides (> 5 µm in size and often aligned in bands along the longitudinal direction), II – pro-eutectoid cementite decorating prior austenite grain boundaries, III – fine spheroidized carbides randomly dispersed in the matrix.

boundary network of proeutectoid carbide is broken down so that a continuous brittle pathway for cracking is avoided. The superior toughness is finally realized by suitably converting the platelet-shaped cementite in the pearlite to a spheroidized form, such that the final structure obtained is essentially spheroidized cementite in a ferritic matrix. In fact this is a general feature of several wootz steel derived steel objects analysed by in-situ metallography[9]. It must be emphasized that the wootz steel worker did not always aim in aligning the bulky carbides in the worked object. It depended on the object that was being fabricated. In case the object was a sword or cutting object, then the watering pattern was maintained such that the alignment of the large carbides were parallel to the direction of the main axis of the blade. This apparently resulted in superior toughness when the cutting object was subjected to impact in a direction perpendicular to the sword axis (i.e. longitudinal direction). In applications where the main requirement was toughness, the wootz steel cake was worked without special care taken to align the bulky carbides. Therefore, one can distinguish between watered and non-watered wootz steel-derived object and this distinction is based on what the final application of the object was.

In the extreme rear of the sword (i.e. away from the cutting edge), one could notice some pearlitic structure while this was generally absent in the thinner sections of the blade. This was due to the conversion of pearlite to spheroidized structure in a matrix of essentially ferrite by thermomechanical processing of the blade.

The nature and distribution of the bulky carbides is of concern, generally based on the debate in the literature on the mechanism for this carbide banding. Therefore, the following discussion will concentrate on these bulky carbides.

Morphology of Bulky Carbides

Inspection of the structure at low magnifications revealed a certain degree of carbide banding. This is evident in Fig. 4. A higher magnification of the boxed region is given in Fig. 5 where the shape of the coarse carbides is more evident.

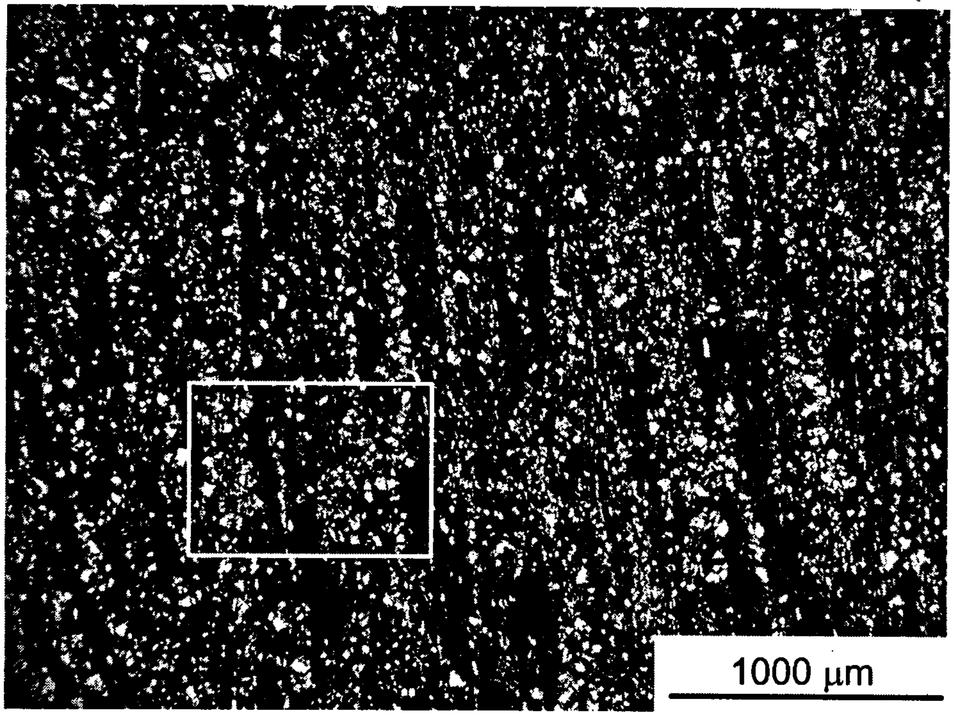

Fig. 4. Low magnification optical microscope image showing carbide banding. The sword long axis is vertical.

