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INVESTIGATION OF PHYSICAL PROPERTIES OF TUNGSTEN-BASED SINGLE CRYSTALS USING AN ULTRASONIC METHOD

PREISKAVA FIZIKALNIH LASTNOSTI MONOKRISTALOV NA OSNOVI VOLFRAMA Z METODO ULTRAZVOKA

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Using an ultrasonic method, the measurement of longitudinal and transversal velocities v of ultrasonic waves in the major crystallographic directions of pure-tungsten single crystals and tungsten single crystals alloyed with Ta and Mo was performed. Single crystals with a [110] crystallographic orientation were prepared by plasma-arc melting. Crystal density ρ was also measured. Crystal elastic constants C_{ij}, anisotropy factors A, Young's modulus E, shear modulus G and bulk modulus B for the given crystallographic directions, and the mean values of the longitudinal and transversal velocities of the ultrasound according to the Fochtu-Roisu-Chilly method, Young's modulus, shear modulus, Poisson's ratio and Debye temperature were calculated from the obtained data. The measurement of ultrasound rates was realized by means of a pulse apparatus with a frequency of 10 MHz to 30 MHz. It was found that the alloying of pure tungsten with the elements such as tantalum and molybdenum led to a decrease in the average magnitudes of v, C_{ij}, and B over various crystallographic and polarization directions, as well as the magnitude of ρ. The effects of the alloying elements on the elastic properties of tungsten crystals were identical. It may be concluded on the basis of the obtained results that the ultrasonic method can be used for the quality control of the purity of tungsten single crystals and tungsten low-alloyed alloys by measuring the attenuation effects of ultrasound waves in various parts of the tested samples.

Keywords: tungsten, single crystal, physical properties, ultrasonic method

Z ultrazvočno metodo je bila izvršena meritev longitudinalne in transverzalne hitrosti v ultrazvočnih valov v glavnih kristalografskih smereh kristalov čistega volframa in volframovega monokristala, legiranega s Ta in Mo. Monokristali s kristalografsko orientacijo [110] so bili izdelani s taljenjem v plazemskem obloku. Izmerjena je bila gostota ρ kristala. Iz dobljenih podatkov so bili izračunani: elastična konstanta C_{ij} kristala, faktor anizotropije A, Youngov modul E, strižni modul G in elastični modul pri stiskanju B pri dani kristalografski smeri in glavne vrednosti longitudinalnih in transverzalnih hitrosti ultrazvoka po Fochtu-Roisu-Chillyjevi metodi, Youngov modul, strižni modul, Poissonovo razmerje in Debyejeva temperatura. Meritev hitrosti ultrazvoka je bila izvršena s pulzatorjem s frekvenco od 10 MHz do 30 MHz. Ugotovljeno je, da legiranje čistega volframa z elementi, kot sta tantal in molibden, povzroči zmanjšanje povprečnih veličin v, C_{ij} in B v številnih kristalografskih in polarizacijskih smereh, kot tudi veličino ρ. Vpliv legirnih elementov na elastične lastnosti kristalov volframa je bil enak. Na podlagi dobljenih rezultatov se lahko sklene, da se ultrazvočna metoda lahko uporabi za kontrolo kvalitete monokristalov volframa in njegovih malo legiranih zlitin z meritvijo oslabitve ultrazvočnih valov v različnih delih preizkušanih vzorcev.

Ključne besede: volfram, monokristal, fizikalne lastnosti, metoda z ultrazvokom

1 INTRODUCTION

The effects of alloying elements and crystallographic orientation on physical properties, particularly the elastic properties of single crystals of refractory metals, widely used for manufacturing cathodes, anodes, blades, nets, heaters and other parts of electro-vacuum devices, cathodes for thermionic converters, high-power electrical contacts, emitters in the detectors of atomic beams, etc., constitute an important area of research[1–3]. Special focus has been devoted to tungsten-based single crystals due to their anisotropy that is close (not equal) to unity[1,2].

