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# Strength of rhenium from x-ray diffraction experiments under nonhydrostatic compression to 250 GPa

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Abstract. Polycrystalline rhenium in the form of a powder contained in a two-stage gasket was compressed in a diamond anvil cell. No pressure medium was used to ensure that maximum nonhydrostatic stresses that rhenium can support were produced. The pressure was increased in steps to a maximum of 250 GPa and the diffraction pattern recorded at each pressure using energy dispersive technique. The differential stress t, a measure of the compressive strength, was determined at any given pressure from the offset between the measured unit cell volume and volume computed from the pressure-volume relation under hydrostatic pressure. The data suggest that t is 2.5 GPa at a pressure of 5 GPa and increases linearly to 26 GPa at 250 GPa. The present data agree well with those obtained from the radial diffraction data to 37 GPa in an earlier study but differ significantly from the results of another study. Though comparable with the theoretical strength of ideal solids, the observed strengths are extremely large for a polycrystalline aggregate of a solid. The pure pressure effect on the strength described by the shear modulus scaling is inadequate to account for such a large increase of strength with pressure. It is suggested that the major contribution to strength comes from the strain hardening of rhenium that arises due to plastic deformation of the sample during nonhydrostatic compression in a diamond anvil cell.

### 1. Introduction

Rhenium, a group-VII transition metal, crystallizes in the hexagonal-close-packed (hcp) structure. Measurements of the volume change produced by static [1] and dynamic [2] pressures indicate that Re is highly incompressible. High-pressure x-ray diffraction studies [3] db not indicate any pressure-induced phase transition up to 216 GPa and suggest a nearly pressure independent *c/a*-ratio. Ultrasonic velocity measurements give high values of the single-crystal elastic moduli confirming the low compressibility of Re [4]. First-principles computations of the elastic moduli [5, 6] and their pressure derivatives are found to be in reasonable agreement with the ultrasonic data From the consideration of the Gibbs free energies of the hcp and body-centered-cubic (bcc) structures, Kaufman [7] suggested

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that Re might transform to the bcc phase at high pressure. However, first-principles calculations predict that hcp Re is stable to pressures in the range of a terapascal [8].

The increase in the yield (flow) stress of Re with increasing plastic deformation, termed strain or work hardening, is found to be the largest of all metallic materials [9, 10]. The successful use of Re as a gasket material in high-pressure studies with a diamond anvil cell is due to the fact that it develops, on compression, high enough compressive strength to retain appreciable thickness even at several hundred gigapascal without any "punch-through" at the edges of the diamond anvils. Two studies [11, 12] carried out in the past reported the strength of Re as a function of high pressure. The first study [11] combined the pressure-volume data measured under nonhydrostatic compression and that under hydrostatic pressure to estimate the strength under pressure up to 120 GPa. The second study [12] used radial diffraction data to determine the strength to 37 GPa. In this study, we derive the compressive strength of Re as a function of pressure up to 250 GPa using an approach that is essentially same as the one used in the earlier study [11]. However, the equations we use to analyze the data are based on the lattice strain theory [13–19] and differ from that used in the earlier study [11].

#### 2. Experimental details

X-ray diffraction experiments were carried out at the wiggler beam line X17C of the National Synchrotron Light Source of Brookhaven National Laboratory, using the energy dispersive x-ray diffraction method. A diamond anvil cell with a pair of bevel diamonds was used. The culet size of one of the diamonds was 0.17 mm flat face and 0.48 mm at the beveled edge and that of the second diamond differed slightly (0.19 mm and 0.49 mm). A two-stage gasket was used to contain the Re sample. The outer gasket consisted of a pre-indented 0.025mm thick stainless steel disk with a 0.090 mm central hole. A 0.025 mm-thick Re disk with a 0.040 mm sample hole was inserted in the hole of the stainless steel gasket. Re powder (99.99%) mixed with Pt-powder was loaded in the 0.040 mm hole. Pt was used as a pressure standard. The primary incident beam slit was  $0.1 \times 0.1 \text{mm}^2$  and the collimator was  $0.010 \times 0.010 \text{ mm}^2$ . The first receiving slit was  $0.15 \times 0.35 \text{ mm}^2$  and the second receiving slit was  $0.1 \times 5 \text{ mm}$ . An intrinsic solid state Ge-detector was used to record the diffraction patterns. A fixed  $2\theta_0 = 20^\circ$  was used in the experiments.