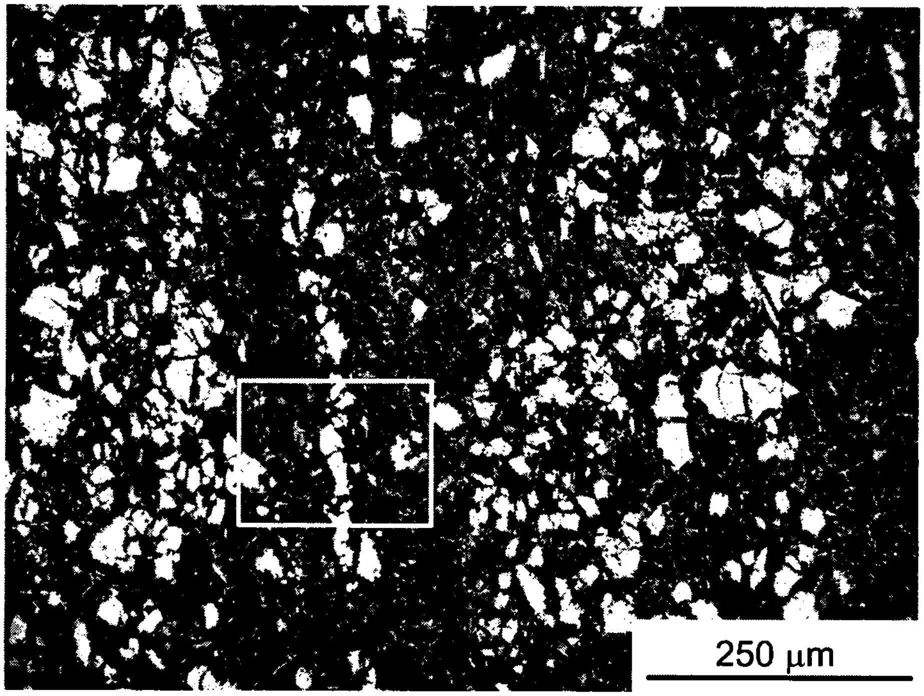

Fig. 5. Higher magnification image of the boxed region in Fig. 4.

At these higher magnifications, cracks can be detected in some of the carbides. These cracks reveal the low ductility of the carbides. They also demonstrate that although the sword was clearly forged at high temperatures, these temperatures were not sufficiently high as to dissolve the coarse carbides. These cracks further suggest that the large particles have been present over a considerable period of the forging and that the forging was sufficiently severe as to cause cracking.

Carbide cracking is more evident when the region boxed in Fig. 5 is further enlarged in Fig. 6. This figure also reveals a pearlitic structure outlined in places by apparently pro-eutectoid cementite. The large carbide particles display cracks predominantly perpendicular to the long axis of the blade. A detailed study of the banding indicated that the carbides varied somewhat in their morphology between the different bands[13]. In some bands, the carbides were consistently larger than in other bands. In other cases, the carbides displayed a more rounded appearance or a more elongated aspect. However, systematic variation was difficult to discern because of the deformation that

