COMPARISON OF LABORATORY-BASED X-RAY MICRODIFFRACTION AND ELECTRON BACKSCATTER DIFFRACTION FOR PHASE IDENTIFICATION

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ABSTRACT

X-ray microdiffraction and electron backscatter diffraction (EBSD) have been compared by analysis of a number of materials, including nanocrystalline particles, thin films, and plasma-sprayed (Zr,Y)O$_{2-x}$. EBSD is capable of phase identification of single particles down to approximately 100 nm in size, and x-ray microdiffraction is capable of phase identification of powders down to tenths of nanograms in mass. EBSD is clearly the better technique for the identification of individual small particles, but cannot be used when all the particles (crystallites) are less than 100 nm in size. X-ray microdiffraction has better precision in the determination of lattice constants, which is important in the case of plasma-sprayed (Zr,Y)O$_{2-x}$.

INTRODUCTION

Two techniques can be readily applied for phase identification of micrometer-sized particles or areas. Scanning electron microscope (SEM) based EBSD has been used primarily for orientation determination, but has recently been extended to phase identification [1]. EBSD uses Kikuchi patterns generated by the electron beam, and phase identification is accomplished by comparing simulated patterns with the experimental pattern. X-ray microdiffraction is a modification of standard powder diffractometry using pinhole collimators or focusing capillaries to achieve a micrometer-sized beam.

EBSD and x-ray microdiffraction are fundamentally different, and as needs for phase identification of small areas or particles grow, it is useful to compare the advantages and limitations of the two techniques. These different capabilities for phase identification are illustrated by direct comparison on selected materials, including nanocrystalline powders, thin-films, and plasma-sprayed (Zr,Y)O$_{2-x}$. The issues that were considered were differences in minimum particle size or mass that could be measured, and the quality of the data obtained.

EBSD

The general advantages of EBSD include a smaller beam size as compared with x-rays (5 nm vs 10 µm), the ability to collect compositional information from the same area probed for diffraction, and SEM imaging capabilities. EBSD is a single-crystal technique and cannot be used when there are multiple crystallites within the sampling volume. The collection depth for EBSD is very shallow with respect to x-ray microdiffraction, with the information coming from depths generally much less than 1 µm [2].

The use of EBSD for orientation imaging of flat, bulk materials is a relatively common technique, but the extension of EBSD to practical phase identification is more recent. The use of
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EBSD for phase identification requires both a higher pattern quality and a link to a database for pattern simulation. The latest development in phase identification using EBSD has been the analysis of micrometer-sized particles [3]. Problems that are unique to the analysis of particles include the collection of appropriate background images and increased noise due to backscattered electron emission from the mounting substrate [3, 4], and result in a loss of pattern quality. The maximum spatial resolution for EBSD reported for bulk samples using field-emission gun SEMs ranges from 50 nm to 500 nm [2, 5], depending on the material, implying that particles with similar sizes can be identified by EBSD if the patterns are of sufficient quality.

To investigate minimum particle sizes, a sample of corundum was prepared from two commercial polishing compounds containing nanometer- to micrometer-sized particles. Particle size and crystallite size can be taken as synonymous in the discussion of EBSD, as single-crystal particles can be identified under the imaging conditions in the microscope. The sample was dispersed onto a pyrolytic carbon substrate, coated lightly with carbon, and analyzed using a Hitachi S-4500 field emission SEM equipped with a NORAN 32 bit Phase ID System optimized for a beam energy of 20 keV. Particles that were 1 µm or larger routinely yielded EBSD patterns of sufficient quality to identify the crystalline phase, as shown in Figure 1 for a nominal 2 µm particle. Particles less than 1 µm in size were more difficult to analyze, and we did not obtain any useable patterns from particles less than approximately 0.5 µm in size. The poor quality of the patterns for the smaller particles was, in this instance, attributed to an increase in noise from the bulk substrate, and so the particles were dispersed onto a thin-film substrate. By employing thin-film rather than bulk substrates, we were able to analyze particles down to 150 nm in size.

