The Phase Diagram of Mo–H Alloys under High Hydrogen Pressures

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The phase diagram of the Mo–H system was determined by *in situ* X-ray diffraction using synchrotron radiation up to 1200°C and the hydrogen pressure to $p(H_2) = 5.3$ GPa. Three phases were found to exist; a bcc phase (α) of low hydrogen concentrations at low hydrogen pressures, and two high-pressure phases, an hcp (ε) phase at lower temperatures and an fcc (γ) phase at higher temperatures, both having a nearly stoichiometeric composition of $x = [H]/[Mo] \sim 1$. A gradual lattice contraction observed in the fcc phase indicates the formation of superabundant Mo-atom vacancies (vacancy-hydrogen clusters).

1. Introduction

At hydrogen pressures of $p(H_2) \geq 1$ GPa, the chemical potential of fluid hydrogen increases steeply, causing drastic enhancements of the solubility in metals and concomitant structural changes of the metal lattice.[1] A systematic investigation of the phase diagram of transition metal-hydrogen (M–H) alloys under extended pressure-temperature conditions ($p(H_2) \leq 6$ GPa, $T \leq 400°$C) was performed by a Russian group, by combination of *in situ* resistometry and X-ray diffraction (XRD) of recovered specimens, and the results were described in their review papers.[2,3] We have succeeded in taking a step forward by developing techniques of *in situ* XRD under more extended $p(H_2)$-T conditions, and reported the phase diagrams for Cr–H,[4] Mn–H,[5] Fe–H[6] and Ni–H[7] systems.

For the Mo–H system at high hydrogen pressures, the Russian group showed that an hcp hydride of a nearly stoichiometric composition [H]/[Mo] ≈ 1 was formed,[8,9] and the bcc (α)-hcp (ε) boundary was located at 250°C, 2 GPa increasing to 450°C, 5 GPa.[10] The octahedral-site occupancy of H atoms was also established.[11] Subsequently, we found that an fcc hydride (γ) was formed at a high temperature and high hydrogen pressure (1000°C and 5 GPa), and additionally, superabundant metal-atom vacancies (SAVs) were formed in the process.[12] The purpose of this paper is to report on the phase diagram of the Mo–H system over a wider range of temperature and hydrogen pressure.

2. Experimental Methods

The experiments were performed at a synchrotron radiation facility (Photon Factory) in Tsukuba, using a cubic-anvil press MAX80 designed for XRD measurements at high p-Ts.

A sample cell assembly was constructed in the following way.[13] A high-purity (99.99%) powder sample was sealed in a capsule of NaCl together with an internal hydrogen source ($NaBH_4$ + $Ca(OH)_2$) and a pressure marker (NaCl diluted with BN to suppress grain growth at high temperatures), and was placed at the center of an 8 mm cube of amorphous B-epoxy resin composite. Pressures up to 6 GPa could be

applied to the sample by compression from six perpendicular directions, and temperatures could be raised to 1200°C by sending an electric current to a graphite tube heater around the capsule. In the course of heating, H_2 was supplied to the sample by the decomposition of the hydrogen source at 200–300°C. The temperature was measured by a C-A thermocouple, and the pressure by measuring the lattice parameter of NaCl using a Decker scale.[14] The validity of the Decker scale under these high $p(H_2)$-T conditions is warranted by the absence of any reactivity of NaCl with H_2.

The XRD was measured by the energy-dispersive method, where diffracted X-rays were energy-analyzed by a solid-state detector placed at a fixed angle ($2\theta \doteqdot 6°$) from the incident beam. With these devices, each measurement was completed in 60–100 s with the accuracy of lattice parameters typically better than 0.1%. Each measuring run was performed under a fixed ram load at appropriate temperature intervals in the course of heating. At each temperature, a sample was equilibrated for at least 10 min (30 min near the phase boundaries) before XRD measurement was started. A phase diagram was constructed from a series of such measurements at several different ram loads.

3. Experimental Results

An example of the XRD spectrum measured at $p(H_2) = 4.7$ GPa and 1000°C is shown in Fig. 1. This is a clear demonstration of the occurrence of the fcc (γ) hydride and also of a high quality of XRD data in the present experiment. The $p(H_2)$-T phase diagram constructed from several heating runs is shown in Fig. 2. The bcc-hcp (α-ε) boundary is in fair agreement with the one reported previously by the Russian group in the low $p(H_2)$-T region.[8,10] The upward extrapolation of the α-ε boundary to lower pressures is simply a guess from the known persistence of the bcc structure to 2617°C (the melting point of Mo) under normal pressure.

