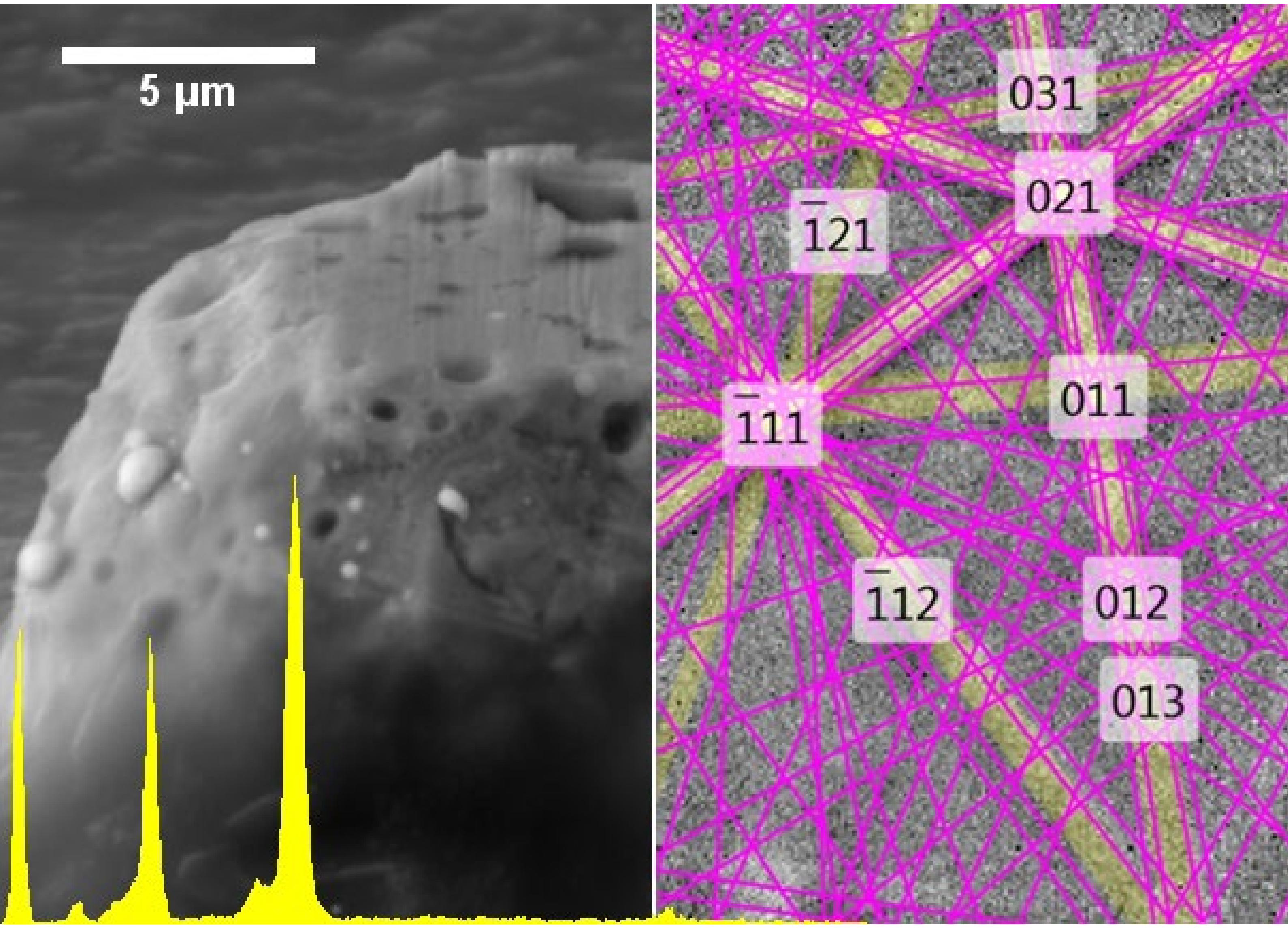

Improved Gun Shot Residual Analysis

Using FIB and EBSD

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Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are well established techniques for the classification of gunshot residue (GSR) in forensic examinations. However, they are often not sufficient to clearly distinguish between GSR and environmental particles. Combining SEM and EDS with focused ion beam (FIB) and electron backscatter diffraction (EBSD) analysis, ZEISS Crossbeam instruments can provide more accurate and reliable GSR characterization.