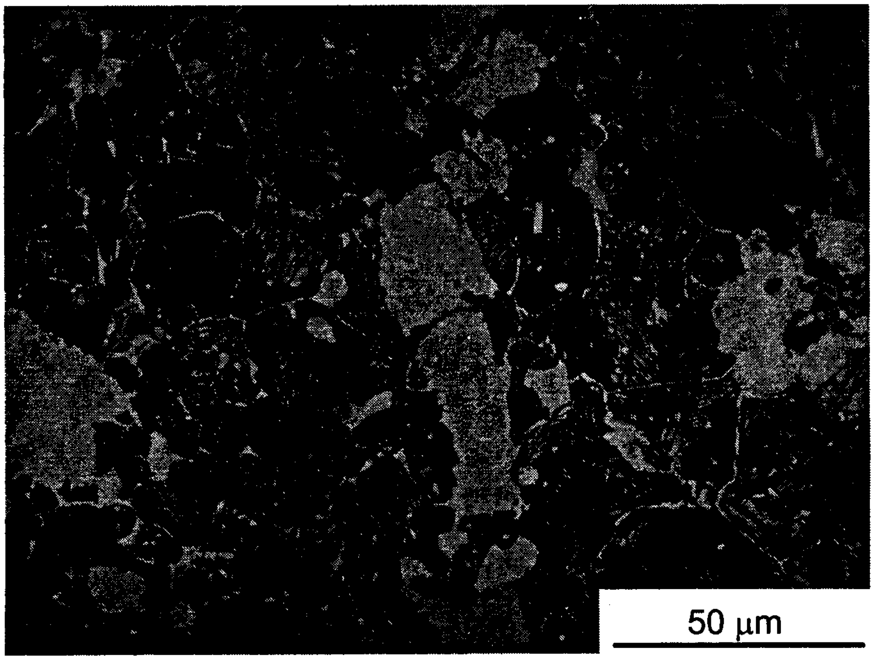

Fig 6. Higher magnification optical microscope image of the boxed region in Fig. 5 showing a large cracked carbide.

was imparted to the sword appears to be fairly even. In contrast, microstructural analysis of partially worked wootz objects, like a wedge-shaped tool (used by toddy collectors to incise sharp cuts on palm fruits) analysed in this volume[16], provide valuable information about type and nature of carbide distribution with degree of deformation. Finally, it is worth noting that in a number of cases some isolated large cementite particles were very difficult to index. This may be indicative of a slight variation in structure and will be taken up for further study.

Bulk Texture of Coarse Carbides

Another advantage of utilizing EBSD mapping is that bulk textures can also be estimated based on the data obtained. Care must be taken in this regard to ensure that sufficient numbers of grains are measured. The grain statistics are low in the present case but it turns out that consideration of a more extensive data set (not considered here for the sake of brevity) yields a similar result to that presented in pole figure format in Fig. 7. It is clear

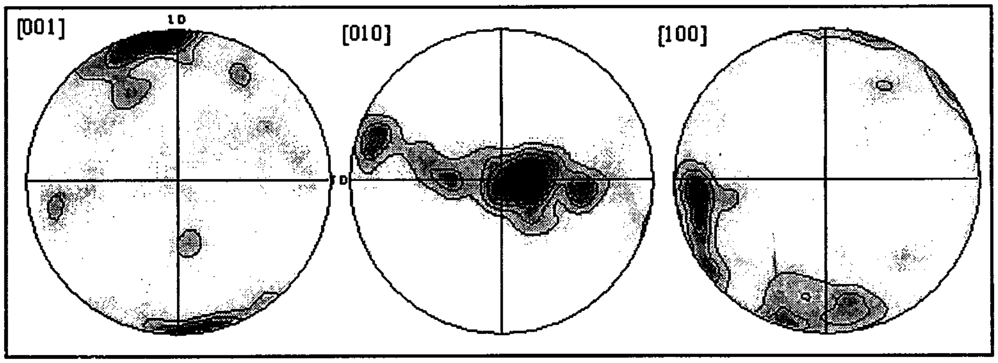

Fig. 7. Crystallographic textures of coarse blocky cementite shown in pole figure representation (contours: 1,2,3,... times random, LD = longitudinal direction, TD = transverse direction).

that there is a preferential grouping of orientations with either their [010] axis parallel to the normal of the blade face or their [001] axis parallel to the longitudinal direction. These textures presumably arise from the repeated working of the particles during forging in similar manner to that seen in conventional metal working processes[12].

Kikuchi Band Contrast Maps

The appearance of the microstructure revealed by the band contrast obtained using EBSD is illustrated in Fig. 8 for a similar though not identical region of the sample. Similar features to those seen in Figs 5 and 6 are evident though a pearlitic structure is not apparent. This point will be considered in detail elsewhere[13] but can be understood as a combination of the variation of the structure and the effect of ferrite erosion during the course of the ferric chloride etch that was employed in the optical analysis. It is quite clear that a good number of the coarse cementite particles display distinctive cracks. It is also evident that some of the coarse cementite particles are darker in shade than others. This may reveal a slight difference in structure. Further work is required on this but it was noticed that these were often more difficult to obtain complete indexing of the Kikuchi patterns.

