The Preparation of Mg, Cd and Zn Samples for Crystal Orientation Mapping with BKD in an SEM

R.A. Schwarzer

Institute of Physics, Clausthal University of Technology
Clausthal-Zellerfeld, Germany
schwarzer@tu-clausthal.de

Backscatter Kikuchi Diffraction (BKD) from crystalline solids has been known since 1928 [1]. But only during the last decade, when sufficiently sensitive cameras, fast PCs and high-performance SEMs have been available, has this technique been developed into an invaluable tool for materials' science and geology. BKD is also known as "*E*lectron *B*ackscatter *D*iffraction" (EBSD) if referred to the commercial trademarked systems OXFORD/HKL "Channel" or EDAX-TSL "OIM". Crystal Orientation Measurement/Mapping (COM), without user intervention, is performed in an SEM by digitally scanning the beam spot across the specimen, acquiring and transferring one Backscatter Kikuchi Pattern (BKP) after another into the computer, indexing it, and calculating the crystal orientation of the grain under the beam spot [2]. The sample is typically tilted by 70° towards a phosphor screen for pattern collection. Spatial resolution is in the range of <0.05 µm and accuracy is better than 0.5°. The speed of on-line measurement is between 30,0000 and 200,000 orientations per hour, depending on the hardware. Close to 2 million BKP can be acquired per hour with a GigE CCD detector NORDIF 500UF [3], but these patterns have to be indexed off-line. If intragranular structure is of no concern, it is sufficient to acquire the orientation of each grain only once, and then apply an iterative mesh refinement procedure [4]. This has proven to be a very effective means to concentrate measurements near grain boundaries and triple points. Mesh refinement is inadequate if the microstructure contains twinned grains or if a broad grain size distribution is present. The study of crystallography and microstructure of polycrystals has never been so easy and efficient.

The principal objectives of COM are: a quantitative description of the microstructure of selected areas on *bulk surfaces,* on a grain-specific level; the determination of quantitative, statistically-significant data sets of crystal orientations; misorientations; the CSL character (Σ) of grain boundaries; local crystal texture (pole figures, ODF, MODF, OCF) and derived entities; and phase discrimination and identification. Additionally, the crystallographic direction of the grain boundary normal ***n*** can be determined by measuring the spatial inclination of the grain boundary plane, *e.g.* by serial sectioning, ion beam slope cutting or FIB milling.

Grain orientations are commonly depicted in pseudo-colors on the scanning grid to form *C*rystal *O*rientation *M*aps, which represent "images" of the microstructure with the advantage of providing quantitative orientation contrast. In a similar way, misorientations across grain boundaries, the Σ values of grain boundaries, or other microstructural characteristics and derived entities are visualized by staining the grains in the micrograph with specific colors. The *P*attern *Q*uality (PQ) reflects the perfection of the crystal lattice in the diffracting volume and is thus a measure of dislocation density and lattice strain.

Magnesium and its alloys have been of interest to material scientists for more than 70 years [5]. They are the lightest commonly used structural metals with the highest mechanical strength to weight ratio and thus have a great potential for substantial weight reduction of manufactured components. Further advantages are: abundant availability from minerals and sea salt, low casting costs, excellent machinability, good damping characteristics, and electromagnetic shielding properties. Drawbacks of magnesium based alloys are: a low resistance to corrosion, creep and notch effects on fatigue life, a very limited ductility and in particular a highly directional anisotropy—which means that they present a severe impediment to cold forming and to the manufacture of structural components. Therefore, the knowledge and optimization of crystal texture on a grain-specific level is of great technical concern. However, sample preparation for BKD is said to be difficult, because plastic deformation artifacts have to be avoided and a clean surface is required. Similar difficulties occur with Cd and Zn. BKD is a surface sensitive technique since the patterns are formed from the top 100 nm of the sample surface.

Sample preparation by CMP

Some hexagonal base alloys are soft and easily undergo plastic deformation by twinning. Therefore, excessive pressure during sectioning, embedding and grinding may alter the true microstructure. The samples are cold-mounted in Lucite resin, ground on SiC abrasive paper with water lubricant in a sequence from 400 down to 1200 mesh using standard metallographic techniques, followed by a mechanical polishing of the samples to a mirror-like flat with diamond paste from 3 µm to 0.25 µm or with an alumina suspension. Between each step, the samples have to be cleaned carefully in an ultrasonic bath.

