

20 Molybdenum

The W–Mo system was reviewed in [1, 2], in "Molybdenum" Suppl. Vol. A 3, 1983, pp. 107/8, "Shunk" (1969), p. 528, "Elliott" (1965), p. 636, "Hansen" (1958), pp. 980/1, and in "Vol" Vol. 2 (1962), pp. 417/22.

20.1 Phase Diagram

Unrestricted solid solubility was found with sintered and annealed samples at 1000 to 1800°C [3], with samples homogenized at $\geq 2000^\circ\text{C}$ [4], arc-cast samples [5], and with samples sintered at $\leq 2600^\circ\text{C}$ [6]. The occurrence of an intermetallic compound $\text{Mo}_{0.5}\text{W}_{0.5}$ was suggested by the results of corrosion tests on arc-melted samples [7] and by the composition dependence of the Hall coefficient R_H of $\text{W}_{1-x}\text{Mo}_x$ alloys prepared by sintering at 2000 to 2200°C. The R_H vs. x curve consists of two linear segments joining at $x \approx 0.5$ [8]. A tendency for segregation was indicated by the diffuse X-ray diffraction from $\text{W}_{0.56}\text{Mo}_{0.44}$ alloys homogenized for 20 h at 1700°C and quenched or annealed at 1350°C for 2 h or at 1100°C for 10 h prior to X-ray diffraction [9]. The oxidation rate of arc-cast (W, Mo) alloys in air at $\sim 955^\circ\text{C}$ has a minimum near 15 wt% W and a rather sharp maximum at ~ 60 wt% W [5].

The solidus ascends nearly linearly with composition (at% W) from 2619°C (Mo) to 3423°C (W) [2]; also see [10] and "Massalski" (1986), pp. 1643, 1645.

The enthalpy of solution of 1 mol liquid solute in liquid solvent at infinite dilution was estimated as $\Delta H = -1\text{ kJ}$ for both Mo in W and W in Mo [11].

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20.2 Ion Implantation

For an FIM study of (W atom) depleted zones formed by 30 keV irradiation of W emitter tips with Mo^+ ions, see Wei, Ch.-Y., Seidman, D. N. (Appl. Phys. Letters **34** [1979] 622/4).

20.3 Adsorption Effects and Adlayer Growth

20.3.1 Molybdenum on Tungsten

FEM and FIM Tips

For FEM and FIM (field electron and ion microscopic) studies of particular W surfaces, see below.

The work function change vs. coverage relationship, $\Delta\Phi$ vs. Θ , was determined from the field emission current from a (100)-oriented W tip exposed to Mo at 77 K. A minimum is passed with $\Delta\Phi \approx -0.6$ eV at $0.4 \leq \Theta \leq 0.5$. Mo deposition at 20 K beyond $\Theta = 0.4$ quenches the Swanson hump in the total energy distribution (TED) of the field-emitted electrons [1]. A monotonous decrease of the work function from the assumed 4.5 eV for the pure W tip to 4.1 eV and 4.2 eV was found for Mo deposition at 77 and 800 K, respectively. The slight difference of the final values was attributed to disorder of the Mo layer near W(100) at 77 K [2]. Annealing a full monolayer at 750 K raised Φ from 4.21 eV (77 K) to 4.3 eV [1]. According to FIM, the Mo layers deposited at 78 K and base pressures $p \approx 10^{-7}$ Torr are very irregular. They contain many random Mo clusters. Mo deposition at 320 K yields similar results, the clusters being somewhat larger. First signs of crystallinity occurred with the tip at 420 K [4]. An FIM technique was also used to study the adlayers produced by deposition of large amounts of Mo onto a W tip at 77 K and background pressures around 10^{-7} Torr. Films some 30 to 40 atomic layers thick were microcrystalline and showed no long-range crystallographic order. On field-desorbing the Mo layer-by-layer, the heavy disorder of the Mo progressively diminished as the W substrate surface was approached (films with $\Theta > 30$ to 40 ruptured under the applied desorption field) [5]. On deposition at 420 K, crystallites first developed on {111} and {100} regions with Mo orientations close to that of the W substrate surface. Annealing at higher temperatures yielded epitaxial and more perfect crystallites [4].

