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Anil K. Singh and Hanns-Peter Liermann

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Strength of polycrystalline niobium from high-pressure x-ray diffraction data: A comparison of results from line-width and line-shift analyses

Anil K. Singh^{1,a)} and Hanns-Peter Liermann²

¹Materials Science Division, Council of Scientific and Industrial Research (CSIR), National Aerospace Laboratories, Bangalore 560 017, India

²Photon Science, Deutsches Elektronen Synchrotron, Notkestr. 85, 22607, Hamburg, Germany

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High purity polycrystalline niobium was compressed in a diamond anvil cell (DAC) without any pressure transmitting medium and the pressure was increased in steps of ~ 5 GPa to the highest pressure of ~ 40 GPa. The diffraction pattern was recorded after each pressure increment using angle-dispersive mode with the conventional diffraction geometry, wherein the primary x-ray beam is parallel to the load axis of the DAC. The strength of niobium as function of pressure was determined using the line-width and line-shift analyses. Both eY and $2eY$, where Y is the aggregate Young's modulus and e is the strain determined from the line-width analysis, have been used as the measure of strength in earlier studies. In this study, it is eY that agrees with the strength determined from the line-shift analysis of the radial diffraction data as well as the data from the conventional diffraction geometry. These results have been discussed and compared with a similar observation made earlier on strength of diamond. This study highlights the ambiguity that presently exists in choosing eY or $2eY$ as a measure of strength while attempting to estimate the strength from the diffraction line width analysis. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4927727>]

I. INTRODUCTION

A polycrystalline sample compressed in a diamond anvil cell (DAC) develops complex stresses and resulting strains.¹ A simplified approach recognizes two types of strains: the micro- and macro-strains—the former results in the broadening of the diffraction lines and the latter in shift of the diffraction lines. The diffraction-line broadening has been used to determine the maximum stress in the stress distribution in the crystallites.^{2–12} The maximum stress $p_{\max}$ ($\cong eY$, where e and Y are the micro-strain and the aggregate Young's modulus, respectively) is often termed the micro-differential stress (micro-DS) and is taken as the measure of compressive strength of the polycrystalline sample material. Some studies used $p_{\max}$ (e.g., Refs. 2 and 5–7), whereas others $2p_{\max}$ (e.g., Refs. 8–12) as the measure of micro-DS. The macro-stresses at the center of the sample compressed in a DAC possess a cylindrical symmetry about the load axis, the axial stress component σ_{33} being larger than the radial stress component σ_{11} . The difference $(\sigma_{33} - \sigma_{11}) = t$, termed uniaxial stress or macro-DS, is another measure of strength at a confining pressure equaling the mean normal stress.^{13–18} Both the measures of strength, the micro- and macro-DS, are under identical confining pressure and must be equal. We determined strength of Nb to be 40 GPa from the angle-dispersive x-ray diffraction patterns taken with the conventional geometry of the DAC by using the methods outlined earlier for micro-DS⁹ and macro-DS.¹⁷ These results have been compared with macro-DS obtained from the radial diffraction data in an earlier study.¹⁹

II. THEORETICAL ANALYSIS

A. Line-width analysis

The model for the microscopic stress distribution in the crystallites of the compressed aggregate assumes that all stresses between zero and a maximum stress $p_{\max}$ occur with equal probability.²⁰ For a predominantly Gaussian profile, the apparent strain $\eta(hkl)$ perpendicular to the plane (hkl) is given by³

$$(2w_{hkl} \cos \theta_{hkl})^2 = (\lambda/D)^2 + \eta^2(hkl) \sin^2 \theta_{hkl}. \quad (1)$$

Here, $(2w_{hkl})$ and θ_{hkl} denote full width at half maximum (FWHM) on 2θ -scale and the Bragg angle of the reflection (hkl) . λ is the wavelength of the x-rays and D is the average apparent size of the crystallites assumed independent of (hkl) . Equation (1) can be rewritten in terms single-crystal Young's modulus $Y(hkl)$ as follows:⁹

$$(2w_{hkl} \cos \theta_{hkl})^2 = (\lambda/D)^2 + \left[\frac{4p_{\max}}{Y(hkl)} \right]^2 \sin^2 \theta_{hkl}. \quad (2)$$

For the cubic system,²¹

$$Y(hkl) = S_{11} - 2 \left(S_{11} - S_{12} - \frac{1}{2} S_{44} \right) \Gamma(hkl). \quad (3)$$

