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Effect of Hydrogen Annealing on the Composition and Particle Size of Molybdenum Nanopowders

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Abstract—We have studied the behavior of molybdenum nanopowder consisting of particles with an average size of 23.7 nm. The powder was prepared by hydrogen plasma reduction of molybdenum trioxide and contained considerable amounts of oxygen in the form of amorphous molybdenum oxides and hydroxides. Annealing in hydrogen for 1 h at temperatures from 300 to 1000°C is shown to cause crystallization of oxides, which then vaporize to form the volatile hydroxide $MoO_2(OH)_2$. Most of the oxygen is removed by annealing below 700°C. Starting at this temperature, particle growth is observed. The main mechanism behind the coagulation of molybdenum particles is vapor transport. Annealing at 1000°C for 30–50 min in hydrogen with a dew point of –5°C increases the particle size by about one order of magnitude.

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INTRODUCTION

A widespread approach to producing nanopowders of refractory metals is the reduction of their oxides in a low-temperature hydrogen plasma [1]. The powders thus obtained contain considerable levels of oxygen. The oxygen can be eliminated—or at least its content can be reduced to an acceptable level—by annealing in a reducing atmosphere. This process, however, leads to coagulation of the metal nanoparticles.

The purpose of this work was to study the behavior of molybdenum nanopowders during hydrogen annealing.

EXPERIMENTAL PROCEDURE AND CALCULATIONAL APPROACH

The starting powder, prepared by plasma reduction of molybdenum trioxide [1], consisted of equiaxed particles and contained 15.0 wt % oxygen. The specific surface area S of the powder before and after storage was 24.8 ± 3 m^2/g, which corresponded to an average particle size d= 23.7 nm.

Loose powder samples were annealed in flowing hydrogen with a dew point of –5°C. The specific surface area of the powder was determined by low-temperature nitrogen adsorption measurements. The average particle size was evaluated as $d = 6/(\gamma S)$ (where γ is the density of molybdenum. Oxygen content was determined on a LECO TC-436 gas analyzer. X-ray diffraction (XRD) characterization was performed with CuK_α radiation. Weight changes were monitored with an analytical balance to an accuracy of 1 mg.

The nondimensional thermodynamic particle-size criterion D_L was calculated by the formula

$$D_L = 1.2 \times 10^{-11}\sigma/(Gb^2d) \qquad (0.1)$$

where σ is the surface energy, G is the shear modulus, and b is the Burgers vector [2]. The particle-size criterion D_L for the as-prepared powder was found to be 11.8. Anneals were carried out for 5–60 min at a fixed temperature from 300 to 1000°C.

RESULTS AND DISCUSSION

The annealing conditions and analysis results for the annealed samples are summarized in Table 1. XRD examination showed that the only crystalline phase in these samples was metallic molybdenum. This implies that oxygen was present in the powder either as adsorbed species or in X-ray amorphous phases.

In addition to about fifteen stable and metastable oxides [3], the system in question contains the $MoO_2(OH)_2$ hydroxide, which has the highest vapor pressure among the phases of this system [4].

Analysis of the data in Table 1 leads us to propose the following sequence of processes that take place during annealing of the as-prepared powder in flowing hydrogen: Heating from room temperature to 600–700°C leads to simultaneous vaporization of amorphous oxides and hydroxides, their crystallization, and reduction with hydrogen. In this process, the particle size remains essentially unchanged. At higher temperatures, particles of almost pure molybdenum coagulate. This sequence is supported by the observed changes in

Table 1. Effect of hydrogen annealing on the properties of molybdenum nanoparticles

Annealing conditions		Weight loss, %	S, m^2/g	d_{meas}, nm	D_L	wt % oxygen	d_{calc}, nm	Phase composition
temperature, °C	time, min							
As-prepared		–	24.8 ± 3	23.7	11.8	15.0	–	–
After storage		–	24.8 ± 3	23.7	11.8	17.7	–	Mo, Mo_2O_3
300	60	5.51	30.4 ± 3	19.3	14.6	–		Mo, Mo_2O_3
400	60	5.93	30.2 ± 3	19.5	14.4	–		Mo, Mo_2O_3
500	60	7.17	15.8 ± 1.8	37.2	7.58	–		Mo, Mo_2O_3
600	60	11.25	18.6 ± 2.6	31.6	8.92	–		Mo, Mo_2O_3
700	60	–	28.2 ± 2.6	20.9	13.5	4.87		Mo
800	15	–	23.0 ± 2.3	25.6	11.0	–	60	–
800	30	–	11.8 ± 1.1	49.9	5.65	–	74	–
800	60	–	10.0 ± 0.9	58.8	4.79	2.58	93	Mo
900	5	29.24	–	–	–	–	–	
900	10	28.15	–	–	–	–	–	
900	15	–	9.9 ± 0.9	59.4	4.74		137	–
900	30	–	5.6 ± 0.7	105.0	2.68		174	–
900	30	24.80	9.4 ± 1.1	62.6	4.50		174	–
900	60	–	7.4 ± 0.8	79.5	3.54	1.24	218	Mo
900*	60	18.74	–	–	–	–	–	Mo
900**	30	5.22	–	–	–	–	–	–
1000	5	22.58	–	–	–	–	–	–
1000	10	21.33	–	–	–	–	–	–
1000	15	–	2.5 ± 0.2	235.3	1.19	–	282	–
1000	15	–	4.3 ± 0.5	136.8	2.06	–	282	–
1000	30	–	3.5 ± 0.3	168.1	1.67	–	355	–
1000	60	–	3.2 ± 0.5	183.8	1.53	0.76	447	Mo

