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Phase stability and the equation of state of the transition-metal alloy Mo-Re at high pressure

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The transition-metal alloy Mo–32 at. % Re was compressed in a diamond anvil cell to 193±8 GPa (volume fraction $V/V_0=0.721$) and studied by x-ray diffraction using a synchrotron source. Copper was used as an internal pressure standard in the experiment. The bcc phase of this Mo-Re alloy was found to be stable to the highest pressure and the expected phase transformation to the hcp phase was not observed. The equation of state of the Mo-Re alloy is compared with its constituent metals. Mo-Re alloys show a rapid decrease in compressibility with increasing Re concentration. The rigid-band model for the alloy along with the first-principles theoretical calculations for pure Mo are not adequate to explain the experimental results.

Transition metals and alloys occupy a unique position in the periodic table because of their high cohesive energies, incompressibilities, and magnetism due to the unfilled *d* shell. Phase transitions in these materials induced by temperature and pressure are of considerable current interest because of their applications as high-temperature, superconducting, and magnetic materials. The dominant role of *d* electrons in providing cohesion and phase stability in transition metals has been well recognized.[1,2] First-principles calculations[3–5] have been done on most transition metals to reproduce the observed trends in crystal structures, cohesive energies, lattice parameters, and bulk modulus. The group-IV metals Ti, Zr, and Hf and group-VI metals Cr, Mo, and W are of particular interest because of their proximity to structural instability. These groups of metals have been the focus of several theoretical and experimental investigations.[6–8] However, transition-metal alloys have not been investigated experimentally or theoretically in the ultrahigh-pressure regime ($P > 100$ GPa).

The present research is motivated by the interplay of alloying and pressure variables in the phase stability of transition metals and alloys. It has been suggested earlier that the application of pressure is equivalent to alloying in the transition metals in the beginning and the middle of the series.[9] This correspondence between pressure and alloying is due to the transfer of *sp* electrons to the *d* bands as a result of compression.[10] The interesting implication is that the transition metals would adopt the crystal structures of their neighbors to the right in the periodic table because of an increase in *d*-band population caused by pressure. Ultrahigh-pressure shock studies on pure Mo indicate the possibility of a solid-solid transition at 210 GPa and 4100 K.[11] For a group-VI metal such as Mo, for example, a structural transition from bcc to hcp phase is calculated to happen when 0.34 electrons/atom are added to the *d* band of Mo.[6] A similar conclusion is also reached by examining the destabilization of the bcc lattice with respect to the hcp in different alloys of Mo and W.[11,12] It is generally seen from the alloy data that addition of 0.5 electrons/atom to the *d* band of Mo would cause phase transformation to the hcp lattice. It is thus expected that the addition of *d*-rich metals to Mo would bring down the bcc-hcp phase boundary to lower pressures. In this context, alloying with Re is most promising because the solubility[13] of Re in solid Mo is as high as 42 at. % at 2500 °C. In this paper, we have investigated the effect of alloying on the phase stability of the Mo-Re system and ultrahigh-pressure studies to 193 GPa are reported.

The Mo–32 at. % Re alloy (Sandvik Rhenium Alloys, Inc., Ohio) was in the form of 25-μm-thick foils suitable for the high-pressure experiments. The ambient pressure x-ray-diffraction study on the Mo–32 at. % Re alloy indicated the sample to be mostly in the bcc phase ($a=3.1337$ Å). Very weak second-phase diffraction lines were observed in the x-ray-diffraction spectra of this alloy, however, this second-phase concentration was too low to be detected in the diamond anvil cell experiments. Type-Ia diamond anvils with 81-μm central flat and 7° bevel angle to 350-μm culet size were used in the present experiments. No special attempt was made to select diamonds with nitrogen platelets for this experiment. This particular diamond design can produce pressures up to 200 GPa on samples of 50 μm diameter. A sample chamber of 40 μm thickness and 50 μm diameter was filled with the alloy sample and copper powder (99.5% purity), which was used as an internal pressure calibrant. Use of Cu as a pressure standard has been suggested[14] and the equation-of-state data[14,15] are available to 1000

GPa. Energy dispersive x-ray-diffraction studies were carried out at the B1 National High Pressure Beam line at Cornell High Energy Synchrotron Source (CHESS). An x-ray-collimated beam of 25 μm nominal size was used in all experimental data.

