Phase transformation in Mo - Ru alloy induced by laser heating at high pressures

1996 J. Phys.: Condens. Matter 8 L647

(http://iopscience.iop.org/0953-8984/8/43/004)

J. Phys.: Condens. Matter **8** (1996) L647–L652. Printed in the UK

LETTER TO THE EDITOR

Phase transformation in Mo–Ru alloy induced by laser heating at high pressures

Steven Beaver†, Jun Liu† Yogesh K Vohra† and H Kleykamp‡

† Department of Physics, University of Alabama at Birmingham (UAB), Birmingham, AL 35294-1170, USA

‡ Kernforschungzentrum Karlsruhe, Postfach 3640, 7500 Karlsruhe, Germany

Received 16 August 1996

Abstract. Phase transformations in the Mo–Ru alloy system were investigated at high pressures and high temperatures in a laser-heated diamond anvil cell. The room temperature compression of Mo–20 at% Ru alloy to 67 GPa revealed that the BCC phase is stable to the highest pressure. Laser heating at high pressures performed without an insulating medium resulted in the formation of Mo_2C phase. However, controlled laser heating to 2200 K at 20 GPa with KCl insulating medium showed that the BCC phase transforms into a mixture of BCC and sigma (σ) phases. The present phase-stability data are discussed within the context of the rigid-band model and electron transfer under high pressures in transition metal systems.

It is well established from first-principles theoretical calculations that the phase transformations in transition metals and alloys are governed by changes in the number of d electrons and their dominant effect on bonding [1, 2]. High-pressure investigations on metals and alloys provide critical data on the stabilities of various crystal structures and their compressibilities as functions of reduced interatomic spacings. Transition metals and alloys occupy a unique position in the periodic table because of their high cohesive energies, high bulk moduli and magnetism caused by the unfilled d shell. In particular, group VI metals (Cr, Mo and W) lie on the stability boundary between the BCC and HCP structures. It has long been speculated from shock compression studies [3, 4] that these group VI metals might undergo BCC $\rightarrow$ HCP transformation under high pressure and high-temperature environments. This has led to experimental activity to detect the BCC $\rightarrow$ HCP transformation in alloys because the transformation pressures for pure elements (Cr, Mo and Ru) are expected to be above 300 GPa [3, 4] and may be hindered by kinetic barriers. Room temperature compression studies have been performed on Mo–32 at% Re alloy, indicating that the BCC phase is stable to compression V/V_0 of 0.681 (a pressure of 259 GPa) [5, 6]. However, all the experimental work to date has focused on high-pressure studies on binary alloys between 4d and 5d metals. In this letter we report the first high-pressure study on a group VI transition metal alloy with both constituent metals from the same row of the periodic table. The phase diagram of the binary Mo–Ru system was determined by Anderson and Hume-Rothery [7] at ambient pressure. Kleykamp [8] investigated the effects of heat treatment on the composition and crystal structure of Mo–Ru alloys at ambient pressure. These earlier studies documented the existence of the BCC (two atoms per cell), HCP (two atoms per cell) and sigma (σ, 30 atoms per cell) phases in the Mo–Ru alloy at ambient pressure. However, the high-pressure phase boundaries in the Mo–Ru system have not yet been established.

