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DAC Measurement of High-Pressure Yield Strength of Vanadium using In-Situ Thickness Determination

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Abstract

The pressure-dependence of the quasi-static yield strength of vanadium in polycrystalline foils and powders has been measured up to 80 GPa at room temperature using an implementation of a non-hydrostatic diamond anvil cell technique [C. Meade and R. Jeanloz, *J. Geophys. Res.* 93, 3261 (1988)]. A new feature of this work is the use of an in-situ determination of the sample thickness. Following an initial increase in the strength with pressure, a decrease in the strength of vanadium was observed beginning at 40~50 GPa.

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Introduction

The mechanical properties of vanadium under pressure are extraordinary, related to a subtle effect in the electronic structure. Its unique properties make it particularly attractive for the study of the effect of elastic anisotropy and weak martensitic phase transformations on material strength. Vanadium is a non-magnetic group VA transition metal possessing a body-centered cubic (bcc) crystal structure and refractory properties at ambient pressure. It has technological applications from structural elements in fusion reactors to use as a bonding agent for titanium and steel, and it is an important alloy component of certain steels. Pure vanadium exhibits elastic anisotropy due to pressure softening of the C_{44} shear modulus¹⁻³ common to the group VA elements, but only in vanadium has C_{44} been calculated to go to zero (and negative) in the zero temperature bcc phase (at ~ 1.4 Mbar). The pressure softening is of interest because of its impact on strength and other mechanical properties³ and also because it enhances the electron-phonon coupling leading to an anomalously high superconductivity transition temperature.⁴ The negative modulus calculated in the theoretical studies¹ suggested a pressure-induced structural instability in vanadium. This prediction was confirmed by recent x-ray diffraction studies, which observed a structural transformation in vanadium from a body-centered cubic (*bcc*) phase to a rhombohedral phase at about 0.69 Mbar.⁵

This unusual behavior may affect the yield strength of vanadium. The yield strength is the minimum stress to induce plastic deformation. Lower stresses only cause reversible elastic deformation. The shear modulus sets a natural scale for material strength,⁶ so it may be expected that the extraordinary softening of the shear modulus will

lead to an effect on the strength at pressure, perhaps even a reduction of the strength at pressure. This decreased strength would be unusual since, as Bridgman observed, metals commonly show enhanced strength and ductility by applying small amounts of load/pressure.⁷ Several mechanisms have been proposed to account for the pressure-dependence of the yield strength applicable to the bcc phase.⁸ The strength may also be affected by the pressure dependence of the order parameter of the rhombohedral phase at pressures above the transition. To date there has been no measurement of the yield strength of vanadium at pressures approaching a Mbar. Here we use the diamond anvil cell to measure the strength of pure vanadium at room temperature at pressures up to 0.8 Mbar. The results provide experimental data to challenge or validate theoretical models and to develop insights into the fundamental mechanisms governing the pressure-dependent yield strength of vanadium.

The diamond anvil cell (DAC) is a useful and extremely versatile instrument for high-pressure experimental studies.⁹ The capability of the DAC to rapidly achieve high pressures and the modern capabilities of 3rd generation synchrotron x-ray sources has enabled studies of the mechanical properties of various materials at high pressures.¹⁰⁻¹²

Previously, Meade and Jeanloz reported yield strength measurements for MgO based on measurement of a sample's thickness and radial pressure gradient.¹³ The radial pressure gradient dP/dr is related to the shear stress σ_{rz} (and strength) of the material through the mechanical equilibrium equations.¹⁴ In axial symmetry such as in an ideal DAC sample, this relationship is given by $\sigma_{rz} \approx (h/2) * (dP/dr)$ where h is the sample thickness. In the middle of the sample, equidistant from the two anvils and the edges of the anvils, the yield stress σ_0 of the sample can be approximated as twice the shear stress

(Tresca yield criterion) under two assumptions, (1) that the normal stress does not vary along the sample depth, and (2) that the radial and azimuthal stresses are approximately equal,^{11,15}

$$Y=2 \sigma_{rz} \approx h \cdot (dP/dr). \quad (1)$$

In this study we determined the radial pressure gradient (dP/dr) by measuring the pressure distribution across vanadium sample in a DAC. Energy- and angle-dispersive diffraction with an x-ray beam focused to a spot size of $\sim 10 \mu\text{m}$ were used to determine the crystal structure and lattice parameters. Using these parameters combined with the known EOS of vanadium yielded the pressure. An in-situ x-ray absorption technique was used to determine the sample thickness h . When an x-ray is transmitted through the sample, the intensity of the transmitted x-ray can be expressed as

