Tungsten

Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds

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30 CHAPTER 1

affect the recrystallization grain morphology and the retained dislocation substructure. In particular, non-sag tungsten is significantly more creep-resistant than pure tungsten, mainly as a result of the interlocking grain structure, which forms on recrystallization and which prevents both grain boundary sliding and diffusional creep. In addition, the fine dispersion of potassium bubbles contributes to the outstanding creep resistance through pinning of dislocations [1.62, 1.66].

Non-sag tungsten wires are the most creep-resistant wires, with the exception of monocrystalline tungsten. They are therefore used for sag-free lamp filaments at service temperatures of up to $3000\,^{\circ}\text{C}$ (0.88 $T_{\rm m}$), and shear stresses in the range of 0.5 to 10 MPa [1.66].

1.2.4. Thermal Properties

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Melting point: 3422 \pm 15 °C (3695 K) [1.67], 3390 \pm 40 °C (3663 K) [1.68], 3423 \pm 30 °C (3696) [1.69].
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The high melting point (highest of all metals) is the most prominent and important property in regard to all applications as refractory metal. It is a consequence of the electron density of states. Small amounts of impurities, such as carbon, lower the melting point.

The molar volume increases by 8% on melting. This is the largest expansion observed for bcc metals [1.70].

The melting curve of W has been determined to 5 GPa [1.71].

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Enthalpy of fusion: 46 \pm 4 \text{ kJ} \cdot \text{mol}^{-1} [1.68].
Entropy of fusion: 14 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} [1.70].
Enthalpy of sublimination: 858.9 \pm 4.6 \text{ kJ} \cdot \text{mol}^{-1} [1.35].
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Vapor Pressure. Tungsten has the lowest vapor pressure of all metals. Within the temperature range from 2600 to 3100 K, it obeys the following equation [1.76]:

$$\log p[Pa] = -45395T^{-1} + 12.8767$$

At 2000 °C, the vapor pressure is 8.15×10^{-8} Pa; at 3000 °C it is 10^{-1} Pa. Experimental data for p over liquid W are not available.

The rate of evaporation in vacuum is about $6.2 \times 10^{-11} \,\mathrm{g \cdot cm^{-2} \cdot s^{-1}}$ at $2000 \,^{\circ}\mathrm{C}$, about $7 \times 10^{-8} \,\mathrm{g \cdot cm^{-2} \cdot s^{-1}}$ at $2500 \,^{\circ}\mathrm{C}$, and about $2.5 \times 10^{-5} \,\mathrm{g \cdot cm^{-2} \cdot s^{-1}}$ at $3000 \,^{\circ}\mathrm{C}$ [1.72]. It is markedly reduced by an inert gas atmosphere (Ar, Kr). Therefore, modern incandescent lamps contain inert gas fillings to avoid enhanced wall-blackening (the rate of evaporation in vacuum is about 500 times larger as compared to an Ar atmosphere of 1.2 bar) [1.73].

Boiling Point: calculated from rates of evaporation of solid tungsten,

5663 °C (5936 K) [1.74],



Critical temperature: $13400 \pm 1400 \text{ K}$ [1.75]. Critical pressure: $(3.37 \pm 0.85) \times 10^8 \text{ Pa}$ [1.75]. Critical density: $4.31 \text{ g} \cdot \text{cm}^{-3}$ [1.35].

Thermal expansion. At room temperature, values between 4.32 and 4.68 \times 10⁻⁶ K⁻¹ were obtained for the linear coefficient of expansion α , depending on the material (P/M sheet, arc-cast sheet, etc.) and the type of measurement. Values for low and high temperatures are listed in Table 1.12. The linear coefficient of expansion can also be calculated according to the following equations [1.76]:

temperature range: 293-1395 K

$$\alpha = 4.266 \times 10^{-6} (T - 293) + 8.479 \times 10^{-10} (T - 293)^2 - 1.974 \times 10^{-13} (T - 293)^3$$

temperature range 1395-2495 K

$$\alpha = 0.00548 + 5.416 \times 10^{-6} (T - 1395) + 1.952$$
$$\times 10^{-10} (T - 1395)^2 + 4.422 \times 10^{-13} (T - 1395)^3$$

temperature range 2495-3600 K

$$\alpha = 0.01226 + 7.451 \times 10^{-6} (T - 2495) + 1.654 \times 10^{-9} (T - 2495)^{2} + 7.568 \times 10^{-14} (T - 2495)^{3}$$

The very low thermal expansion of tungsten makes it compatible with glass and ceramics in high temperature applications.