Misorientations and Local Orientation Groupings

The internal structure of the coarse bulky cementite particles reveals a substructure comprised of low angle boundaries (Fig. 9). These boundaries

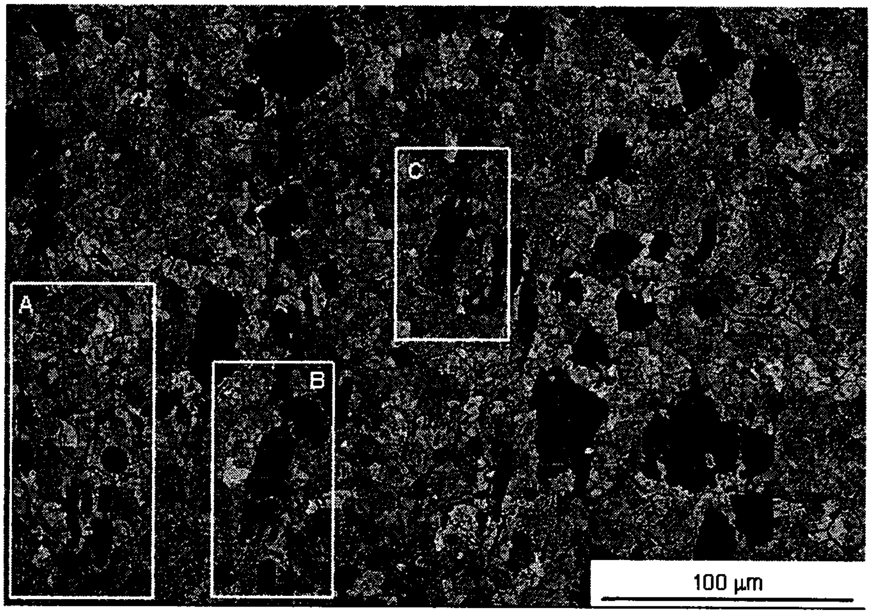

Fig. 8. Kikuchi band contrast image of the microstructure. In this case, the carbides are darker than the ferrite, in reverse to the optical images presented above.

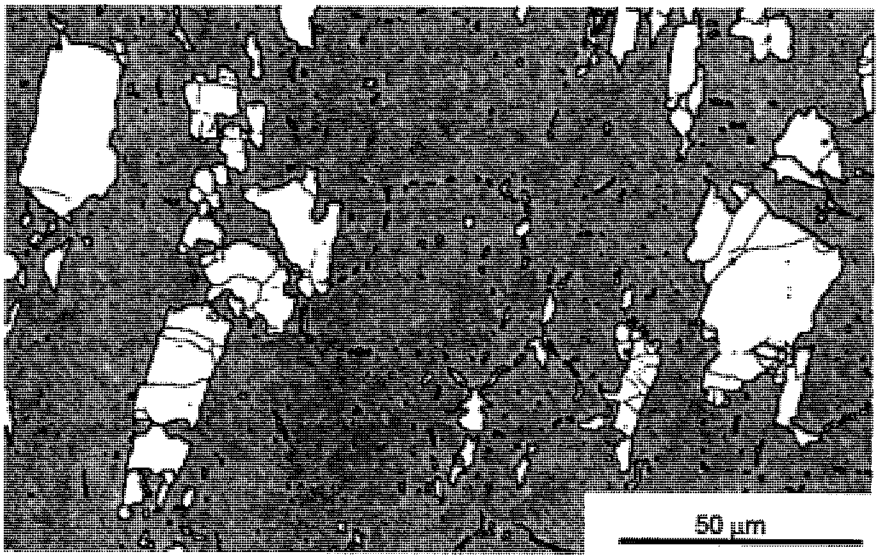

Fig. 9. EBSD map of the region displaying the boundaries observed in the coarse bulky cementite particles. The boundaries greater than 15° in misorientation are seen in bold and those greater than 1.5° in misorientation are shown by fine lines.

frequently span the width of the particle. Such a substructure is likely to be a consequence of dynamic recovery during hot working. Although the particles have cracked, the presence of a substructure (assumed to be comprised of "recovered" dislocations) implies some degree of dislocation induced plasticity.