Mo deposition at 370 to 850 K resulted in films that withstood the rupturing action of the desorption field better than did the 77 K films. Up to 60 atomic layers could be investigated. The upper portions yielded irregular FIM images, the perfection improving as field desorption proceeded. The layers close to the W substrate were well-ordered and oriented in the same way as the substrate surface. This epitaxial portion of the Mo film included the first layer. Raising the tip temperature during deposition increased the thickness of the well-ordered, epitaxial portion, which comprised 20 and 40 atomic layers for 500 and 750 K, respectively [5]. The “epitaxial temperature” is ~ 400 K [4].

On heating Mo layers with $0.8 \leq \Theta \leq 1.2$ to 750 K, a field-dependent resonance develops in the TED at about 0.17 to 0.18 eV below the Fermi level. It is identified with the resonance from Mo(100). Heating deposits near monolayer coverage at 750 K produces very stable, ordered Mo layers. The Mo resonance in the TED and the $\Phi = 4.3$ eV value (see above) persist up to 1300 K [1]. Mo layers with $\Theta \approx 10$ were deposited at 600 K and annealed for a few seconds at 1000 K. After field desorption of 5 to 8 Mo layers, the FIM image of the tip resembled that of a pure Mo tip and the remaining Mo was oriented in the same way as the W substrate. The ion image of the first Mo monolayer, however, resembled more closely that of the W substrate than that of an Mo tip [4].

Heating to 1200 K the Mo layers deposited at 77 K resulted in film structures similar to those of films deposited at 370 to 850 K. Pulse heating for 1 s at 1000 K of the 77 K layers resulted in films that were epitaxial at the bottom and disordered at the top. Anneals lasting for 6 min at 1200 K produced large {211} and {110} facets [5].

Epitaxial Mo single crystals free of dislocations grew on W FIM tips at 923 to 1073 K from $\text{Mo}(\text{CO})_6$ vapor at background pressures of $\sim 10^{-7}$ Torr. No orientation misfit occurred between the substrate and overgrowth within accuracy limits of $\pm 2^\circ$. The {110} surfaces were the last to be coated. At 1113 to 1163 K single crystalline Mo films formed, usually epitaxial, which contained extensive dislocations. Spirals on and around W(110) surfaces occurred having Burgers vectors of $(\text{a}/2) \times \langle 1\bar{1}0 \rangle$ or $(\text{a}/2) \times \langle 111 \rangle$ type, the dislocation lines being close to $\langle 110 \rangle$. At 1173 to 1273 K amorphous layers formed right from the substrate surface. At 1273 to 1403 K epitaxial single crystals could again be deposited, but the density of imperfections was some 10 times larger than below 800°C [6].

W(110) Face

Pairs of Mo atoms were detected on W(110) surfaces after Mo deposition onto FIM tips at 78 K. They are more stable against field desorption than single Mo atoms. The dumbbell is in most cases oriented along [1 $\bar{1}$ 0] and less frequently along [1 $\bar{1}$ 1]. Pairs oriented along [001] were never seen. The Mo adsorption sites on W(110) are "surface sites" rather than "lattice sites", from which they differ by slight displacements [7].

The intrapair atomic distance in the [1 $\bar{1}$ 0]-oriented dumbbells is estimated as ~ 4.47 Å. The bond length in the [1 $\bar{1}$ 1]-oriented pairs is estimated as 5.48 Å, twice the substrate nearest neighbor distance. The [1 $\bar{1}$ 0]-oriented pairs dissociate in a narrow temperature range above 230 K; the resulting Mo atoms apparently are field-desorbed. The binding energy of these pairs is estimated as 0.12 eV. Occasionally, more than two pairs coalesced on heating at or above the pair dissociation temperature. Clusters of Mo atoms form on heating at 300 K; among these are chains of Mo atoms oriented along [1 $\bar{1}$ 0]. The chains are stable below ~ 280 K and dissociate at higher temperatures. Rhombic clusters of four Mo atoms form most frequently above 300 K. These Mo_4 clusters never migrated nor dissociated on heating at 312 K and did not adsorb any further Mo atoms [7].

W(211) Face

Mo atom pairs occurred on the W(211) surfaces of an FIM emitter tip [7 to 9]. Mo–Mo pairs were observed both with the Mo atoms in the same channel (parallel to [111]) of the (211) surface or in adjacent channels. Pairs with the atoms confined to a single channel always had Mo–Mo distances larger than 2.74 Å, the closest conceivable approach [7, 8], even on heating to temperatures that allowed Mo diffusion within the surface channel [7]. Apparently, the Mo atoms which approach each other more closely form a bond with concomitant weakening of the Mo-to-substrate bonds [8]. Such close Mo–Mo pairs seem to be field-desorbed easily [8, 9].

