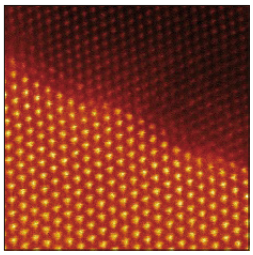

A New Analysis Technique for Polycrystalline Grain Boundaries Combining STEM and EBSD

Koji KURAMOCHI*, Takashi SEKIYA, and Hirofumi YAMAMOTO

Scanning transmission electron microscopy (STEM), characterized by its high spatial resolution, is a indispensable tool for atomic-level structural analysis of crystalline materials. Particularly in polycrystalline materials such as metals and ceramics, grain boundaries often determine material properties. However, due to the randomness of grain orientations, efficient extraction of grain pairs for grain boundary analysis has been a challenge. In response, we have developed a new technique for crystal orientation analysis using electron backscatter diffraction (EBSD). By applying two types of EBSD methods, reflective and transmission, to sintered tungsten carbide (WC) and cobalt (Co), we confirmed that transmission EBSD can find suitable grain pairs with practical throughput. In addition, STEM analysis successfully detected step structures and Co segregation at WC grain boundaries. The integration of STEM and EBSD analysis developed in this study presents a highly effective approach to structural analysis of polycrystalline grain boundaries for material property improvement.

Keywords: grain boundary, STEM, EBSD, cemented carbide

1. Introduction

Scanning transmission elecctron microscopy (STEM) has been widely used for structural analysis of various crystalline materials, due to the recent progress of spherical aberration correction technology*1 that has significantly improved spatial resolution. For example, in semiconductor devices, epitaxially grown single crystals with different compositions such as InGaAs/InP are often used. In the evaluation of compositional steepness at the crystal interface, which affects device characteristics, STEM is an indispensable tool.(1) On the other hand, in the case of polycrystalline materials including metals and ceramics, crystal grains of the same or different species are bonded to each other in a random orientation. Crystal orientation, compositional change, segregation of specific elements, and flatness at the grain boundary are thought to affect material properties significantly. In order to improve these properties, analytical technologies that can precisely evaluate these "grain boundary structures" are of fundamental importance.

Generally, in STEM-based grain boundary structure analysis, electron beams are irradiated onto two crystal grains across the grain boundary, to project a sequence of atoms and to observe their periodic alignment. The observation procedure requires starting from the crystal zone axis. In ordinary polycrystals, however, there is no correlation between the orientations of the two neighboring grains and it is often impossible to observe both grains simultaneously from the zone axis. For example, Fig. 1 shows a high angle annular dark field (HAADF) STEM image*2 obtained from the grain boundary of a tungsten carbide (WC) sample. In Fig. 1 (b), the lower grain was successfully observed from the [01-10] orientation and the arrangement of W atoms are visualized as periodic white dots. On the other hand, observation of the upper grain from the zone axis was so difficult that the atomic arrangement could not be confirmed. As a result, no detailed structural analysis was carried out for the grain boundary.

Due to the aforementioned problems, in many studies in the past, so-called "bicrystal"*3 samples with adjusted crystal orientation were prepared, to analyze structure of a model grain boundary.(2),(3) However, in industrial material development, analyzing model samples is of no use. To obtain knowledge that leads to improvement in product properties, analytical data on a variety of interfacial structures from a number of prototypes are required, whereas using STEM to discover grain pairs with appropriate orientations from among a large number of grain boundaries is not practical from the viewpoint of throughput.

To address the issue described above, we focused on electron backscattered diffraction (EBSD), which can analyze the orientations of all crystalline grains in a probing area with a single measurement. By combining EBSD with STEM, we aimed to establish a technique to analyze the grain boundary structure of polycrystalline materials with high precision and efficiency. The newly developed technique was applied to a cemented carbide material for a cutting tool, which is one of our main products.