For final chemical polishing and etching we have tried various solutions, depending on the alloy and degree of deformation, for example, mixtures of:

a. nitric acid in methanol (volume ratio 1:50)
b. nitric acid and hydrochloric acid in methanol (volume ratios between 2:1:7 and 1:2:7)
c. nitric acid, acetic acid, ethanol and ethyl glycol (volume ratios about 1:10:10:30)
d. acetic acid and picric acid in ethanol (volume ratios about 1:1:10).

As well as electrochemical polishing in:

e. nitric acid in methanol (volume ratio 1:2)
f. perchloric acid in ethanol (volume ratios from 1:9 to 1:5)

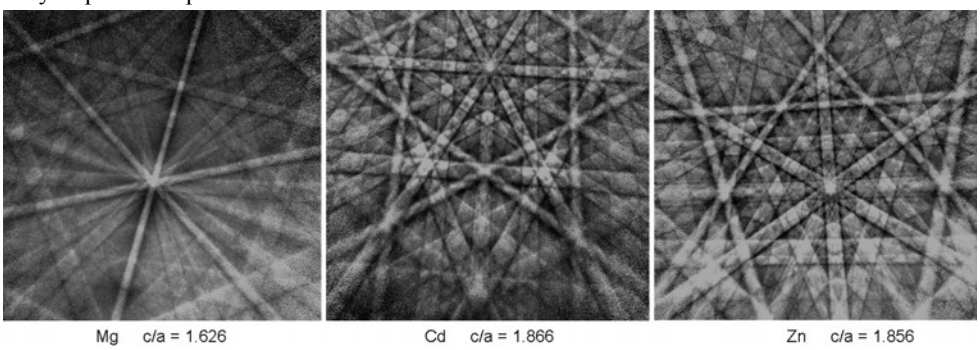

Fig. 1 Backscatter Kikuchi patterns from a CPM polished (a) Mg, (b) Cd, and (c) Zn sample.

g. perchloric acid, butyl cellusolve, water and ethanol (volume ratio 1:2:2:10).

The addition of butyl cellusolve to the mixtures and cooling the polishing baths often helps smooth the surfaces. Immediately after the polishing processes, the samples were rinsed several times in ethanol and then dried in a stream of warm air. Although the surfaces seemed to have an excellent mirror-like finish in the optical and in the scanning electron microscope, the results with BKD were disappointing. The patterns were diffuse, or even in worst cases, no patterns were seen at all. The raster spots where the primary beam had hit the surface turned bright in imaging mode. A thin residue layer had obviously formed during or after final polishing. We supposed traces of water or humid air to be the "malefactor".

So we worked out a simple finishing technique, which excludes the effect of water. The embedded samples were subjected to a conventional final mechanical polishing to a flat with a slurry of alumina in soapy water, or with diamond paste, down to 0.25 µrn as described above. It is advantageous to use vibration polishing for about one or two hours with a few ml of 1% nitric acid in methanol added to the polishing suspension for the last 10 minutes. The samples were then cleaned in an ultrasonic bath, rinsed with ethanol and placed over night on a heater plate or the central heating of the laboratory at about 50 °C. We are aware that a thin oxide or hydroxide layer will form on the polished surface using this protocol.

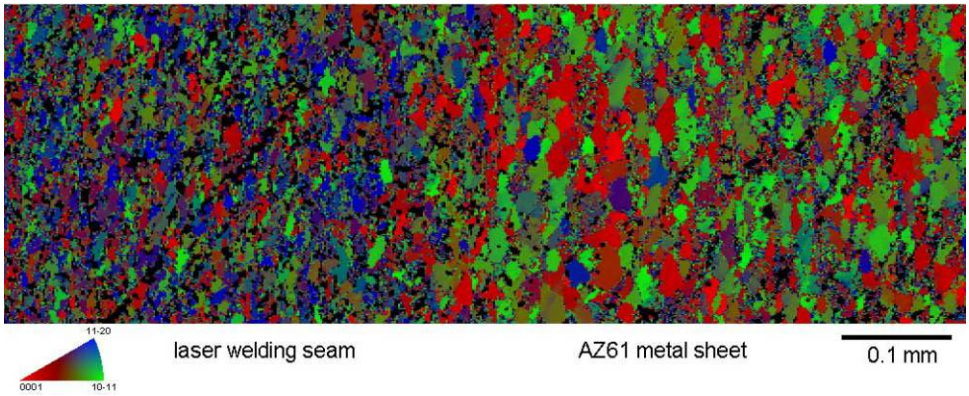

Fig. 2 Crystal orientation map of a laser welding seam in an AZ61 sheet metal.