Pairs of Mo atoms situated in adjacent channels occurred frequently both in the as-deposited condition (78 K) and after heating at 240 K. These pairs are oriented along [1 $\bar{1}$ 0] (normal to the channel direction) with Mo–Mo distances of 4.77 Å ("straight configuration") or with distances of ~ 5.24 Å ("oblique configuration"). The pairs easily switch between the straight and the oblique configurations. The surface migration of these pairs is activated by ~ 0.74 eV (which is also the estimated minimum energy for pair dissociation) [7]. The boundaries at the edges of the W(211) surfaces do not reflect the Mo pairs. Rather, below ca. 350 K, the pairs are trapped. On heating above 400 K the trapped pairs are liberated and diffuse to the interior of the (211) surface [8].

W(100) Face

Single crystalline W films, apparently exposing (100) surfaces and $\sim 1000 \text{ \AA}$ thick, were annealed in vacuum at 1000°C . Mo was deposited onto these films at 800 to 1000°C by electron-beam evaporation. For $\leq 100 \text{ \AA}$ Mo thickness, coherent matching of the films is achieved, the misfit being relieved by elastic strain, and no misfit dislocations occur. With thicker Mo layers, the Mo-W interface contains systems of misfit dislocations with Burgers vector $\frac{1}{2}\langle 111 \rangle$. The dislocation lines are oriented mostly along $\langle 210 \rangle$, $\langle 110 \rangle$ orientations being also observed [14].

Binding Energies

From an FIM study with H_2 as imaging gas, the desorption fields for single Mo adatoms from various W surfaces were determined relative to the W desorption fields, and the binding energies of Mo atoms on various W surfaces were derived as follows [10]:

| substrate plane | W(110) | W(211) | W(100) | W(111) |
|-----------------------------|--------|--------|--------|--------|
| Mo desorption field | 0.885 | 0.912 | 1.018 | 0.960 |
| Mo binding energy in eV ... | — | 8.3 | 10.5 | 8.7 |

In addition to these data the value 9.5 eV was given for the binding energy of Mo on W(110) in [3].

AES Studies

Mo sputter-deposited onto W (presumably polycrystalline) forms uniform, smooth films [11]. The thickness dependence of the AES (Auger electron spectroscopy) signal is given for ≤ 30 Mo monolayers in [12]; also see [13]. The sputter removal of the deposited Mo from the W substrate proceeds nearly as if the Mo was sputtered from bulk Mo [11].

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20.3.2 Tungsten on Molybdenum

Mo(110) Face

Terrace-like W layers form by vapor deposition at 1200°C. With the impinging W atom beam approximately parallel to an Mo [111] direction, the resulting W layer had a strong [110] texture with a weak [100] component. With the W atom beam aligned nearly parallel to an Mo [100] direction, a [100] texture in the W layer resulted [1].

Mo(100) Face

The $\Delta\Phi$ vs. Θ curve passes a maximum at $\Theta = 0.3$ and $\Delta\Phi \approx 0.5$ eV for W deposition at 77 K onto a (100)-oriented Mo FEM tip. The curve levels off at $\Delta\Phi = 0.3$ eV for $\Theta \geq 0.6$. Heating a monolayer to 880 K results in an increase to $\Delta\Phi = 0.4$ eV. This value persists up to 1300 K, suggesting that it is due to ordering of the layer rather than to W diffusion out of the Mo(100) plane. This conclusion is corroborated by the total energy distribution curves of the field-emitted electrons [2].

Pseudomorphic growth of W films occurs for up to ~ 1000 Å thickness by vapor deposition onto (100)-oriented Mo foils at 200 to 1000°C. On raising of the Mo temperature, the density D of growth dislocations diminishes. A value $D \approx 10^9/\text{cm}^2$ is found at 900°C and a W thickness of 1000 Å [3].

Other Studies

For the Θ dependence of various W AES signal intensities and of the 120 eV Mo intensity at $\Theta \leq 16$, see [4]. For the formation of epitaxial W films from W(CO)₆ on Mo substrates, see [5].