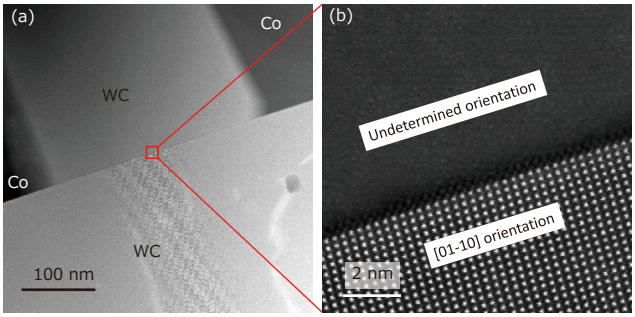

Fig. 1. Example of HAADF STEM image of WC crystal
(a) 500,000 times (b) 20 million times

2. About EBSD

EBSD is one of the functions incorporated in scanning electron microscopes (SEM). In an EBSD analysis, a few nanometer-sized electron beam is irradiated onto a crystal sample. Then, the diffraction pattern from each crystal grain is detected to determine its orientation. EBSD can be classified into two methods, reflection and transmission, depending on the arrangement of the electron beam, sample, and detector, as shown in Fig. 2. In the reflection method, an electron beam is irradiated onto a sample and electrons reflected at the sample surface are detected. In the transmission method, it is necessary to thin the sample in advance so that the transmitting electrons can be detected.[4] In both methods, diffraction patterns from crystals known as Kikuchi bands*4 are utilized to determine the crystal orientations. The reflection method, which needs no thinning process, is more widely used than the transmission method. However, the transmission method can suppress the spread of electron beams within the sample, as shown in Fig. 2 (b). This results in a very high spatial resolution of about 20 nm, compared to the approximately 100 nm that is achievable with the reflection method.

In this study, we attempted to establish a technique to efficiently extract grain boundaries with an appropriate orientation relationship to be analyzed by STEM. We examined which of the two methods described above could extract the grain boundaries more efficiently.

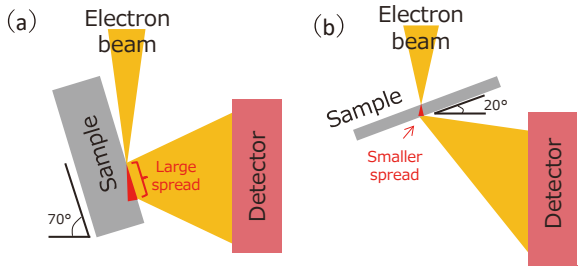

Fig. 2. Schematic diagram of (a) reflection EBSD and (b) transmission EBSD

2-1 Comparison of reflection EBSD and transmission EBSD

Figure 3 shows the analysis flows of grain boundaries. Although both EBSD methods start with pre-processing of the samples, the transmission method requires more time due to the thinning process, as mentioned above. However, to perform a STEM analysis, the reflection method also requires an additional thinning process using focused ion beam (FIB). Furthermore, the FIB thinning should be done for each grain boundary. This means that the number of thinning processes increases as the number of grain boundaries to be analyzed increases. In terms of process steps, the transmission method is more efficient than the reflection one. On the other hand, the reflection method has a wide probing area and can extract many grain boundaries compared to the transmission method, which can analyze only a limited part of the thinned sample (less than 50 nm thick).

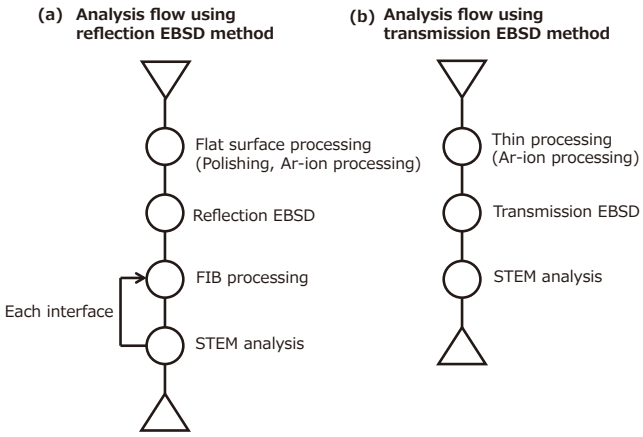

Fig. 3. Comparison of analytical flow using reflection/transmission EBSD

Regarding spatial resolution, the transmission method is suitable for analyzing fine crystalline materials. In the case of coarse crystalline materials, the reflection method is considered superior.

