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Determination of the five parameter grain boundary character distribution of nanocrystalline alpha-zirconium thin films using transmission electron microscopy

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ABSTRACT

Grain boundary engineering and other fundamental materials science problems (e.g., phase transformations and physical properties) require an improvement in the understanding of the type and population of grain boundaries in a given system – yet, databases are limited in number and spare in detail, including for *hcp* crystals such as zirconium. One way to rapidly obtain databases to analyze is to use small-grained materials and high spatial resolution orientation microscopy techniques, such as ASTAR™/precession electron diffraction. To demonstrate this, a study of grain boundary character distributions was conducted for α-zirconium deposited at room temperature on fused silica substrates using physical vapor deposition. The orientation maps of the nanocrystalline thin films were acquired by the ASTAR™/precession electron diffraction technique, a new transmission electron microscope based orientation microscopy method. The reconstructed grain boundaries were classified as pure tilt, pure twist, 180°-twist and 180°-tilt grain boundaries based on the distribution of grain boundary planes with respect to the angle/axis of misorientation associated with grain boundaries. The results of the current study were compared to the results of a similar study on α-titanium and the molecular dynamics results of grain boundary energy for α-titanium.

1. Introduction

Grain boundary engineering (GBE) is used to improve certain material properties by controlling the population of grain boundary types [1–5]. For instance, the intergranular stress corrosion cracking in nickel-based alloys can be reduced by increasing the fraction of low Σ coincidence site lattice (Σ CSL) boundaries where Σ is the reciprocal of the number fraction of coincident sites [6]. For GBE to be successful, a comprehensive knowledge of the grain boundary structure and the population is required [7] as is their influence on the properties of interest. However, developing the requisite knowledge of the grain boundaries, especially when considering large populations, has some intrinsic challenges [8–10]. For example, the three misorientation parameters used to determine the CSL boundary types are not sufficient to specify the coincidence degree in the grain boundary plane [11]. In addition, it has been shown that to interpret some phenomena (e.g., stored elastic strain [11]; pronounced differences in energies of coherent twin (i.e., Σ3 boundary with a {111} boundary plane) as well as incoherent twin (i.e., Σ3 boundary on a {112} boundary plane) [12]; and, intergranular stress corrosion [13]) both the misorientation and grain boundary plane distribution should be considered. Therefore, it is necessary to characterize both the grain boundary plane and the grain boundary misorientation to adequately characterize the boundaries so that precise interpretations can be made, and GBE can be affected [13].

The study of grain boundaries ranges from calculations of the atomic bonding and assessment of the chemical composition of the

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grain boundaries [14] to geometrical attributes including microscopic boundary parameters (e.g., translations between lattices form a grain boundary) [15] and macroscopic boundary parameters (e.g., misorientation between adjacent grains) [16]. The distribution of macroscopic grain boundary parameters may be determined from the orientation of the locations where grain boundaries intersect the plane of observation using a stereological method [17]. Each grain boundary is identified by five characteristic parameters. Three of these parameters specify the lattice misorientation Δg between the two crystals across a grain boundary. The misorientation space is parameterized into cells (or bins) with a specific discretization (e.g., 10°) using Bunge Euler angles (φ_1, Φ, φ_2). The misorientation domain is parameterized by φ_1, $\cos(\Phi)$ and φ_2 within the range of 0 to $\pi/2$, 0 to 1 and 0 to $\pi/2$, respectively [18]. The other two parameters determine the inclination of the grain boundary normal n. The inclination of the boundary normal in the crystal reference frame is parameterized using two angles (i.e., θ and φ) in the spherical coordinate system. The two angles are parameterized by $\cos(\theta)$ and φ within the range of 0–1 and 0 to 2π, respectively. When parameterizing grain boundary space, the cell size should be large enough to contain a considerable number of observations per cell (or per bin) and small enough to represent the textural features at a sufficient resolution [18]. The grain boundary character distribution (GBCD) method is based on partitioning the boundary parameter space into bins of equal volume. Recently, a new GBCD method has been proposed which determines the grain boundary distribution based on counting boundaries which are closer than an angular distance threshold value to a specific point in the boundary space [19]. The grain boundary character distribution is defined as the distribution (λ) of boundaries with the misorientation of Δg and the boundary normal of n (i.e., $\lambda(\Delta g, n)$). GBCD is measured in the unit of multiples of a random distribution (MRD). Distribution values larger than one indicate frequencies of occurrence more than expected in a random distribution.

