# Interface Stress in Polycrystalline Materials: The Case of Nanocrystalline Pd

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(Received 7 December 2001; published 6 May 2002)

Based on a generalization of a capillary equation for solids, we develop a method for measuring the absolute value of grain-boundary stress in polycrystalline samples having a large interface-to-volume ratio. The grain-boundary stress in nanocrystalline Pd is calculated from x-ray diffraction measurements of the average grain size and the residual-strain-free lattice spacings, yielding a value of 1.2 ± 0.1 N/m. The random distribution of crystallite orientations in the sample suggests that this value is characteristic of high-angle grain boundaries in Pd.

DOI: 10.1103/PhysRevLett.88.206104 PACS numbers: 68.35.Gy, 81.07.Bc

When a solid with a fine-scale microstructure is elastically deformed, work is performed against volume (bulk) forces and interface forces. Even if there is no external load applied, mechanical equilibrium prescribes that stresses in the bulk are required to compensate interface stresses. In a conventional polycrystalline material, the bulk stresses arising from interface stresses are negligible; however, for a solid with a nanometer-scale microstructure, interface stresses can no longer be neglected, because they induce bulk stresses on the order of $f/L$, where $f$ is the scalar interface stress and $L$ denotes a characteristic length scale of the microstructure (such as the average crystallite size). Classically, the interface stress $\mathbf{f}_{ij}$ is defined as the derivative of the interfacial free energy $\gamma$ with respect to the elastic strain $\mathbf{e}_{ij}$ tangential to the interface plane: $\mathbf{f}_{ij} = \partial\gamma/\partial\mathbf{e}_{ij}$ [1–3]. Unlike $\gamma$, which is a scalar quantity and always positively valued, the interface stress $\mathbf{f}_{ij}$ is a tensor with entries that may have either sign. A more general notion of interface stress permitting a discontinuity in the displacement across an internal interface has been discussed by Gurtin *et al.* [4].

The rapid development in our theoretical and experimental understanding of stresses at solid surfaces and the role they play in phenomena such as surface reconstruction, epitaxial growth, and the self-organization or stabilization of mesoscopic structures have been reviewed by Ibach [5]. Comparatively rudimentary is our understanding of the influence of internal interfaces on intrinsic stresses and their consequent impact on the properties of materials with a large interface-to-volume ratio, such as multilayered thin films or nanostructured materials [6]. Equations for calculating the volume stresses induced by interface stresses have been derived for special sample geometries [7] and for general microstructures subjected to a hydrostatic load [8]. Several recent experiments have taken advantage of such relations to obtain experimental values for $f$ [9–13]; in particular, the relative change of grain-boundary stress upon hydrogen loading of nanocrystalline Pd has been investigated [11]. Nevertheless, many aspects of the interface stress remain largely unexplored in experiment, such as the absolute value of $f$ obtained from the study of its direct mechanical action on the crystallites adjoining a grain boundary.

In this paper we describe a method for determining the absolute value of the grain-boundary stress in a polycrystalline sample made up of nanometer-sized grains (crystallites), i.e., a so-called nanocrystalline (NC) material. Our approach is based on a generalized capillary equation derived by Weissmüller and Cahn [8] using the principle of virtual work. Their central result was obtained by relating the hydrostatic components of the volumetric stress tensor averaged over all of the grains in a polycrystalline solid, $\boldsymbol{\sigma}_{ij}$, to the integrated (average) stresses of the interfaces contained within the sample:

$$\langle \Delta P \rangle_V = \frac{2}{3}\left(\frac{A}{V}\right)\langle f \rangle_A \,. \tag{1}$$

In Eq. (1), $\langle \Delta P \rangle_V$ denotes the volume-averaged difference between the local pressure $P^{\text{int}}$ in the sample and an externally applied hydrostatic pressure $P^{\text{ext}}$, i.e., $\Delta P = P^{\text{int}} - P^{\text{ext}}$. The quantity $\langle f \rangle_A$ is the area-averaged interface stress; in analogy to the scalar pressure $P$ in the theory of bulk elasticity, in which $P = -\text{Tr}(\boldsymbol{\sigma}_{ij}/3)$, the scalar interface stress (interface pressure) $f$ is defined as $f = \text{Tr}(\mathbf{f}_{ij}/2)$. Finally, $A/V$ represents the total interface area divided by the total grain (bulk) volume. In Eq. (1), contributions to the volume stress arising from interface junctions, which are one-dimensional elements of microstructure and second order in $A/V$, are neglected. We see from this equation that the mean pressure is independent of the spatial arrangement, orientation, and curvature of the interfaces.