In this study, cemented carbide or sintered alloy of WC and cobalt (Co) was prepared as the target of analysis. The main component is WC, the average grain size of which is approximately 500 nm. The grain boundary of WC was analyzed by both the reflection and transmission methods, in order to confirm which one is more efficient.

2-2 Analysis by reflection EBSD

For analysis of reflection EBSD, the sintered WC-Co sample was first mechanically polished. Then, the surface was planarized by Ar ion polishing, using a “Cross Section Polisher” from JEOL, Ltd. In the EBSD analysis, an SEM (GeminiSEM450) from Carl Zeiss Co., Ltd. and a “Symmetry” detector from Oxford Instruments plc. were employed. Measurements were performed at an acceleration voltage of 15 kV and an area of approximately 120 μm square was scanned with 100 nm steps.

The obtained diffraction patterns were analyzed using Oxford Instruments plc’s “AZtecCrystal Version 3.1” analysis software and crystal orientation data for approximately 40,000 WC grains were successfully obtained.

For STEM analysis of the grain boundary structure, the orientation deviation of adjacent grains must be within 1°. However, the orientations of the neighboring grains do not necessarily have to be the same. For example, <01-10>//<0001> are available. Although various combinations of crystal orientations are possible, we chose three major orientations, <0001>, <01-10>, and <11-20>, with which it is relatively easy to confirm atomic arrangement in STEM observation. The orientations of 40,000 crystal grains were analyzed and grain boundaries where any of the above three orientations were aligned within 1° were found within the data. As a result, five grain boundaries were extracted.

Figure 4 (a) shows an inverse pole figure map, which represents the color-coded orientation of each crystal grain obtained by reflection EBSD. Figure 4 (b) is an enlarged view of one of the five extracted grain boundaries and the corresponding SEM image. The extracted grain boundaries are indicated by yellow arrows.

In addition, in order to observe the grain boundary by STEM, a cross-sectional thinning sample was prepared by FIB using a "Quanta 3D" (QuantStudio 3D Digital PCR System) from Thermo Fisher Scientific, Inc. The acceleration voltage was 30 kV at first and lowered to 8 kV for the final treatment to remove the damaged surface layer. STEM observations were performed using "GRAND ARM2" (JEM-ARM300F2) from JEOL Ltd. at an acceleration voltage of 200kV. The results are shown in Fig. 4 (c). The position of the grain boundary is indicated by the black line in the figure. The upper and lower grains were observed from [11-20] and [0001] orientations, respectively. As a result, the atomic arrangement near the grain boundary was successfully visualized.