Thermodynamic functions [1.35]. Thermodynamic functions for solid tungsten are listed in Table 1.13. For more details and data for liquid tungsten, see elsewhere [1.10].

TABLE 1.12. Thermal Expansion Coefficient for Low and High Temperatures [1.35]

T (K)	$10^6 \cdot \alpha(K^{-1})$	T (K)	$10^6 \cdot \alpha(K^{-1})$
10	0.006	160	3.82
15	0.019	190	4.06
20	0.048	220	4.20
25	0.102	260	4.32
30	0.20	300	4.49
40	0.53	600	4.75
50	0.90	1000	5.02
60	1.43	1400	5.46
70	1.88	1800	6.11
80	2.30	2200	6.89
100	2.82	2600	7.76
130	3.42	3000	9.05
		3400	11.60



TABLE 1.13. Thermodynamic Functions [1.35]

T	$H_T - H_{298.5}$	$H_{\rm T} - H_{\rm 0}$	S	$S-S_0$	C _p	C _v
(K)	(kJ·mol ⁻ ')	(kJ · mol ⁻¹) (kJ·mol ⁻ '·K ⁻ ')	(kJ·mol ⁻¹ ·K ⁻¹)) (kJ · mol ⁻¹ · K ⁻¹) (kJ·mol ⁻¹ ·K ⁻¹)
298.15	0	4.970	32.640	32.618	24.10-24.42	23.96
500	5.022-5.024	10.007	45.516	45.457	24.33-25.44	25.16
1000	18.23-18.25	23.142	63.658	63.686	27.19-27.60	26.70
1500	32.33-32.62	37.249	75.068	75.099	29.23-29.86	28.12
2000	47.59-48.11	52.599	83.881	83.585	31.37-32.13	29.80
2500	64.52-64.78	69.476	91.399	91.397	34.67-36.00	_
3000	83.10-83.88	88.310	98.254	98.442	39.25-41.80	35.91
3500	105.19	109.845	104.880	_	46.49-50.85	-
3600	110.5-111.8	114.574	106.212	106.89	48.11–54.68	_

Analyses of thermodynamic properties of tungsten at high temperatures are available [1.77, 1.78].

The heat capacity at low temperatures is:

The heat capacity of liquid tungsten is $35.564 \,\mathrm{J}\,\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$ [1.10]

Self-diffusion [1.35]. At a certain temperature, the diffusion process is characterized by the diffusion coefficient D. Its temperature dependency is given by the Arrhenius equation $D = D_0 \exp(-Q/R \cdot T)$ with D_0 a constant in $\text{cm}^2 \cdot \text{g}^{-1}$, T the absolute temperature, R the molar gas constant in $J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and Q the activation enthalpy in $kJ \cdot \text{mol}^{-1}$.

Activation enthalpies for the lattice (volume) diffusion were derived between 586 and 628 kJ·mol⁻¹ for single crystals and between 502 and 586 kJ·mol⁻¹ for polycrystalline tungsten. Accordingly, the following equations were set up [1.79]:

Self-diffusion in tungsten single crystals: $D = 42.8 \exp(-640/RT)$. Self diffusion in polycrystalline tungsten: $D = 54 \exp(-504/RT)$.

Over the range of 1900 to 2800 °C, a linear relationship between $\log D$ and 1/T was obtained for polycrystalline tungsten.

The self-diffusion parameters D_0 and Q are influenced by the impurity content of the diffusion zone. Higher values for both were obtained for impure tungsten. This effect is more pronounced at low temperatures and vanishes above 2043 K. (It is assumed that impurities attract vacancies and the higher vacancy concentration disturbs the diffusion process).

The fact that lower Q values were obtained for polycrystalline tungsten than for single crystals, especially for $T < 0.7T_{\rm m}$, is due to a more or less significant contribution of grain



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