Another advantage of EBSD is that maps of local orientation may be generated by assigning a colour or a grey scale to selected crystallographic orientations. This method is frequently used to reveal groupings of similar orientation. In the present case, this method can be used to understand the orientation relationships between the bulky coarse carbide particles strung out along the length of bands.

The regions boxed in Fig. 8 are subjected to further analysis in Fig. 10. This figure plots interphase boundaries (ferrite-cementite) and orientations within 25° of the blackened cementite particles are shaded with an increasingly lighter grey the greater the misorientation from the black region. Thus, all of the shaded carbides share a closer orientation to the black orientation than the unshaded regions.

The images shown in Fig. 10 reveal some splitting up of the orientation within a single carbide. This is most obvious in region B. However, it is also

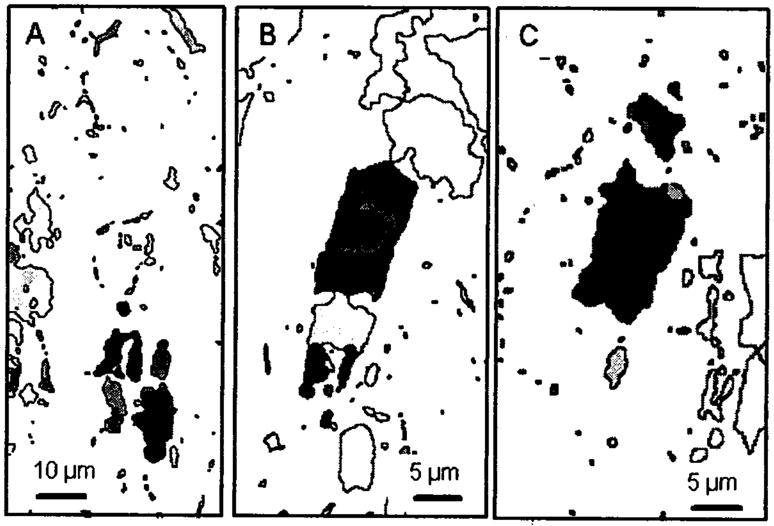

Fig. 10. Images produced using EBSD displaying boundaries between ferrite and cementite (carbide) and shaded according to the proximity of the orientation to the black "central" orientation. The images correspond to the regions boxed in Fig. 6.

evident that cracked portions of the carbides can retain similar orientations. This is not surprising. Indeed, in the present case the morphology of the carbides and the clear cracks frequently allows one to identify certain neighbouring particles that must have previously been one. However, with information of the carbide orientation, it is possible to identify carbides of similar orientation that may have had a common carbide "ancestor" despite not otherwise appearing to do so. This may well be the case for the carbide groups evident in regions A and C in Fig. 8.

New Insights

Although this may seem a subtle point, such inferences about the microstructural ancestry of microstructure features permit one to draw conclusions with regard to processing history. In the present case, both orientation data and the obvious cracks reveal that the carbides have existed through a high portion of the forging. If high temperatures were employed, the carbides would have dissolved only to re-form upon cooling. In such cases cracks and groups of neighbouring particles with similar orientations are far less likely. The simplest interpretation of this is that the neighbouring particles were once part of a single particle and that while fracturing and elongation of the cluster has occurred during forging, a more or less constant crystallographic orientation has been maintained. If these carbides were completely dissolved during the repeated reheating cycles during forging it might not be expected that they would form such strong orientation groupings.

CONCLUSIONS

The electron backscattering diffraction technique can provide useful insight into the metallurgical history of ancient metallic artefacts.

The EBSD technique has been applied for the first time to provide new insights on carbides, specifically bulky carbides, in a wootz steel derived sword.

The blade examined in the present study revealed three types of carbides: coarse, fine and pro-eutectoid.

The coarse carbides were very clearly subjected to heavy degrees of working as shown by the cracking of some of the carbides.

The bulky carbides did undergo plastic deformation at the forging temperature based on dislocation activity in the carbides revealed by the presence of sub-grain boundaries.

The close orientation relationships between neighbouring fractured segments of bulky carbides confirm the use of low forging temperatures.

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