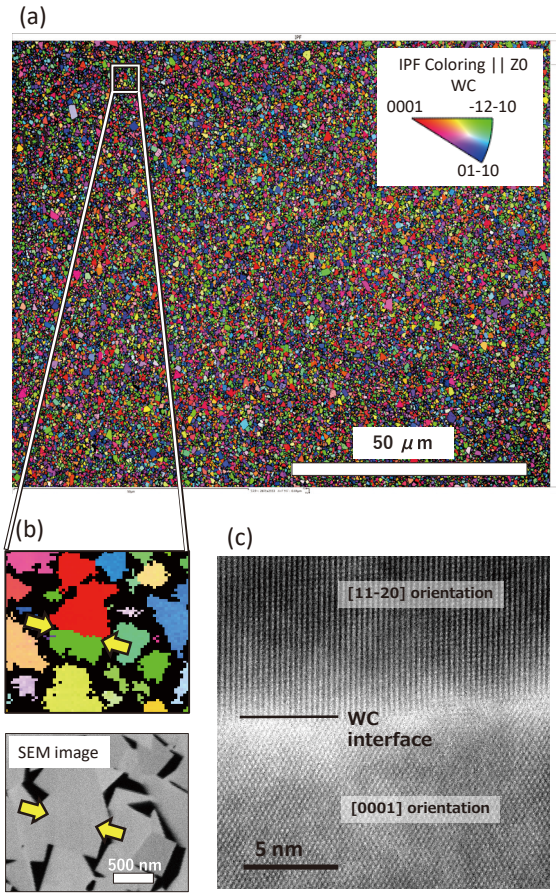

Fig. 4. (a) Cross-sectional EBSD measurements of WC-Co alloy (inverse pole figure map). (b) Partial enlargement of inverse pole figure and corresponding SEM image. (c) STEM image of the extracted grain boundary of WC.

2-3 Analysis by transmission EBSD

As already mentioned, transmission EBSD requires samples thinned to approximately 50 nm. Since the size of the field of view is limited to around 10 μm × 10 μm in the FIB process, we attempted to apply Ar ion which enables processing of a wider area. In this case, we utilized the "Ion Slicer" from JEOL Ltd. The process started at an acceleration voltage of 6 kV, and then the damaged layer was removed under a softer condition of 2 kV.

Figure 5 shows a wide-area SEM image of the sample processed as described above. The schematic cross-section corresponding to the yellow line in the SEM image is illustrated on the right side of the image. In this case, the cross-sectional shape was found to be a wedge with a pointed top. The results of transmission EBSD measurements conducted on the blue frame in the SEM image are shown at the bottom of Fig. 5. It was possible to obtain diffraction patterns by transmitting the electron beam through the wedge-shaped ultrathin region at the edge of the sample and the orientations were successfully analyzed. In a view area of approximately 150 μm × 5 μm, two analyzable grain boundaries, (1) and (2), were successfully extracted. The extraction conditions were the same as those used for the previously mentioned reflection EBSD, with an angular deviation of ±1° or less for adjacent grains in the three major orientations. This measurement was performed at an acceleration voltage of 30 kV.

Figure 6 shows the results of STEM observations of the two extracted grain boundaries, (1) and (2). Both of these were observed from the [01-10] and [0001] orientations across the grain boundary, but the bonding crystal planes were found to be different. As described thus far, the combined use of EBSD and STEM made it possible to analyze the grain boundary structure of polycrystalline materials.

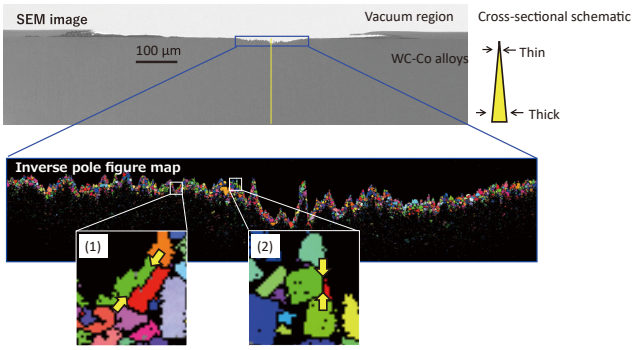

Fig. 5. Wide-area SEM image of the sample analyzed by transmission EBSD and the results of transmission EBSD measurement in the blue framed area (inverse pole figure map). Yellow arrows indicate the extracted grain boundary of WC.

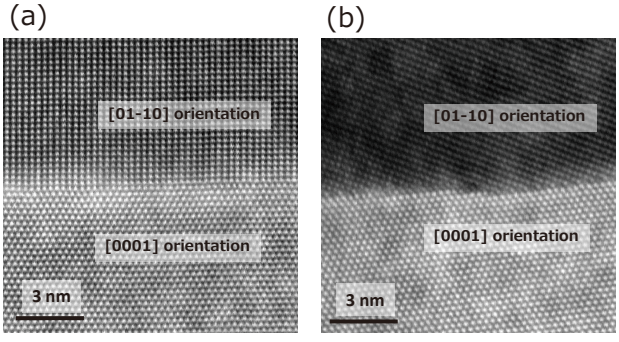

Fig. 6. (a) HAADF STEM image of the grain boundary of WC shown in (1) of Fig. 5. (b) HAADF STEM image of the grain boundary of WC shown in Fig. 5 (2).