In order to devise a method for measuring the interface stress in a nanocrystalline sample, we express Eq. (1) in terms of experimentally accessible quantities. The stereological identity $A/V = 2/\langle L \rangle$ relates $A/V$ to the average grain intercept length $\langle L \rangle$, which can be obtained directly from a Fourier analysis of Bragg-peak profiles [14]. Concerning $\langle \Delta P \rangle_V$, we can derive a relation between the mean pressure in the bulk and the sample lattice parameter, which can be measured with high accuracy in a diffraction

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experiment. By inserting the definition of the isothermal bulk modulus, $K^{-1} \equiv -V^{-1}(\partial V/\partial P)|_T$, into Eq. (1) and making use of the relation $\langle \Delta P \rangle_V = \langle P^{\rm int} \rangle_V - P^{\rm ext}$ (see Eq. (8) in Ref. [8]) together with $(\Delta V)/V = 3\langle (\Delta a)/a \rangle_V$, in which $\langle a \rangle_V$ is a nonlocal, volume-averaged lattice parameter, we obtain

$$\frac{\langle a_{\rm NC} \rangle_V - a_0}{a_0} = -\frac{4}{9K} \langle f \rangle_A \frac{1}{\langle L \rangle}, \tag{2}$$

where $\langle a_{\rm NC} \rangle_V$ denotes the lattice parameter of the nanocrystalline solid with average grain intercept length $\langle L \rangle$, and $\langle a_0 \rangle_V = a_0$ is the lattice parameter of the interface-free reference state (i.e., $\langle L \rangle \to \infty$) . We note that for noncubic polycrystalline microstructures an effective bulk modulus $K^\star \neq K$ should appear in Eq. (2), but for cubic materials $K^\star = K = (C_{11} + 2C_{12})/3$, with elastic constants $C_{ij}$ expressed in the Voigt notation [15]. Equation (2) implies that the interface stress $\langle f \rangle_A$ can be obtained from the slope of a plot of measured values of $\langle a_{\rm NC} \rangle_V$ versus $1/\langle L \rangle$.

Before attempting to carry out such measurements, it is important to realize that Eqs. (1) and (2) are valid only when the volume average extends over the entire specimen rather than merely a portion of it. Equation (1) was derived using the principle of virtual work by summing up the individual amounts of work performed by external, internal, and interface stresses during a homogeneous deformation. For sufficiently small deformations, the total work must vanish in mechanical equilibrium. In general, the internal stress field $\boldsymbol{\sigma}_{ij}(\mathbf{r})$ of a heterogeneous solid is a linear superposition of two stress fields with different physical origins: (i) the stress conjugated to the strain $\boldsymbol{\varepsilon}_{ij}(\mathbf{r})$ resulting from an externally applied load, and (ii) the stress conjugated to the residual strain $\boldsymbol{\varepsilon}_{ij}^{\rm res}(\mathbf{r})$ arising from the elastic response of a material to an inhomogeneous distribution of nonelastic strains, such as plastic strains or those induced by thermal expansion, phase transformations, etc. [16]. As a consequence, the work $W_V$ performed by the total internal stress can be formally written as

$$W_V = \int_V \boldsymbol{\sigma}_{ij}(\mathbf{r}) \boldsymbol{\varepsilon}_{ij}(\mathbf{r})\, dV + \int_V \boldsymbol{\sigma}_{ij}^{\rm res}(\mathbf{r}) \boldsymbol{\varepsilon}_{ij}(\mathbf{r})\, dV, \tag{3}$$

with summation over repeated indices. Owing to the self-equilibrating nature of the residual stresses, the second integral in Eq. (3) vanishes as long as the range of integration extends over the entire sample volume [15], thus explaining why residual stresses do not appear in Eq. (1).

If x-ray diffraction is used to determine the lattice parameters appearing in Eq. (2), it may be impossible, depending on the specifics of specimen geometry, beam cross section, and available radiation energy, to carry out a measurement that averages over the entire sample volume. In such a case, the second integral in Eq. (3) no longer vanishes, and a derivation analogous to that of Eq. (2), involving work integrals extending over the irradiation volume $V_{\rm irr}$, yields an expression for $\langle f \rangle_{A_{\rm irr}}$ that depends on the typically unknown value of the residual strain, rendering a determination of the interface stress from lattice-parameter and grain-size data impossible.

