Electron backscatter diffraction analysis of non-conductive samples using in-situ charge compensation

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Abstract

Electron backscatter diffraction (EBSD) is a powerful technique for structural characterization of micro- or nanocrystalline samples in the scanning electron microscope (SEM). Reliable EBSD analysis of non-conductive samples has so far required the use of conductive coatings or variable pressure (VP) SEM. An in-situ charge compensation system provides improved EBSD analysis of non-conductive samples without the drawbacks of these conventional methods. Similar to VP-SEM, charge neutralisation is achieved by gas ionization, but at negligible loss of resolution due to a significantly reduced interaction volume of beam and backscattered electrons with gas particles.

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Introduction

Diffraction patterns formed by electrons backscattered from a crystalline material in an SEM can be recorded with a dedicated EBSD detector that consists of a scintillator screen, a CCD camera and coupling optics. Characteristic dark and bright line pairs in the recorded diffraction patterns, called Kikuchi bands, relate to phase and orientation of the underlying crystal. The analysis of these bands in multiple measuring points provides crystallographic orientation mapping, grain size mapping, grain boundary characterization, phase discrimination and distribution, and inter-phase orientation relationships with high lateral resolution in 2D, or, if combined with serial sectioning using a focused ion beam (FIB), in 3D. Using in-situ sample modification techniques, EBSD can even be used to investigate the microstructural evolution of the sample under high temperature or mechanical strain.

Raw EBSD patterns usually do not show strong enough diffraction contrast to reliably perform Kikuchi band detection and indexing. They require extensive pre-processing, such as background removal and automatic pattern-by-pattern contrast optimization. Sophisticated and fast algorithms are available for pre-processing as well as the pattern analysis itself, but the quality of the raw data is fundamentally limiting the analysis results.

Non-conductive samples such as ceramics, polymers, and most biological samples typically charge up negatively during EBSD measurements. Accumulated surface charges act as a retarding field for the beam electrons. They will also deflect the backscattered electrons and, thus, degrade and shift the diffraction pattern. Without any countermeasures to mitigate sample charging, insulators do not provide sufficiently good diffraction patterns for consistent and reliable indexing.

In conventional SEMs, EBSD of non-conductive materials can only be done after deposition of a conductive coating of, e.g., a few nm of carbon or gold. However, it is difficult to adjust the correct coating thickness. If the layer is too thick, the signal to noise ratio of the diffraction patterns will decrease significantly, especially if low acceleration voltages are required. If it is too thin, the charge will not be sufficiently dissipated. Both will result in poor EBSD results.

In a VP-SEM, EBSD analysis of non-conductive samples can be done under low vacuum conditions. Here, the SEM chamber is flooded with water vapour or nitrogen. Electrons leaving the sample surface collide with gas molecules and ionise them. Positive ions are attracted to the negatively charged sample surface and balance out the charge. However, electrons produced during ionization will interact with more gas molecules, so that a cascade of charged particles is produced. Collisions of the beam electrons with these particles in a large interaction volume will broaden the beam (‘skirt effect’), and collisions of the electrons backscattered from the sample will degrade the diffraction pattern. Vapour pressure, acceleration voltage, beam current and dwell times have to be iteratively adjusted on a given sample to balance the pattern degradation by low vacuum and the pattern improvement by surface charge reduction.
Both methods described above allow EBSD analysis of non-conductive samples only at the expense of decreased measurement sensitivity. Furthermore, both require tedious and time-consuming optimization of experimental parameters in order to achieve the best results.

A dedicated gas injection system that provides a highly localized, adjustable nitrogen gas flow onto the sample surface, such as the in-situ charge compensation (CC) system available for Carl Zeiss FE-SEM and FIB-SEM systems, solves this problem (Figure 1a). Such a CC system not only allows SEM imaging, but also EBSD analysis of non-conductive samples. While the mechanism of charge neutralisation by gas ionisation is the same as in a VP-SEM, the low vacuum is limited to a small volume around the region of interest. Thus, detrimental interaction of beam and backscattered electrons with gas particles is drastically reduced compared to a VP system. Since the rest of the chamber remains close to high vacuum conditions, no special VP detectors are needed. Image quality and resolution remain largely unchanged. Pneumatic insertion and retraction of the device, as well as the gas flow, are controlled from the software of the microscopes. Charge compensated conditions, as well as restoration of the high vacuum, are achieved in seconds by simply switching the gas flow on and off.