Here, S_{ij} are the single-crystal elastic compliances, and

$$\Gamma(hkl) = (h^2 k^2 + k^2 l^2 + l^2 h^2) / (h^2 + k^2 + l^2)^2. \quad (4)$$

Equation (2) suggests that the $(2w_{hkl} \cos \theta_{hkl})^2$ versus $[\sin \theta_{hkl} / Y(hkl)]^2$ plot is a straight line and $p_{\max}$ in terms of the slope $m(1)$ is given by

^{a)}Author to whom correspondence should be addressed. Electronic mail: singhna1@yahoo.com

$$p_{\max} = \sqrt{m}(1)/4. \quad (5)$$

Often, the elastic compliances S_{ij} are not known. In such cases, the following equation obtained by replacing η_{hkl} in Eq. (1) by the average value $\langle\eta\rangle$ can be used. This leads to the following relation:

$$(2w_{hkl} \cos \theta_{hkl})^2 = (\lambda/D)^2 + \langle\eta\rangle^2 \sin^2 \theta_{hkl}. \quad (6)$$

The average apparent strain $\langle\eta\rangle$, $p_{\max}$, slope $m(2)$, and aggregate Young's modulus Y are related by

$$p_{\max} = \langle\eta\rangle Y/4 = Y\sqrt{m(2)}/4. \quad (7)$$

The equivalent equations applicable to energy dispersive diffraction technique can be found in the literature.²²

It is to be noted that the apparent strain η , the strain e produced by $p_{\max}$, and the root mean square strain ε are related by²³

$$\eta = 4e = 2(2\pi)^{1/2}\varepsilon. \quad (8)$$

The strain e is denoted by ε in Refs. 5–7. References 11 and 12 use the same symbol ε to denote $2e$. It is seen from Eq. (8) that $p_{\max} = eY$.

B. Line-shift analysis

It has been shown that the lattice parameter $a_m(hkl)$ measured using the angle-dispersive conventional geometry of the DAC plotted as function $3(1 - 3 \sin^2 \theta)\Gamma(hkl)$, termed gamma plot, is a straight line with a slope M_1 and intercept M_0 on the ordinate.¹⁷ The parameter t is given by

$$t = -\frac{3M_1}{\alpha M_0(S_{11} - S_{12} - S_{44}/2)}. \quad (9)$$

Here, α is a weight parameter discussed at length in an earlier article.²⁴

III. EXPERIMENTAL DETAILS

The experiments were performed using stainless steel gaskets with the following dimensions: thickness—290 μm , thickness in the indented region—35 μm , and central hole diameter—85 μm . A piece measuring $\approx 80 \times 80 \mu\text{m}^2$ was cut from the as-supplied Nb rod and placed in the central hole. The Nb samples from Alfa-Aldrich had trace metal impurities (in ppm) below 1000, the major ones being Ta—700, Si—180, Mg—5, and Ca—2. No pressure medium was used to obtain nonhydrostatic stresses characteristic of Nb. The primary beam (cross-section $15 \times 15 \mu\text{m}^2$ and wavelength of 0.03678 nm) from HPCAT beam line was used. The pressure was increased in steps of ~ 5 GPa and the diffraction pattern recorded at each pressure on a Mar345 image plate.

The diffraction images were integrated using fit2d program²⁵ to give intensity versus 2θ diffraction profile (Fig. 1). The FWHM and $2\theta_0$ of each diffraction line were determined by fitting a four-parameter pseudo-Voigt function to the diffraction data using the PeakFit program. To assess the diffraction-data quality and fit agreement of the diffraction

FIG. 1. The diffraction patterns of Nb from ambient pressure to 41.4 GPa as recorded with conventional diffraction geometry of the DAC.

peaks, the patterns at ambient pressure and at 41.4 GPa were selected. First five peaks with adequate background were separated (Figs. 2 and 3). A function of the type given below was fitted to each peak

$$I = I_0[\eta L(2\theta) + (1 - \eta)G(2\theta)] + 2\theta m + n, \quad (10)$$

where

$$L(2\theta) = [1 + (2\theta - 2\theta_0)^2/w^2], \quad (11)$$

and

$$G(2\theta) = \exp[-(\ln 2)(2\theta - 2\theta_0)^2/w^2]. \quad (12)$$

$L(2\theta)$ and $G(2\theta)$ are the Cauchy and Gaussian functions, respectively.²⁶ The terms I_0 , $2\theta_0$, $2w$, and η are the peak intensity, peak position, FWHM, and weight parameter (shape factor), respectively. The last two terms in Eq. (10) represent linear background, the m and n being constants. The background-corrected peak-only profile agreement index²⁷ R'_p was used to assess the goodness of fit. R'_p is defined by the relation

$$R'_p(\%) = \left[\sum_i |I_{io} - I_{ic}| / \sum_i |I_{io} - I_{ib}| \right] \times 100. \quad (13)$$