2-4 Comparison of orientation analysis accuracy

Table 1 compares the results of crystal orientation analysis using the two EBSD methods. Although the measurement area and number of grains analyzed by the reflection method were 20 to 30 times larger than those by the transmission method, the number of extracted grain boundaries of the former was only about twice as large as the latter. Regarding the number of extracted grain boundaries per unit area, the transmission method realized one order of magnitude larger than the reflection method. This is attributed to the higher spatial resolution of transmission EBSD, which improves the accuracy of the analysis. Examining the results of the orientation analysis by reflection method in Fig. 4 (b), we can observe numerous black areas between the colored grains. These are the areas where orientation analysis was not possible at the grain boundary of WC and the areas of Co that appear black contrast in the SEM image. If an orientation analysis cannot be performed near the grain boundary, it is not included in the extraction of the grain boundary, which leads to numerous extraction omissions. Although the cleanup process is carried out to compensate for missing analysis data, the Co region is also forcefully supplemented, resulting in incorrect extraction, which requires confirmation by SEM observation to eliminate the incorrect extraction. This problem could be solved if orientation analysis could be applied to the Co region as well. However, this is very difficult because of the narrowness of the Co region in relation to the spatial resolution and the crystalline nature of Co.

Table 1. Comparison of grain boundary extraction results between reflection EBSD and transmission EBSD

	Reflection EBSD	Transmission EBSD
Measurement area	15,000 μm^2	750 μm^2
Number of grains	40,000	1,400
Number of extracted grain boundaries	5	2
Number of extracted grain boundaries per area	0.0003 [pcs/μm^2]	0.003 [pcs/μm^2]

In this study, transmission EBSD has been confirmed superior to the reflection method for the cemented carbide with an averaged WC grain size of about 500 nm, due to accuracy issues caused by spatial resolution. On the other hand, for coarse polycrystalline materials with an average grain size of 10 μm or so, the importance of spatial resolution decreases and its superiority is considered to be reversed.

3. Grain Boundary Structure Analysis by STEM

For the grain boundary shown in Fig. 6 (b), we carried out structural analysis in detail. Figure 7 (a) shows a high-resolution HAADF STEM image. Local observation of the grain boundary shows that the lower and upper crystal grains are bonded at the (10-10) and (10-12) planes, respectively, as indicated by the black dashed line. However, the presence of the steps indicated by the yellow arrows suggests that they are actually bonded by a higher-order crystal plane. In this case, the structure of the grain boundary has been visualized at the atomic level.

Figure 7 (b) is the result of energy dispersive X-ray spectroscopy (EDX)*5 at the grain boundary of the same sample. The position of the grain boundary is indicated by dashed lines. In the lower crystal grain, W is distributed at the position shown in white in the STEM image, while in the upper one, the distribution of W is unclear. This is because the orientation of the upper and lower crystal grains is slightly tilted, and the electron beam was irradiated along the orientation of the lower crystal during the analysis. If we can extract grain boundaries with better alignment in their orientations, it will be possible to analyze the distribution of W more clearly in both the upper and lower crystals. The present results were obtained using EBSD to extract grain boundaries with major orientation differences within ±1°, but it will be possible to select grain boundaries that can be observed more clearly if extraction conditions are made stricter. On the other hand, focusing on the elemental distribution at the grain boundary, it was found that Co segregated at the grain boundary with a thickness of only 0.5 nm.

