Structure and mechanical properties of formed tungsten based materials

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Abstract

High-melting metals belong to transitional metals that are characterised by strong atomic bond in crystal lattice and thus by high-melting temperatures, high strength and heat resistance. These metals considerably surpass other metallic structural materials by their absolute strength level and relative strength (ratio of ultimate strength to density). High corrosion resistance in concentrated acids and some physical properties of high-melting metals, such as high electric resistance, high electron emissivity, etc. also belong to their sought-after properties.
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1. Introduction

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High corrosion resistance in concentrated acids and some physical properties of high-melting metals, such as high electric resistance, high electron emissivity, etc. also belong to their sought-after properties.

These metals are characterised not only by these highly appreciated physical and mechanical properties, but also by some specific features which cause certain problems at their production and treatment. Firstly, they intensively oxidise at increased temperatures (low refractoriness). Oxygen and nitrogen diffuse into tungsten even at low temperatures and create with it solid interstitial solutions and some chemical compounds (oxides, nitrides) that are located particularly at the grain boundaries and thus weaken bonds between them.

Formation of interstitial solid solutions and also of chemical compounds is accompanied by a pronounced loss in mechanical properties, so-called cold brittleness appears (high transition temperature). Transition temperature is not a strictly bound value but it can vary in a broad temperature interval in dependence of contents of impurities, on grain size, production and treatment methods as well as on contents of alloying additions.

2. Structure and properties of tungsten and alloys

Tungsten is characterised by high temperature of melting with high modulus of elasticity. Low compressibility factor, high density and resistance to neutron and gamma radiation are its other valued properties it is also characterised by high electric resistance. Owing to these properties tungsten belongs to important electric materials. Its combination of high-melting properties with high strength is also very advantageous [1]. These properties make tungsten very advantageous and perspective material for manufacturing of strong and heat-resistant alloys. Low refractoriness, decreased deformability and also brittleness at room temperature belong to disadvantages of tungsten.

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Table 1
Impact of impurities content on tungsten's transition temperature

Production method	Content of impurities in mass (%)				Transition temperature (°C)
	C	O	N	H	
Powder metallurgy	0.040	0.023	0.002	0.0003	500
Vacuum melting	0.030	0.004	0.001	0.0002	200
Zone melting	0.024	0.001	0.001	0.0001	100

Owing to tungsten's brittleness its treatment is realised at temperatures that are higher than brittleness limit. This temperature varies for commercially pure tungsten (99.95%) in the interval between 300 and 400 °C, in case of re-crystallised tungsten around 500 °C.

Tungsten's mechanical and physical properties are significantly influenced by undesirable admixtures: oxygen, nitrogen, carbon. They precipitate mainly at the grain boundaries in the form of oxides, nitrides and carbides. By this they considerably decrease mechanical and technological properties of tungsten and also increase its transition temperature, see Table 1.

Carbon is partly dissolved in tungsten's solid solution and besides that creates with it high-melting and hard carbides: W_2C (3.16% C) and WC (6.13% C). The maximum carbon solubility in tungsten is achieved at eutectic temperature (2690 °C) and makes 0.06% (mass). The solubility decreases with decreasing temperature and at room temperature is less than 0.001%.

Carbon content in commercially pure tungsten varies from 0.002 to 0.03% in dependence on production method. Brittle carbide phases precipitate at cooling at the grain boundaries and considerably weaken bonds between grains and significantly increase transition temperature. Tungsten with carbon content under 0.001% has transition temperature approximately −196 °C, and its ductility ranges from 10 to 12%.

Oxygen in low concentrations (under 0.001%) dissolves in tungsten and also forms many oxides with it, e.g., WO_2, WO_3. When the oxygen content is higher than the limit of solubility, the formed oxides precipitate at the grain boundaries. Oxygen bound to solid solution increases tungsten's strength and hardness. Lattice of oxides at the grain boundaries strongly reduces deformability and increases transition temperature.