The parameters I_o , I_c , and I_b are the observed, calculated from Eq. (10) with the fitted parameters, and the background intensities, respectively. The results of the fit are shown in Table I. The results obtained from the PeakFit program are also shown for comparison. Small values of R'_p indicate an excellent overall fit of Eq. (10) to the diffraction data. Further, as judged from the standard errors, the two parameters $2\theta_0$ and $2w$ that are used in the computation of $p_{\max}$ and t are estimated with high degree of precision. It is seen from Table I that the individually fitted peak-parameters agree

FIG. 2. The expanded views of intensity- 2θ profiles of the first five peaks (dots) recorded at ambient pressure. Continuous lines—fit of Eq. (10); unfilled circles— $(I_o - I_c)$ versus 2θ plots.

very well with the corresponding values obtained from the PeakFit program. Other patterns at the intermediate pressures give similar results.

IV. RESULTS AND DISCUSSION

The ambient pressure single-crystal elastic moduli and their pressure derivatives needed to compute $Y(hkl)$ and Y were taken from ultrasonic velocity measurement experiments.²⁸ The elasticity data at high pressure were derived from a third order finite strain equation.^{29,30} It may be noted that the use of Eq. (9) requires the knowledge α_0 , the value of α relevant for Nb. A three-parameter exponential decay function was fitted through the α_0 versus pressure data taken from an earlier study.¹⁹ This function was used to compute the α_0 -value at any required pressure.

Typical results of fitting Eqs. (2) and (6) to the line width-data are shown in Figs. 4(a) and 4(b), respectively. It is noted that the scatter in Fig. 4(b) is much larger than that

FIG. 3. The expanded views of intensity- 2θ profiles of the first five peaks recorded at 41.4 GPa. Symbols have the same denotation as in Fig. 2.

in Fig. 4(a). This is understandable as Eq. (6) ignores the $Y(hkl)$ -dependence of strain²⁰ that appears as the scatter in the fit. Fig. 5 shows typical gamma plots. The runs at pressures lower than 5.4 GPa were discarded as the gamma plots for these runs were of poor quality. Fig. 6 shows the micro-DS derived from Eqs. (5) and (7) and t (macro-DS) from Eq. (9). Also shown in Fig. 6 are t versus pressure data obtained from the analysis of the radial diffraction patterns.¹⁹ It can be seen that $p_{\max}$ determined from Eq. (5) are marginally lower than those determined using Eq. (7). The t - P data derived using Eq. (9) and the radial diffraction data¹⁹ agree well with $p_{\max}$.

Standard tensile tests at ambient pressure and temperature show that the yield stress of Nb is sensitive to the impurity levels.³¹ The samples with an impurity level of 1500 ppm is 0.08 GPa and increases to 0.21 GPa for samples with impurity level of 6500 ppm. The estimated strength at ambient pressure from the present data is $0.2 (\pm 0.1)$ GPa. Considering large errors in the estimated strength at ambient

TABLE I. The parameters obtained by fitting Eq. (10) to the intensity—2 θ data at ambient pressure and 41.4 GPa. The standard error (S.E.) for each parameter is listed in the lower row. The numbers between the square brackets are obtained from the PeakFit program.

		111	200	211	220	310
I_0	0 GPa	26946	2819	3175	917	1209
S.E.		123	10	6	2	2
$2w$		0.0694	0.0834	0.1186	0.1316	0.1318
		[0.069]	[0.083]	[0.119]	[0.132]	[0.131]
S.E.		0.0004	0.0004	0.0004	0.0004	0.0002
		[0.000]	[0.001]	[0.001]	[0.002]	[0.002]
η		0.65	0.47	0.57	0.65	0.50
S.E.		0.02	0.02	0.01	0.01	0.01
$2\theta_0$		9.0428	12.8056	15.6936	18.1388	20.3045
		[9.0427]	[12.8055]	[15.6936]	[18.1387]	[20.3045]
S.E.		0.0001	0.0001	0.0001	0.0001	0.0001
		[0.0001]	[0.0001]	[0.0002]	[0.0002]	[0.0007]
m		-91.1	-70.0	-7.7	-27.7	-21.8
S.E.		39	9	3	1	1
n		2031	2010	1095	1451	1350
S.E.		350	113	52	25	19
R_p (%)		5.8	2.2	1.8	1.4	1.6
I_0	41.1 GPa	10203	1785	1168	390	603
S.E.		57	7	4	2	2
$2w$		0.1656	0.1128	0.3104	0.3178	0.2734
		[0.116]	[0.113]	[0.311]	[0.327]	[0.276]
S.E.		0.0012	0.0006	0.0014	0.0026	0.0014
		[0.001]	[0.001]	[0.002]	[0.007]	[0.005]
η		0.46	0.59	0.50	0.69	0.70
S.E.		0.03	0.02	0.02	0.03	0.02
$2\theta_0$		9.5746	13.5910	16.6262	19.2205	21.5431
		9.5745	[13.5908]	[16.6268]	[19.2190]	[21.5419]
S.E.		0.0004	0.0002	0.0005	0.0007	0.0004
		[0.0003]	[0.0003]	[0.0007]	[0.0019]	[0.001]
m		-94	-94	-19	-26	-29
S.E.		19	4	1	1	1
n		2195	2395	1339	1475	1549
S.E.		182	52	22	16	20
R_p (%)		6.2	3.4	4.2	4.8	3.6

