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A novel approach to measure grain boundary segregation in bulk polycrystalline materials in dependence of the boundaries' five rotational degrees of freedom

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We demonstrate a simplified nondestructive 3-D electron backscatter diffraction (EBSD) methodology that enables the measurement of all five degrees of freedom of grain boundaries (GBs) combined with segregation analysis using atom probe tomography (APT). The approach is based on two 2-D EBSD measurements on orthogonal surfaces at a sharp edge of the specimen followed by site-specific GB composition analysis using APT. An example of an asymmetric Σ9 boundary exhibiting GB segregation emphasizes the need for complete GB characterization in this context.

Keywords: Grain boundary crystallography; Electron backscatter diffraction; Atom probe tomography; Segregation

There is considerable evidence in the literature suggesting that the segregation of solute elements at grain boundaries (GBs) largely depends on the structure and character of these boundaries [1–5]. Historically, GBs have been broadly classified into two categories, namely coincidence site lattice (CSL) boundaries and random high-angle boundaries (HAGBs). More accurately a third category, referred to as vicinal boundaries, needs to be introduced, describing boundaries that deviate to a certain degree from perfect CSL boundaries [6]. CSL boundaries are often assumed to be more resistant to segregation compared to random HAGBs. Grain boundary engineering has been employed in the past to enhance the resistance of materials to segregation [7,8]. The majority of these studies are based on the objective of increasing the proportions of low Σ (Σ⩽29) CSL boundaries as these are often considered as low-energy "special boundaries" (SBs). This is, however, an over-simplification. A GB is crystallographically defined by five rotational degrees of freedom (DOFs). Three independent parameters are required to describe the misorientation between grains (e.g. two DOFs for the misorientation axis and one for the misorientation angle), while the remaining two independent parameters describe the orientation of the GB plane. Since the value of Σ represents only the mutual misorientation of two adjoining crystal lattices, it does not provide any information on the orientation of the GB plane and the degree of coherency in it. Due to these shortcomings, the CSL model fails in correctly classifying GBs (i.e. SBs or random) in many situations [9,10]. This emphasizes that the occurrence of a certain coincidence lattice is not a sufficient criterion for a GB to be special.

This means that the GB plane should also be considered along with the misorientation when defining a GB as "random" or "special". Consequently, the concept of "grain boundary plane engineering" has recently been suggested [11]. However, experimental data correlating the five-parameter GB character and properties (e.g. segregation) has rarely been reported. This is attributed to the fact that metallographic techniques often applied for the characterization of microstructures are on 2-D surfaces, which allows a maximum of four parameters to be determined, namely the misorientation (three parameters) and the trace vector of the boundary on the surface (one parameter). If a sufficiently large number of GBs in an equilibrated microstructure is studied, a stereological technique enables one to quantify the five-parameter grain boundary distribution from 2-D observations [12]. However, such measurement provides information about the statistical distributions of planes, but not for specific boundaries. Although it is possible to determine all five DOFs of a GB by employing 3-D electron backscatter diffraction (EBSD) [13,14] of serial

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sections, this method is destructive and hence cannot be utilized to study the properties of the investigated boundaries, e.g. composition, which requires the use of atom probe tomography (APT). One approach to determine all five DOFs of a GB while preserving its structure is to employ transmission electron microscopy (TEM) on an APT microtip [15]. However, determination of the complete crystallography of internal interfaces by TEM is generally a complex and tedious procedure. Recently, Baik et al. [16] have combined EBSD and focused ion beam (FIB) to characterize a GB's five DOFs and subsequently performed APT to determine GB composition. Alternatively, here we propose a "pseudo" 3-D EBSD approach for measuring all five DOFs of GBs while preserving the boundaries for subsequent APT analysis. The methodology is based on the 2-D EBSD measurement on two orthogonal surfaces of "sharp edge" rectangular specimens (Fig. 1a). The approximate areas of interest near the sharp edge "XY" are marked by the dotted red lines. On each of these two surfaces a trace belonging to the same GB can be determined from which the boundary plane can be evaluated. The concept of determining the GB plane orientation from observations on orthogonal sections was first suggested by Randle [17]. The approach requires that the GB segment be reasonably flat close to the edge. Such a measurement strategy essentially allows us to obtain the GB misorientation as well as the GB traces on the two orthogonal directions. From these measurements, all five DOFs of those boundaries intersecting the edge can be evaluated. Site-specific APT analyses of the pre-characterized GBs can be carried out to estimate how the GB segregation depends on the five DOFs.

