

ON THE CONTRIBUTION OF TRIPLE JUNCTIONS TO THE STRUCTURE AND PROPERTIES OF NANOCRYSTALLINE MATERIALS

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Nanocrystalline materials, having a crystal size less than ~10 nm, have been shown to possess unusual properties [1-3]. These properties are primarily the result of a substantial fraction of the atoms (20 - 50%) lying in intercrystalline regions [3]. On the basis of x-ray scattering [4], EXAFS [5], hydrogen solubility [6], small angle neutron scattering [7], and self diffusivity measurements [8] conducted on bulk nanocrystalline materials, it has been suggested [3] that the grain boundaries in these materials are more disordered than those in conventional polycrystals. Recent studies [9,10] involving direct observation of nanocrystalline interfaces by HREM, provide contradictory results. Wunderlich and co-workers [9] have shown that interfaces in nanocrystalline Pd show an 'extended' structure not typically observed in conventional systems. However, Thomas et al [10] observed that the interfacial structure of nanocrystalline Pd is consistent with that typically observed in coarse-grained materials.

A microstructural element, which has been largely overlooked in the interpretation of nanocrystal properties, is the triple junction (i.e., intersection line of three (or more) adjoining crystals). Bollmann [11-13] has demonstrated that triple lines can be described as line defects (i.e., disclinations), which complete the representation of polycrystalline materials as a balanced network of dislocations (i.e., lattice dislocations, grain boundary dislocations, triple line disclinations) [13]. Bollmann [12] has shown that the structure of triple junctions is dependent on the specific crystallographic arrangement of adjoining crystals, with the defect character of these lines being enhanced with increased randomness in the orientation of adjacent crystals.

We have recently reported [14-16] on a significant triple line structure-dependence for localized corrosion in coarse-grained high purity nickel, whereby the electrochemical characteristics of the triple junctions were determined to be quite distinct from that of the adjoining grain boundaries and crystal lattices [16]. Schaefer and co-workers [17] investigated the structure of nanocrystalline Fe by positron lifetime spectroscopy, and found a distinct positron lifetime, intermediate with a shorter-lived grain boundary contribution, and longer-lived macrovoid contributions, associated with positron trapping at grain boundary intersections (i.e., triple lines). The authors [17] attributed this phenomenon to a relatively large effective free volume at the triple junctions, arising from misorientation-induced atomic instability at these sites.

In considering triple junctions to be distinct microstructural elements of polycrystalline materials, their influence on nanocrystal properties is ultimately dependent on their relative contribution to the high intercrystalline volume fraction associated with these materials. Mutschele and Kirchheim [18] have used the following relation to evaluate the volume fraction (C_t) of nanocrystalline materials associated with intercrystalline regions,

$$C_t = 3\Delta/d \quad (1)$$

where Δ is the average grain boundary thickness and d is the average diameter of the grains. Equation 1 is derived from considering grains having the shape of spheres or cubes. Neither of these grain shapes is suitable for deriving triple junction volume fractions since (a) the cube shape yields quadruple junctions,

which are uncommon in conventional polycrystalline systems [19], and (b) the sphere yields unrealistically large triple junction volume fractions since the grain boundary component can only be considered as the singular points of contact between spheres.

In an attempt to evaluate the grain size dependence of volume fractions associated with both grain boundaries and triple junctions, we have considered the regular fourteen sided tetrakaidecahedron as the grain shape [20], where the hexagonal faces represent grain boundaries, and edges correspond to triple junctions. By considering the grain size to be represented by the maximum diameter (d) of an inscribed sphere, and the intercrystalline component assessed as an outer 'skin' of the tetrakaidecahedron having a thickness of $\Delta/2$, where Δ is the grain boundary thickness, the following relation is obtained for the total intercrystalline volume fraction (V_t^{ic}).

$$V_t^{ic} = 1 - [(d - \Delta)/d]^3 \quad (2)$$

The grain boundary component can be assessed as hexagonal prisms of thickness, $\Delta/2$, extending from the faces of the inner tetrakaidecahedron which defines the interface between perfect crystal and the interfacial 'skin'. This yields the following relation for grain boundary volume fraction (V_t^{gb}).

$$V_t^{gb} = [3\Delta(d - \Delta)^2]/d^3 \quad (3)$$

The volume fraction associated with triple junctions (V_t^{tl}) is then given by,

$$V_t^{tl} = V_t^{ic} - V_t^{gb} \quad (4)$$

Equations 2,3 and 4 are valid under conditions where $d > \Delta$.

Figure 1 shows a schematic representation of this model, with a cross-sectional view, along an edge, where three adjoining tetrakaidecahedra form a triple junction. As indicated in this figure, the triple junction is assessed as a triangular prism (i.e., extending into the page), shared equally between the three adjoining tetrakaidecahedra. It should be noted that the grain size (d) is defined with respect to the center of the intercrystalline region.