Gunshot residue analysis

GSR particles originate from partially reacted components of explosive primer and propellant, as well as from the metallic components of the ammunition and the firearm. GSR may be found on the skin, hair or clothing of the person who fired the gun, on an entrance wound of the victim, or on other persons and objects at the scene. It can be very helpful in connecting the firearm to the culprit, and may help in eliminating the probabilities when there are more than one suspect.

GSR particles range in size from sub-micrometer to several hundred micrometers. They are collected in the field directly on sample mounts with adhesive coating, or on adhesive tape. For their identification mainly the elemental primer components in the particles are used [1]. There are several classes of primers with different compositions that can be retrieved in the GSR particles. Primers based on the Sinoxid formulation mainly contain Pb, Sb, and Ba, but can as well contain small amounts of S, Si, or Ca. Heavy metal free primers known as Sintox contain Ti and Zn. Some ammunitions manufactured for use by police are tagged with specific elements, such as Gd.

Typically, the particles are classified as characteristic of GSR if their composition is rarely found in particles from any other source, or as indicative for GSR if their composition can also be found in particles from a number of common non-firearm sources, such as starter pistols, signal guns and flares, cartridge-operated nail guns, and vehicle air bags. Furthermore, they can be classified as environmental if they have a composition similar to GSR but do not fit into one of the two former groups.

For the examination and analysis of GSR, the combination of SEM and EDS has been widely accepted as the optimum technique. It allows to identify very small amounts of evidence with a high level of confidence by analyzing surface morphology and composition of individual GSR particles [2]. Automated EDS systems have been developed for rapid and effective GSR particle detection and classification. They automatically search the sample surface for particles of interest using the backscattered electron (BSE) contrast, then automatically analyse and classify particles according to their morphology and chemistry. Using a FIB additionally allows to cross-section individual particles to analyse their subsurface morphology [3].

Since the 1980s, the composition of many ammunitions has been changed. Heavy metals have been avoided to comply with environmental standards, and stabilizers and plasticizers have been added during the manufacturing process for safety reasons. Thus, it has become more difficult to classify particles and the reliability of GSR analysis by SEM and EDS has decreased. This has raised the need for advanced techniques to obtain more detailed subsurface structural and compositional information from the GSR particles to avoid producing false positive or false negative results. For instance, Ti and Zn oxides in Sintox particles are not specific and can also appear in environmental particles. Examining their crystalline properties is essential for identification as GSR.

Solution

Crossbeam instruments allow in-situ analysis of the internal crystalline microstructure of GSR particles by EBSD. Complementing EDS by this powerful analytical technique results in accurate phase characterization by combining chemical and crystallographic information. EBSD analysis probes a shallow region a few ten nanometers below the surface only. Therefore, it cannot be applied to entire GSR particles. Cross-sectioning them with the FIB of the ZEISS Crossbeam, however, exposes their internal structure and allows EBSD analysis with high lateral resolution.

The first two steps of such a combined analysis process are identical to conventional, automated SEM-EDS analysis. GSR particles are identified using the backscattered electron image, then analysed by EDS and classified according to elemental composition criteria. Particles requiring FIB cutting with subsequent cross-sectional EDS and EBSD analysis can then be identified in the classification list by the operator and relocated using their stored stage coordinates.

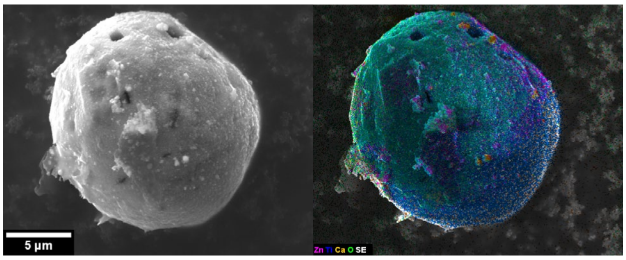

Figure 1. *SE micrograph of a particle (left) from a test shot sample collected. Same image with superimposed EDS map (right) that is consistent with Sintox primer.*