According to the current theory of solids the values of elastic constants are related to the electron structure of a metal. However, at present there are no methods for quantitative calculations of these constants that would be based on the concepts of the electron structure of a metal (Fermi level, Brillouin zone, etc.).

In this paper, the results of measuring velocity v of longitudinal and transverse ultrasonic waves propagating along the three main crystallographic directions in the tungsten-based single crystals with a [110] crystallographic orientation using a non-destructive ultrasonic method[4] are described. Based on the wave velocity and density data, crystal elastic constants C_{ij}, anisotropy factor A, Young's modulus E, bulk modulus of elasticity B, shear modulus G, Debye temperature Θ_D and Poisson's ratio v of single crystals were calculated.

2 EXPERIMENTAL WORK

Tungsten rods after the second re-melting (99.99 %) with a diameter of 4 mm, and Ta or Mo wires (diameter < 1 mm) were used as the initial materials. Highly pure and perfect single crystals of tungsten with the [110] crystallographic orientation were applied as seed crystals, forming the basis of the relevant alloys. For obtaining single crystals of tungsten alloys, an original re-melted tungsten rod was combined with the wires made of molybdenum or tantalum in the amount corresponding to the calculation of the composition of a particular alloy. The plasma-arc melting[1,5] with a mixture of inert gases – helium and argon (in the volume ratio of 1 : 5) – was applied for the preparation of these tungsten-based single crystals – W, W-1.5 % Mo and W-1.5 % Ta (the nominal chemical composition). The melting conditions were as follows: the plasma-arc current – 200 A, the voltage between the electrodes (the cathode plasma torch and the grown crystal) – 20 V, the growth rate – 1.5 mm/min. The experimental specimens were cut from the beginning of single crystals (near the seed) in the form of cylinders or right-angled parallelepipeds. The X-ray reflection-mode topography (a modified Berg-Barrett technique) and the K_α and K_β radiations produced by a sharp-focus X-ray tube (the focus diameter is 40–50 μm) were applied to determine the angular disorientations of the subgrains in the given single crystals[1,3]. The back-reflection Laue method (an X-ray beam perpendicular to the face-end section) was used to determine their crystallographic orientation. The microstructure study was carried out using a light microscope (LM), Olympus GX-51, connected with a digital camera DP12.

The ultrasonic measurements were carried out on a pulsed facility developed at the G. V. Kurdyumov Institute for Metal Physics, N.A.S.U. The working frequency was f = 10–30 MHz. The error of measuring v was 10^{-4} rel. units for a period 10 μs and it diminished with the lengthening of the period. The density ρ was measured hydrostatically using the germanium or fused-quartz standards. The measuring error of the absolute density of specimens 10 g did not exceed 10^{-4} rel. units. The test temperature T was (20 ± 0.5) °C. The elastic constants and parameters were calculated from the velocities of the longitudinal (v_l) and transverse (v_t) ultrasonic waves and the density magnitudes, using the following well-known relationships applicable to cubic crystals[4,6]:

$$\rho v^2_{l[001]} = C_{11} \tag{1}$$

$$\rho v^2_{l[110]} = \frac{C_{11} + C_{12} + 2C_{44}}{2} \tag{2}$$

$$\rho v^2_{l[111]} = \frac{C_{11} + 2C_{12} + 4C_{44}}{3} \tag{3}$$

$$\rho v^{2[00\bar{1}]}_{t[110]} = C_{44} \tag{4}$$

$$\rho v^{2[1\bar{1}0]}_{t[110]} = \frac{C_{11} - C_{12}}{2} \tag{5}$$

$$\rho v^{2[1\bar{1}0]}_{t[111]} = \frac{C_{11} + C_{44} - C_{12}}{3} \tag{6}$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{7}$$

$$B = \frac{C_{11} + 2C_{12}}{3} \tag{8}$$

$$\overline{E} = \rho \overline{v}_t^2 \frac{(3a^2 - 4)}{(a^2 - 1)} \tag{9}$$

$$\overline{G} = \rho \overline{v}_t^2 \tag{10}$$

$$\overline{v} = \frac{a^2 - 2}{2(a^2 - 1)};\ a = \frac{\overline{v}_l}{\overline{v}_t} \tag{11}$$

$$\overline{\Theta}_D = \frac{h}{k}\left(\frac{9N\rho}{4\pi A_\Sigma}\right)^{\frac{1}{3}}\left(\frac{1}{\overline{v}_l^3} + \frac{2}{\overline{v}_t^3}\right)^{-\frac{1}{3}} \tag{12}$$