References:

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20.4 Diffusion

20.4.1 Bulk Diffusion

Interdiffusion

The interdiffusion coefficient \tilde{D} has been measured with diffusion couples. These were prepared by welding Mo with W [1 to 3], W(110) with Mo(100) surfaces [4 to 6], single crystalline W and Mo [3, 7], or by deposition of thin layers. Chemical vapor deposition (CVD) by reduction of WF₆ with H₂ was used to deposit W onto Mo in [1, 8, 9] and a sputtering technique to deposit Mo and W films onto W(110) and Mo(100) surfaces, respectively, in [4]. The temperature ranges of the diffusion anneals were as follows:

| | | | | | | | |
|----------------------------|-------|------|------|------|--------|------|------|
| t_{\min} in °C | ~1630 | 1700 | 1730 | 1800 | 1900 | 2080 | 2100 |
| t_{\max} in °C | ~2175 | 2400 | 2400 | 2200 | 2250 | 2080 | 2500 |
| Ref. | [9] | [3] | [2] | [1] | [5, 6] | [7] | [8] |

Diffusion profiles were determined by electron microprobe analysis [2 to 9]. They were asymmetric [1, 4 to 6] and evaluated by Matano's method [1 to 6]. The Matano plane is at an Mo content of ~60 at% [9], at 64 at% [6], ~65 vol% [5]. Pore formation occurred in the couples near the interface on the Mo-rich side [1, 5, 6, 8, 10], at 20 wt% W [1], indicating that the Mo is the faster-diffusing species [5, 8]. Facets and smooth surfaces form at the Mo-rich and W-rich sides of the pores, respectively. The pores nucleate at imperfections and foreign particles [1], and in the CVD-produced couples the deposition conditions have a strong effect on the pore formation [9] by influencing the grain growth process in the tungsten layer [1]. No porosity was observed in samples that were electropolished before tungsten deposition. At 1650°C the main process producing a layer of pores is grain boundary diffusion of Mo in the W layer [1].

The composition dependence of \tilde{D} in $\text{Mo}_{1-x}\text{W}_x$ alloys is exponential, $\tilde{D}(x) = \tilde{D}(0) \cdot \exp(-\alpha x)$ with $\tilde{D}(0) = D_W^0$, the impurity diffusivity of W in Mo (see below) [1]. The values given for α are 4.4 [1], ~4 [2], and 3.85 [4, 5], revising the 3.45 given in [6]. For plots of \tilde{D} vs. composition, see also [7, 9].

The interdiffusion is thermally activated, $\tilde{D}(x, T) = \tilde{D}_0 \cdot \exp(-E_A/RT) = \tilde{D}(0) \cdot \exp(-\alpha x) \cdot \exp(-E_A/RT)$ with $\tilde{D}(0) = 0.14 \text{ cm}^2/\text{s}$, $\alpha = 3.85$, and $E_A = 126 \text{ kcal/mol}$ [4, 5]. $\tilde{D}_0 = 140 \text{ cm}^2/\text{s}$ and $E_A = 136 \text{ kcal/mol}$ [1]. For 10 to 70 wt% W, \tilde{D}_0 ranged around $0.1 \text{ cm}^2/\text{s}$ and E_A ranged between ~100 and 105 kcal/mol [2]. The rather low value $E_A = 92.4 \pm 7.6 \text{ kcal/mol}$ given for 80 wt% W [2] and the $E_A = 4 \text{ eV} \approx 92.2 \text{ kcal/mol}$ given in [9] suggest substantial grain boundary diffusion. The $\tilde{D}(x, T)$ values determined on powder metallurgical samples in [3] are omitted here. They were always larger than the results obtained with zone-melted single crystals of Mo and W [3] evaluated in the following table:

| | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| wt% W | 10 | 10 | 20 | 20 | 30 | 30 | 40 | 40 | 50 |
| E_A in kcal/mol | 120 | 117.2 | 119 | 114.9 | 118.2 | 109.6 | 114 | 109.3 | 111.3 |
| \tilde{D}_0 in cm^2/s ... | 4.8 | 4.48 | 4.3 | 2.41 | 2.73 | 0.64 | 1.18 | 0.48 | 0.59 |
| Ref. | [3] | [8] | [3] | [8] | [3] | [8] | [3] | [8] | [3] |
| wt% W | 50 | 60 | 60 | 70 | 70 | 80 | 80 | 90 | 90 |
| E_A in kcal/mol | 107.7 | 107.7 | 105.4 | 107.2 | 104.7 | 102.5 | 102.7 | 98.6 | 100.8 |
| \tilde{D}_0 in cm^2/s ... | 0.30 | 0.37 | 0.17 | 0.09 | 0.14 | 0.01 | 0.08 | 0.003 | 0.05 |
| Ref. | [8] | [3] | [8] | [3] | [8] | [3] | [8] | [3] | [8] |

The $\tilde{D}(x, T) = 0.00063 (\text{cm}^2 \cdot \text{s}^{-1}) \cdot \exp[-79.8(\text{kcal} \cdot \text{mol}^{-1})/RT]$ relationship determined using tungsten wires [27] is obviously severely influenced by grain boundary effects; also see [28].