Although determination of the residual-strain tensor of a given sample is a challenging task, standard methods for residual-stress analysis [17] allow one to identify scattering geometries in which residual-strain-free lattice spacings can be measured by diffraction, despite probing a confined scattering volume $V_{\rm irr}$. In these geometries, the residual-stress contribution to $W_V$ vanishes even when $V_{\rm irr} < V$, because the integrand of the second integral in Eq. (3) is identically zero. Consequently, we can still use Eq. (2) to compute the interface stress, provided the quantity $\langle a_{\rm NC} \rangle_V$ is replaced by the residual-strain-free lattice parameter $[\langle a_{\rm NC} \rangle_{V_{\rm irr}}]_0$.

The theory of stress analysis by x-ray diffraction provides an explicit protocol for extracting $[\langle a_{\rm NC} \rangle_{V_{\rm irr}}]_0$ values from measurements of $hkl$-dependent lattice spacings $d^{hkl}$. For a polycrystalline specimen, average values of the latter can be related to the average strain according to

$$[\langle \boldsymbol{\varepsilon}'_{33} \rangle_{V_{\rm irr}}]^{hkl}_{\phi,\psi} = \frac{[\langle d \rangle_{V_{\rm irr}}]^{hkl}_{\phi,\psi} - d^{hkl}_{\rm ref}}{d^{hkl}_{\rm ref}}, \tag{4}$$

where the prime signifies a laboratory coordinate system oriented with the $z$ axis parallel to the scattering vector and azimuthal ($\phi$) and polar ($\psi$) angles defined relative to the plane of the sample surface. The term $d^{hkl}_{\rm ref}$ denotes the lattice spacings of a reference state, which may be chosen without loss of generality to correspond to the residual-strain-free state, i.e., strain contributions arise only from the homogeneous deformation of all grains by interface-stress-induced forces. The applicability of such a reference state to a given experiment must be justified *a posteriori*. The scattering geometry ($\phi$, $\psi$) permitting measurement of residual-strain-free (but interface-stress-modified) $hkl$ lattice spacings is specified by the condition

$$[\langle \boldsymbol{\varepsilon}'_{33} \rangle_{V_{\rm irr}}]^{hkl}_{\phi,\psi} \equiv 0. \tag{5}$$

As demonstrated in Ref. [18], Eq. (5) may be solved by considering the ensemble-averaged (i.e., $\phi$-averaged) strain $[\overline{\langle \boldsymbol{\varepsilon}'_{33} \rangle}_{V_{\rm irr}}]^{hkl}_{\psi} = (1/4) \sum_{n=0}^{3} [\langle \boldsymbol{\varepsilon}'_{33} \rangle_{V_{\rm irr}}]^{hkl}_{n\pi/2,\psi}$, which can be shown to vanish for $\psi$ values equal to $(\psi_0)^{hkl} = \arcsin[2\nu^{hkl}/(1 + \nu^{hkl})]^{1/2}$. The $\nu^{hkl}$ parameters are $hkl$-dependent Poisson numbers, which can be computed for a given material according to the theory of x-ray elastic constants [19]. This solution to Eq. (5) relies upon the applicability of Hooke's law and equations of mechanical equilibrium in conjunction with the supposition that the nanocrystalline solid is statistically homogeneous and isotropic within $V_{\rm irr}$. A sample characterization must be carried out to determine whether or not these requirements are met. We conclude that the lattice parameters appearing in Eq. (2) can be replaced by their irradiated-volume-averaged equivalents, provided residual-strain-free values $[\langle a_{\mathrm{NC}}\rangle_{V_{\mathrm{irr}}}]_0$ are determined from lattice spacings $[\overline{\langle d_{\mathrm{NC}}\rangle_{V_{\mathrm{irr}}}}]^{hkl}_{(\psi_0)^{hkl}}$, where an average is performed at each $hkl$ over the scattering geometries $[n\pi/2, (\psi_0)^{hkl}]$ for $n = 0, 1, 2, 3$.

We now demonstrate the applicability of this approach to the experimental determination of the interface stress $\langle f\rangle_A$ in a sample of nanocrystalline Pd. A disk-shaped specimen 8 mm in diameter and about 0.1 mm thick was prepared by the inert-gas condensation technique and subsequently preannealed at 60 °C for 24 hours in order to equilibrate the grain boundaries [20]. Lattice constants were extracted from diffraction measurements performed on a Huber powder x-ray diffractometer equipped with a Eulerian cradle and pinhole collimators. The Cu-$K\alpha_{1,2}$ radiation scattered by a sample held at 20 °C with a stability of ±0.01 °C was detected by an energy-dispersive solid-state detector. Statistical isotropy of the specimen was verified by the radial symmetry of the isointensity contours of (111) pole figures. The average grain intercept length $\langle L\rangle$ was found to be $\sim$10 nm by means of the standard Warren-Averbach analysis (compare details in Ref. [14]). Annealing the sample in a sealed quartz tube filled with He (99.999%) induced grain growth [21], corresponding to marked increases in $\langle L\rangle$.