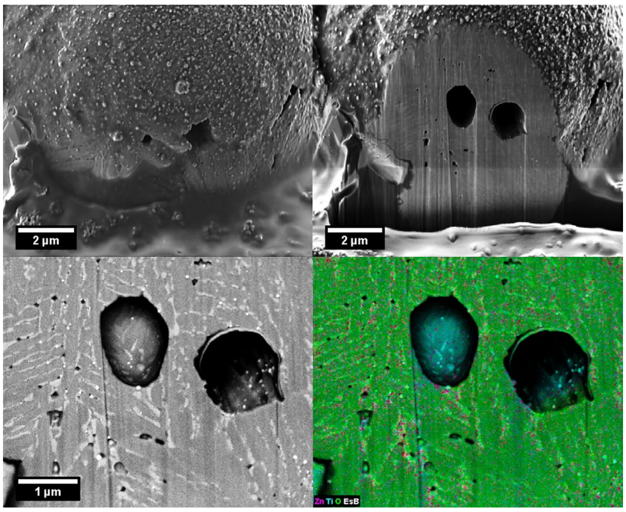

Figure 2. *SE micrograph of the particle shown in Figure 1 before (top left) and after (top right) FIB cross-sectioning. Detail SE micrograph of the cross-section (bottom left), and same image with superimposed EDS map (bottom right). While indicative for gunshot provenience, environmental origin cannot be excluded.*

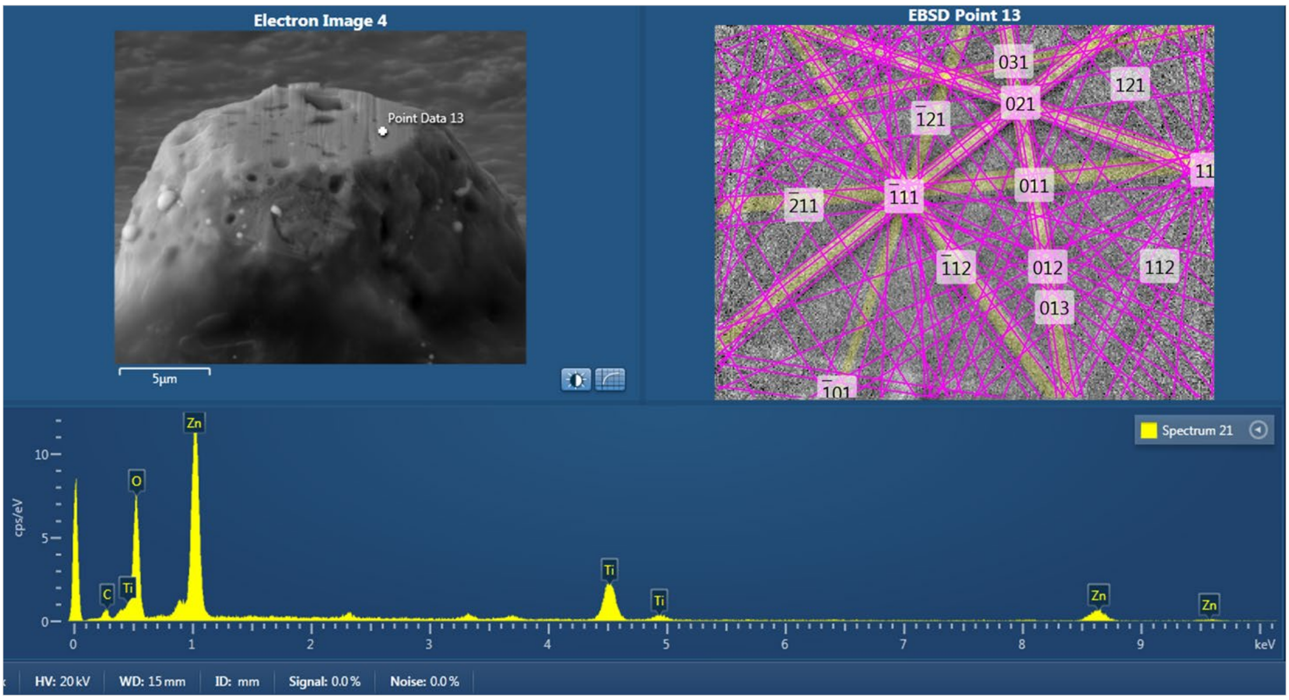

Figure 3. *Another particle from the same sample after FIB cross-sectioning (top left) with simultaneous EBSD (top right) and EDS (bottom) point analysis.*

For the EBSD analysis, diffraction patterns formed by electrons backscattered from crystalline material are recorded with a dedicated detector that consists of a scintillator screen, a CCD camera and coupling optics. Characteristic dark and bright line pairs in the recorded patterns, so-called Kikuchi bands, relate to phase and orientation of the underlying crystal [4]. 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.