Note: d_{meas} and d_{calc} are the average particle sizes, and D_L is the particle-size criterion.
*Powder compact with an initial relative density of 20%.
**Annealing in helium.

sample weight, phase composition, specific surface area, and oxygen content.

Only two crystalline phases were identified in our samples by XRD: molybdenum and Mo_2O_3. Note that Mo_2O_3 was not detected in earlier structural studies of molybdenum oxides prepared by a method other than plasma reduction [4]. It is, however, completely identical to the Mo_2O_3 obtained by a plasma process and described by Tsvetkov et al. [1]. It seems likely that this oxide is a metastable form of Mo_4O_{11} [4].

Even though the as-prepared powder contained 17.7 wt % oxygen and consisted of fine particles, its XRD pattern showed sharp, narrow peaks from only one phase, molybdenum, with very weak, broad reflections from Mo_2O_3. Therefore, nearly all of the bound oxygen in the powder was present in the form of amorphous oxides and hydroxides.

After heating at 200–600°C for 1 h, the samples consisted of two crystalline phases: Mo and Mo_2O_3. The contents of these phases, evaluated from the intensity of XRD peaks from molybdenum ($d = 2.22$ Å) and Mo_2O_3 ($d = 3.44$ Å), are listed in Table 2. At annealing temperatures of 700°C and above, the samples consisted entirely of Mo. The observed weight loss was due to the removal of volatile species from the powder.

Control experiments with loose powder samples and with the powder compacted to a relative density of 20% (marked by an asterisk in Table 1) showed approximately the same weight loss. Raising the temperature from 300 to 600°C (1-h anneals) leads to a systematic increase in weight loss, which nevertheless remains below the initial oxygen content of the powder. Given that it is in this temperature range that the amorphous oxides and hydroxides in Mo_2O_3 crystallize, we think that the weight loss is due to the removal of the water of hydration and hydrogen reduction of Mo_2O_3. At temperatures of 700–800°C and above, the weight loss corresponding to the removal of all the oxygen is 25–30%. This considerably exceeds the initial oxygen content of the powder. The reason for this is that the removal of the water of hydration and the reduction of oxides are accompanied by the vaporization of the oxides and the volatile hydroxide $MoO_2(OH)_2$.

Heating at 700°C for 1 h and even at 800°C for 15 min has little or no effect on the specific surface area of the powder. Annealing at 800°C for a longer time or at 900 and 1000°C for any of the annealing times tested reduces the specific surface area as a result of particle coagulation. The oxygen content of the powder drops rapidly at annealing temperatures above 700°C, but remains appreciable even after annealing at 1000°C, which may be caused by partial oxidation of the completely reduced molybdenum during cooling in flowing hydrogen containing trace levels of moisture.

Coagulation of molybdenum particles during hydrogen annealing at temperatures from 800 to 1000°C may proceed through the growth of the contact necks between the particles as a result of volume and surface diffusion and vapor transport. The time needed for particle coalescence through volume and surface diffusion was evaluated as [5]

$$t = \left(\frac{\Delta L}{L_0}\right)^{\frac{5}{2}}\left(\frac{2RTr^3}{5\sigma V_0 D_{\mathrm{vol}}}\right), \tag{1}$$

$$t = (r^4 RT)/(D_{\mathrm{surf}}\sigma V_0 \delta). \tag{2}$$

Here, L is the center-to-center distance between neighboring particles, $L_0 = 2r_0$ is the initial distance, V_0 is the molar volume, D_{vol} and D_{surf} and the volume and surface diffusion coefficients, R is the gas constant, T is the absolute temperature, r is the particle radius, and δ is the thickness of the surface diffusion layer.