$$I=I_0 \exp (-\mu \cdot \rho \cdot h) \quad (2)$$

where I is the transmitted intensity, I_0 is the incident intensity, μ is the mass absorption coefficient, ρ is the sample density, and h is the sample thickness. The values of I and I_0 were measured. μ is assumed to be pressure-independent and was calculated from the slope of the absorbance ($A=-\log I/I_0$) as a function of foil thickness for a set of reference foils at ambient conditions. We also corrected for the effect of the absorption due to the diamond anvils themselves. Before applying pressure the initial absorption was measured, which corresponded to the sum of the absorption due to both the diamond anvils and the foil. This initial measurement served as a calibration to correct for the diamond absorption in subsequent measurements. The sample density, ρ , was determined by in-situ x-ray diffraction. An unknown sample thickness, h , can then be obtained from Eq. (2), from the known values of μ and ρ and the measured absorbance.

Experimental

We used two experimental approaches for our measurements. In one case we used an energy dispersive x-ray diffraction (EDXD) system (16BMB at HPCAT/Advanced Photon Source/Argonne National Laboratory). This experiment was performed with 200 μm diameter diamonds mounted in a DAC. A rhenium gasket, pre-indented to a thickness of 25 μm and drilled with a ~ 80 μm diameter hole, was packed with vanadium powder (99.99% Alfa Aesar ~ 325 mesh, ~ 36 micron grain size). EDXD patterns for pressure determination were collected at a spatial resolution and with an x-ray beam size of ~ 10 μm (FWHM) and a Ge point detector positioned at 12° from the direct beam ($E \cdot d = 59.3073$). Incident and transmitted intensities of the x-ray beam were measured using two MIC-205 ion chambers from Advanced Design Consulting USA, Inc. Data were collected up to a pressure of 80 GPa. To estimate the sample thickness, absorption of the rhenium gasket was measured. A number of rhenium foils indented to various thicknesses were used to get an effective mass absorption coefficient for a white beam. In this case the sample thickness was assumed to be homogeneous and independent of the radial location along the sample. X-ray diffraction patterns and the absorption were collected at several points separated by 10 μm along the gasket hole diameter and perpendicular to the diamond culet.

The second experimental approach utilized an angle dispersive x-ray diffraction (ADX) system (16BMD at HPCAT/Advanced Photon Source/Argonne National Laboratory). This experiment was carried out with 300 μm culet diamonds. Instead of

studying vanadium powder packed in a gasket hole, a 100 μm -thick vanadium foil was squeezed between the 300 μm culet diamonds. A series of vanadium foils of 100, 75, 50 and 25 μm thicknesses (99.8% purity with <50 ppm Al, Ca, Cr, Cu, Ni, Sn and 150 ppm Mo, Si and Ti and 200 ppm Fe, ESPI metals) were used to calibrate the absorption measurements with PDC254d-PN diodes (Detection Technology). We used an incident monochromatic x-ray beam with a size of ~ 10 μm (FWHM), $\lambda = 0.387451$ \AA and an image plate detection system (MAR3450 imaging plate detector). Incident and transmitted intensities of the x-ray beam were measured as described above. One difference in this set of experiments was the use of a series of vanadium foils instead of rhenium foils to calibrate the sample thickness measurement as a function of pressure. This approach allowed us to measure the thickness through the sample. The pressure in the DAC was incrementally increased. Following each pressure increment, x-ray diffraction patterns and the absorption scans were collected at several points spaced by 30 μm across the diameter of the diamond culet to determine the pressure, radial pressure gradient and thickness across the sample. The maximum pressure for this set of data was 65 GPa. X-ray diffraction patterns were converted from 2-dimensional images to intensity versus 2θ with the Fit2D program¹⁶ and then the structure and lattice parameters were determined using the XRDA¹⁷ program.

The vanadium EOS reported by Ding et al.⁵ was used to calculate the pressure from our measurement of the lattice parameters of vanadium. It is important to note that in the work of Ding et al. the rhombohedral and cubic phases lie, within experimental accuracy, on a single pressure-volume EOS curve. Over a broad range following the bcc-rhombohedral transition, the diffraction patterns of these phases are very similar; the

diffraction pattern of the high-pressure rhombohedral phase differs from the bcc phase in line broadenings rather than well resolved peak splittings.⁵ Thus we have made all of our pressure and density evaluations from the diffraction measurements using the bcc structure and the non-hydrostatic EOS of Ding et al.⁵ Thus we avoid complications related to identifying the precise transition pressure, which are difficult to discern given the resolution of our diffraction measurements. The analysis methodology for the yield strength is not affected by this simplification, since it does not depend on the crystal structure, only the thickness and pressure gradient.