In equations (1) to (7) for the longitudinal or transverse velocities of ultrasonic waves, the subscripts indicate the wave-propagation vectors; the subscript indexes indicate the polarization vectors.

3 RESULTS AND DISCUSSION

The binary systems of W-Ta and W-Mo create ideal types of phase diagrams with unlimited solubility of the components in the liquid and solid states[1]. Under normal temperatures, the structures of both systems are formed as a result of substitution of the solid solution of tungsten, which may be formed within the concentration interval of the alloying element from 0 % to 100 %. During the investigation of the macrostructure on the surfaces of the single crystals of tungsten, alternating light and dark strips were observed as a result of various etchings of the edges (**Figure 1**). Some subgrain boundaries of the 1st order[1,3] were also observed without any additional magnification aids (visually), indicating their relatively high disorientation.

These preliminary results are consistent with the results of the study of the crystal structure with X-ray topography (**Table 1**). As an example, a topogram taken

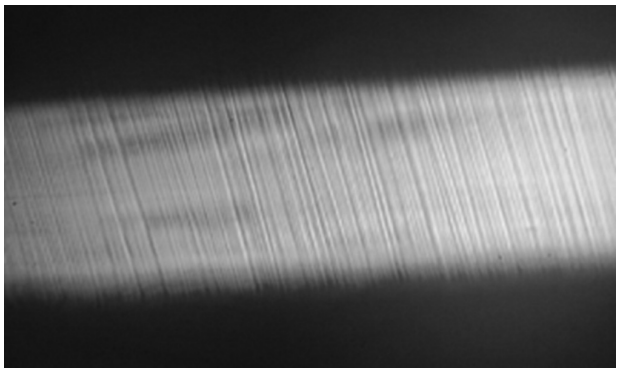

Figure 1: Surface morphology of W-1.5 % Ta single crystals
Slika 1: Morfologija površine monokristala W-1,5 % Ta

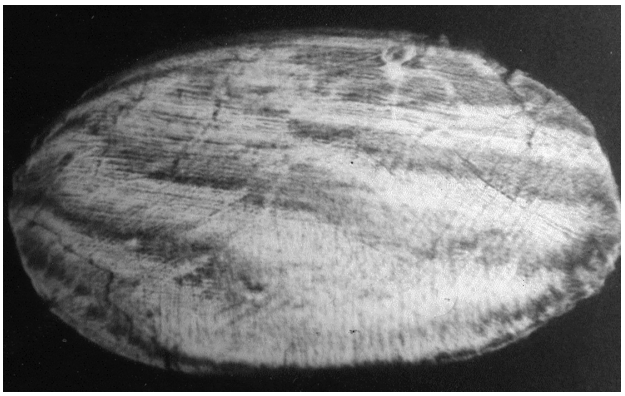

Figure 2: X-ray topogram taken from the beginning of W-1.5 % Ta single crystal with a [110] growth-axis orientation (cross-section)
Slika 2: Rentgenski topogram iz začetka monokristala W-1,5 % Ta z osjo rasti [110] (prečni prerez)

from the beginning of the single-crystalline W-1.5 % Ta alloy is shown in **Figure 2**. Generally, the fragmentation of the substructure and the misorientation of the subgrains at the end part of single crystals are higher than at the beginning – there are distinctly visible wide boundaries between the blocks, which, in principle, are characteristic of most methods of single-crystal growth.