Content of impurities in tungsten depends on method of its production. It is possible to obtain a high-purity tungsten by zone melting, tungsten with higher content of impurities is produced by powder metallurgy.

2.1. Structure

Failure of poly-crystalline tungsten of commercial purity originates always at the grain boundaries where impurities usually accumulate; limits of inter-crystalline and transcrystalline failure depend on oxygen and carbon content and on grain size. At given content of impurities in tungsten the finer the grain, the smaller the relative content of impurities,

segregations and compounds containing impurities per unit of grain boundary surface and thus the smaller material brittleness. There exists direct linear dependence between logarithm of grain size and transition temperature independently on treatment, by which the grain was obtained. Literature [2] gives the following relation for dependence between transition temperature T_x (plastic state–brittle state) and grain dimension d_z:

$$T_p^{-1} = C_1 - C_2 \log d_z \qquad (1)$$

Relation $T_p = 5.7 + 198.9 \log d_z$ is valid for commercially pure, deformed and annealed tungsten. Experimental results [3] prove that impact of grain dimension on transition temperature cannot be separated from influence of history of preceding treatment and from quantity and character of impurities distribution at the grain boundaries, which is formed at a given treatment.

One of the methods used for reduction of transition temperature is intensive forming of the structure. It is possible to reduce the transition temperature of commercially pure tungsten by forging at temperature of approximately 1550 °C and $\varepsilon = 50\%$ from 600 to 300 °C [3], as a result of extrusion at 1600 °C and rotary swaging at temperatures 1550–1450 °C the transition temperature drops to 150 °C. Dependence of transition temperature of tungsten produced by powder metallurgy on deformation magnitude is shown in Fig. 1.

Annealing at temperatures below the re-crystallisation temperature (800–1400 °C) increases initial transition temperature approximately by 40 °C (WRe5 alloy).

The transition temperature after re-crystallisation annealing at temperatures 1800–2400 °C quickly increases up to the temperature of 240 °C. These values are valid for commercially pure tungsten.
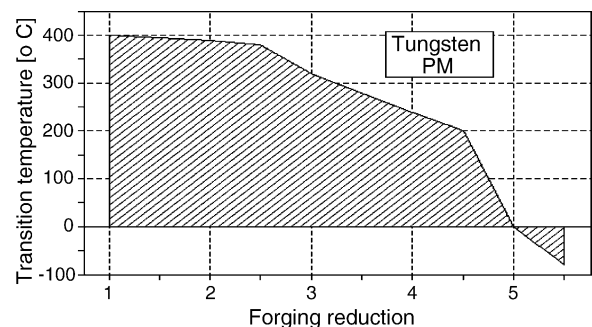

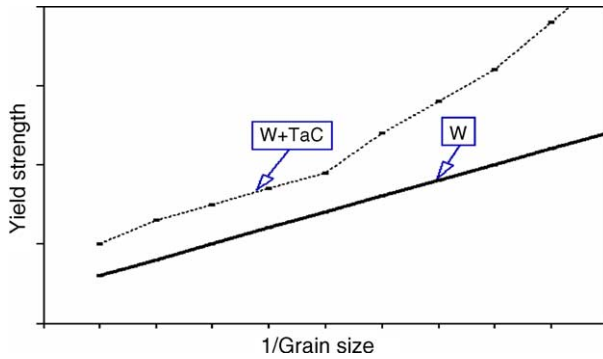Fig. 1. Dependence of transition temperature on forging reduction.

Fig. 2. Dependence of yield point on grain size.

2.2. Grain size

Impact of grain size d_z on yield point can be in accordance with the Hall–Petch model expressed by the equation:

$$\sigma_k = \sigma_o + k d_z^{-\frac{1}{2}} \qquad (2)$$

where σ_k, yield point in torsion; d_z, grain size; k, a constant.