Although the true lattice parameter of a crystalline material is independent of the Miller indices $hkl$, the same does not in general apply to the lattice constants $a^{hkl}$ computed from individual lattice spacings $d^{hkl}$. A reliable estimate for the $hkl$-independent lattice parameter is obtained by plotting the $a^{hkl}$ values against an appropriate extrapolation function [22]. Such a procedure is illustrated in Fig. 1 for nanocrystalline Pd in the as-prepared state, where the extrapolation function was chosen to correct the error induced by displacement of the specimen from the focal plane of the diffractometer. Each data point represents the average over four diffraction measurements carried out at the angles $\phi = n\pi/2$ $(n = 0, 1, 2, 3)$ and $(\psi_0)^{hkl}$, the values of which are given in Table I. The strong scatter in the raw data points of Fig. 1 was found to arise from the presence of stacking faults in the specimen. After correcting the lattice constants for stacking faults as described in Refs. [23–25], we obtain a set of data points lying nearly along a straight line. The $y$ intercept of a linear fit to the latter gives the residual-strain-free lattice parameter $[\langle a_{\mathrm{NC}}\rangle_{V_{\mathrm{irr}}}]_0 = \langle a_{\mathrm{NC}}\rangle_V$ of the nanocrystalline solid. For a sample containing two-dimensional faults, the Warren-Averbach analysis yields the average intercept length of the coherent scattering domains, the so-called effective intercept length $\langle L\rangle^{\mathrm{eff}}$, which is smaller than the true intercept length $\langle L\rangle^{\mathrm{true}}$, owing to the peak broadening induced by stacking faults and/or twin boundaries incorporated in the individual nanocrystallites [23]. The quantity $\langle L\rangle^{\mathrm{true}}$ was determined from $\langle L\rangle^{\mathrm{eff}}$ using the procedure of Ref. [23], thus permitting $\langle a_{\mathrm{NC}}\rangle_V$ to be plotted as a function of $1/\langle L\rangle^{\mathrm{true}}$ (Fig. 2). The slope of a fit of Eq. (2) to the data points gives $\langle f\rangle_A = 1.2 \pm 0.1$ N/m for $K = 192 \pm 2$ GPa [26]; possible small contributions of two-dimensional faults to $\langle a_{\mathrm{NC}}\rangle$ have been neglected. From Eq. (1) we compute a compressive bulk pressure of 0.17 ± 0.03 GPa in the as-prepared state. In the limit $\langle L\rangle^{\mathrm{true}} \to \infty$, $\langle a_{\mathrm{NC}}\rangle_V$ should tend toward the lattice parameter of a Pd single crystal, $a_0 = 389.019 \pm 0.002$ pm [27]; extrapolation of the fit line in Fig. 2 yields a value of 389.02 pm for $a_0$, which is in remarkably good agreement with the literature value. Moreover, independent measurement of a disk-shaped coarse-grained reference sample of Pd found a lattice parameter of 388.99 pm. This consistency justifies both the assumption of statistical homogeneity as well as the supposition that interface stress generates a homogeneous deformation of the nanocrystallites upon which it acts. Finally, our analysis suggests that the interface stress value as determined from the slope of Fig. 2