Table 1: Structure parameters of tungsten-based single crystals
Tabela 1: Parametri strukture monokristalov na osnovi volframa

Sample	Disorientation of subgrains (°)		Size of subgrains (mm)	
	1st order	2nd order	1st order	2nd order
W-1.5 Mo	0.35–1.0	0.06–0.2	2.0–4.0	0.3–0.5
W-1.5 Ta	0.1–0.25	0.03–0.06	1.5–3.0	0.3–0.5
W	0.1–0.25	0.1	1.0–3.0	0.13–0.5

A single-crystalline structure of tungsten-based alloys was also confirmed during the study of the sections using LOM (**Figure 3**). The subgrains in the shape of polygons in the cross-section and long columnar subgrains elongated in the direction of growth formed during crystallization due to plasma heating in the longitudinal sections are visible in the photos of these single-crystal microstructures. A lower structural perfection of these single crystals is associated with a considerable disturbance of the melt by the plasma arc, large temperature gradients and the cooling rate of the growing single crystals due to "air rinsing" of their surfaces by the plasma-forming gas.

The data on the longitudinal (v_l) and transverse (v_t) velocities of the ultrasonic waves at 20 °C for different crystallographic directions and densities (ρ) are given in **Table 2**. **Table 3** shows elastic constants and related parameters C_{11}, C_{44}, C_{12}, B, A and Θ calculated from the data given in **Table 2**. **Table 4** includes the average velocities of longitudinal and transverse ultrasonic waves, and the average values of E, G and ν. The data on Young's modulus E and shear modulus G for different crystallographic directions are presented in **Table 5**. It is evident from the obtained results that in the case of tungsten-based single crystals, as a result of alloying with molybdenum or tantalum, the density slightly decreases (ρ_W = 19.26 g/cm^3) in comparison with pure tungsten.

Table 2: Magnitudes of v_l and v_t for different crystallographic orientations, and density of tungsten-based single crystals at 20 °C
Tabela 2: Veličina v_l in v_t pri različnih kristalografskih orientacijah in gostota monokristalov na osnovi volframa pri 20 °C

Sample	ρ/ (g/cm^3)	$v_{l[110]}$/ (m/s)	$v_{t[110]}^{[00\bar{1}]}$/ (m/s)	$v_{t[110]}^{[1\bar{1}0]}$/ (m/s)	Anisotropy v_t/%
W-1.5 Mo	18.97	5250.1	2893.8	2896.6	0.095
W-1.5 Ta	19.10	5235.1	2881.7	2889.3	0.263
W	19.26	5241.6	2894.4	2879.5	0.517

The alloying of tungsten with small amounts of molybdenum or tantalum led to a decrease in elastic coefficients C_{11}, C_{44}, C_{12} in comparison with single crystals of pure tungsten, while the obtained values of the coefficients for the alloyed samples of single crystals are very