Energy dispersive x-ray-diffraction (EDXD) studies on this sample at low pressures in a diamond anvil cell indicated the copper marker diffraction peaks to be typically 25% of the Mo-Re sample diffraction peak and that the sample was a homogeneous mixture. The (111), (220), (311), and (222) diffraction peaks were observed from the fcc phase of copper marker. The (200) diffraction peak of fcc copper was obscured by the Mo K fluorescence lines and (222) diffraction peak of fcc copper overlapped with a (310) Mo-Re diffraction peak at ultrahigh pressures. Figure 1 shows the EDXD pattern of the Mo-Re alloy and Cu at a pressure of 193±8 GPa. This pressure of 193 GPa is obtained from the measured lattice parameter of Cu in the diffraction pattern ($a=3.112$ Å, $V/V_0=0.638$) and using the equation of state[14] of Cu to calculate the pressure. The uncertainty of 8 GPa is due to random errors in the lattice parameter measurement of Cu and does not include any systematic errors in the equation of state of Cu. For pressure calculations, we fitted the room temperature (300 K) P-V data between 0 and 1000 GPa for Cu (Ref. 14) to the following modified universal equation of state[16] (MUEOS)

$$\ln H = \ln P_0 + \eta(1-X) + \beta(1-X)^2 \ , \qquad (1)$$

$$H = PX^2/3(1-X) \ , \qquad (2)$$

$$X^3 = (V/V_0) \text{ is the volume compression } . \qquad (3)$$

The parameters $P_0=223.1$, $\eta=0.120$, and $\beta=21.242$ in Eq. (1) describe the P-V data of Cu in the extended pressure range to 1000 GPa. The room-temperature P-V data from earlier shock studies on Cu (Ref. 15) to 240 GPa is within 5% of the recent data[14] in the overlap region of 95–240 GPa. The consistency of equation-of-state data from different sources and the stability of the fcc phase in Cu make it a good choice as a calibrant in ultrahigh-pressure studies.

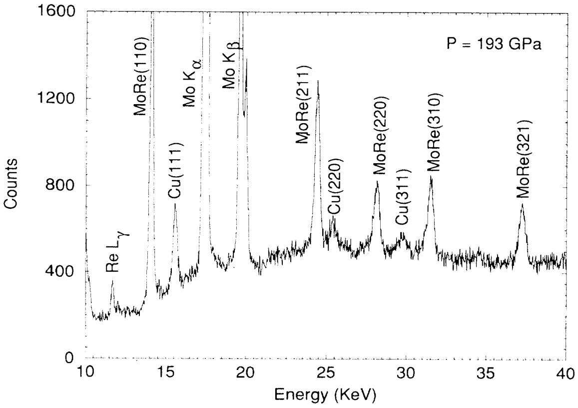

FIG. 1. Energy dispersive x-ray-diffraction pattern of Mo–32 at.% Re alloy sample and copper (Cu) pressure marker at 193±8 GPa in a diamond anvil cell. Mo-Re diffraction peaks are indexed based on a bcc phase and Cu diffraction peaks are indexed based on a fcc phase. The product of energy and interplaner spacing for this spectrum is $Ed=27.968\pm0.005$ KeV Å.

All the five distinct diffraction peaks (110), (211), (220), (310), and (321) in Fig. 1 from the Mo-Re alloy index very well to the bcc cubic phase indicating that no phase transformation has occurred to the highest pressure achieved in this experiment. The measured lattice parameter of the Mo-Re alloy at 193 GPa is 2.810 Å and volume compression $V/V_0=0.721$.

