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Interactions of lattice distortion fields in nano polycrystalline materials revealed by molecular dynamics and X-ray powder diffraction



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ABSTRACT

Interacting distortion fields from local and diffuse structural defects in metal nanomaterials were investigated via atomistic simulations supported by X-ray powder diffraction (XRPD) analysis. Numerical models of several large nano polycrystalline Pd microstructures embedding a wide range of defect types and densities were equilibrated via molecular dynamics (MD) to evaluate the interaction effects of various structural defects on the deformation-field components. Microstrain contributions from crystallite grain boundaries (GBs), line dislocations, and vacancies were determined from analysis of line broadening in Debye-simulated XRPD profiles. Dynamic disorder was investigated across the crystallites, revealing anisotropic vibrational components of atoms at the GBs. Although the estimated structural and microstructural properties agreed globally with the ideally expected parameters directly calculated from numerical models, widely dispersed values were observed among the assemblage of crystallites. Estimated dynamic and static Debye-Waller parameters used to account, respectively, for atomic thermal vibration and disorder across the GBs were in excellent agreement with experimental values observed by Inagaki et al. (*J. Mater. Sci.*, 18 (1983) 1803) for Pd metal powders. However, the static component decreased with environmental temperature and increasing interaction between defects in different crystallites, approaching zero in the limit.

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1. Introduction

Relaxation of unsatisfied atomic bonds at crystallite surfaces (i.e., grain boundaries) primarily affects the lattice-distortion field [1] and thus the energy density in nanomaterial systems [2]. In addition to crystallite size distribution and shape variations [3–6], the deformation field and the energy distribution are significantly affected by structural defects [7–9]. Although weakly stable in single nanoparticles [10], a high density of dislocations and vacancies is stabilized in polycrystalline microstructures due to grain boundary (GB) constraints [11,12]. However, despite the long-range deformation field resulting from line dislocations [13], the lattice distortion field across the microstructure has been usually investigated assuming the *superposition principle*, ignoring any interaction between local defects across different crystalline domains (e.g., grains) [14]. Hence, understanding cross contributions from defects

over incoherent crystallites is crucial for the accurate characterization of structural disorder-related properties in nanomaterials [15–17].

In addition to readily providing estimates of the *microstrain* within a system [18–24], X-ray powder diffraction (XRPD) techniques have been extensively employed to investigate the lattice-distortion field in nanomaterials by exploiting a physically meaningful characterization of line broadening [25]. Structural and microstructural properties of nanomaterials have been simultaneously investigated by whole-powder-pattern-modelling (WPPM [26,27]) via the convolution of their physical attributes to the XRPD line profiles. Accurate crystallite shape and size distribution contributions to observed XRPD profiles have been determined [28–31], achieving statistical agreement with other experimental observations [32]. Line broadening resulting from the structure deformation field over crystalline domains has been characterized either by the density of dislocations and the corresponding characteristic region of influence [33], or alternatively by means of the root-mean-square (RMS) atomic relative displacement as a function of the atom pair distance [34,35]. The behavior of XRPD profiles

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was related to structural anisotropy [36] and possibly to the nature of the defect(s) [35], according to structural disorder and strain profile shapes [35,37,38]. An accurate temperature diffuse scattering (TDS) model [39,40] characterized by the Debye-Waller parameter B [41–43] has been used to evaluate individual atomic thermal vibration contributions to line broadening, exploiting high-order factors to account for the restriction on phonon wavelength for the atomic vibrations in a powder of small crystallites [44]. However, as estimated values were found to be significantly larger than expected (i.e., than the corresponding values for bulk materials) and sensitive to the physical state of the sample [45], the Debye-Waller parameter for nano polycrystalline aggregates has been assumed to be composed of two components [46], namely (i) dynamic thermal atomic vibrations (B_d); and (ii) a thermal-like static disorder (B_s) due to incoherent lattice-distortions.

The need for sensitivity and accuracy when evaluating properties has led to the use of combined techniques to evaluate data and to make phenomenological behavior interpretations [32,47–49]. Atomistic simulations provide the opportunity to study material properties with high precision and the ability to control environmental conditions, sample inhomogeneity, experimental set-up, and data analysis assumptions and approximations [50–52]. In addition, XRPD methods have been successfully used to establish links between experimental data and molecular dynamics (MD) simulations, extending studies of investigated properties to the atomic-resolution scale [13,24,38,44,53,54] and explaining conflicting experimental results [55]. In particular, the larger Debye-Waller coefficient (B) for nanomaterials than for bulk materials was shown to result primarily from static atomic disorder at the GBs [46]. However, although simulated and experimental data were in good agreement, these studies primarily focused on single crystallites, ignoring the behavior of the polycrystalline microstructure as a whole [12,55]. The contributions to XRPD profiles from cross interaction of structural defects embedded in different crystalline domains are indeed neglected by currently available line broadening models.

