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Electron backscattering diffraction as a complementary analytical approach to the microstructural characterization of ancient materials by electron microscopy

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ABSTRACT

Since the development of electron backscattering diffraction (EBSD), scanning electron microscopy (SEM) has become a powerful tool for characterizing the local crystallography of bulk materials at the nanoscale. Although EBSD is now a well-established characterization method in materials science, it has rarely been used in art and archaeology, and nearly exclusively in metallic materials. However, EBSD could also be exploited to characterize ancient materials and to highlight their local crystallography (e.g., in the study of natural or artificial pigments). We discuss the potential of EBSD, as outlined in studies and from its application with an ancient material – Egyptian blue – in identification of crystalline phases, drawing phase maps, and the extraction of several microstructural parameters (e.g., the grain size and the aspect-ratio distribution of phases).

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Contents

1. Scanning electron microscopy and electron backscattering diffraction

Scanning electron microscopy (SEM) has long been used due to its unmatched ability, on both powdered and bulk samples, to combine high-resolution images with elemental chemical analysis by means of energy-dispersive spectroscopy (EDS). The spatial resolution of the images obtained in current field-emission SEM is below 1 nm, whereas EDS systems can now detect elements heavier than boron ($Z = 5$) and draw compositional maps with a spatial resolution below 1 µm. However, for decades there was no means to obtain crystallographic information in a SEM specimen in a fast, simple manner. Researchers interested in combining high-resolution images and elemental chemical analysis with crystallographic information were thus forced to use only transmission electron microscopy (TEM). TEM is very powerful, but having to work with electron-transparent specimens involves difficult sample preparation and limits the observation to small areas of the sample. However, since the development of electron backscattering diffraction (EBSD) in the 1990s, SEM has become a powerful tool for characterizing the local crystallography in large areas of bulk materials with a spatial resolution as small as ~10–20 nm [1]. Although EBSD is now a well-established characterization method in materials science, in the rare cases where it has been used in art and archaeology, these have been nearly exclusively in metallic materials [2].

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EBSD is based on the acquisition of divergent beam electron-diffraction patterns in a SEM, called Kikuchi patterns after their first description by Seishi Kikuchi [3], in back-reflection geometry. Although the acquisition of EBSD patterns was reported in the 1950s [4] and scanning electron microscopes became commercially available in the 1960s, the use of EBSD in materials science was very limited until the development of high-sensitivity recording cameras and fast automated computerized methods for on-line pattern analysis. Methods for the fully-automated indexation of EBSD patterns were developed in the 1990s [5] through the Hough transformation of the patterns [6]. Commercial EBSD systems soon became available and the so-called orientation-imaging microscopy (OIM) rapidly spread throughout materials-characterization laboratories. Commercial EBSD systems are now a common, moderately-priced SEM accessory. Currently, they can be used to record, store and index individual EBSD patterns in about 10 ms and to plot large-area maps of bulk samples representing the crystallographic orientation of each pixel and other microstructural parameters. The development of modern EBSD is the result of the collective efforts of many scientists, and readers interested in this matter can consult the excellent review written by one of them, D.J. Dingley [7].

In an EBSD experiment, the vertical electron beam hits the sample surface at an angle of about 70° (the sample is tilted towards the EBSD detector), producing diffracted electrons. These diffracted electrons form a pair of Kossel cones (hkl and $\bar{h}\bar{k}\bar{l}$) for each reflecting plane. The projection of the Kossel cones on the EBSD detector screen produces pairs of Kikuchi lines, also known as Kikuchi bands, including the region between them (Fig. 1). Although the mechanisms related to the formation of band contrasts are quite complex, it is easier to understand that, as the Kossel cones are centered at a point on the diffracting planes, they reflect the crystal symmetry of the electron-interaction point, thus enabling spatially-resolved crystallographic identification in the SEM. The position of the Kikuchi bands in the detector screen also reveals the crystallographic orientation of the analyzed grains.