General dependence of the Eq. (2) for commercially pure tungsten and for the WTaC alloy is shown in Fig. 2. Magnitude of factors σ_o and k is sensitive both to quantity and kind of additions in the basic material, as well as on structure and state of deformation.

According to [2], the characteristic $d_z^{-1/2}$ can be put into correlation with the transition temperature (tenacious state–brittle state), with hardness or possibly with fatigue.

2.3. Conditions of deformation

Rate of deformation does not significantly influence the transition temperature, but influences tungsten's yield point and deformation resistance. It is possible to express this dependence for tungsten (and also for other high-melting metals with the KSC lattice) by the following relation:

$$\sigma_d = (\varepsilon'^{Q/RT})^n \qquad (3)$$

where σ_d is deformation stress; ε', rate of deformation; n, deformation rate index; T, deformation temperature; Q, activating energy.

Impact of deformation rate ε' on deformation behaviour of tungsten can be also described the equation

$$\sigma = A\dot{\varepsilon}^{m_1} \qquad (4)$$

where A is material constant; m_1, material dependant exponent which in principle expresses material sensitivity to rate of deformation. It varies for commercially pure tungsten around the value $m \leq 2$. Stress σ_d can at certain values of deformation rates surpass the brittle fracture stress and influence thus the transition temperature. Transition temperature is related to the rate of deformation by the relation
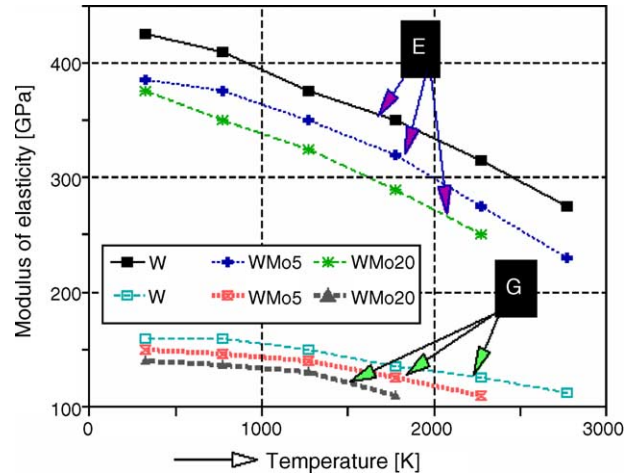
Fig. 3. Dependence of modulus of elasticity in tension (E) and in shear (G) on temperature.

$$T_p^{-1} = A - B \log\varepsilon \qquad (5)$$

where A, B are material constants.

Thus, e.g., the transition temperature for PM tungsten of the grade WA tungsten at the change of the rate of deformation from 0.2 to 320 s^{-1} increases from 120 to 375 °C. With the increase of the rate of deformation for re-crystallised tungsten from 0.001 to 1.5 s^{-1} the transition temperature increases from 200 to 400 °C [4].

2.4. Elasticity

Modulus of elasticity of tungsten produced by PM and deformed in traction at room temperature varies around $E = 4.1 \times 10^5$ MPa, modulus of elasticity of re-melted tungsten is $E = 4.2 \times 10^5$ MPa. Modulus of elasticity in shear is $G = 1.65 \times 10^5$ MPa. Dependencies E and G on temperature are given in Fig. 3.

2.5. Deformation resistance

Increase of tungsten's resistance to deformation is subject to increase of its yield point. It is possible to increase deformation resistance by deterioration of conditions for generation and movement of dislocations. Resistance of an ideal lattice against movement of dislocations (Peierls–Nabarro stress) can be increased by four principal ways that deteriorate conditions for generation and movement of dislocations.

(1) Reciprocal interaction of dislocations.
(2) Interaction of dislocations with particles of the other phase.
(3) Interaction of dislocations with atoms of additions.
(4) Interaction of dislocations with arrangement zones.