0953-8984/96/430647+06$19.50

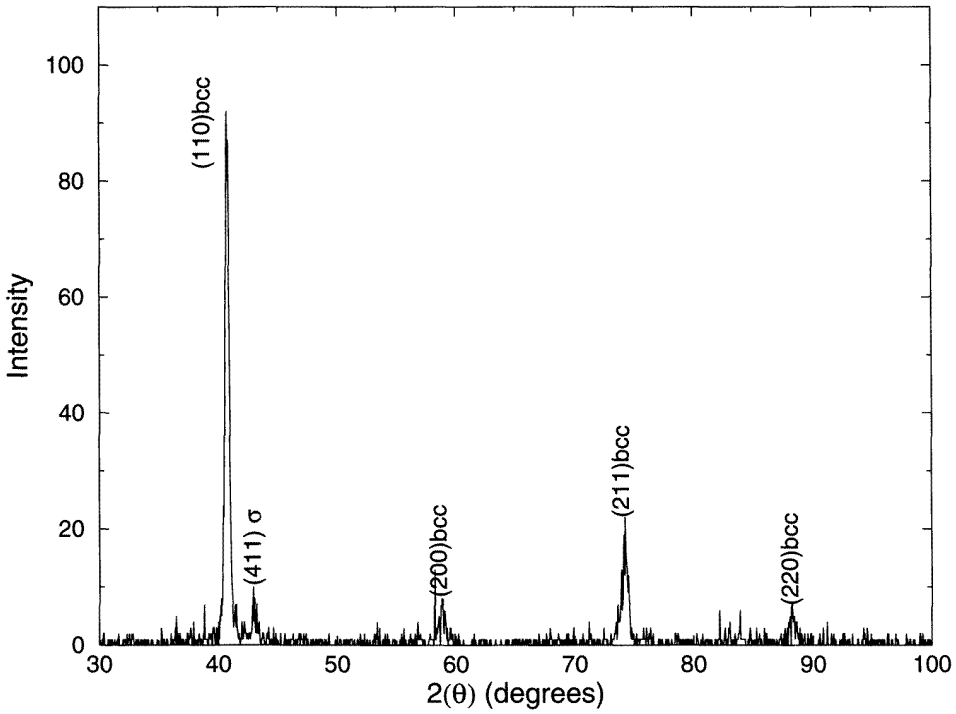

Figure 1. The angle-dispersive x-ray diffraction of the arc-melted Mo–20 at% Ru alloy under ambient conditions. The sample is largely in the BCC phase with some residual sigma phase. The x-ray wavelength $\lambda = 1.50$ Å.

Mo–Ru alloys were fabricated by arc-melting under reduced argon pressure using a tungsten electrode. Mo–Ru ingots with Ru compositions 10, 20 and 35 at% were prepared. X-ray diffraction studies were first performed at ambient pressures and temperatures. These studies indicated that Mo–20 at% Ru alloy was largely single-phase BCC with lattice parameter $a = 3.1290$ Å. There was some residual sigma (σ) phase, as shown in figure 1, in which a weak (411) peak at 2.100 Å can be observed. Therefore, Mo–20 at% Ru alloy was chosen for detailed investigations. Several high-pressure experiments were performed in a diamond anvil cell (DAC). The first experiment was performed at ambient temperature to 67 GPa using a mixture of Mo–Ru alloy and copper as a pressure standard. The high-pressure equation of state of copper by Kinslow was used in the present experiments [9]. Figure 2 shows the compression curve for the BCC phase of Mo–20 at% Ru alloy at room temperature. The full curve in figure 2 is the fit to the first-order Birch equation

$$P(X) = \tfrac{3}{2}B_0\big(X^{-7} - X^{-5}\big)\big[1 + \tfrac{3}{4}\big(B_0' - 4\big)\big(X^{-2} - 1\big)\big]$$

where $X = (V/V_0)^{1/3}$, pressure P is in gigapascals, B_0 is the bulk modulus and B_0' is the pressure derivative of the bulk modulus at ambient pressure. The fitted curve in figure 2 was obtained by fixing $B_0' = 4$ and led to a best-fit value of $B_0 = 300$ GPa.

In experiments involving laser heating, the sample pressure was measured by a ruby fluorescence technique [10]. In the second experiment, laser heating was performed at a pressure of 30 GPa in a DAC to a temperature of 3300 K. Energy dispersive x-ray diffraction studies performed after laser heating showed that the spectrum is dominated by