The Co distribution is biased toward the upper side of the grain boundary indicated by the dashed yellow line, and the intensity of W detection decreases in the region where Co is distributed. The surface energy of WC is higher for the (10-12) plane than the (10-10) plane. Consequently, it can be inferred that the more unstable structure of the (10-12) plane is disturbed at the grain boundary, leading to the diffusion of Co, which results in a more stable structure.

Although we evaluated samples without additive elements in this study, we believe that analyzing the behavior of additive elements at the grain boundary in the future will provide useful information in interpreting the stability of the grain boundary structure and bond strength.

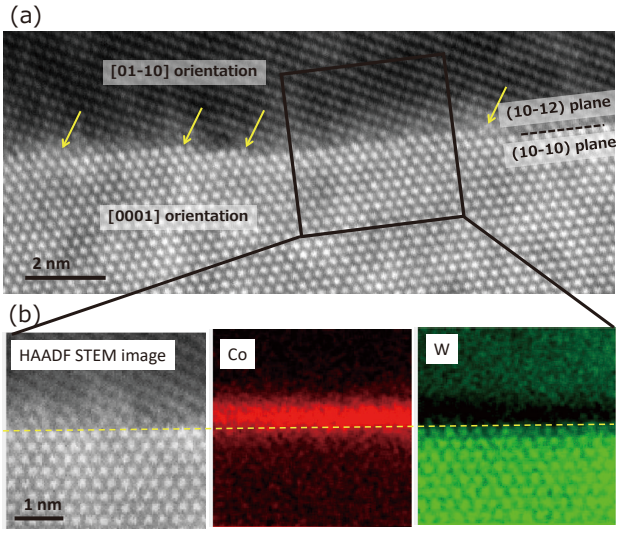

Fig. 7. (a) HAADF STEM image of the enlarged grain boundary of WC in Fig. 6 (b). (b) EDX mapping result of the black framed area in (a).

4. Conclusion

We have developed a new analysis technique for the grain boundary structures in polycrystalline materials, which greatly affect the material's properties. Using sintered WC-Co alloy samples for tools, two types of EBSD methods were applied to efficiently extract adjacent crystal grains with an orientation deviation of 1° or less from the numerous grain boundaries, which can be analyzed by STEM. Although the reflection EBSD method was found to be capable of analyzing the grain boundaries, it was demonstrated that its accuracy was not sufficiently high due to the low spatial resolution and that there were many omissions in the extraction of grain boundaries. On the other hand, transmission EBSD was confirmed to be more efficient in extracting the grain boundary with fewer omissions. Regarding the sample preparation for STEM analysis, reflection EBSD requires FIB processing for each grain boundary, which increases the process steps compared to transmission EBSD. However, for polycrystalline materials composed of coarser grains, reflection EBSD, which can analyze a larger area, is considered superior because the spatial resolution is less important. STEM analysis was also applied to the extracted grain boundary of WC, and it was confirmed that there is a step structure and that the position of Co precipitates at the locally identified WC(10-10)/WC(10-12) grain boundary is biased toward the (10-12) plane. Although the samples evaluated in this study did not contain any additive elements, analyzing the behavior of additive elements at the grain boundary in the future is expected to provide valuable insights into interpreting the stability of the grain boundary structure and bonding strength.

Technical Terms

∗1 Spherical aberration correction technology: Technology to correct spherical aberrations, which cause deviation from ideal image formation, in condenser lenses and magnetic field lenses in electron microscopes. By correcting spherical aberrations, atomic-level image observation and elemental analysis become possible.

∗2 HAADF STEM image: STEM image obtained by detecting high-angle scattered electrons with an annular detector. The contrast is proportional to the atomic weight.

∗3 Bicrystal: A crystal made by bonding two single crystals with different crystal orientations.

∗4 Kikuchi Band: A band-like diffraction pattern formed when incident electrons are inelastically scattered in a sample and then diffract on a crystal plane.

∗5 EDX: A method for elemental analysis done by detecting characteristic X-rays generated when a sample is irradiated with electron beams.

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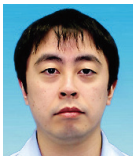

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