### 3. Lattice strain equations

The stress state of a solid sample under nonhydrostatic compression is axially symmetric about the load axis of the diamond anvil cell and is described by two equal stress components  $s_{11}$  along the two orthogonal set of axes parallel to the anvil face and a component  $s_{33}$  along an axis parallel to the load axis. The off-diagonal terms in the stress tensor are assumed to be zero. This assumption is not always valid in practice. The effect of the breakdown of this assumption on the lattice strain theory has been discussed in detail elsewhere [20, 21]. The difference ( $s_{33} - s_{11}$ ) is denoted by t, and its maximum value is limited by the compressive yield strength at the confining pressure that equals the mean normal stress ( $2s_{11} + s_{33}$ )/3. At a given pressure, the unit cell volume  $V_m$  measured under nonhydrostatic compression is larger than  $V_P$ , the unit cell volume under hydrostatic compression. As shown earlier [14], t is given by the relation

$$t = \frac{V_{\rm m} - V_{\rm P}}{V_{\rm P}} \frac{3K}{\langle (1 - 3\sin^2 \boldsymbol{q}_0) \rangle} \left[ \frac{1 - 2\boldsymbol{n}}{1 + \boldsymbol{n}} \right]$$
(3.1)

In terms of the shear modulus, equation (3.1) can be expressed as

$$t = \frac{V_{\rm m} - V_{\rm P}}{V_{\rm P}} \frac{2\boldsymbol{m}}{\langle (1 - 3\sin^2 \boldsymbol{q}_0) \rangle}$$
(3.2)

K, m and n denote the aggregate bulk modulus, shear modulus and Poisson's ratio, respectively. The negative sign in Eq. (33) of the earlier paper [14] appears because the convention of taking

compressive stress as negative was used. Noting that the pressure offset is given by  $\Delta P = K [(V_m - V_P) / V_P]$ , equation (3.1) can be rewritten as

$$t = \frac{3\Delta P}{\langle (1 - 3\sin^2 \boldsymbol{q}_0) \rangle} \left[ \frac{1 - 2\boldsymbol{n}}{1 + \boldsymbol{n}} \right]$$
(3.3)

Here,  $\Delta P = (P_{\rm m} - P_{\rm h})$ . The terms  $P_{\rm m}$  and  $P_{\rm h}$  are pressures computed from the *P*-*V* relation measured under nonhydrostatic and hydrostatic compressions, respectively, at a fixed  $V/V_0$ . Equations (3.1), (3.2) and (3.3) are equivalent if *P* at which  $V_{\rm m}$  and  $V_{\rm P}$  in (3.1) are computed is chosen at  $(P_{\rm m} + P_{\rm h})/2$ . It may be noted that the elastic moduli in these equations are to be taken at the relevant pressure.

#### 4. Results

The diffraction pattern recorded at 251 GPa is shown in figure 1. The pressure in each run was determined by using the measured volume compression of Pt in the equation of state proposed by Holmes et al [22]. The cell volumes  $V_{\rm m}$  were determined from the measured *d*-spacings. These values together with the data obtained by Jeanloz et al [11] are shown figure 2. To determine *P*-*V*<sub>P</sub> data under hydrostatic pressure the fourth order Birch equation given below was used

$$F = \frac{P}{3f(1+2f)^{5/2}} = K_0[1+a_1f+a_2f^2]$$
(4.1)

$$f = [(V_0 / V)^{2/3} - 1]/2$$
(4.2)

Here, *F*, and *f*, are the normalized pressure and Eulerian strain, respectively.  $K_0$  is the zero-strain bulk modulus, and  $a_1$ , and  $a_2$  are functions of  $K_0$ ,  $K_0'$ , and  $K_0''$  [23]. The single and double primes indicate the first and second pressure derivatives of the bulk modulus at zero strain. Equation (4.1) was fitted to the pressure-volume data obtained from shock wave measurements [2]. This gave  $K_0=364.97(\pm 0.64)$ ,  $a_1=0.48(\pm 0.05)$  and  $a_2=-2.03(\pm 0.33)$ . The *P*-*V*<sub>P</sub> data computed from equation (4.1) with these constants are shown in figure 2 by continuous lines. It may be noted that the constants in equations (4.1) used by Jeanloz et al [11] are significantly different from those used in this study. However, the *P*-*V*<sub>P</sub> data computed from the constants used by Jeanloz et al [11] do not show any significant difference with the present data up to 150 GPa. The strength *t* was determined from equation (3.2). The pressure dependent  $\mu$  required for these calculations was determined using  $\mu_0=179$  GPa and  $\mu_0'=$ 1.8 in the Birch equation [24] viz.:

$$\mathbf{m} = \mathbf{m}_0 x^{5/3} [1 + \frac{1}{2} (3K_0 \mathbf{m}_0 / \mathbf{m}_0 - 5)(x^{2/3} - 1)]$$
(4.3)

The term  $(1 - 3\sin^2 q_0)$  appearing in equation (3.2) equals 0.91 here and is constant for all reflections. The compressive strength *t* determined in this study as a function of pressure is shown in figure 3. The error bars indicate standard errors arising only from the uncertainty in  $V_m$ . Uncertainties in  $\mu$  and  $V_P$  are hard to estimate. The strength data from the earlier studies [11, 12] are also shown in figure 3.