Figure 2 shows the results of this analysis, applying a boundary thickness (Δ) of 1nm [18,21]. The effect of grain size (d), in the range 2nm to 1000nm(1 μ m), on the calculated volume fractions corresponding to intercrystalline regions, grain boundaries, and triple junctions, are shown. The total intercrystalline component is shown to be consistent with the previous suggestion [3] of a 20%-50% intercrystalline volume fraction with materials having a grain size less than 10nm. The intercrystalline component increases from a value of ~0.3% at a grain size of 1 μ m, to a maximum value of 87.5% at a 2nm grain size. The volume fractions associated with intercrystalline regions and perfect crystal are equivalent (i.e., 50%) at a grain size of ~5nm. In assessing the individual elements of the intercrystalline fraction, it is noted that the triple junction volume fraction displays a greater grain size dependence than that of the grain boundaries. In the range 100nm to 2nm, the triple junction volume fraction increases by three orders of magnitude, while the grain boundary volume fraction increases by little over one order of magnitude. In the nanocrystal range (i.e., $d \leq 10$ nm), the grain boundary fraction only increases from ~27% at 10nm, to a maximum value of ~44% at 3nm. Over the same range of grain sizes, the triple junction fraction increases from ~3% to a value of 50%. It is interesting to note that the grain boundary volume fraction decreases at grain sizes less than 3nm, while the triple junction fraction continues to increase. The physical significance of this phenomenon is not yet known. As demonstrated in this figure, the most significant contribution of triple junctions to bulk properties is expected to occur with materials having grain sizes ≤ 10 nm. It should be noted that the determined triple junction volume fractions may represent a conservative estimate, since these junctions may be better represented as 'tubes' circumscribing the triangular prisms depicted in Fig.1.

On the basis of the calculated volume fractions shown in Figure 2, it is apparent that variations in the bulk properties of nanocrystalline materials with grain size in the nanocrystal range (i.e., ≤ 10 nm) are more likely

the result of triple junction contributions than grain boundary effects. Chokshi and co-workers [22] found a decrease in room temperature microhardness with decreasing grain size in nanocrystalline Cu and Pd, which they attributed to Coble creep [23]. McMahon and Erb [24] observed similar effects in nanocrystalline Ni-P prepared by electrodeposition, which they attributed to the development of preferred crystallographic orientations in the electrodeposits. In these studies [22,24], observed deviations from expected Hall-Petch behaviour [25,26] may be justified on the basis of results from this study (Fig. 2), whereby both (1) minimal variation in grain boundary volume fraction, and (2) a large increase in triple junction volume fraction is expected with decreasing grain size in the nanocrystal range.

Consideration of triple junctions as distinct crystalline defects, comprising a significant fraction of the total volume of nanocrystalline systems, may allow for a better understanding of the structure and (unusual) properties of these novel materials. Furthermore, experimental studies involving bulk nanocrystalline materials, will likely provide greater insight into the structure and properties of triple junctions in polycrystalline materials.

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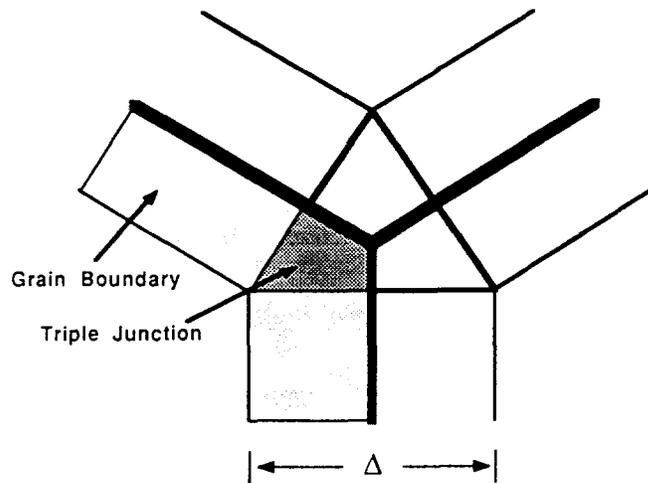


Figure 1. Schematic representation of the three - dimensional model used to evaluate the volume fractions of the microstructural elements. Shown is a cross-sectional view of the intersection of three adjoining tetrakaidecahedra (along a polyhedral edge), where the triple junction is considered a triangular prism extending into the page. Shaded regions represent the considered intercrystalline volumes.

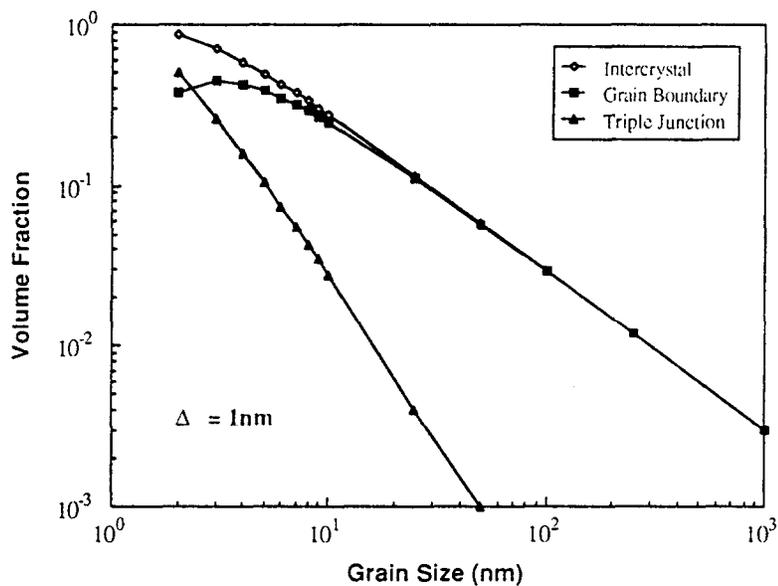


Figure 2. The effect of grain size (d) on calculated volume fractions (eqns. 2,3 and 4) for intercrystalline regions, grain boundaries, and triple junctions, assuming a grain boundary thickness (Δ) of 1nm.