EBSD experiments are performed on flat faces of cleaved crystals or, more commonly, on polished specimens. EBSD analysis of non-flat samples is also possible, but shadowing of the backscattered electrons in the sample itself prevents orientation maps from being obtained and limits these experiments to the acquisition of diffraction patterns of protruding grains for phase identification. The polished EBSD specimens are generally prepared using conventional metallographic methods. The only special care needed is to ensure that the sample surface is free of damage, because the EBSD patterns are generated from the top surface layer (~40 nm) [8]. The strains introduced by overly aggressive sample polishing would blur the Kikuchi bands. Thus, the specimen is prepared using a progressive lapping and polishing method to eliminate any strain created in the previous step. For a common ceramic sample, two grinding and two polishing steps using a low load-and-rotation speed of the polishing wheel, followed by a final polishing using colloidal silica, are generally sufficient. The same methods that produce well-prepared specimens for high-contrast SEM backscattering observations using low-energy incident electrons, which are the most sensitive to the quality of the specimen surface, are often good choices for EBSD-sample preparation.

However, differential polishing needs to be kept to a minimum to prevent shadows in the grain boundaries due to the tilted position of the sample. This effect limits the minimum grain size in the orientation maps. Special care should be taken to adjust the duration of the final step using colloidal silica, and long polishing times result in good quality patterns, but can lead to differential polishing between the phases. Colloidal silica should also be avoided if there are components that are sensitive to the alkaline pH of the solution in the sample, in order to avoid chemical reactions that may modify the composition. In this case, other polishing compounds, such as acidic alumina suspensions, could be used. In our experience, EBSD-specimen preparation of a common sample is not much more difficult than for daily SEM, and certainly less difficult than for TEM. However, it is true that EBSD-specimen preparation of delicate samples, mixing small grains of hard and soft phases, is always very challenging. Compared to TEM-specimen preparation, the quality of the surface finish is similar, though luckily only one side needs polishing and, even better, a thin film does not need to be prepared.

The spatial resolution of the EBSD technique is limited to 10–20 nm by the effect of the electron dispersion in the bulk sample [9], while the spatial resolution in modern TEMs using convergent beam electron diffraction (CBED) is limited by only the need for a minimum number of atoms to behave like a crystal, the practical limit being about 1 nm. Electron diffraction has been conventionally used in TEM for decades. Unlike TEM, with EBSD, large areas of bulk samples can be studied with fast, automated acquisition and analysis of the patterns. Both techniques have developed counter-attack strategies to overcome their own limitations. On the one hand, in TEM, it is now possible to plot orientation maps in an automated way using the precession electron diffraction (PED) technique [10], where the focused beam is scanned at a constant angle around the optic axis [11]. Using a slower procedure than EBSD, they achieve a spatial resolution of up to 1 nm. On the other hand, it is now possible to perform EBSD experiments in SEM in transmission mode {t-EBSD, also referred to as TKD [12]} to improve the spatial resolution below 10 nm. Generally speaking, SEM-EBSD is better for fast, large automated electron-diffraction maps of bulk samples, whereas TEM-PED is more appropriate for high-resolution orientation maps of small, thin-film samples (roughly tens of square micrometers).

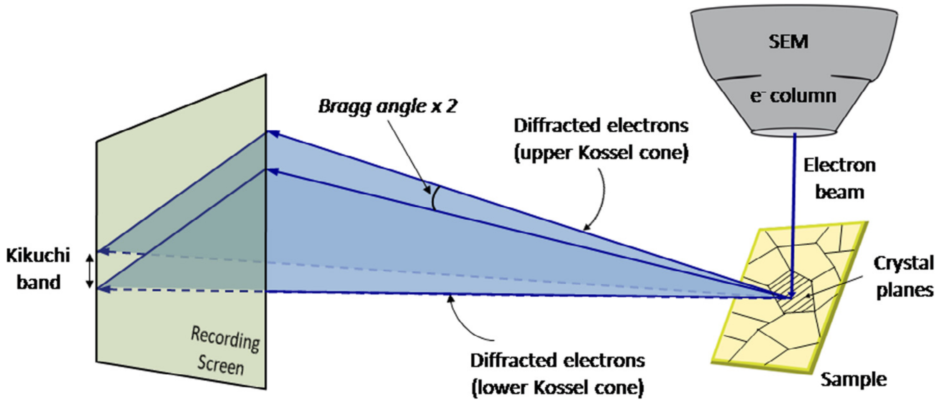

Fig. 1. Projection of the Kossel cones on the EBSD detector screen, showing the pair of Kikuchi lines and the region included between them (Kikuchi band).

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