#### 5. Discussion

The pressure-volume data from this study and an earlier measurements to 119 GPa [11] are shown in figure 2. To compare the data from two studies we fitted the third-order Birch-Murnaghan equation to each set of data. The computed  $V_0/V_m$  from this study is larger than that from [11] by 0.3% at 20 GPa and increases to 0.6% at 120 GPa. Though not relevant to this comparison, the difference begins to decrease above ~150 GPa and vanishes at ~225 GPa. The trend is reversed above 225 GPa. These differences are small in comparison with the combined errors of measurements in the two studies. It is seen that at any given pressure,  $V_m > V_P$  due to the effect of nonhydrostatic compression.





Figure 1. Diffraction pattern of Re.

Figure 2. Volume compressions data under nonhydrostatic (symbols) and hydrostatic pressure.



**Figure 3.** Strength of Re as function of pressure. Dots – present data, circles – Duffy et al. [12], triangles – Jeanloz et al. [11], and squares – recomputed from equation (3.2) using measured  $V_m$  from [11]. Solid line – straight line fit through dots, circles, and squares gives t = 2 + 0.096P. Dashed line – shear modulus scaling taking ambient pressure strength as 1 GPa.

Duffy et al [12] used radial diffraction data to determine the strength. It is seen from figure 3 that the strength data of Duffy et al [12] are in good agreement with the present data. This agreement is not surprising as both the present set of formulae and those used by Duffy et al are based on the same lattice strain theory. The results of Jeanloz et al. [11], however, show large differences. Since the measured unit cell volumes under nonhydrostatic compression and the computed  $V_{\rm P}$  in [11] are in excellent agreement with those in this study, the differences in estimated strength solely arise due to the fact that the formula used to derive the strength differed in the two studies. It can be easily verified that equation (4) of [11] gives *t* that is ~3-times larger than *t* obtained from equation (3.3) for any given set of experimental data.

The pure pressure effect on yield strength is given by shear modulus scaling [25]. The ambient pressure yield strength of Re reported in the literature varies in the range 0.7-1.3 GPa [9]. Taking the ambient-pressure shear modulus as 179 GPa and yield strength as 1 GPa, the shear-modulus scaling suggests that the strength of Re under pressure is given by 0.006m Considering the pressure dependence of m, this effect predicts strength of ~5 GPa at 250 GPa. The strength measured in this study varies from 0.01m at 2.5 GPa to 0.04m at 250 GPa. These magnitudes, though comparable with the strength of ideal solids [26–28] are extremely large for the polycrystalline aggregate of a real solid. The plastic deformation during nonhydrostatic compression of the sample in a diamond anvil cell is an important factor in the interpretation of strength derived from the diffraction data. It changes the state of the sample in two ways: The crystallite size [29–31] and the sample thickness decrease with increasing compression. This decrease in grain size results in an increase in strength following the Hall-Petch relation [32, 33]

$$\boldsymbol{s}_{\rm Y} = \boldsymbol{s}_0 + K_{\rm HP} / D^{1/2} \tag{5.1}$$

Here,  $S_0$  is the yield strength at one atmosphere and *D* is the grain size, which is taken as the crystallite size determined from diffraction line-width analysis [29–31]. The term  $K_{\rm HP}$  is a material-dependent constant called strengthening coefficient or the Hall-Petch parameter. In absence of the information on the grain-size reduction under nonhydrostatic compression and  $K_{\rm HP}$  of Re, the quantitative estimate of the grain-size contribution to strength is not possible. However, the magnitude of strengthening from this source can be estimated by assuming the value of  $K_{\rm HP}$  for pure Re as 12 GPa/ $\sqrt{nm}$ , a value close to those for hexagonal metals. With this value of  $K_{\rm HP}$ , a grain size in the range of 10-20 nm at 250 GPa would account for a strength increase in the range of 3–4 GPa. Thus, the contribution to strength from both the shear modulus scaling and grain-size factor together is ~10 GPa at 250 GPa. The major contribution to strength of Re comes from the effect of plastic deformation on the flow (yield) stress known as strain or work hardening. The strain hardening effect is described by the relation [34],

$$\boldsymbol{s}_{\mathrm{fY}} = k\boldsymbol{e}^n \tag{5.2}$$

Here,  $\mathbf{s}_{\text{fY}}$  is the flow or yield stress, k and n are material constants, and e is the plastic strain. With the experimenta values [10], k = 28.7 GPa and n = 0.78 [10], Re shows the highest strain hardening effect of all metals. Equation (5.2) suggests that plastic strain of ~50% at 250 GPa can result in a strengthening of ~16 GPa. Such large plastic strains are not inconceivable at high nonhydrostatic compression. The constants k and n are expected to be pressure dependent [35].

In conclusion, the strength of Re at high pressure determined by x-ray diffraction is found to be extremely large. The increased strength under pressure cannot be explained by shear-modulus scaling. It is pointed out that the nonhydrostatic compression, which is essential for the strength determination by the diffraction method, causes severe plastic deformation of the sample. This results in the reduction of the crystallite size and sample thickness leading to strengthening due to grain size and work hardening. In the case of Re, work hardening effect appears to be the dominant factor leading to strengthening under pressure.

## 6. References

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