Substituting $\frac{\Delta L}{L_0} = 0.5$, $r = 12$ nm, $\sigma = 1.915$ J/m^2, $V_0 = 9.42 \times 10^{-6}$ m^3/mol, $\delta = 10^{-9}$ m, $D_{\mathrm{vol}} = 1.448 \times 10^{-21}$ m^2/s, and $D_{\mathrm{surf}} = 100 D_{\mathrm{vol}}$ into Eqs. (1) and (2), we find that at 100°C the coalescence time must be 13.8 h for volume diffusion and 23.3 h for surface diffusion. Both values far exceed those determined experimentally. Therefore, the contribution of solid-state diffusion to coagulation is negligible.

The main mechanism behind the coagulation of molybdenum particles is vapor transport. At atmospheric hydrogen pressure and a bulk density of 0.05, the mean free path of molecules of volatile compounds is much smaller than the interparticle distance in the range of particle sizes studied. Therefore, the coagulation process is mediated by the diffusion flow caused by the difference between the pressure of the volatile molybdenum compound over a flat surface and that over particles of radius r.

Table 2. XRD results for the molybdenum nanopowders annealed in hydrogen for 1 h

Annealing temperature, °C	$I_{Mo}/I_{Mo_2O_3}$	Weight percent	
		Mo	Mo_2O_3
As-prepared	50	100	Traces
200	1.5	76	24
300	1.4	74	26
400	1.5	75	25
500	0.92	65	35
600	1.75	77	23
700	∞	100	0
800	∞	100	0
900	∞	100	0

Note: $I_{Mo}/I_{Mo_2O_3}$ is the intensity ratio of the Mo line with $d = 2.22$ Å to the Mo_2O_3 line with $d = 3.44$ Å.

It is convenient to consider coagulation kinetics using the Livshits–Slezov equation in differential form:

$$\frac{dr}{dt} = \frac{4}{27}\frac{\sigma V_0 C_\infty D_{\mathrm{vol}}}{r^2 RT}, \tag{3}$$

where C_∞ is the equilibrium concentration of particles with $r \longrightarrow \infty$ in the host solution.

In this equation, the term $2\sigma V_0/(rRT)$, which represents the solute concentration gradient, must be replaced in the case of vapor transport by the product of the gradient of the number density of particles and the volume per particle, V_a. Given that $\mathrm{grad}\, nV_a = \mathrm{grad} pV_a/(kT)$, $\mathrm{grad}\, p = \Delta p/z$, and $\Delta p = 2\sigma V_a p_\infty/(rkT)$, we have

$$\mathrm{grad}(nV_a) = \frac{2\sigma V_a^2 P_\infty}{r^2 (kT)^2} = \frac{2\sigma V_0^2 P_\infty}{r^2 (RT)^2}. \tag{4}$$

It follows from Eqs. (3) and (4) that

$$\frac{dr}{dt} = \frac{4}{27}\frac{\sigma V_0^2 P_\infty}{r^2 (RT)^2} D_t, \tag{5}$$

$$\bar{r}^3 = \overline{r^3} + \frac{4}{9}\sigma\left(\frac{V_0}{RT}\right)^2 D_\Gamma P_\infty t. \tag{6}$$

Here, D_g is the diffusion coefficient of atoms (molecules) in the gas phase.

The main point in evaluating the coagulation rate by Eq. (6) is to determine the nature and p_∞ of the atoms (molecules) responsible for vapor transport. In the system under consideration, mass transport in the vapor phase may be due to molybdenum atoms and molecules of various oxides and hydrates.

In the range 800–1000°C, the equilibrium molybdenum vapor pressure is so low that substituting it in

Eq. (6) gives values many orders of magnitude below those observed in experiment. Therefore, in what follows the effect of transport via molybdenum vapor can be neglected.

As shown by Jehn [4], the presence of solid molybdenum in the Mo–O–H system leads to the formation of solid MoO_2 (the lower molybdenum oxide) and $MoO_2(OH)_2$ vapor even at very small amounts of oxygen and, accordingly, a low p_{H_2O} partial pressure and small p_{H_2O}/p_{H_2} ratio. Vapor transport and growth of powder particles proceed with the participation of $MoO_2(OH)_2$ molecules, which form by the reaction

$$MoO_2(s) + 2H_2O(g) = MoO_2(OH)_2\,(g) + H_2, \quad (7)$$

$$K_{p(7)} = \frac{p_{MoO_2(OH)_2}p_{H_2}}{p^2_{H_2O}}. \quad (8)$$

The temperature dependence of this constant was determined by Jehn [4].

In addition, the vapor phase contains a variety of oxide species. Mo_3O_9, one the most stable oxides, with the highest partial pressure, may form by the reaction

$$3Mo_3O_2(OH)_2(g) = Mo_3O_9(g) + 3H_2O. \quad (9)$$

The equilibrium constant of this reaction is such that, even at low water partial pressures (10^3 Pa), the $Mo_3O_9(g)$ partial pressure is three orders of magnitude below the $Mo_2(OH)_2(g)$ partial pressure.