In the following paragraphs, we present a comparison of EBSD patterns and grain orientation maps recorded at different acceleration voltages with and without CC, but otherwise identical conditions from the same samples. As typical application examples, an Al$_2$O$_3$-Er$_3$Al$_5$O$_{12}$-ZrO$_2$ (AEZ) directionally solidified eutectic ceramic (DSEC) and a sample of textured hexagonal silicon nitrate beta-Si$_3$N$_4$ were used. DSEC materials are highly textured composites whose properties strongly depend on their orientation relationships, EBSD being an essential tool for their characterization. Al$_2$O$_3$-based DSEC present outstanding mechanical properties up to temperatures very close to the melting point. In addition they present excellent microstructural and chemical stability, which make them promising materials for structural applications at high temperatures. Recently, the incorporation of rare earth ions in the eutectic composition also allows their use as selective thermal emitters in thermophotovoltaic devices. Silicon nitrides have a high technological relevance as engineering ceramics for engine parts and bearings, high temperature parts and cutting tools, as well as in semiconductor technology for isolation and passivation. In addition, textured Si$_3$N$_4$ is an excellent test specimen for EBSD, as it has a strongly anisotropic microstructure with highly oriented grains and a very high dielectric constant. We have used such a sample to assess the effectiveness of the CC system at different acceleration voltages.

**Materials and methods**

The AEZ rods for the application example were directionally solidified by the laser-heating floating zone method using a continuous wave CO$_2$ laser at a growth rate of 25 mm/h. Details of the sample preparation procedure can be found in [8]. The EBSD experiments were performed on transverse cross-sections after progressive lapping and polishing. The polishing sequence was designed to finally get a thin surface layer (~40 nm thick) free of strains. The presence of strains in the layer where the diffraction patterns are produced would blur the Kikuchi bands, preventing proper indexation. To
this end, the sample was polished first using SiC paper (15 µm and 10 µm particle size, polishing wheel at 40 rpm, 2.5 N load), subsequently with diamond paste (0.3 µm and 0.1 µm particle size, 120 rpm, 2.5 N) and finally with colloidal silica (100 rpm, 2.5 N) for 15 min.

The measurements on this sample were made using a Carl Zeiss MERLIN FE-SEM equipped with a Nordlys EBSD detector from Oxford Instruments. The sample was tilted 70° to the electron beam and placed at 14.5 mm of working distance. To accommodate the high specimen tilt angles necessary for EBSD and to avoid shadowing of the diffraction patterns, the CCs’ standard gas injection nozzle was replaced by a suitably shaped one (Figures 1 b and 2 a). EBSD grain orientation maps were recorded from a selected region of the sample (Figure 2 b) at 15 kV accelerating voltage, 0.8 nA probe current and 280 ns pixel dwell time with the CC gas flow switched on and off. For data acquisition and processing, the Flamenco-Channel5 software was used.

From an uncoated sample of textured hexagonal $\beta$-Si$_3$N$_4$, EBSD orientation maps were acquired in a Carl Zeiss Ultra 55 Plus FE-SEM equipped with an Oxford Instruments Nordlys EBSD detector. The measurements were made at 5, 15 and 20 kV acceleration voltage, approximately 1.5 nA beam current, a working distance of 11.7 mm, and a pixel dwell time of 100 ns. The Oxford Instruments Flamenco software was again used for data acquisition and processing.

**Results**

In Figure 3, diffraction patterns recorded at 15 kV acceleration voltage from the sample with and without in-situ CC are compared (336 x 256 pixel, 280 ms acquisition time). Patterns recorded with CC showed higher contrast and better-defined Kikuchi lines over a larger angular range than patterns recorded without CC. Moreover, the latter showed charging artefacts that saturated the detector.