The material studied here is an austenitic stainless steel type 304L containing Fe–17.6Cr–13.7Ni–0.017C–0.089P–0.025Mn–0.003S–0.01Si–0.0045N–0.0028Co (all in wt.%). A large amount of P was added intentionally to produce pronounced GB segregation. To homogenize the steel, hot rolling (thickness reduction from 60 to 6 mm) at 1373 K was performed on the as-cast material. The hot-rolled plate was subsequently solution-annealed at 1323 K for 60 min followed by water quenching to room temperature. Long-term annealing (at 923 K for 100 h) was performed to promote strong equilibrium segregation of P. Specimens for GB determination were prepared by standard mechanical grinding and polishing procedures with a 50 nm colloid suspension of SiO_2 as a final polishing step. Extreme care was taken during polishing to preserve and prepare a "sharp edge" (edge radius <0.5 μm). EBSD scans were performed on orthogonal surfaces of the sharp edge with a Zeiss XB1540 microscope, using a step size of 0.5 μm at an electron beam accelerating voltage of 15 kV. The collected EBSD data were analyzed using TSL OIM 6.2 analysis software. For identifying CSL boundaries, Brandon's criterion was used [18]. Site-specific lift out was carried out on pre-characterized (with respect to all the five DOFs) boundaries along the sample edge using a dual-beam FIB (FEI Helios NanoLab™ 600*i*). APT was performed with a local electrode atom probe (LEAP™ 3000X HR, Cameca Instruments) in voltage mode at ~60 K. The pulse fraction and repetition rates employed were 15% and 200 kHz, respectively [19]. Data reconstruction and analysis was carried out using IVAS 3.6.6 software.

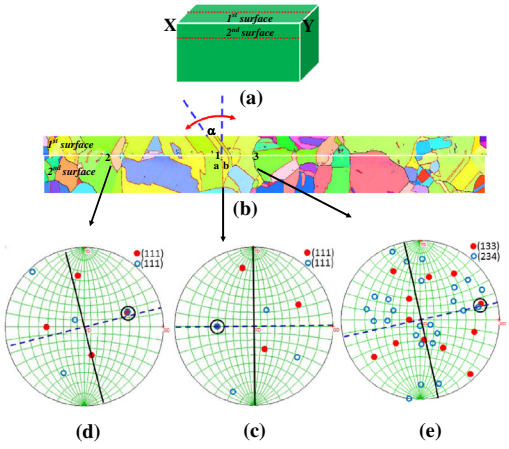

Figure 1. (a) Schematic illustration of a "sharp edge" specimen showing the approximate location (by red dotted line) where EBSD measurements were carried out. (b) Two IPF maps (with the sample edge direction as common reference direction) for the two mutual perpendicular surfaces near the sharp edge (boundary color code: Σ3, red; Σ9, blue; other HAGBs, black). (c–e) Stereographic projections for three representative GBs displaying the two abutting crystals, the boundary traces (black lines) and potential boundary normals (dashed blue lines); filled red circles and open blue circles in (c–e) represent all the potential symmetrically equivalent planes from the 1st and 2nd crystals, respectively, whereas the open black circle indicates the actual boundary plane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Figure 1b shows the inverse pole figure (IPF) maps displaying the crystallographic direction parallel to the edge direction of the sample of the two mutually perpendicular surfaces (denoted as the 1st and 2nd surface, respectively) near the sharp edge. The boundary traces on both surfaces were identified from the IPF maps. A graphical procedure to evaluate the boundary plane of individual GBs is explained in the following. The plane of boundary 1 (which is likely to be a coherent twin boundary as it has straight traces, see Fig. 1b) is evaluated first. The boundary has a misorientation of 59.6°<1 1 −1> and deviates by 0.4° from the exact Σ3 relationship as per Brandon's criterion. The orientations of the two neighbouring face-centered cubic crystals of the boundary 1 (i.e. crystals a and b in the lower IPF of Fig. 1b) are plotted in a stereographic projection (Fig. 1c). The trace of the boundary from the IPF map of the 2nd surface is plotted onto the stereographic projection as a black line (Fig. 1c). Since the boundary plane normal is perpendicular to its trace, it is obvious that the plane normal of boundary 1 lies somewhere along the dashed blue line (Fig. 1c). In addition, the inclination of the boundary plane is measured on the 1st surface to evaluate the exact position of the boundary plane normal. The vertical inclination angle of the boundary trace in the IPF map of the 1st surface (i.e. the angle α, see Fig. 1b) is measured to be 40°. This indicates that the boundary plane normal lies 40° away from the X-reference axis (as shown by the open black circle in Fig. 1c) which overlaps exactly (with <1° deviation) with the superimposing (1 1 1) poles from both adjoining crystals. Hence, the Miller indices of boundary 1 are (1 1 1) for both grains as highlighted in the stereograph (Fig. 1c). The results of the five-parameter study confirmed that the boundary 1 is a coherent Σ3 twin. Applying the same procedure, all five DOFs of the other boundaries were evaluated. Two representative boundaries are shown