In Fig. 3, the atomic volume (volume per Mo atom) measured in the four heating runs (in Fig. 2) is shown as a function of temperature. In all the three phases, the atomic volumes observed at different pressures are closely the same, and stay nearly constant (except for small thermal expansion effects). This indicates that the hydrogen concentration also stays constant in each phase. ([H]/[Mo] ≈ 0 in the α phase
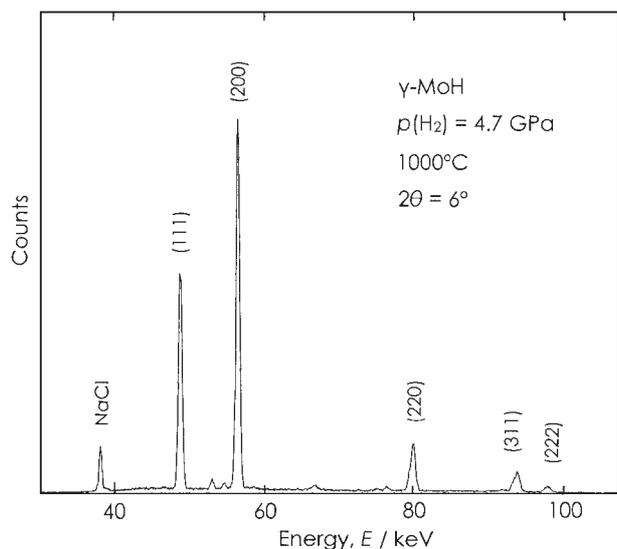
Fig. 1   The XRD spectrum of the fcc monohydride γ-MoH$_{\sim 1}$ at $p(H_2) =$ 4.7 GPa and 1000°C. A diffraction angle $2\theta = 6°$ and a measuring time = 90 s.

Fig. 3   Temperature dependence of the atomic volume (volume per Mo atom) measured in four different runs ($p(H_2) =$ 2.1–2.4 GPa, 3.0–3.4 GPa, 3.5–4.3 GPa and 4.4–5.2 GPa), encompassing three different phases; bcc (α), hcp (ε) and fcc (γ). A curve drawn in the lower part of the figure represents the thermal expansion of metallic Mo at ambient pressure.[15]
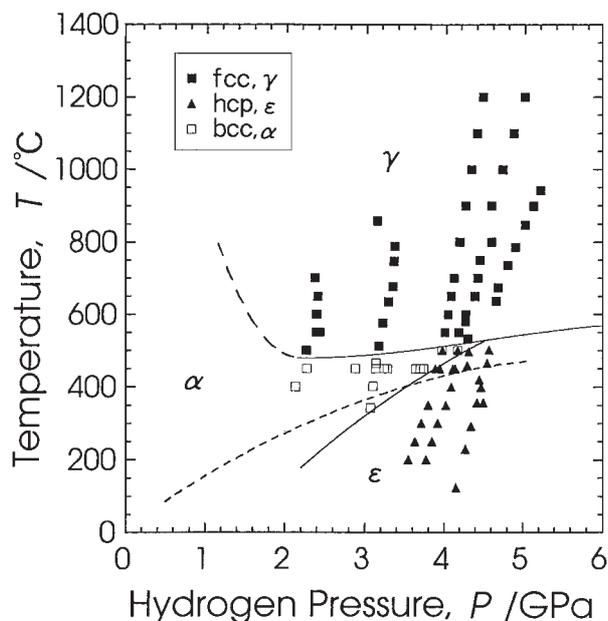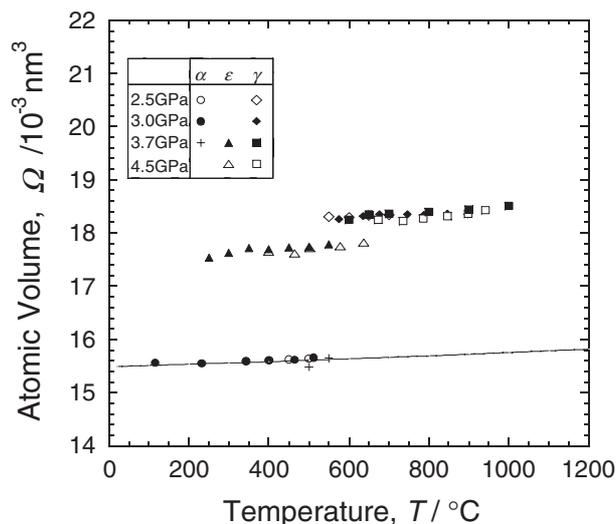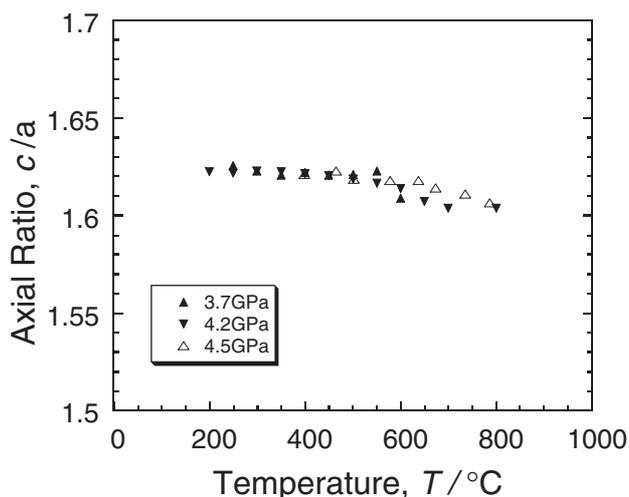