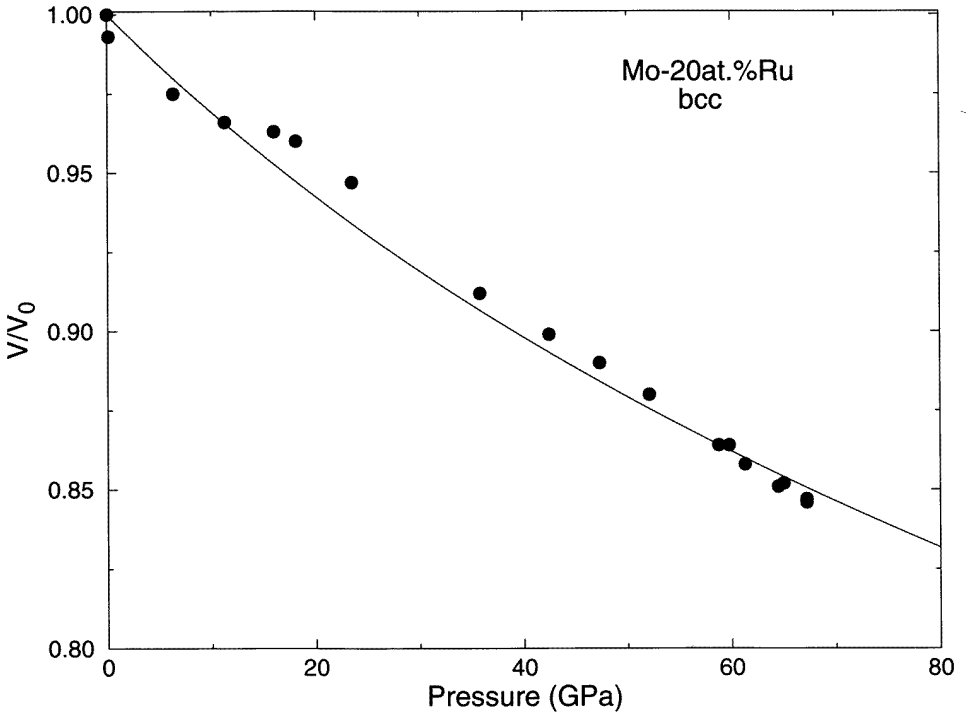

Figure 2. The measured pressure-volume relation (equation of state) for the Mo–20 at% Ru alloy at 300 K. The BCC phase is stable in the entire pressure region. The full curve is the fit to the first-order Birch equation described in the text.

the hexagonal Mo_2C phase with lattice parameters $a = 2.810$ Å and $c = 4.475$ Å at 30 GPa. This phase resulted due to a chemical reaction between the molten Mo–Ru and diamond. In the next study, care was taken to improve the thermal insulation between the diamond and the hot sample with the use of an alkali halide (KCl) as a thermal insulator. Figure 3 shows the linearized black-body spectrum emitted by the laser-heated sample at 20 GPa. This linearization was achieved through the method introduced by Heinz and Jeanloz [11], whereby the output of the spectrometer $I(\lambda, T)$ is used to yield a plot of $J(\lambda, T)$ via the relations

$$J(\lambda, T) = \ln\left[I(\lambda, T)\lambda^5/\left(2C_1F(\lambda)\epsilon_0(\lambda, T_0)\right)\right]$$
$$\omega(\lambda) = C_2/\lambda$$

where $F(\lambda)$ is the efficiency of the measuring system, $\epsilon(\lambda, T)$ is the sample emissivity and both C_1 and C_2 are constants. The (linear) parametric form of J immediately follows as

$$J(\lambda, T) = (-1/T)\omega(\lambda) + \ln\left(\epsilon(\lambda, T)/\epsilon_0(\lambda, T_0)\right)$$

where it is assumed that the argument of the logarithm is constant in λ. This method gave T for the sample as approximately 2200 K at a sample pressure of 20 GPa.

Figure 4 shows the energy dispersive x-ray diffraction spectrum obtained at the X-17C beamline, Brookhaven National Laboratory after laser heating at 20 GPa. Detailed phase analysis was performed on this spectrum. It showed a mixture of a B2 phase of the KCl pressure medium with lattice parameter $a = 3.346$ Å and the BCC phase of Mo–Ru with