At this time, 100 nm to 150 nm seems to be the approximate minimum size required for EBSD phase identification of particles. Two additional samples, quartz (Minusil®) and m-ZrO₂, that have average particle sizes less than 100 nm, were deposited onto the thin-film substrate and analyzed by EBSD. Although the particle size range included particles of approximately 100 nm, we were not able to obtain any useable EBSD patterns for either sample. This could be due to factors other than particle size, as EBSD is sensitive to any surface disturbance of the crystalline lattice, and there could be an amorphous component on the particle surface.

The quality of the EBSD data as given in Figure 1 is sufficient for an identification of corundum, given the additional constraints imposed by the composition. In general, the measurement of lattice constants by use of Kikuchi lines is limited to an uncertainty of approximately 5 % [6]. The error in the reduced cell volume from the simulation in Figure 1 is approximately 1 %, which is in agreement with the general capabilities of the technique. Although there has been considerable work in establishing uncertainties in measurements of angles between zone axes using EBSD [6, 7], calibration procedures for phase identification by EBSD are only starting to be developed, due to the novelty of the technique. Our system happens to have some unique geometrical constraints that induce a distortion in the pattern, which is compensated by the software and results in the noise feature seen in the top right corner of the EBSD pattern. Even after this correction, there are errors related to position in the image, as seen by the change across

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1 Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
the image in the degree of correspondence between the simulation and the observed pattern. Improvements in the quality of data obtained by EBSD are under development, including the use of High Order Laue Zone (HOLZ) rings for improved resolution of lattice constants [6, 8], and ab-initio cell calculations from EBSD patterns [8].

![Image of corundum particle (a) with corresponding EBSD pattern as collected (b) and with overlay of simulated corundum pattern (c). The simulation uses data from PDF card 10-0173 and an intensity cutoff of 11%.

Figure 1. SEM image of corundum particle (a) with corresponding EBSD pattern as collected (b) and with overlay of simulated corundum pattern (c). The simulation uses data from PDF card 10-0173 and an intensity cutoff of 11%.

**X-RAY MICRODIFFRACTION**

X-ray microdiffraction has the advantages over EBSD of mature data analysis (if the problems due to low crystallite number can be overcome) and greater precision in lattice parameter determination. X-ray microdiffraction depends on sampling a large number of crystallites, although the problem of low crystallite number can be ameliorated by using area detectors. Since x-ray microdiffraction is not a single crystal technique, it is more useful to discuss minimum detection limits in terms of mass, rather than particle size, as the particles must necessarily comprise many crystallites.

The same materials analyzed by EBSD (quartz, corundum, and $m$-ZrO$_2$) were prepared for x-ray microdiffraction by packing the loose powders into brass holders. The analysis was performed on a Rigaku microdiffractometer mounted on an 18 kW rotating anode using a total internal reflection collimator with a 10 μm exit diameter. The beam diameter was measured with an x-ray imager and found to be 10 μm ± 2 μm. The x-ray imager consists of a 5 μm thick Gd$_2$O$_2$S
phosphor layer on a magnifying inverse tapered fiber optic plate coupled to a CCD camera. The data were generated at 40 kV and 200 mA and collected for 1 hour on a position sensitive detector. All three materials produced diffraction patterns under these conditions that are representative of the given phase, with all peaks above a relative intensity of 5% easily discernable, and the relative intensities in general agreement with those for the ideal, random orientation case. The crystallite size of the three materials is small enough that a sufficient number of crystallites are contained within the sampling volume (Table 1), producing continuous Debye rings that can be adequately sampled by the linear detector. The continuity of the Debye rings was independently tested by collecting the data on a phosphor imaging plate.