Based on GBCD studies in a wide range of materials (e.g., Al [20], $MgAl_2O_4$ [21], MgO [18], $SrTiO_3$ [22], TiO_2 [23], Fe-1%Si [24]), it was noticed that the distribution of grain boundary planes is anisotropic, where low-energy and low-index habit planes are more favorable and grain boundary energy (i.e., γ (Δg, n)) is inversely correlated to the grain boundary character distribution (i.e., $\lambda(\Delta g, n)$) [25–27] for randomly textured materials. GBCD studies of materials with *hcp* crystal structure are very limited. The limited research on the *hcp* systems includes the work of Kelly et al. [28] who showed that prismatic grain boundary planes are more prevalent than basal grain boundary planes for α-titanium. In this work, the population of 180°-twist and 180°-tilt grain boundaries was shown to be greater than what is expected for the random distribution for this material. Another GBCD study of α-titanium by Randle et al. [29] attributed the plane population peak associated with the 60°–65°/$\langle 2\bar{1}\,\bar{1}0\rangle$ misorientation to the *bcc* to *hcp* (β to α) phase transformation in titanium. Beladi et al. [30] showed that the distribution of intervariant crystallographic planes in martensite for a Ti-6Al-4V alloy showed strong texture for prismatic planes, {hki0}. They also showed the highest intervariant boundary populations were associated with 63.26°/$[\bar{1}0\,5\,5\bar{3}]$ and 60°/$[11\bar{2}0]$ which terminate on $(4,\bar{1},\bar{3},0)$ [2] and $(\bar{1},0,1,1)$. Notably, most of the GBCD studies have been conducted on cubic materials with the average grain size above the micron scale and very few GBCD investigations have been performed on nanocrystalline materials, although where studies have been made, the GBCD of the nanoscaled material and microscaled material have been in agreement.[3] For instance, GBCD results of nanocrystalline copper films [31] showed that a strong (111) peak for 60°/[111] which is in accordance with a similar study on copper [32] with the average grain size far larger than the nanocrystalline copper films. Similarities between the GBCD results of metallic materials with nano and micron grain sizes were observed for nanocrystalline tungsten as well [33].

In general, electron backscattered diffraction (EBSD), a scanning electron microscope based orientation microscopy method, cannot be used for the characterization of grain boundaries in microstructures where the average grain size of less than a critical dimension, as there is a minimum number of indexed points required for subsequent analyses. For example, this critical dimension has been reported to be ~100 nm for iron, and is attributed to the spatial resolution in the x direction (35±5 nm) and in the y direction (90±15 nm, i.e., the lateral resolution) [31,34]. The precise spatial resolution in EBSD is primarily a function of the atomic number and the accelerating voltage, but can be calculated easily using Monte Carlo approaches of electron beam/specimen interactions. Also, it is important to note that there is an apparent inconsistency between the spatial resolution and the grain size that may be studied. In reality, this minimum grain size is likely to approach ~500 nm, once the number of measurements/grain is sufficiently large for statistically reliable analyses. This relatively poor spatial resolution results in an inability to detect fine features (e.g., nanotwins) [35,36]. Recently, transmission EBSD (t-EBSD) [37] or transmission Kikuchi diffraction (TKD) [38] technique has been developed which enjoys the spatial resolution of ~2 nm. However, due to the unusual projection geometry, the angular resolution of this SEM based orientation microscopy technique is reported to be reduced to ~1° [39].

ASTAR™/precession electron diffraction (ASTAR™/PED) is a relatively new orientation microscopy technique that is implemented onto transmission electron microscopes and makes possible the characterization of very fine features due to the spatial resolution of ~2 nm [40] and the angular resolution of ~0.3° [41] or ~0.8° [40]. This technique has been used successfully to characterize materials which cannot be studied by EBSD (e.g., severely deformed metallic materials [42] or grain growth characterization at the nanoscale regime [43]). By precessing the direct beam, the accuracy of indexing improves considerably as any dynamical diffraction effects are reduced or eliminated, and a quasi-kinematical diffraction condition [41,44] operates, which makes the acquired diffraction patterns sharper and reduces/removes Kikuchi lines, double diffraction events, and significantly reduces the background from the recorded diffraction patterns [45]. Also, by precessing the direct beam, the 180° ambiguity problem of indexing spot diffraction patterns is avoided, as higher order Laue zone reflections are excited in addition to zero order Laue zone reflections [46].

The orientation datasets used for GBCD studies have been prepared by different characterization techniques. For instance, EBSD technique was used to prepare 2D orientation datasets [12] while the combination of EBSD and serial sectioning technique using focused ion beam was used to prepare 3D orientation datasets for materials with the average grain size of few microns [47]. However, since the preparation of 3D datasets using the combination of focused ion beam and EBSD techniques is very time-consuming, recently Xe plasma focused ion beam was used to prepare 3D orientation datasets in a considerably shorter time [28]. For the

[2] It is common to deviate from low index poles when conducting GBCD studies. To ease in the readability of planes, the authors have adopted the style of including commas in the Miller indices designations for *hcp* four-index notation.

[3] It is expected that small differences in solute levels of elements that partition to the grain boundaries may influence the GBCD of some systems.