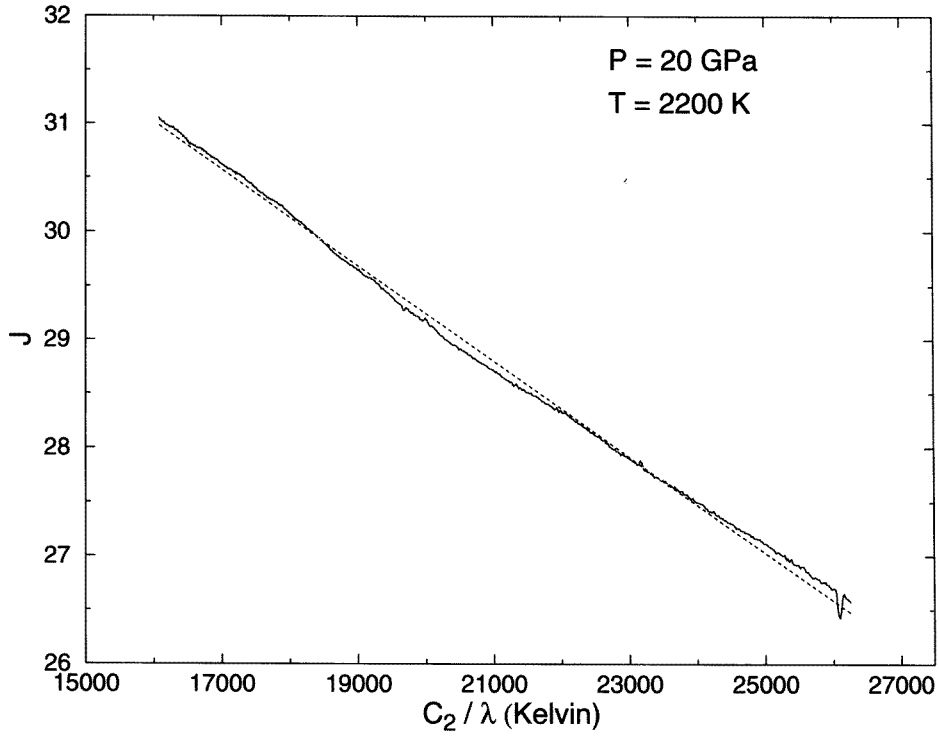

Figure 3. The linearized black-body spectrum J from the Mo–Ru sample laser-heated at 20 GPa. J itself is dimensionless. The broken curve is the linear fit used to obtain the temperature of the hot sample (2200 K in this case).

lattice parameter $a = 3.072$ Å. The measured compression of the KCl pressure medium was $V/V_0 = 0.606$. (This is in part due to the large volume change at the B1 to B2 phase transition.) The measured compression of the Mo–Ru alloy was $V/V_0 = 0.946$. Assuming a c/a ratio of 0.516, the (411) peak provides the σ phase lattice parameters $a = 9.317$ Å and $c = 4.807$ Å. The measured compression for the σ phase was $V/V_0 = 0.926$.

Using a simple band model we can estimate the electron transfer from the s band to the d band induced by the application of pressure. Simple model calculations [5] indicate that the electron transfer rate for group VI metals is $\mathrm{d}n/\mathrm{d}(\ln(V)) \approx 0.8$ electrons per atom. The total number of electrons transferred is $0.8\mathrm{d}V/V_0 = 0.8(1 - V/V_0)$. Using our $V/V_0 = 0.846$ at 67 GPa, we estimate the electron transfer to be 0.12 electrons per atom. The total electron transfer including the effect of 20% alloying and pressure is estimated to be 0.32 electrons per atom. This is still below the critical value of 0.5 electrons per atom required for phase transformation in Mo [3, 4]. Thus the simple model calculation predicts the BCC phase to be stable within the pressure range achieved in the present experiments.

We offer the following conclusions.

(i) The high-pressure studies at room temperature on Mo–20 at% Ru alloy show that the BCC phase is stable up to compression $V/V_0 = 0.846$ (a pressure of 67 GPa). The measured value of B_0 from the equation of state is 300 GPa with a fixed value of $B_0' = 4$.

(ii) Laser-heating studies at 20 GPa indicate that the BCC phase is stable to 2200 K and the BCC $\rightarrow$ HCP transformation was not observed. Instead, thermal annealing at high