It was proved [5] that it is possible to achieve strengthening at which the yield point varies around 700 MPa by any of these methods.
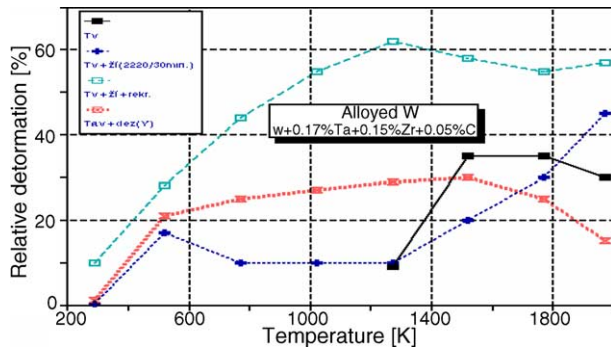
Fig. 4. Dependence of tungsten's ductility on temperature and production technology.

In case of tungsten there are used methods of strengthening by oxides (K_2O, SiO_2, ThO_2), that are introduced into the material before sintering. Thorium strengthened tungsten has increased strength characteristics at preserved or increased plastic properties of material.

2.6. Plasticity

Tungsten's ultimate plasticity is characterised by forming of microscopically detectable cohesion failure in the critical point of deformed volume. Measure of ultimate plasticity is magnitude of deformation till fracture which is expressed by deformation intensity. Ultimate plasticity of tungsten and its alloys depends on structural influences grain size and precipitated impurities at the grain boundaries, as well as on thermomechanical conditions of forming and on state of stress. Value of ultimate plastic deformation (Fig. 4) at continuous hot deformation, at which occurs dynamic re-crystallisation depends on Zener–Hollomon's parameter, on intensity of the state of stress at stabilised deformation and on physical properties of investigated tungsten.

If an intermittent hot deformation is applied (deformation on rotary forging machines), then the ultimate plasticity increases with decrease of values of individual deformations and with duration of pause between individual deformations. If duration of the pause corresponds with the time necessary for static re-crystallisation, then interruption of deformation does not have the influence described above. Impact of the state of stress on the tungsten deformability is partic-

ularly important [6]. Tungsten's deformability increases at high hydro-static pressure.

3. Tungsten alloys

The first tungsten alloys represented possibilities of increase of tungsten's strength and plastic characteristics.

It is possible to divide the used tungsten alloys into two basic groups:

(a) single-phase alloys of the type of solid solutions;
(b) heterogeneous alloys, which are strengthened by dispersion particles, namely by carbides and oxides.

Alloying influences tungsten's strength properties as well as its deformability. Niobium, tantalum, molybdenum, zirconium, hafnium, rhenium, boron, carbon and other elements are used as alloying additions. Table 2 gives composition of some tungsten alloys. In case of tungsten low-alloyed, e.g., by molybdenum the strength properties slightly decrease (Fig. 5), in case of alloying by tantalum or rhenium the substitution atoms in solid solution contribute to increase of the yield point approximately by 10–15%.

Addition atoms, especially those of interstitial elements can, however, significantly influence properties of grain boundaries and thus, e.g., deteriorate deformability of tungsten. C and O_2 and their compounds that segregate at the grain boundaries with concentration up to 2 orders higher than there overall average content, have this impact.

Tungsten produced by powder metallurgy and alloyed by additions of Al_2O_3, CaO has been industrially used for a long time already for manufacturing of bulb filaments. Commercially pure tungsten has been used in recent years also for manufacturing of rocket engine components.