A roughly tenfold increase in $\tilde{D}(x)$ is said to occur at 1600°C for ≤ 3 at% W if the diffusion couple is exposed to an He glow discharge (300 to 1000 V; 20 to 60 mA/cm²) rather than to vacuum [34].

The partial diffusion coefficients D_{Mo}^p and D_W^p were determined from Kirkendall marker shifts and from tracer diffusivities (see below). Results obtained by the two methods are compared in the following table [4]:

| t in °C | x in $\text{Mo}_{1-x}\text{W}_x$ | D_{Mo}^p in $10^{-12} \text{ cm}^2/\text{s}$ from marker shifts | D_{Mo}^p in $10^{-12} \text{ cm}^2/\text{s}$ from tracer | D_W^p in $10^{-12} \text{ cm}^2/\text{s}$ from marker shifts | D_W^p in $10^{-12} \text{ cm}^2/\text{s}$ from tracer |
|------------|-------------------------------------|---|--|---|--|
| 1900 | 0.12 | 3.5 | 3.7 | 0.43 | 0.65 |
| 2045 | 0.20 | 7.4 | 12.4 | 2.7 | 2.7 |
| 2150 | 0.21 | 21 | 37 | 8.8 | 9.0 |
| 2250 | 0.27 | 36 | 68 | 22 | 20 |

Tracer Diffusivities D^*

The papers dealing with the impurity diffusivities (diffusion coefficients) $D_W^*(Mo)$ and $D_{Mo}^*(W)$ in the pure components of the W–Mo system are treated separately below.

For intermediate compositions $Mo_{1-x}W_x$, $D_{Mo}^*(x)$ was determined using ^{99}Mo [11 to 16, 30, 31]. The electrodeposition of the ^{99}Mo is described in [11]; also see [12]. Polycrystalline samples containing 0, 45, 48, 56, 80, 95, and 100% (apparently at%) W were studied between 1900 and 2400°C. At 1900°C, $D_{Mo}^*(x)$ decreases exponentially as x increases from 0 to 80% W. There is an even stronger decrease at $x = 95$ and 100%. This seems to be due to grain boundary effects, since the Mo diffusivities in W single crystals are $\sim \frac{1}{3}$ those in W polycrystals [11]. $D_{Mo}^*(x, T) = D_0^*(x) \cdot \exp(-E_A(x)/RT)$ with $D_0^*(x)$ and $E_A(x)$ as follows [11]:

(at?) % W 45 56 100 100 (single crystal)

$D_0^*(x)$ in cm^2/s 0.12 0.17 3.7 0.05

$E_A(x)$ in kcal/mol ... 103 107 110 121

$Mo_{1-x}W_x$ wires were prepared by powder metallurgical methods in [12] and the spreading of the ^{99}Mo along the wire was measured between 1400 and 2800°C; the temperature ranges covered at least 600 K for each composition [12, 13]:

| | | | | | | | | | | | |
|--------------------------------------|-----|-----|-----|----|----|----|-----|------|-------|------|--------|
| at% W | 0.1 | 15 | 20 | 25 | 35 | 50 | 65 | 75 | 80 | 85 | 99.9 |
| $D_0^*(x)$ in cm^2/s | 142 | 265 | 146 | 47 | 28 | 12 | 1.3 | 0.2 | 0.112 | 0.08 | 0.0025 |
| $E_A(x)$ in kcal/mol | 112 | 106 | 102 | 95 | 92 | 88 | 86 | 84.5 | 82 | 80 | 78 |

This table also takes account of the results of [14 to 16, 30, 31]. To avoid surface effects, thin layers were removed from the annealed wires by electropolishing prior to the activity measurements [12] (see also [13]), but the low activation energies suggest severe grain boundary effects for ≥ 25 at% W.

Based on impurity diffusivities and on the exponential composition dependence of D_{Mo}^* found by [11], the estimate $D_{Mo}^*(x, T) = 3.99(\text{cm}^2 \cdot \text{s}^{-1}) \cdot \exp(-3.28x) \cdot \exp[-(138 - 11.5x) (\text{kcal} \cdot \text{mol}^{-1})/RT]$ was given in [4, 5].