Results

Angle-dispersive powder x-ray diffraction patterns for vanadium at 1.5 GPa and at 65 GPa with $\lambda = 0.38745 \text{ \AA}$ are shown in Fig. 1a. Selected EDXD patterns up to 80 GPa are stacked in Fig. 1b. Here asterisks denote small peaks from the rhenium gasket. When the cubic phase (a_C, b_C, c_C) distorts to the rhombohedral phase (a_R, b_R, c_R) = ($-\frac{1}{2}a_C + \frac{1}{2}b_C + \frac{1}{2}c_C, \frac{1}{2}a_C - \frac{1}{2}b_C + \frac{1}{2}c_C, \frac{1}{2}a_C + \frac{1}{2}b_C - \frac{1}{2}c_C$), the $(110)_C$ line splits to $(100)_R$ and $(1-10)_R$, and the $(211)_C$ line splits to three lines [$(110)_R, (2-10)_R$ and $(2-1-1)_R$], whereas the $(200)_C$ line remains a single line $(1-11)_R$. We do not observe that the (110) or (211) peaks of the *bcc* phase split into multiple peaks up to 65 GPa, in the ADXD data.

Since pressure increased very slowly, strain rates are expected to be very small ($\sim 10^{-3} \sim 7 \times 10^{-2} \text{ s}^{-1}$).^{13,18} We assume the yield strength (Y) is equivalent to the sample thickness multiplied by the radial pressure gradient as shown in Eq.(1).¹³ Figure 2 (a) shows the ADXD measured pressure (solid squares) and sample thickness (open

triangles) as a function of radius along the horizontal diameter of the 300 μm culet for a given DAC load. The radial pressure gradient was obtained from the slope of the pressure as a function of the radius. Using Eq. (1), the yield strength at each DAC load was calculated by multiplying the radial pressure gradient and the thickness (Fig. 3). The pressure at the center of the sample is taken as the nominal pressure for a given DAC load. Similarly, the thickness value was measured at the sample center. For the example shown in figure 2, the pressure is 39.8 GPa. The average dP/dr is 0.194 GPa/ μm from the slope of the radius and the pressure. The yield strength as a function of pressure from a sequence of DAC loads is shown in Fig. 3. Figure 2b shows the yield strength as a function of the radius at the given DAC load, 39.8 GPa. The yield strength at each point is obtained by multiplying the tangent of the pressure as a function of radius and the thickness at the given point. The maximum yield strength at the given DAC load, 39.8 GPa is 4.158 GPa as shown in Fig. 2b. In Fig. 4, this maximum yield strength is within the error range at the given DAC load, 39.8 GPa.

Our experimental yield strength values at ambient condition are 0.336 GPa for ADXD and 0.488 GPa for EDXD while the shear modulus of polycrystalline vanadium at the ambient pressure is reported as 39 GPa.⁴ The yield strength is very small compared to that of high strength steels at ambient pressure, 2.5 GPa. This softness is consistent with the use of vanadium as bonding material. Steinberg, Cochran and Guinan suggested that $Y_L/Y_0 = G_V(P)/G_V(0) = (1 + A_0 P(V/V_0))^{1/3}$ where Y and G are the yield strength and the polycrystalline shear modulus at given pressure P .¹⁹ However, in our study we find that the vanadium yield strength does not adhere to this idealized case.

For the EDXD experiment using a powder sample, the rhenium gasket thickness was assumed to be the same as the sample thickness. Since the powder becomes more efficiently packed above 10 GPa and vanadium is a soft material, the sample in the experimental pressure range is expected to behave as a thin foil. As demonstrated elsewhere,¹¹ plots of 100 μm -thick foil and powder samples represent extreme cases of high strain and low strain.