3.1. Alloys of the W–Mo type

Tungsten forms together with molybdenum a continuous line of solid solutions. Melted tungsten alloys with 10 and 15% Mo as well as alloys produced by powder metallurgy containing 25–50% Mo are used in industrial scale [7]. These alloys can be classified on the basis their structure to solid

Table 2
Chemical composition of selected tungsten alloys

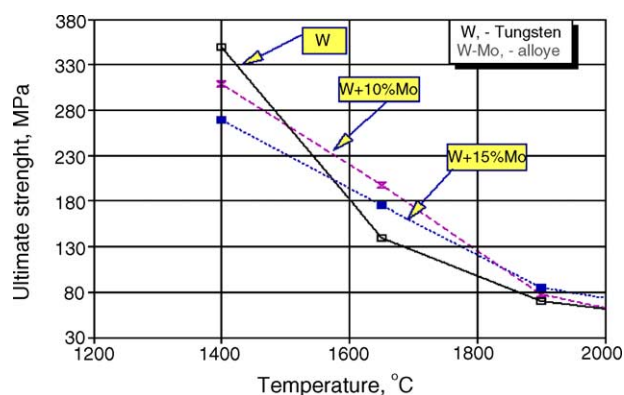| Type of alloy	Chemical composition in mass (%)				Strengthening phase	Undesirable impurities
	Nb	Zr	Mo	Ta		
W–Nb	0.6–0.9	0.1			0.1 Hf 0.001 B	0. 001–0.02 O 0.001 C
W–Mo		0.11	50			
			25			0.05 C
			15			
W–Ta–C				0.2 Ta	0.1–0.15 C	
				0.38		0.05 C
				TaC		
W–Ta–Zr–C				0.2	0.15–0.20 ZrC	0.05 C

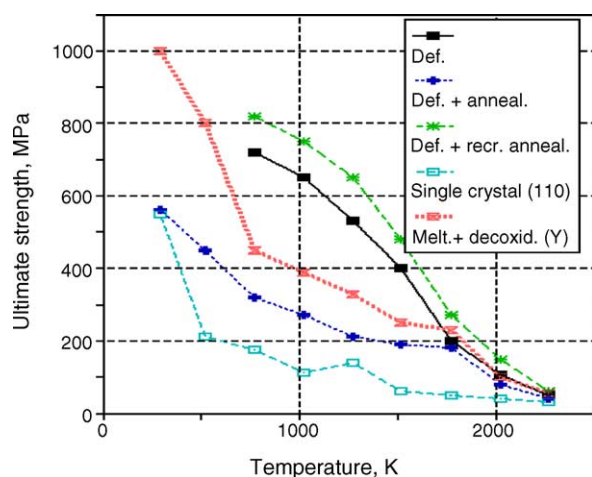Fig. 5. Dependence of ultimate strength of the w-mo type alloy on the temperature in °C.

Fig. 6. Dependence of tungsten's ultimate strength on temperature and production technology.

solutions. Ultimate strength of these alloys is given in Fig. 6. Apart from the types of alloys mentioned above there are industrially used also tungsten alloys with molybdenum and rhenium.

3.2. Alloys of the W–Ta–C type

Tungsten alloy containing 0.2% Ta and 0.05–0.1% C, or alloy containing 0.4% Ta and 0.01–0.02% C are often used. Both alloys belong to heterogeneous alloys with carbides strengthening. Basic strengthening phase in both alloys is tantalum carbide. Alloying of tungsten by tantalum carbide has impact on re-crystallisation temperature. Mechanical properties are given in of these alloys. Comparison of properties shows that the transition temperature of non-alloyed tung-

sten is approximately 100–200 °C higher than that of alloyed alloys [8].

3.3. Alloys of the W–Ta–Zr–C type

Alloying by zirconium enables achievement of higher values of strength characteristics and plasticity of the W–Ta–C type alloys. It is possible to obtain in this way finer grain; grain growth is also slowed down at high temperatures. This type of formed tungsten alloys is used in electrical engineering and machine industry for heating elements, for rocket engine components.

4. Conclusions

The submitted paper analysed and discussed selected mechanical-metallurgical problems concerning relations between ways of production, chemical composition, forming parameters and obtained technically significant properties of tungsten based high-melting materials. Available structural formed tungsten alloys fulfil at present the requirements for their utilisation in transport and in other industrial branches. Their use in given structures is limited by their higher price and also by the state of the industry.

Acknowledgements

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