The tracer diffusivity $D_W^*(x)$ of ^{185}W in $Mo_{1-x}W_x$ was determined by [12 to 17, 30, 31]. While wire samples were used by [12 to 16, 30, 31] (see above), a series sectioning technique was applied to platelets by [17]. The method used for electrodeposition of the ^{185}W onto the wires is referred to in [12]. The diverging results of the two sets of experiments ([12 to 16, 30, 31] and [17]) are given in the following tables.

| Diffusivities $D_W^*(x)$ at 1900°C are: | | | | | | | | | |
|--|---------------|------|------|----------------|--------------|----------|---------------|----------------|------|
| at% W | 0 | 0.1 | 10 | 15 | 20 | 20 | 25 | 25 | 30 |
| $D_W^*(x)$ in $10^{-12} \text{ cm}^2/\text{s}$ | 5.35 ±0.25 | 827 | 7.88 | 78400 ±1.05 | 9.35 | 59300 | 43300 | 43600 ±0.31 | 7.40 |
| Ref. | [17] | [12] | [17] | [12, 15] | [17] | [12, 31] | [12] | [16] | [17] |
| at% W | 35 | 50 | 50 | 65 | 70 | 75 | 80 | 100 | |
| $D_W^*(x)$ in $10^{-12} \text{ cm}^2/\text{s}$ | 2750 ±0.47 | 6.15 | 3730 | 866 | 5.28 ±1.3 | 540 | 2.25 ±0.12 | 1.65 ±0.17 | |
| Ref. | [12, 14] | [17] | [12] | [12] | [17] | [16] | [17] | [17] | |

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For $D_w^*(x, T) = D_0^*(x) \cdot \exp(-E_A(x)/RT)$, the following parameters were determined [12, 13]:

| | | | | | | | | | | | |
|--|--------|-----|------|-----|-----|----|-----|-----|-----|-----|------|
| at% W | 0.1 | 15 | 20 | 25 | 35 | 50 | 65 | 75 | 80 | 85 | 99.9 |
| $D_0^*(x)$ in cm^2/s ... | 0.0085 | 1.4 | 1.7 | 2.2 | 6.9 | 14 | 16 | 20 | 22 | 25 | 24 |
| E_A in kcal/mol .. | 71 | 73 | 74.6 | 77 | 85 | 95 | 102 | 116 | 119 | 122 | 130 |

The orders of magnitude larger $D_w^*(x)$ values obtained by [12 to 16] suggest that grain boundary diffusion was substantial in the wire samples prepared by powder metallurgy and that the $D_0^*(x)$ and $E_A(x)$ values given above [12, 13] should be taken with due reservation. Also see the following results on impurity diffusivities.

Impurity Diffusivities $D_{\text{Mo}}(\text{W})$ and $D_{\text{W}}(\text{Mo})$

The impurity diffusivity (diffusion coefficient) of Mo in (nearly) pure W was determined from the penetration profile of thin Mo layers sputter-deposited onto W(110) surfaces and diffusion-annealed at ($\pm 20^\circ\text{C}$) 2008 to 2255°C [4, 5]. Diffusion anneals at 1700 to 2100°C yielded the results given in [18], presumably determined by a serial sectioning technique with ^{99}Mo . Electron microprobe analysis was used to establish the diffusion profiles after anneals at 1730 to 2400°C [2]. Powder-metallurgically prepared W wire samples of 99.9 at% purity as described above were used by [12, 13]. Thermodynamic data were used to calculate the values given by [19]. The parameters D_0 and E_A in $D_{\text{Mo}}(\text{W}) = D_0 \cdot \exp(-E_A/RT)$ are as follows:

| | | | | | |
|---------------------------------------|----------|------|------------------|-------|-----------------|
| D_0 in cm^2/s | 0.0025 | 0.3 | 2.94 | 0.87 | 0.15 ± 0.01 |
| E_A in kcal/mol .. | 78 | 101 | 102.1 ± 10.3 | 109.9 | 126.5 ± 3.4 |
| Ref. | [12, 13] | [18] | [2] | [19] | [4, 5] |

Theoretical values are $D_0 = 0.87 \text{ cm}^2/\text{s}$, $E_A = 110 \text{ kcal/mol}$ [32]. For a $D_{\text{Mo}}(\text{W})$ vs. $1/T$ plot, see also [33].

