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Examination of the energy phase space of mixed copper grain boundaries by EBSD and the sphere-on-a-plate method

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Abstract

This article reports on an experimental study of the energy phase space of mixed copper grain boundaries by a combination of electron backscatter diffraction (EBSD) and the so-called sphere-on-a-plate method. Single crystal copper spheres with diameters of a few microns were sintered onto flat single crystal {1 1 1} copper plates, resulting in random initial grain boundary configurations. EBSD measurements together with an assumption about the grain boundary plane orientation were used for the determination of the five macroscopic degrees of freedom of the grain boundaries. The tilt and twist components of the grain boundaries were calculated making use of the interface plane scheme representation of grain boundaries. Upon annealing, the spheres rotated along gradients in the grain boundary energy phase space. Thus, points of the trajectories of single spheres could be recorded between the single annealing steps, allowing for tracing the path of single spheres towards and into energy minima regions. The results gathered from 13 spheres underline a strong complexity of the grain boundary energy phase space.

Keywords: Grain boundary energy; Grain boundary energy phase space; EBSD; Sphere-on-a-plate method

1. Introduction

The physical properties of polycrystalline materials are influenced to a large extent by their inherent defects [1]. One of these are the grain boundaries, which separate single crystalline regions of different orientation but the same chemistry. The contribution of the grain boundaries to a material's properties stems from their volume fraction and their specific properties. It has been shown that extrema of grain boundary properties are often related to energy minima [2]. Thus, the grain boundary energy seems to be the decisive parameter, usually written as an excess Gibbs free energy term G^{gb}:

$$G^{gb} = \gamma \cdot A \tag{1}$$

where γ denotes the specific grain boundary energy and A is the grain boundary area.

Principally, γ depends on eight degrees of freedom (DOF), which are necessary for a complete geometrical characterization of a grain boundary. Several descriptions of the five macroscopic DOF are possible, which emphasize different aspects [3]. The coincidence-site lattice (CSL) scheme focuses on the misorientation of the adjacent crystallites (three DOF, one angle Θ_{mis} and one axis $\vec{r}_{mis}$), while neglecting the orientation of the grain boundary plane (two DOF and a normal unit vector $\vec{n}$ related to one of the grains) [4]. The inverse volume density of CSL sites is denoted by the parameter Σ. An alternative parameterization of the macroscopic DOF, the interface plane scheme, highlights the importance of the grain boundary plane orientations in both crystals by assigning four DOF to the two

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grain boundary normal unit vectors $\vec{n}_{1,2}$ and one DOF to an angle ϕ_{twist} [3,5] (see also Appendix A.2). The three microscopic DOF are referred to mutual translations of the two grains, forced by atomic relaxation processes during the equilibration of the grain boundary core region, and are of no further interest in what follows.

The consequently hyperdimensional grain boundary energy phase space might be summarized qualitatively in a simple picture, as shown in Fig. 1. The essential implications therein are: apart from the global energy minimum, the single crystalline state, there are a number of local energy minima located at special subsets of the five macroscopic DOF. The functional form of the minima regions is believed to be of a cusp-like shape, i.e it resembles a singularity, as a result of a dislocation model of grain boundaries.

In a seminal paper, Read and Shockley presented an energy calculation for small angle pure tilt grain boundaries that were modelled as infinite periodic lattice dislocation walls [6]. The energy was calculated from the long-range elastic strain fields, taking account of the boundary plane orientation and assuming a constant dislocation core energy. It is solely the elastic energy part that is responsible for the cusp-like shape of the energy minimum regions through a $(-\Theta_{\text{mis}} \ln \Theta_{\text{mis}})$ dependency.

While the calculations had been done for the small angle region, Read and Shockley suggested that in the large-angle region local energy minima exist with similar cusp-like behaviour for all configurations that cannot be built up by regularly spaced, periodic lattice dislocation arrangements. Such deviations were proposed and proven later to be accommodated by so-called secondary grain boundary dislocations [7–9]. Hence, similar to the small angle case, Read–Shockley types of local energy minima regions arise around special Σ misorientations, where the secondary dislocations accommodate the mismatch to the perfect CSL as the primary lattice dislocations do for the perfect crystal lattice.

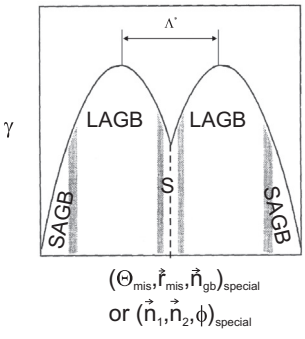

Fig. 1. Sketch of the present view of grain boundary energy phase. Basically, it is divided into three regions: SAGB (small-angle grain boundaries), LAGB (large-angle grain boundaries) and S (special low-energy regions around special subsets of the macroscopic DOF, indicated by the dashed line) [2]. Λ^* denotes the catchment area of an energy minimum, where driving forces for sphere rotations are given.

The experimental determination of absolute or relative grain boundary energies for a series of pure tilt and twist boundaries with fixed low-index grain boundary planes in various face-centred cubic (fcc) metals and other materials provides evidence for the existence of local energy minima for a number of special CSL configurations, e.g. Σ3, 9, 11 for Cu [10–13]. Due to the experimental approaches, these investigations automatically put the focus on the degrees of freedom related to the misorientations. However, the strong influence of grain boundary inclination on the energy of Σ3 boundaries in Cu was revealed by U. Wolf et al. [14]. D. Wolf and Merkle performed extensive computer simulations on fcc Cu and Au as well as body-centred cubic Fe and Mo, also investigating mixed boundaries with fixed tilt component and varying twist, further stressing a strong influence of the grain boundary plane orientations [15]. Recently, new atomistic simulations have been performed to calculate grain boundary energies in fcc metals, sampling a larger part of the phase space than was possible before [16]. In the last decade, automated methods have been developed to extract the five-parameter grain boundary character distribution from 3-D sampling using electron backscatter diffraction (EBSD) and serial sectioning methods, and to combine it with measurements of dihedral angles at triple junctions in order to determine relative grain boundary energies with respect to the five macroscopic DOF [17,18]. The results from large numbers of grain boundaries again support the view that grain boundary energy anisotropy seems to be much more strongly influenced by variations in the grain boundary plane orientation than by variations in the lattice misorientation (for an overview, see Ref. [19]). High-energy X-ray diffraction (XRD) microscopy has also been used recently for a non-destructive 3-D microstructure reconstruction that can be used to extract five-parameter grain boundary character distributions [20].

Unlike the aforementioned approaches, the so-called sphere-on-a-plate method dispenses with an explicit energy determination. This method comprises thermally induced free rotations of single crystalline spheres that are sintered onto flat single crystal substrates to form flat grain boundaries between sphere and plate. The rotations are driven by grain boundary energy gradients, directing the spheres into energy minima positions in phase space (for details see Section 3). The evolution of single grain boundaries occurs without constraints imposed by a microstructural grain boundary network and can be traced, principally. Originally proposed by Shewmon [21], the group of Gleiter applied the sphere-on-a-plate technique by first performing XRD texture measurements on large Cu and Ag sphere ensembles with random initial misorientations between spheres and substrate (e.g. [22–24]). The analysis of the final misorientations revealed the existence of many CSL related local energy minima using low-index substrate orientations. Erb investigated the temperature dependency of the Cu grain boundary energy and revealed that with increasing temperature a decreasing number of energy