Discussion

We observed that vanadium strength decreases in the pressure range of 40~50 GPa. This type of pressure-dependent yield strength behavior is not uncommon. Bridgman's work on nickel, molybdenum, and tungsten also reported decreases in the yield strength.⁷ He called it strain-softening and interpreted this behavior as inhomogeneity (or damage) in highly strained samples; this would be called strain localization in tensile tests. A second order phase transition of vanadium was reported at 35~69 GPa.^{5,20,21} This bcc to rhombohedral phase transition is expected to be a martensitic transformation in which the cubic symmetry is reduced to a trigonal symmetry through a diffusion-free distortion of the lattice.^{22,23} It is widely believed that particular features of the Fermi surfaces (FS) could cause a pre-martensitic phonon softening and lead to martensitic transformation.²⁴ Recent *ab-initio* calculations on vanadium elastic constants and shear modulus^{1,3} support the hypothesis that vanadium goes through a mechanical instability in C_{44} through a FS effect. Thus, vanadium undergoes both structural and yield strength changes over this pressure regime. It is

plausible that the decrease in strength is coincident and a feature of the structural change. Unfortunately our work was not able to resolve the subtle changes in the diffraction pattern associated with the bcc-rhombohedral transition.

Changes or non-uniform distributions of the intensity around Debye-Scherrer diffraction rings are indicators of the texture/preferred orientation. The ADXD experiment allowed us to observe this texture/preferred orientation effect under uniaxial compression. From our studies, figure 4 shows selected images of the two dimensional diffraction patterns of a vanadium foil in a DAC at the sample center ($r=0$). Several arcs of (110) and (200) diffraction rings of the vanadium foil are indicated with arrows. Their intensities relative to the rest or the arcs change significantly as pressure increases from 1 GPa, to 5 GPa to 40 GPa. This suggests that the degree of preferred crystallographic orientation in the sample is enhanced as pressure increases. Some researchers propose that this texture/preferred orientation of the sample may cause strain softening in the yield strength,^{11,13} an effect that may be particularly strong in vanadium at high pressure due to its elastic anisotropy.²

Tantalum (Ta), in the same periodic table group Va as vanadium, is also predicted to exhibit an anomaly in C' and C_{44} at high pressure in which the pressure hardening ceases as the shear moduli plateau in the range of 1 to 2 Mbar.²⁵ The yield strength of Ta was reported in various experiment conditions; nonhydrostatic condition using powders by Cynn²⁶ and hydrostatic condition with single crystals by Dewaele.¹⁰ The yield strength in both experiments exhibits 2.6~3 GPa at 50 GPa which is comparable to that of vanadium. Furthermore tantalum shows a smooth increase in its yield strength as the pressure increases up to ~1 Mbar, while vanadium shows decrease at 40~50 GPa. This

difference in properties may originate from the structural stability differences between tantalum and vanadium. Tantalum is stable as bcc up to a few Mbar and higher while vanadium transforms to a rhombohedral structure at much lower pressure.

Conclusions

We have measured the yield strength of vanadium up to 80 GPa under non-hydrostatic conditions. In this study, we used x-ray diffraction and absorption techniques to make in-situ measurements of the pressure gradient and the sample thickness. These measurements were used to evaluate the pressure-dependence of the material strength. We observed a decrease in the yield strength of vanadium over the pressure range of 40-50 GPa. We propose that this change in the yield strength pressure-dependence is an indicator of the phase transition from bcc to rhombohedral.

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Figure captions

Figure 1. (a) Angle dispersive powder x-ray diffraction patterns of vanadium foil with $\lambda=0.3875\text{\AA}$. Top and bottom lines correspond to the patterns at 65 GPa and 1 GPa, respectively. (b) Selected energy dispersive powder x-ray diffraction patterns of vanadium powder are stacked.

Figure 2. For a given DAC load, the pressure (GPa) and thickness (μm) as a function of the distance from the center (μm). (b) The strength calculated by multiplying the pressure gradient and the thickness at a given position according to Eq. (1). The pressure, thickness and strength are represented by solid squares, open triangles and solid circles. For this load as an example, the maximum yield strength is 4.158 GPa at the loading pressure of 39.8 GPa.

Figure 3. The yield strength as a function of pressure obtained by multiplying the average dP/dr as shown in Fig. 2a and the sample thickness. Solid squares and open circles represent the points from ADXD with foil and from EDXD with powder.

Figure 4. X-ray diffraction patterns of vanadium foil sample at (a) 1 GPa, (b) 5 GPa, (c) 40 GPa and (d) 64 GPa on MAR3450 image plates. Arrows are used to indicate the arcs of the (110) and (200) rings which show intensity changes.