Fig. 2   The phase diagram of the Mo–H system as a function of hydrogen pressure and temperature. The crystal structures are bcc (α), hcp (ε) and fcc (γ). The short dashed line represents the α-ε boundary reported in Refs. 8–10), and the long dashed line is a guess from the known persistence of the bcc structure to 2617°C (the melting point of Mo) at $p(H_2) = 0$ GPa.

Fig. 4   Temperature dependence of the axial ratio of the hcp phase (ε) measured in three different runs ($p(H_2) =$ 3.5–4.0 GPa, 3.8–4.6 GPa and 4.5–5.0 GPa).

and [H]/[Mo] ≈ 1 in the ε and γ phases as shown in the next section).

The temperature dependence of the axial ratio in the hcp (ε) phase is shown in Fig. 4. The ratio is nearly constant and slightly smaller than the ideal ratio $c/a = 1.633$ at all temperatures and pressures. Note that the points above 550°C are those taken from the remnant hcp phase above the phase boundary.

The temporal variation of the lattice parameter measured in the fcc (γ) phase at 1000°C under $p(H_2) = 5$ GPa is shown in Fig. 5. The observed lattice contraction indicative of SAV formation will be discussed later.

4.   Discussion

The composition of the observed phases can be deduced from Fig. 3.

The fact that the bcc data points lie closely on the thermal expansion curve of metallic Mo at ambient pressure[15] indicates that H concentrations are very low. As the pressure-induced volume change estimated from the bulk modulus of Mo ($K_0 = 271$ GPa[16]) amounts to only -0.17×10^{-3} nm^3 at 3 GPa, the thermal expansion curve under normal pressure can be taken to be a good measure of the reference volume. Thus, the H-induced volume expansion, which is scarcely visible, can be roughly estimated to be $\Delta\Omega < 0.2 \times 10^{-3}$ nm^3. This value can be converted into the H concentration, [H]/[Mo] $< 7 \times 10^{-2}$, by using a typical value for the H-
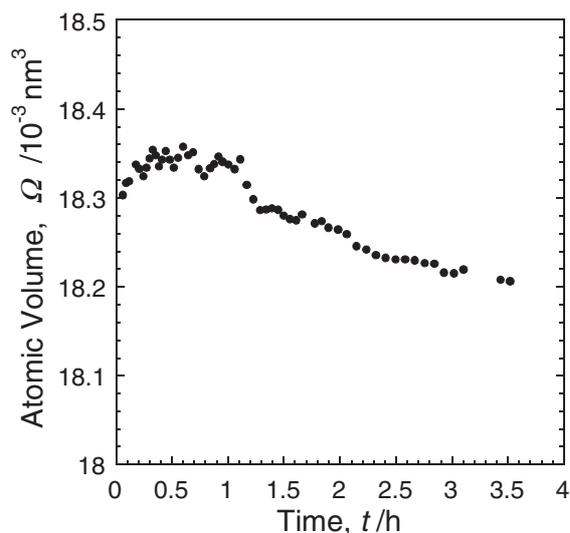
Fig. 5 Atomic volume (volume per Mo atom) of fcc (γ) hydride as a function of holding time at 1000°C and $p(H_2) = 5$ GPa.

induced volume in the bcc lattice ($\sim 3 \times 10^{-3}$ nm³/H-atom).[1] The solubility calculated using the heat of solution of 56 kJ/mol H ([H]/[Mo] = (3 $\sim$ 8) $\times 10^{-3}$ for 4–6 GPa at 500°C[17]) is consistent with this result.