Figure 2 shows all the observed interplaner spacings as a function of pressure for the Mo-Re alloy to 193 GPa. The (200) diffraction peak is observable only in a narrow pressure range because of the nearby Mo fluorescence peaks and the (222) diffraction peak is too weak to be observed above 15 GPa. The continuous decrease with increasing pressure of all the observed interplaner spacings is a clear indication that the much anticipated hcp phase has not nucleated to these extreme pressures.

The measured P-V curve or equation of state of Mo–32 at.% Re is shown in Fig. 3 to 193 GPa at 300 K. The experimental P-V data for the Mo-Re alloy is listed in Table I. Figure 3 also shows the comparison between the alloy data and the room-temperature equation of state of constituent metals Mo and Re to 200 GPa obtained from shock studies.[15]

All the (P-V) equation-of-state data shown in Fig. 3 and listed in Table I for the Mo-Re alloy were well represented by the universal equation of state (UEOS) of the form suggested by Vinet *et al.*[16]

$$\ln H = \ln B_0 + \eta(1-X) \ . \qquad (4)$$

H and X are given by Eqs. (2) and (3), respectively, and

$$\eta = 3/2(B_0' - 1) \ . \qquad (5)$$

V_0, B_0, and B_0' are the atomic volume, bulk modulus, and its pressure derivative, respectively, at ambient pressure and temperature. The fitted values for B_0, B_0', and V_0 in the UEOS equation for Mo, Re, and the Mo–32 at.% Re alloy are listed in Table II.

First-principles theoretical calculations of Mo indicate that a transfer of 0.34 electrons/atom would transform[6] it from the bcc phase to the hcp phase. The alloying of Mo with 32 at.% Re adds 0.32 electrons/atom to the d band

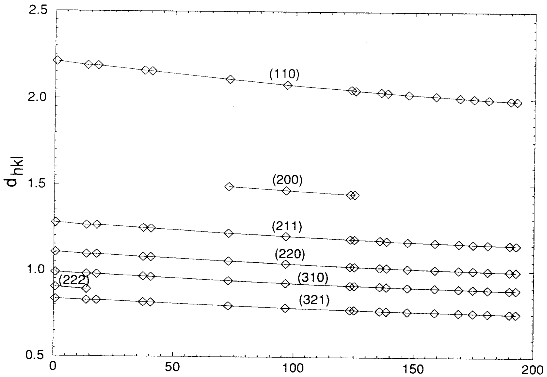

FIG. 2. The observed interplanar spacings (d_{hkl}) for the bcc phase of the Mo–32 at.% Re alloy to 193 GPa. The (200) diffraction peak of the alloy is obscured by the fluorescence peaks at pressures not indicated. The (222) diffraction peak is only observed at low pressures.

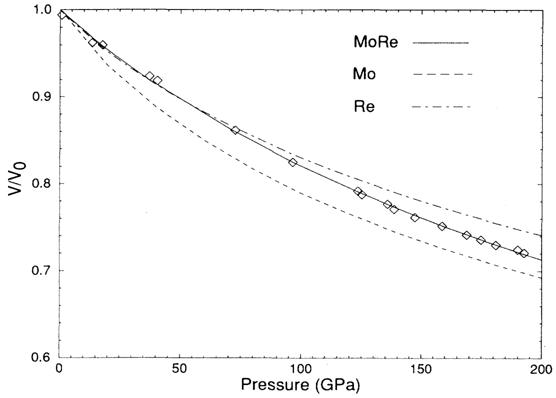

FIG. 3. The measured equation of state of the Mo–32 at. % Re alloy sample to 193 GPa (diamond symbols) at 300 K. The solid curve is the UEOS fit to the experimental data. The dashed curves represent the UEOS fits to the room-temperature equation-of-state data for pure Mo and Re metals obtained from shock studies (Ref. 15).