Application example

For the following application example, an Oxford Instruments X-Max80 EDS detector with x-stream2 pulse processor and INCAGSR analysis software was used. The EBSD detector used was a NordlysNano. The samples originated from test shots done at the German Federal Office of Criminal Investigation (Bundeskriminalamt) and the State Office of Criminal Investigation (Landeskriminalamt) Düsseldorf, Germany. The particles were collected by picking up GSR residual with adhesive carbon tabs on aluminum SEM stubs without further preparation.

The conventional EDS analysis of a whole particle from this sample shown in Figure 1 indicates the presence of Zn, Ti, O, and some Ca. Although this is indicative for Sintox primer, it is not sufficient to exclude an environmental origin of the particle without further information on the internal morphology of the particle. After FIB cross-sectioning the particle perpendicular to the substrate, SEM reveals its inner structure and EDS shows the internal distribution of chemical elements (Figure 2). Presumably Ti and Zn oxides are present, but this imprecise information is still not sufficient to unequivocally assign this sample to a gunshot or environmental source. The presence of amorphous $Zn_2Ti_3O_8$ would point to an environmental particle. Crystalline $TiZn_2O_4$ in spinel phase, however, would unambiguously identify the particle as resulting from a gunshot, as this phase will only form under the high temperature and pressure conditions present in a firearm discharge.

Figure 3 shows another particle from the same sample. Its top portion was milled away almost parallel to the substrate surface, which allows simultaneous EDS and EBSD analysis after tilting the sample to a high angle.

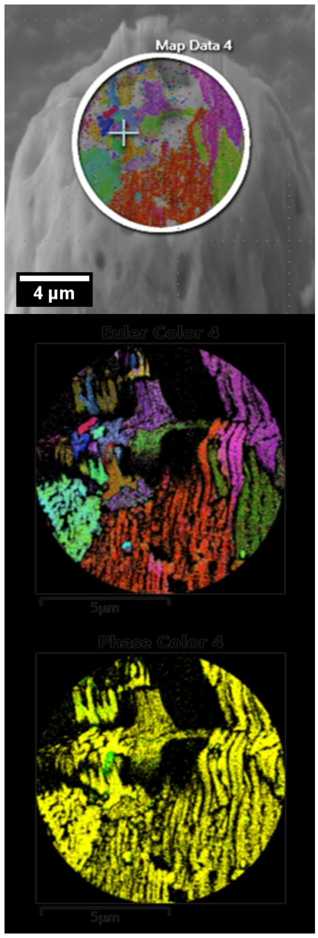

Figure 4. EBSD grain orientation (middle) and phase map (bottom) from the FIB cross-section (top) of the particle shown in Figure 3.

A Ti, Zn and O-rich spot was identified using EDS point measurements. EBSD analysis was performed at the same spot to verify if the material was crystalline and if so, to identify its crystalline phase (spinel, cubic or tetragonal). It was found to be crystalline and spinel was identified as the most probable phase.

In order to obtain information from a larger part of the cross-section, grain orientation and phase maps were produced by recording and processing EBSD patterns while scanning the electron beam over the sample. The results are shown in Figure 4. For the most part, the cross-section exhibits the same spinel phase with different orientations of the grains. Thus, the particle could be classified as originating from a gunshot with ammunition using Sintox primer.

Conclusion

Complementing SEM and EDS with FIB and the powerful analytical technique of EBSD in a Crossbeam enables complete forensic characterization of GSR particles. With new data on their internal crystalline properties available, better insight in their genesis is provided. The application example presented here showed that spinel phase of Ti-Zn-oxides could be identified to discern GSR from environmental particles.

This method can be extended to other types of GSR, e.g., from specifically tagged ammunition. In this case, unequivocal identification by SEM and EDS is not straightforward, as the EDS signal of the tracer element is often weak.
As crystalline species are usually not found in such GSR particles, EBSD can exclude the absence of typical crystalline phases and increase the reliability of tagged ammunition identification.

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