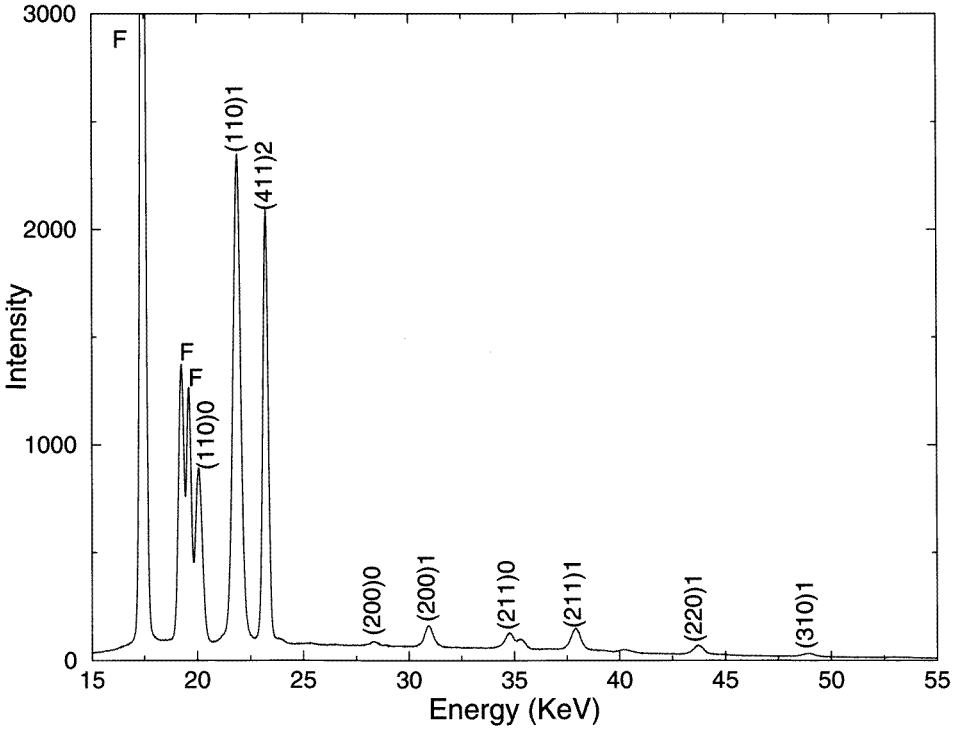

Figure 4. The energy-dispersive x-ray diffraction spectrum for the Mo–20 at% Ru alloy and KCl medium at a pressure of 20 GPa after laser heating to 2200 K. The product of energy (E) and interplanar spacing (d) is $Ed = 47.491$ keV Å. Peaks marked F are the characteristic x-ray fluorescence lines; the diffraction lines are assigned to various phases in the sample (phase 0 is the B2 phase of KCl, phase 1 is BCC Mo–Ru and phase 2 is σ phase Mo–Ru).

pressures of 20 GPa resulted in an increase in the sigma phase content, as detected by the x-ray diffraction studies. The BCC $\rightarrow$ sigma phase transformation was observed under high-pressure and high-temperature conditions in Mo–Ru alloy.

This research was supported by the National Science Foundation (NSF) grant DMR-9403832. The authors acknowledge the use of the X-17C beamline at the NSLS, Brookhaven National Laboratory.

References

[1] Shriver H L 1985 *Phys. Rev.* B **31** 1909
[2] Moriarty J A 1992 *Phys. Rev.* B **45** 2004
[3] Hixson R S, Boness D A, Shaner J W and Moriarty J A 1989 *Phys. Rev. Lett.* **62** 637
[4] Shaner J W 1990 *Shock Compression of Condensed Matter – 1989* ed S C Schmidt *et al* (Amsterdam: North-Holland) p 121
[5] Gu G and Vohra Y K 1993 *Phys. Rev.* B **47** 11 559
[6] Gu G 1995 *PhD Thesis* University of Alabama at Birmingham
[7] Anderson E and Hume-Rothery W 1960 *J. Less-Common Met.* **2** 443
[8] Kleykamp H 1988 *J. Less-Common Met.* **136** 271

[9] McQueen R G, Marsh S P, Taylor J W, Fritz J M and Carter W J 1970 *High Velocity Impact Phenomenon* ed R Kinslow (New York: Academic) ch VII
[10] Bell P H, Xu J A and Mao H K 1985 *Shock Waves in Condensed Matter* ed Y M Gupta (New York: Plenum) p 125
[11] Heinz D L and Jeanloz R 1987 *High-Pressure Research in Mineral Physics* ed M H Manghnani and Y Syono (Washington, DC: American Geophysical Union) pp 113–27