of Mo at ambient conditions assuming a rigid-band model. Further model calculations combined with experimental data predict the electron transfer rate to be $dn/d\ln V=0.8$ electrons/atom[17,18] for group-VI transition metals. Using this transfer rate and the volume compression of 0.721 gives electron transfer by pressure to be 0.22 electrons/atom. These estimates are consistent with the first-principles calculations of Godwal and Jeanloz[19] for pure Mo. Combining the alloying and pressure effects, we estimate that 0.54 electrons/atom are added to the *d* band of Mo at a pressure of 200 GPa for the Mo–32 at. % Re alloy.

The estimated *s*-*d* electron transfer of 0.54 electrons/atom achieved in the Mo–32 at. % Re alloy at 200 GPa far exceeds the critical value of 0.34 electrons/atom required for the bcc-hcp phase transition.[6] It appears that the assumption of a rigid-band model is not justified in this case and the addition of Re distorts the *d* band of pure Mo and the *spd* hybridization is significantly altered in the alloy. This is somewhat expected because of the differing *d* band width in 4-*d*- and 5-*d*-band transition metals. Also, at high alloy concentrations such as 32 at. % Re in the present study, materials effects such as clustering may play a significant role in modifying the *d*-band density of states and hence the *d*-band occupation at ambient and high pressures. Therefore, the rigid-band-model predictions of the transition pressure for alloys are to be considered only as an estimate.

TABLE I. Pressure-volume data for the Mo–32 at. % Re alloy to 193 GPa at 300 K. The pressures are measured by the lattice parameter of the copper pressure standard and by using the shock equation of state (Ref. 14).

Pressure (GPa)	Volume (Å^3/atom)
0	15.387
0.7	15.29
13.6	14.81
17.8	14.77
37.4	14.21
40.5	14.14
72.5	13.25
96.6	12.69
123	12.18
125	12.12
136	11.95
138	11.87
147	11.72
159	11.57
169	11.41
175	11.32
181	11.23
190	11.15
193±8	11.09±0.01

TABLE II. The parameters for the universal equation of state fits to the equation of state of Mo, Re, and the Mo–32 at. % Re alloy. The alloy data are from the present static pressure experiments while the Mo and Re data are from the shock experiments (Ref. 15).

	Mo	Re	Mo–32 at. % Re
B_0 (GPa)	268	365	402
B_0'	3.977	4.352	2.346
V_0 (Å^3/atom)	15.583	14.713	15.387

It is also interesting to note from Fig. 3 that the initial compression of the Mo–32 at. % Re alloy to 50 GPa follows closely the compression of pure Re. This is also reflected in the bulk modulus (B_0) value of the Mo–32 at. % Re alloy of 402 GPa which is closer to the Re value (365 GPa) and is substantially higher than the value for pure Mo (262 GPa) as shown in Table II. An earlier study[8] for a lower Re concentration alloy, i.e., Mo–26 at. % Re alloy, reported a value of 325 GPa for B_0. The combination of all the data indicates that there is a rapid decrease in compressibility with increasing Re concentration in Mo-Re alloys.

We offer the following conclusion.

(1) The bcc phase Mo–32 at. % Re alloy shows extensive stability in the bcc phase and the anticipated phase transformation to the hcp structure was not observed to 193±8 GPa. Use of the electron transfer rate and the rigid-band model indicates that 0.54 electrons/atom have been transferred to the *d* band of Mo at the highest pressure. The discrepancy with pure Mo calculations and the failure of the rigid-band model point out the need to perform first-principles theoretical calculations on the alloys.

(2) The addition of substitutional Re to the Mo lattice gives rise to rapid stiffening of the alloy as demonstrated by the increase in the bulk modulus. A bulk modulus comparable to pure Re was obtained in the Mo–32 at. % Re alloy. First-principles calculations of the bulk properties of the alloy are needed to make contact with the experiments.

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