pressure from high-pressure data, this estimate is in reasonable agreement with the ambient pressure strength data.

The strength increases steeply as the pressure is increased from the ambient, reaches a local maximum, and drops before it registers a monotonous increase beyond 15 GPa. This feature persists in the strength-pressure data derived from the line-width as well as the line-shift analyses. The pressure-dependence of strength in the 5–15 GPa region is anomalous. It may be noted that a similar trend in strength-pressure data was observed in an earlier study except that the minimum in the strength-pressure plot occurred at much higher pressure.¹⁷ The origin of this anomaly is not clear at present.

In a study on the strength of MgO by line width analysis,⁹ $2p_{\max}$ was found to agree well with the strength-pressure data determined from the analysis of the radial diffraction data.³² The estimation of strength of Fe in the hexagonal phase³³ showed that it was $2p_{\max}$ that agreed with the strength derived from the radial diffraction data.³⁴ These two

FIG. 4. Typical fits of (a) Eq. (2) and (b) Eq. (6) to the line-width (in arc radian) data. Because of large scatter, no line fitted through the data points at 41.4 GPa in (b) is shown.

FIG. 5. The measured lattice parameter $a_m(hkl)$ versus $3(1 - 3 \sin^2\theta)\Gamma(hkl)$ plots, termed gamma-plots, at different pressures.

FIG. 6. Comparison of micro- and macro-differential stresses, $p_{\max}$ and t .

examples probably led to a generalization that $2p_{\max}$ is the correct measure of strength and would match the strength derived from the radial diffraction data. More recently, $2p_{\max}$ was found to agree well with t derived from the radial diffraction data on silica.^{35,36} Many other studies (e.g., Refs. 10–12) used $2p_{\max}$ as the criterion of strength. In the present study, the use of $2p_{\max}$ as the measure of strength will result in large disagreement with the macro-DS obtained either from Eq. (9) or from the radial diffraction data.¹⁹ Such differences between $2p_{\max}$ and the macro-DS have been observed earlier in case of diamond.¹² It was suggested¹² that this difference arose due to cupping of the diamond anvils at high pressure, which constrained the radial flow of the diamond sample and prevented t from reaching the limiting value. However, this fails to explain the fact that the differences between $2p_{\max}$ and macro-DS in case of both diamond and Nb persist down to the lowest pressures where the cupping of the anvil faces would tend to become insignificant. Another factor that could influence the estimates of strength from the radial diffraction data is the interference from the gasket that can prevent t from reaching its maximum value.³⁷ The gasket interference can become so dominant that it can result in negative t , as was observed in the compressibility studies of Nb.³⁸ It is interesting to note that in both cases, the present data and those on diamond, the use of $p_{\max}$ as the criterion of strength brings in a better agreement with the macro-DS. In case of Nb, taking $2p_{\max}$ as the measure of strength leads to another inconsistency in that the estimated strength at ambient pressure from $2p_{\max}$ versus pressure data would reach 0.5 GPa, which is too large to match the strength obtained from the ambient pressure tensile tests.³¹ This supports the assumption that $p_{\max}$ represents the strength of Nb.

V. SUMMARY

The strength versus pressure data of Nb derived from the line-shift data are found to be in good agreement with $p_{\max}$. The ambient pressure strength estimated from the strength-pressure data is in good agreement with the yield strength determined from the standard tensile tests. This study highlights the ambiguity that exists in the criterion to be used while estimating the strength from the diffraction line-width analysis; many studies reported in the literature use $p_{\max}$ while others $2p_{\max}$ as a measure of strength. Present understanding of the nature of micro-stresses in the sample and relation thereof with macro-DS does not appear to be adequate. Another area that lacks proper understanding is the role of the gasket in determining the deformation behavior of the sample.

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