The impurity diffusivity $D_{\text{W}}(\text{Mo})$ of W in (nearly) pure Mo was determined from the penetration profile of Mo-W couples [1], W(110)-Mo(100) couples [4, 5] by reevaluation of the data in [6], and from the penetration profile of sputter-deposited thin W layers on Mo(100) [4, 5]. The diffusion of ^{185}W in Mo was studied by [12, 13, 17, 18, 20 to 24, 33]. Mo single crystals were used by [20, 24]; the polycrystals used in addition had grain sizes between 80 and $200 \mu\text{m}$ [24]. The grain sizes in [21] ranged from 0.5 to 1 mm. The serial sectioning technique was used by [17, 20, 22 to 24], supplemented by autoradiographic studies in [21]. The parameters D_0 and E_A in $D_{\text{W}}(\text{Mo}) = D_0 \cdot \exp(-E_A/RT)$ are given in the following tables. Theoretical values are $D_0 = 0.50 \text{ cm}^2/\text{s}$, $E_A = 105.7 \text{ kcal/mol}$ [32].

For Mo single crystals:

| | | | | |
|---------------------------------------|-------------------|-------------------|-----------------------|--------------------------------|
| D_0 in cm^2/s | 5.89 | 3.97 | 3.6 ± 0.5 | $(2.3 \pm 2.7) \times 10^{-2}$ |
| E_A in kcal/mol | 125.4 | 123.2 | 123.2 ± 7.5 | 100 ± 3 |
| t_{\min} in $^\circ\text{C}$ | 1900 | 1900 | ~ 1900 | 1700 |
| t_{\max} in $^\circ\text{C}$ | 2250 | 2268 | ~ 2270 | 2150 |
| Ref. | [5] ^{a)} | [5] ^{b)} | [4] ^{a), b)} | [24] ^{c)} |

^{a)} W(110) welded on Mo(100). – ^{b)} Thin W layer on Mo(100). – ^{c)} (1 to 5) $\times 10^7$ dislocations per cm^2 .

For Mo polycrystals:

| | | | | | | | | | |
|-------------------------------------|------|------------------------|------------------|------------|----------------|--------------------------------------|--------|---------|----------|
| D_0 in cm^2/s ... | 140 | $2.64^{+1.49}_{-0.95}$ | 3.18 | ~ 1.7 | 0.19 | $(5.26^{+26}_{-4.3}) \times 10^{-3}$ | 0.0005 | 0.00045 | 0.0085 |
| E_A in kcal/mol | 136 | 119.3 ± 1.9 | 112.9 ± 1 | 110 | 102 ± 7 | 91 ± 8 | 78 | 77.5 | 71 |
| t_{\min} in $^\circ\text{C}$ | 1800 | 1660 | 1700 | 2075 | 1730 | 1700 | 1750 | 1700 | 1800 |
| t_{\max} in $^\circ\text{C}$ | 2200 | 2230 | 1900 | 2260 | 2400 | 2150 | 2150 | 2150 | 2400 |
| Ref. | [1] | [20] | [21] | [22] | [2] | [24] | [23] | [18] | [12, 13] |

Activation energies below 80 kcal/mol obviously are due to grain boundary diffusion.

At 1900°C $D_W(\text{Mo}) = (5.35 \pm 0.25) \times 10^{-12} \text{ cm}^2/\text{s}$ [17].

Grain Boundary Diffusion

Any of the above data of large diffusivities or low activation energies are under suspicion of being affected by grain boundary diffusion.

Mo in W. Artificial grain boundaries were produced in W by diffusion-bonding W(110) with W(111) surfaces, i.e., heating at 1650°C for 3 h under 49 at (700 psi) at 10^{-5} Torr. The resulting specimen was cut perpendicular to the bonding plane. A thickness of 1 μm Mo was evaporated onto the polished cut and the sample diffusion-annealed at 10^{-7} Torr and ($\pm 20^\circ\text{C}$) 1840, 1960, and 2090°C for up to 200 h. Then the penetration profiles were determined by electron microprobe analysis in a cut perpendicular to both sample surface and artificial grain boundary. The activation energy was ca. 27 kcal/mol [25].