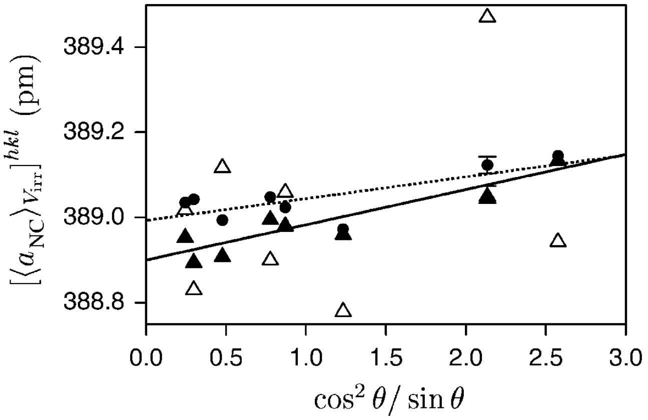

FIG. 1. Lattice constants $[\langle a_{\mathrm{NC}}\rangle_{V_{\mathrm{irr}}}]^{hkl}$ plotted relative to the extrapolation function $\cos^2\theta/\sin\theta$, where $\theta$ denotes the Bragg angle. All $[\langle a_{\mathrm{NC}}\rangle_{V_{\mathrm{irr}}}]^{hkl}$ values were determined at the corresponding angles $(\psi_0)^{hkl}$ listed in Table I (△: raw data; ▲: data corrected for stacking faults). The $y$ intercept of the least-squares fit line (solid line) yields the lattice parameter $\langle a_{\mathrm{NC}}\rangle_V$ of the nanocrystalline solid. For comparison, we include the lattice parameters of a sample annealed at 600 °C for use as a reference material (●, dashed line).

TABLE I. X-ray elastic constants $\nu^{hkl}$ of Pd, computed for the various $hkl$ lattice planes according to the method in Ref. [19]. The angles $(\psi_0)^{hkl}$ were calculated from the $\nu^{hkl}$ constants using the formula given in the text.

| $hkl$ | $\nu^{hkl}$ | $(\psi_0)^{hkl}$ (deg) |
|---|---|---|
| 111 | 0.36 | 46.7 |
| 200 | 0.41 | 49.5 |
| 220 | 0.38 | 47.6 |
| 311 | 0.39 | 48.5 |
| 222 | 0.36 | 46.7 |
| 400 | 0.41 | 49.5 |
| 331 | 0.37 | 47.4 |
| 420 | 0.39 | 48.4 |

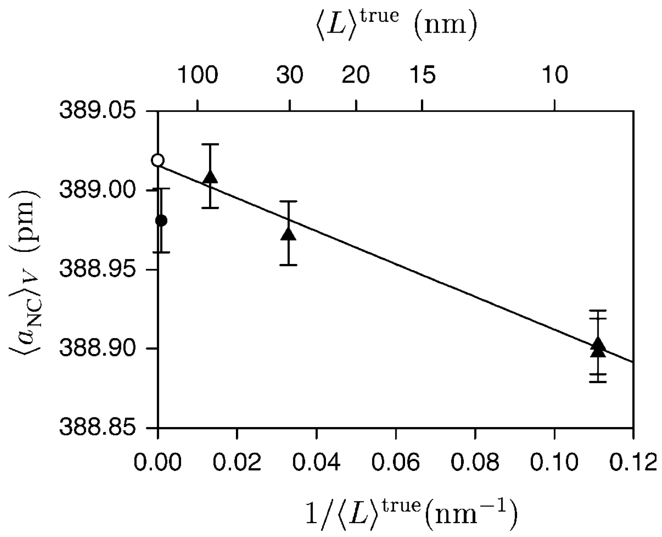

FIG. 2. Lattice parameter $\langle a_{\rm NC}\rangle_V$ of nanocrystalline Pd (▲) plotted as a function of the reciprocal average grain intercept length. The solid line is a least-squares fit to the data points. Also shown are the literature value for Pd (○) and the lattice parameter measured for the coarse-grained reference sample of Fig. 1 (●).

is independent of grain size for all grain sizes larger than 10 nm.

Since $\langle f\rangle_A$ represents an orientational average over many different interfaces, we may assume that its value is characteristic of the predominant type of grain boundary—namely, high angle [28]—in the specimen. This conclusion is supported by the fact that calorimetric measurements performed on an as-prepared nanocrystalline Pd sample yielded a value of 0.8 ± 0.1 J/m$^2$ for the enthalpic part of the area-weighted grain-boundary energy $\langle\gamma\rangle_A$ (compare details in Ref. [29]), which agrees well with typical values for high-angle grain boundaries in Pd [30,31].

Finally, we note that the value obtained in this paper for the interface stress in nanocrystalline Pd differs significantly from $\langle f\rangle_A = 0.1 \pm 0.1$ N/m, as measured by Weissmüller and Lemier [11]. This discrepancy is most likely caused by the presence of irreversibly dissolved hydrogen in their specimens [32], since it was found that the sign and magnitude of the interface stress is significantly affected by the segregation of hydrogen to the core region of grain boundaries.

The authors are obliged to C. E. Krill, A. Tschöpe, and J. Weissmüller for critical readings of the manuscript and helpful suggestions. We are indebted to Professor H. Ruppersberg for his guidance in setting up the stress measurements and in interpreting the residual-strain data. This research was supported by the Deutsche Forschungsgemeinschaft (Grant No. Bi 385/13, Sonderforschungsbereich 277).

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