In hcp (ε) and fcc (γ) phases, the fact that the atomic volumes stay very nearly constant, independent of $p(H_2)$, T, indicates that the composition has reached the stoichiometric limit [H]/[Mo] = 1.0. This is consistent with the earlier result of the Russian group,[8,9] in which they determined the composition of ε-MoH$_x$ by quenching under pressure to be close to $x \approx 1$. The atomic volumes of ε and γ phases are larger than that of the α phase by 2.1×10^{-3} and 2.7×10^{-3} nm³, respectively, independent of pressure or temperature. Assuming a reference volume of (hypothetical) hcp and fcc Mo to be larger than bcc Mo by $\sim 0.4 \times 10^{-3}$ nm³, based on the band-theoretical calculation on fcc and bcc Mo,[18] we obtain the H-induced volume of 1.7×10^{-3} and 2.3×10^{-3} nm³/H-atom, respectively, for hcp and fcc Mo. The small value for the hcp phase is consistent with the known data for H atoms occupying octahedral sites in the hcp lattice (1.66 for Mn–H,[2] 1.82 for Co–H,[2] 2.19,[19] 1.6–1.7[20,21] for Re–H and 1.86×10^{-3} nm³ for Tc–H[19]).

The phase diagram shown in Fig. 2 is very similar to that of the Cr–H system.[4] In both cases, the bcc structure transforms to monohydrides of hcp and fcc structure at high hydrogen pressures, with the triple point located at 500°C and 4.5 GPa in the Mo–H system, and 900°C and 3.7 GPa in the Cr–H system. The appearance of the fcc monohydride as a high-temperature phase at high hydrogen pressures has in fact been found in many other transition metal-hydrogen systems as well (Mn–H,[5] Fe–H,[6] V–H, Nb–H and Ta–H[22]), and is believed to be one of the common trends in the hydride phase relations. Another general feature of metal-hydrogen alloys, the reduction of the melting point, was not observed in the present experiment. Apparently, the melting point of Mo (2617°C at ambient pressure, and ~ 100°C higher at several GPa) is too high to be made accessible by dissolution of hydrogen.

A small discrepancy in the α-ε boundary existing between the two groups of data may be attributed to some uncertainties arising from the sluggishness of the transitions. In our experiments, as small amounts of low-temperature phases often persisted to high temperatures, we located the phase boundary at the point of onset of the transition. Similar experience was reported by the Russian group.[8,10] They observed a very large hysteresis in the α-ε transition in compression-decompression cycles at fixed temperatures. The hysteresis amounted to ~ 3 GPa at 100°C, but nearly disappeared at ~ 500°C. They determined the α-ε boundary in the decompression process, according to the conventional wisdom that a locus of hydride decomposition should represent more closely the true phase boundary. This conventional wisdom may not, however, be totally reliable under high pressures where any structural changes tend to be retarded by mechanical constraints, often resulting in large hysteresis in transition pressures (or temperatures). For example, in the p-T phase diagram of Fe, a large hysteresis in terms of pressure was observed for the bcc-hcp transition below 500°C, amounting to 3 GPa at 100°C.[23] More efforts are needed to eliminate the discrepancy in the α-ε boundary.

The observed lattice contraction $\Delta\Omega/\Omega = -8.2 \times 10^{-3}$ due to the formation of vacancy-H clusters (Fig. 5) divided by the relaxation volume of a vacancy calculated for a hypothetical fcc Mo $v^R/\Omega = -0.40$[18] leads to the concentration of vacancy-hydrogen clusters $x_{cl} = 0.02$. This value is smaller than the equilibrium concentrations observed in other fcc hydrides; $x_{cl} = 0.09$ for Cr–H,[4] 0.1 for Mn–H,[13] 0.19 for Fe–H,[6] 0.10 for Co–H,[13] 0.30 for Ni–H[24] and 0.10 for Pd–H.[25] Considering the extreme sluggishness of atomic processes experienced in phase determinations, it appears very probable that the equilibrium cluster concentration was not yet achieved in the experiment shown in Fig. 5. Further investigation is needed for clarifying the process of SAV formation in Mo–H alloys.

5. Summary and Conclusions

By *in situ* X-ray diffraction at high hydrogen pressures and temperatures, it has been shown that monohydrides of Mo having hcp and fcc structures can be formed. A $p(H_2)$-T phase diagram consisting of these three phases has thus been constructed in the range $p(H_2) \leq 5.3$ GPa and $T \leq 1200$°C. A gradual lattice contraction observed at 1000°C and $p(H_2) = 5$ GPa indicates the formation of superabundant vacancies (Vac-H clusters) of Mo atoms in the fcc phase, with concentrations amounting to ~ 2 at%.

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