The masses measured under the conditions stated above are calculated in Table 1, assuming the density of the pure phase. Clearly, in a packed powder the density will be less than that for the pure phase, but the calculation is a reasonable approximation. The estimated masses are quite small, much smaller than the cited limits of 10 µg from early microdiffraction experiments [9]. In order to investigate the possibility of analyzing deposits thinner than the estimated beam penetration, the EBSD preparations on the thin-film substrates were analyzed. The loadings on some areas of the preparations were sufficient to form coherent masses at least 10 µm wide, but the thicknesses could not have exceeded approximately 20 µm. Under these conditions we were able to get a diffraction pattern for the quartz sample that contained only the two most intense peaks, but were unable to get any useable patterns from the corundum or m-ZrO₂ samples. Assuming a depth of 20 µm indicates that we were measuring approximately 0.4 ng of quartz. We also analyzed a sample of a 300 nm thick BaTiO₃ (BT) film on MgO, and were able to obtain a diffraction pattern containing the (002)/(200) BT reflection. In this case the estimated mass is 0.1 ng (Table 1), but our ability to detect the phase was enhanced by the preferred orientation of the crystallites. [EBSD analysis of the BT thin film was not possible, probably due to the small crystallite size.]

Table 1. Calculated mass and crystallite number available for x-ray diffraction assuming a 10 µm wide cylindrical beam and 100 nm wide spherical crystallites.

<table>
<thead>
<tr>
<th>Phase</th>
<th>density, g/cm³</th>
<th>beam penetration†, µm</th>
<th>mass, ng</th>
<th># of crystallites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>2.65</td>
<td>210</td>
<td>43.8</td>
<td>3.15 x 10⁷</td>
</tr>
<tr>
<td>Corundum</td>
<td>3.987</td>
<td>159</td>
<td>49.7</td>
<td>2.38 x 10⁷</td>
</tr>
<tr>
<td>m-ZrO₂</td>
<td>6.031</td>
<td>33</td>
<td>15.4</td>
<td>4.88 x 10⁶</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>6.012</td>
<td>0.3</td>
<td>0.1</td>
<td>4.50 x 10⁴</td>
</tr>
</tbody>
</table>

†Calculated as 2(1/µ) where µ is the linear attenuation coefficient calculated for Cu Kα using the NIST XCOM database [10] and the density of the pure phase.
‡Taken as the thickness of the film.

APPLICATION TO (ZR,Y)O₂-x THERMAL BARRIER COATINGS
A sample of plasma-sprayed (Zr,Y)O₂-x was analyzed by electron microprobe compositional mapping and found to contain discrete 10 µm wide areas that have much lower Y₂O₃ concentrations than the bulk material. Such low stabilizer compositions would normally be attributed to the monoclinic phase, but m-(Zr,Y)O₂-x was not detected above trace levels in the
bulk material using x-ray or neutron diffraction. The bulk diffraction patterns were analyzed using Rietveld refinement and indicated the presence of both the tetragonal and cubic phases [11].

To resolve this discrepancy, x-ray microdiffraction and EBSD were applied to determine the phase composition of the low Y$_2$O$_3$ areas. Although EBSD patterns were obtained from areas of higher Y$_2$O$_3$ content, none could be obtained from the areas of interest. It is unclear whether the inability to obtain EBSD patterns from the low Y$_2$O$_3$ areas relates to crystallite size, or is perhaps a result of some surface imperfection. For the EBSD patterns that were collected, it was not possible to distinguish between the tetragonal and cubic phases, as there is, at most, a 2% difference in the $a$ dimension. In the case of x-ray microdiffraction, however, the analysis of the low Y$_2$O$_3$ areas yielded a tetragonal pattern (Figure 2) although there could be some cubic phase in addition to the tetragonal phase. The monoclinic phase is not present above detection limits (≈ 0.01 mass fraction) in the low Y$_2$O$_3$ areas. The collection depth for microdiffraction is much larger than the 1 µm depth represented by the electron microprobe data (Table 1), which is an issue we will be addressing in the future.

CONCLUSIONS
EBSD and x-ray microdiffraction are both useful techniques for phase identification of small areas or particles. EBSD has advantages in phase identification of small particles if the crystallite size is 100 nm or larger. X-ray microdiffraction is useful when the crystallite size is less than 100 nm, and when the lattice constants must be measured precisely.

![Figure 2](image)

Figure 2. X-ray microdiffraction pattern of 10 µm wide low-yttria area of plasma-sprayed (Zr,Y)O$_{2-x}$ sample. Reference patterns of t- (top) and m- (bottom) (Zr,Y)O$_{2-x}$ from PDF database.
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REFERENCES