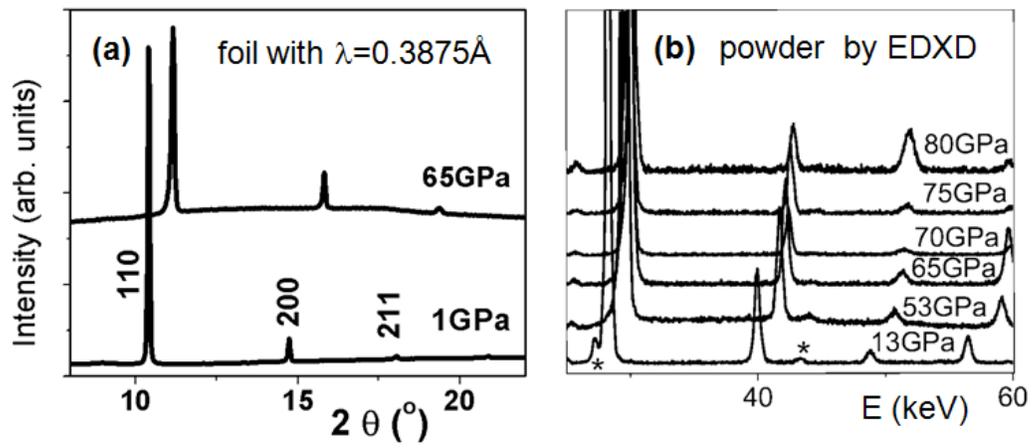


Figure 1.

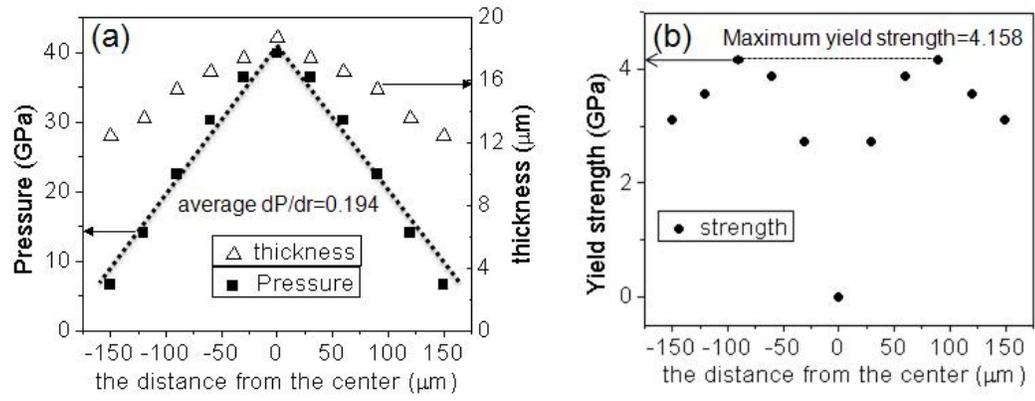


Figure 2.

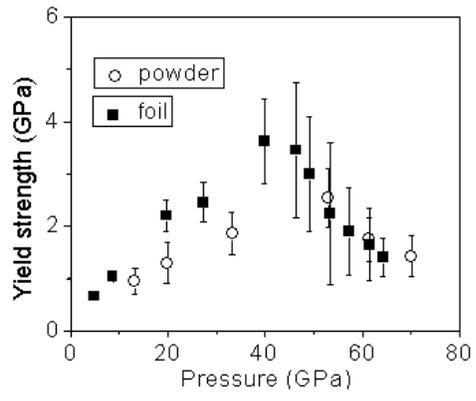


Figure 3.

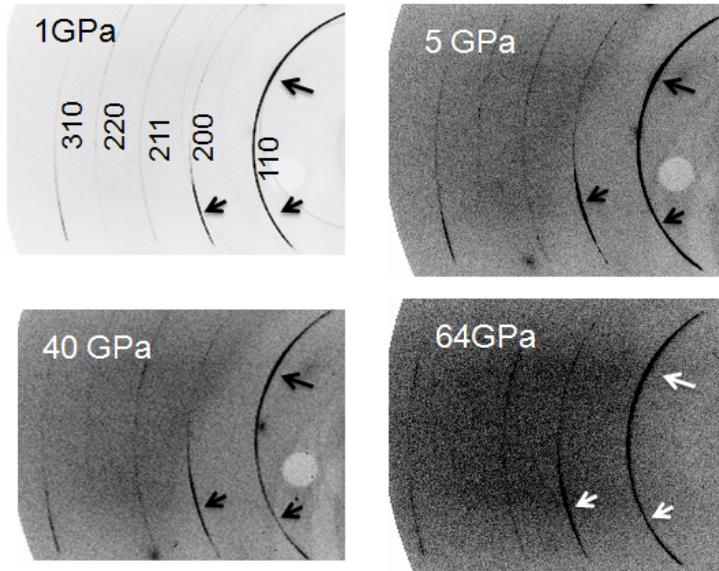


Figure 4.