Volatile molybdenum oxides may also form through direct reaction between condensed molybdenum and oxygen impurities, which are always present in gases nonreactive with molybdenum. As shown in our experiments, the weight loss during annealing in helium (marked by two asterisks in Table 1) is substantially lower than that in hydrogen, and therefore the mass transport is predominantly due to $MoO_2(OH)_2$ molecules.

The gas-phase diffusion coefficient of $MoO_2(OH)_2$ was evaluated using the well-known formula $D_g = \bar{u}\lambda/3$, where $\bar{u}$ is the average speed of diffusant molecules in the gas phase (m/s):

$$\bar{u} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}},$$

$$\lambda = \frac{kT}{\sqrt{2}\pi(r_{MoO_2(OH)_2} + r_{H_2})^2 p_\Sigma}.$$

Here m is the molecular mass of the diffusant (kg), M is its molar mass (kg/mol), λ is the mean free path of diffusant molecules (m), $r_{MoO_2(OH)_2}$ is the molecular radius of $MoO_2(OH)_2$ (3×10^{-10} m), r_{H_2} is the molecular radius of hydrogen (1.35×10^{-10} m), and p_Σ is the total pressure in the system (1.013×10^5 Pa).

At 800, 900, and 1000°C, the D_g of $MoO_2(OH)_2$ molecules is 2.17×10^{-5}, 2.48×10^{-5}, and 2.80×10^{-5} m^2/s, respectively.

Under the conditions of our experiments, p_{H_2} and p_{H_2O}, needed to find $p_{MoO_2(OH)_2}$ by Eq. (8), may depend on two factors. First, the starting hydrogen has a certain humidity. In flowing hydrogen, to this humidity corresponds a constant water vapor pressure over the molybdenum powder. Second, the starting powder contains oxygen, and its traces are present in the final product. This suggests that, throughout a given experiment, the water vapor pressure may be determined by equilibrium in the hydrogen reduction of the lower molybdenum oxide.

In the former case, the water vapor pressure must be constant, independent of the annealing temperature and duration. For hydrogen with a dew point of –5°C, the water pressure is 4.162×10^{-3} Pa. Substituting this water vapor pressure and a hydrogen pressure of 10^5 Pa into Eq. (8) and using the temperature dependence of the equilibrium constant of reaction (7), we find that $p_{MoO_2(OH)_2}p_\infty$ at 800, 900, and 1000°C is 8.7×10^{-8}, 7.8×10^{-7}, and 4.9×10^{-6} Pa, respectively. Substituting these p_∞ values and the corresponding D_g values into Eq. (6) gives an increase in the radius of molybdenum particles below the experimentally determined value by more than one order of magnitude.

In the latter case, the hydrogen pressure is determined by equilibrium in the reaction

$$0.5MoO_2(s) + H_2(g) = 0.5Mo + H_2O(g). \quad (10)$$

The equilibrium constant of this reaction, $K_p = p_{H_2}/p_{H_2O}$, as a function of temperature has the form [5]

$$\log K_p = 0.8799 - \frac{1383.2}{T}. \quad (11)$$

Combining this equation with (5) and taking into account that the total pressure is 10^5 Pa, we find that $p_{MoO_2(OH)_2}$ at 800, 900, and 1000°C is 5.5×10^{-4}, 7.5×10^{-3}, and 6.8×10^{-2} Pa, respectively, which is about four orders of magnitude higher in comparison with the former case.

The $p_{MoO_2(OH)_2}$ and $D_{g\ MoO_2(OH)_2}$ values thus obtained were used to evaluate the increase in particle size by Eq. (6) with $V_0 = 2.02 \times 10^{-5}$ m^3/mol and $\sigma = 1.0$ J/m^2. The calculated particle sizes of the annealed samples d_{calc} are listed in Table 1. The experimentally determined average particle sizes are of the same order as the values calculated by Eq. (6). This provides solid evidence that the main mechanism behind the coagulation of molybdenum particles during hydrogen annealing at temperatures from 800 to 1000°C is mass transport by $MoO_2(OH)_2$ vapor.

CONCLUSIONS

Heating of molybdenum powder in hydrogen below 700°C leads to Mo_2O_3 crystallization, a gradual decrease in oxygen content through removal of the water of hydration, and vaporization of molybdenum oxides and hydroxides. After heating to above 700°C, the powder consists almost entirely of molybdenum, with trace amounts of oxygen.

Considerable coagulation of molybdenum nanoparticles begins above 700°C and proceeds through vaporization.

Molybdenum is transported through the gas phase primarily by $MoO_2(OH)_2$ molecules.

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