The trick is now to remove this layer right before the sample is placed in the SEM for orientation measurement. For this purpose, the sample is subjected to a short Chemical-Mechanical Polishing (CMP) operation on a rotating disk @ 150 rpm using a diamond cloth that had been wetted with about 10 ml *of afresh* mixture of 0.5 % concentrated nitric acid in *dehydrated methanol.* No diamond paste needs to be added. The specimen, gently pressed on the cloth, is slowly moved counterclockwise at a speed of 1 cycle per second against the rotation of the disk. About 5 to 10 seconds of polish are sufficient. In the beginning, the surface may turn yellowish brown, in that case, CMP has to be continued until this color has disappeared. If the sample is etched too much, the final steps of mechanical polishing, including dry-storing the sample and CMP, have to be repeated. Directly after CMP, the samples are rinsed several times in dehydrated methanol, dried in a stream of warm air and immediately placed in the SEM. In general, wide areas of the sample will produce excellent patterns. If this is not the case, a short sequence of CMP can be repeated.

It is worth noting that this technique works well *only* with dehydrated methanol—not with ethanol, which usually contains about 5 % water. If the methanol in the lab is not dry, Mg shavings can be added to the stock bottle. It is not wise, in any case, to use ethanol for the electrolyte because the mixture with a few percent of concentrated nitric acid may explode.

Fig. 1 shows typical backscatter Kikuchi patterns from Cd, Mg and Zn samples that have been prepared with the CMP process described above. The patterns have been collected with a video CCD camera WATEC 902H at 20 kV on a JEOL JSM 6400 SEM. Extended sample areas can be investigated as is demonstrated by the crystal orientation map of a laser-welding joint in a MgAl6Zn1 (AZ61) metal sheet (Fig. 2). As a rule, digital beam scans in z larger than 0.5 mm should not be done without the three dynamic operations of the BKD system (calibration, focus and background correction) individually performed at every raster point [2,4]. These dynamic control operations are implemented in advanced BKD systems. It is strongly suggested to always perform these corrections at every data collection point to obtain reliable results. If PQ is calculated from the height or slope of some Hough peaks using a simple algorithm, the index may be affected by the dynamic background correction. Hence, determination of PQ from a ID FFT of Radon peaks is superior [6]. A fixed focus, static value for the pattern center, and only one flat background determined at the pattern center during system setup and applied at all raster points are insufficient.

The pseudo-colors of the COM in Fig. 2 indicate the crystallographic directions perpendicular to the sheet plane. The orientation data have not been filtered. Dark spots are pixels where indexing had not been possible due to heavy local deformation (along a polishing scratch forming a line of dark spots) or a second phase (isolated dark spots at segregations of $Mg_{17}Al_{12}$). These β particle inclusions are considerably harder than the AZ61 alloy matrix. They tend to jut out of the flat after CMP and cast shadows on the steeply tilted surface in the SEM. ■

References

[1] S. Nishikawa and T. Kikuchi: The diffraction of cathode rays by calcite. *Proc. Imperial Academy (of Japan)* **4** (1928) 475-477.

[2] R.A. Schwarzer: Automated crystal lattice orientation mapping using a computer-controlled SEM. *Micron* **28** (1997) 249-265.

[3] J. Hjelen, private communication

[4] R.A. Schwarzer: Advances in the analysis of textures and microstructures. *Archives of Metallography and Materials* **50** (2005) 7-20.

[5] A. Beck: *Magnesium und Magnesiumlegierungen.* Springer-Verlag 1939 (reprint by Springer Heidelberg, 2nd edition, 2001. Reihe Klassiker der Technik). A. Beck: *The Technology of Magnesium and Its Alloys.* Kynock Press London 1943

[6] R.A. Schwarzer and J. Sukkau: Automated evaluation of Kikuchi patterns by means of Radon and Fast Fourier Transformations, and verification by artificial neural networks. *Advanced Engineering Materials* **5** (2003) 601-606.