EBSD orientation maps recorded at 15 kV from the same region of the AEZ sample with and without CC are shown in Figure 4 (20.7 µm x 16.1 µm map area, 100 nm step size, 2h 46 min total acquisition time). For obtaining these maps diffraction patterns, such as the ones shown in Figure 3, were automatically processed to detect seven Kikuchi bands and indexed to identify their crystallographic phase and orientation. Post-processing filtering was applied to eliminate the noise in the orientation map. In the experiment without CC, the map quality was good at the beginning of the acquisition (top right of the map), but progressively deteriorated during the acquisition due to charge accumulation. The software was not able to find consistent indexing solutions in about half of the patterns of this map, and the grain shape appeared distorted. However, a consistent, non-distorted and well-defined orientation map was obtained from the patterns recorded with CC. The unassigned pixels were in this case only about 16% and mainly corresponded to interface areas, where the patterns from different phases overlapped.

Figure 5 presents orientation maps recorded from the Si$_3$N$_4$ sample at 15 and 5 kV acceleration voltage with CC, and at 20 kV with and without CC. Again, using the CC results in a significant improvement of the orientation maps. Even at 5 kV, consistent indexing and orientation map computation was possible.
Discussion

The improvement in the quality of EBSD raw data obtained from non-conductive samples by using in-situ CC becomes clear when comparing single diffraction patterns acquired with and without CC in our experiments. Consequently, crystal orientation mapping is strongly improved, as shown by the grain orientation maps acquired with and without CC from the AEZ ceramic sample. No apparent degradation of the spatial resolution was observed by using the CC.

Moreover, the acquisition time used in the AEZ application example, less than 3 hours, is not a long time for EBSD maps. Acquisition times of more than 8 hours are very usual. In this case, the charge accumulation and, as a consequence, the percentage of non-indexed patterns would be higher and the map distortion would be even more severe than shown here.

The results obtained from a Si₃N₄ sample show that the mentioned improvement is not restricted to the high acceleration voltages typically used for EBSD analysis. Successful orientation mapping was possible even at a voltage as low as 5 kV. Due to the small electron-sample interaction volume at this low voltage, the corresponding orientation map shows a particularly high spatial resolution. It would not have been possible without the CC system.

Conclusions

EBSD analysis of non-conductive samples presents an experimental challenge, as the low quality of diffraction patterns from such samples usually requires time-consuming charge mitigation techniques that decrease measurement sensitivity. In the above examples, we have shown that an in-situ CC system allows EBSD orientation mapping of insulating, nano-crystalline samples without special sample preparation or further countermeasures to eliminate specimen charging. The pattern contrast and quality obtained with the CC system is comparable to those from conductive samples and good enough to ensure phase discrimination and accurate crystallographic orientation.

The restrictions of sample coating or using VP-SEM also apply to energy dispersive X-ray spectroscopic (EDS) analysis of non-conductive samples. It can be improved by in-situ CC as well. Using it for simultaneous EDS and EBSD analysis to couple crystallographic and chemical information enables unambiguous phase identification of insulating materials.

Clean sample surfaces are an essential requirement to successful EBSD analysis. The CC system provides the additional benefit of being able to remove carbon contamination from the in-situ specimen surface. To this end, the region of interest is flooded with oxygen instead of nitrogen, while being exposed to the electron beam. Thus, cleaning of the sample before loading is avoided, and its surface can be repeatedly cleaned whenever necessary between EBSD measurements.
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Figure 1: (a) Schematic drawing of the charge compensation system configuration. (b) View of the experimental setup inside the SEM chamber.
Figure 2: (a) SEM micrograph of the AEZ sample with CC nozzle in operating position. (b) SEM micrograph of the AEZ sample with region of interest where the EBSD maps were acquired indicated by a rectangle.
Figure 3: Diffraction patterns recorded at 15 kV acceleration voltage from the AEZ sample without (a) and with CC (b). Bright spot in the non-CC pattern indicates detector saturation due to strong specimen charging.
Figure 4: EBSD orientation maps recorded at 15 kV acceleration voltage from the same region of an AEZ sample without (top) and with CC (bottom).
Figure 5: EBSD orientation maps recorded in the marked areas of a Si$_3$N$_4$ sample without (a) and with CC with (b, c and d) at different acceleration voltages.