W in Mo. The diffusion of ^{185}W in Mo polycrystals was studied by [21, 24, 26]. The grain sizes ranged from 0.08 to 0.2 mm in [24] and from ~ 0.5 to 1 mm in the autoradiographic study [21]. The Mo single crystal used by [24] for comparison had $(1 \text{ to } 5) \times 10^7$ dislocations per cm^2 [24]. The parameters d_0 and E_A in $a \cdot D_{gb} = d_0 \cdot \exp(-E_A/RT)$ are as follows (a = diffusion width of the grain boundary):

| | | | | |
|--|-------------------|-------------------|-----------------|-------------|
| d_0 in $10^{-6} \text{ cm}^2/\text{s}$... | 30^{+100}_{-23} | 1.1×10^6 | $1^{+5}_{-0.8}$ | 0.068 |
| E_A in kcal/mol ... | 105 ± 6 | 77 | 76 ± 7 | 69 ± 18 |
| t_{\min} in $^\circ\text{C}$ | 1700 | 1750 | 1700 | — |
| t_{\max} in $^\circ\text{C}$ | 2150 | 1900 | 2150 | — |
| Ref. | [24]*) | [21] | [24] | [26] |

*) Single crystal.

For a study using W layers deposited on Mo by pyrolysis of $\text{W}(\text{CO})_6$ or by reduction of WF_6 with H_2 , see [29].

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20.4.2 Electrotransport in (Mo, W) Alloys

The electrotransport in $\text{Mo}_{1-x}\text{W}_x$ alloys was studied for $x = 0.001$ to 0.999 at temperatures between 1400 and 2800°C [1, 2]. For each composition the temperature interval studied spanned at least 600 K. For all temperatures and compositions studied, the Mo atoms were transported to the anode and the W atoms to the cathode [1] when a direct current passed through the wire samples, which were prepared by powder metallurgical methods [3]. For $x = 0.15$, see also [4], for $x = 0.25$ and 0.75 , see also [5]. The effective charges on the Mo and W atoms in the alloys as evaluated in [1, 2, 4, 5] are based on tracer diffusivities which were obviously strongly affected by grain boundary effects (see p. 128).

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20.4.3 Surface Diffusion

FIM Studies

The Mo diffusion on W tips in field ion microscopes was studied at residual gas pressures in the low 10^{-10} Torr range. Clean field-evaporated tips were used, and a few Mo atoms were deposited on the W tip at liquid nitrogen temperature [1, 2], in the case of [1] under image gas pressure, i.e., $p(\text{He}) \leq 10^{-2}$ Torr. Contaminants from the tip shank were not mobilized below ~ 400 K [1].

W(110) Face. The diffusion of single Mo atoms on this plane started at ≥ 218 K, which suggested an activation energy of diffusion of about 0.65 eV [3].

W(211) and W(321) Faces. One-dimensional (1-dim) diffusion of Mo was observed on W(211) [1 to 4] and on W(321) [1, 4] surfaces. The diffusion proceeded along the [111]-oriented ridges and troughs that exist on these surfaces [1 to 4]. The widths of the observed jumps are integral multiples of 2.74 Å on both surfaces [1].

For the 1-dim diffusivity $D = D_0 \cdot \exp(-E_A/kT)$, the parameters $D_0 = 9.3 \times 10^{-7}$ cm 2 /s and $E_A = 0.57$ eV were determined at $235 \text{ K} \leq T \leq 285 \text{ K}$ [4], in fair agreement with the 2.4×10^{-6}

cm^2/s and 12 kcal/mol ($\sim 0.52 \text{ eV}$) of the earlier study [1], which also covered a ca. 50 K range [1]. At 280 K the diffusing single Mo atoms were reflected at the edges of the W(211) plane. At 330 K, on the other hand, they appeared to be adsorbed at the ends of the W atom rows (ridges). The potential step at the W(211) plane edge (activation energy for overcoming the step from the inside of the plane) therefrom is estimated at $\sim 0.73 \text{ eV}$. The potential well trapping the Mo atoms at the end of the steps is deeper than 0.54 eV [2].

Mo atoms located on adjacent channels of the W(211) surfaces and forming pairs with interatomic distances $d = 4.47$ and 5.24 \AA have 1-dim diffusivities D (in cm^2/s) = $(2.3 \times 10^{-12}) \cdot \exp(-0.26/kT)$ with the activation energy in eV [4]. The "oblique" pairs with $d \approx 5.24 \text{ \AA}$ (see p. 124) migrate activated by $\sim 0.74 \text{ eV}$ according to [3].

On W(321) the 1-dim diffusivity D (in cm^2/s) = $(1.2 \times 10^{-7}) \cdot \exp(-0.55/kT)$ was determined at $235 \text{ K} \leq T \leq 295 \text{ K}$ [4].

FEM Studies

Field emission microscopic and field emission spectroscopic studies indicate that some of the Mo deposited on W(100) at 20 to 77 K diffuses out of the W(100) plane when heated up to 750 K [5].

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