In the present work, the interaction of lattice distortion fields across different crystalline grains resulting from a wide range of defect types and densities was incorporated into atomistic models of nano polycrystalline Pd microstructures. The effects of these distortion fields were revealed using state-of-the-art line profile analysis (LPA) of virtual XRPD profiles [22–24,41,56,57] for the entire aggregate and, independently, for all crystalline domains within. Estimated properties for the whole systems were in agreement with expected ideal values, regardless of defects' thermodynamic stability [55], but significant fluctuations were observed for single domains and GB structural disorder parameters as a function of the defects embedded in the surrounding environment. Although static and dynamic structural disorder in defect-free atomistic simulations were in excellent agreement with Debye-Waller parameters measured for Pd powders by Inagaki et al. (1983) and Eastman et al. (1992) [46,58], both the equilibration temperature and the dislocation density were observed to affect the static disorder, providing a partial explanation for deviations from the expected trend of experimental observations for metal alloy powders [59,60].

2. Methods

Large atomistic models of Pd nano polycrystalline materials (composed of ~12 million atoms, Table S1) were built accommodating a wide range of structural defects into an ideal defect-free microstructure. A cubic box with periodic boundary conditions (PBCs) was divided via the constrained modified Voronoi tessellation method [61,62] to 50 cells with minimum surface-to-volume

ratio (i.e., spherical shape) and lognormal size distribution (Fig. S1). The Voronoi cells (VCs) were filled with randomly oriented [63] periodic *fcc* crystal structures of unit-cell side length $a = 0.389070$ nm, excluding atom positions closer than 85% of the crystallographic minimum interatomic pair distance [64]. Line dislocation or vacancies defects were then alternatively embedded in the defect-free grains' crystal structure.

Dislocation defects with Burgers vector $\mathbf{b} = 2 \cdot [110]$ of modulus $a/\sqrt{2}$ were modelled as follows:

- (i) Edge line dislocation: two consecutive half $(1\bar{1}0)$ planes of atoms above the dislocation line belonging to the $[\bar{1}\bar{1}2]$ crystallographic direction were removed, and the nearest 10 planes on both sides were progressively rearranged to recover the remaining empty region.
- (ii) Screw line dislocation: atoms were shifted along the $[110]$ crystallographic direction by $\mathbf{b} \cdot \psi/2\pi$.

Dislocation lines were arranged crossing the mass center of the crystallites to promote their stability [10,55,65] and to produce a meaningful contribution to the deformation field [66] (i.e., the crystal structure was compressed in half of the crystallite and expanded in the other half). Although a detailed study of the effect of the dislocation line lying on alternative equivalent crystallographic directions within the largest crystallite was discussed in Leonardi et al. (2015) [53] for the same polycrystalline microstructure, slip orientations were randomly chosen to exclude any preferential strain geometry. Vacancies were further obtained by removing randomly chosen atoms with 1.6 nm minimum pair distance from the crystallite core region, taking care to avoid affecting the GB structure (i.e., at a minimum distance from the VC surface of 0.8 nm). An average vacancy density of 0.013 nm^{-3} was used in these simulations to account for lower formation energy in the subsurface layers than in bulk [67] and to accentuate the contribution to the lattice-distortion field [60] (see [Supplementary materials section 2](#) for further details). As no more than one defect was embedded per crystallite, only the interaction of deformation fields across different crystalline domains was expected to affect the grains' structural disorder as a function of increasing density of dislocations (e.g., the ratio between the cumulative dislocation line lengths and crystallite volumes). In particular, although defects were accommodated into randomly choosing grains, the same defect types on the same dislocation lines were considered for the largest and smallest grains (i.e., G35 and G24 of ~15 and ~23 nm, respectively) to directly isolate the alteration of the local lattice distortion field due to the surrounding environment (see [Table 1](#) for a detailed list of the investigated numerical models).

MD simulations of the as-built ideal microstructures were performed using the software LAMMPS [68], employing the embedded atom method (EAM) [69] to describe atom-atom pair interactions. In particular, the Pd EAM pair potential from Sheng et al. (2011) [70] was used because of the optimal agreement with experimental observations [54,70] (lattice dynamics, thermal behavior, mechanical and defect properties). After energy minimization, equilibrium was attained using a 1 ns dynamic at constant pressure (0 Pa) and temperature (300 K), employing the Nose-Hoover style non-Hamiltonian thermostat [71,72] with a time integration of 1 fs (Fig. S2). The ideal defect-free microstructure was also equilibrated at 100, 200, 400, 500 and 600 K by independent dynamics. A set of 100-atom arrangements in space (i.e., single frames - SFs) was then sampled over a 0.1 ns dynamic at 1 ps constant time-step (i.e., time trajectory). Thus, average atom coordinates were calculated over the time trajectory, retrieving the averaged-position (AP) configurations free of any dynamic contribution [24,73–75].

XRPD patterns of the atomistic models were simulated by

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