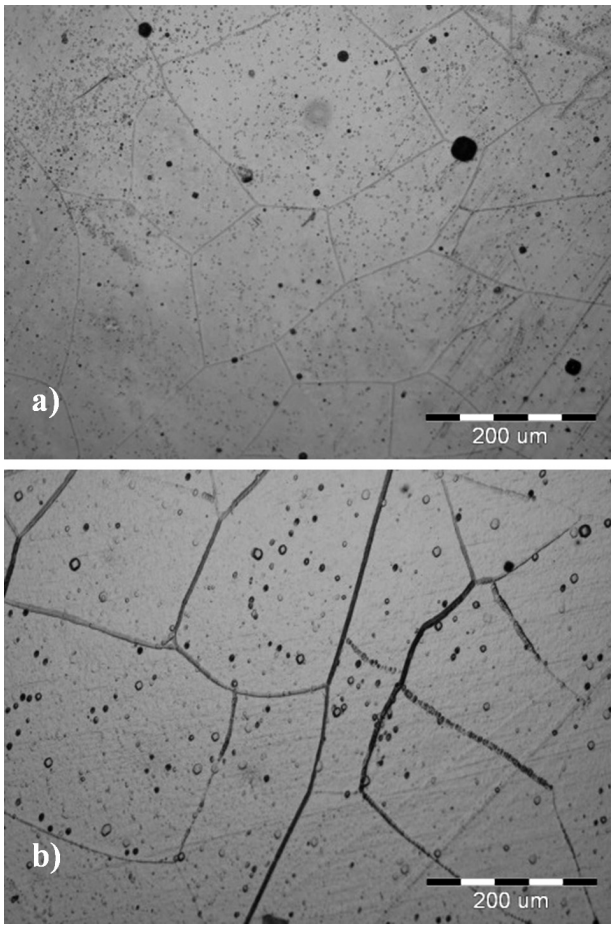

Figure 3: Microstructure of tungsten-based single crystals with a [110] crystallographic orientation: a) W-1.5 % Mo, b) W-1.5 % Ta (cross-section)
Slika 3: Mikrostruktura monokristalov na osnovi volframa s kristalografsko orientacijo [110]: a) W-1,5 % Mo, b) W-1,5 % Ta (prečni prerez)

close (similar). Determined elastic coefficients for single crystals of pure tungsten, as well as the values of the speed of ultrasound waves v_l and v_t correlate very well with the results of the other authors[6,7]. The average values of the Young's modulus, shear modulus and bulk modulus for single crystals of pure tungsten are also in a very good agreement with the literature data[1].

Table 3: Magnitudes of C_{ij}, B, A and Debye temperature Θ_D of tungsten-based single crystals

Tabela 3: Veličine C_{ij}, B, A in Debyejeva temperatura Θ_D monokristalov na osnovi volframa

Sample	C_{11}/ (GPa)	C_{12}/ (GPa)	C_{44}/ (GPa)	B/ (GPa)	A	Θ_D/ (K)
W-1.5 Mo	522.4	204.8	159.1	310.7	1.002 (0.2 %)	382.4
W-1.5 Ta	522.5	205.4	159.4	311.1	1.005 (0.5 %)	381.6
W	527.5	208.1	161.3	314.6	1.010 (1 %)	381.6

It is evident from **Table 4** that an addition of molybdenum or tantalum led to a decrease in the values of the mentioned moduli. A slight dependence of Young's modulus and shear modulus on the crystallographic direction of the measurement was manifested in all the investigated samples of single crystals (**Table 5**). The highest values of Young's modulus were determined in the [110] crystallographic direction, while for the shear modulus it was the [111] crystallographic direction.

Table 4: Average values of E, G, v_l, v_t and Poisson constant v of tungsten-based single crystals

Tabela 4: Povprečne vrednosti E, G, v_l, v_t in Poissonova konstanta v monokristalov na osnovi volframa

Sample	$\overline{E}$/(GPa)	$\overline{G}$/(GPa)	$\overline{v}_l$/(m/s)	$\overline{v}_t$/(m/s)	$\overline{v}$/–
W-1.5 Mo	407.5	159.0	5249.8	2895.5	0.281
W-1.5 Ta	407.7	159.1	5234.3	2886.3	0.281
W	411.9	160.7	5239.9	2888.4	0.282

Table 5: Young's modulus E and shear modulus G for the main crystallographic orientation of tungsten-based single crystals

Tabela 5: Youngov modul E in strižni modul G za glavne kristalografske orientacije monokristalov na osnovi volframa

Sample	E/(GPa)			G/(GPa)		
	[111]	[100]	[110]	[111]	[100]	[110]
W-1.5 Mo	407.1	407.6	407.8	159.1	159.0	158.9
W-0.5 Ta	406.6	408.0	408.5	159.4	159.0	158.9
W	409.7	412.4	413.4	161.3	160.5	160.2

The obtained results confirm the fact that the anisotropy of elastic properties of tungsten approach one[1,2]. The Poisson constant for individual samples of single crystals, depending on the ratio between v_l and v_t, was equal to 0.28 ± 0.001. It may be therefore stated that the amounts of the alloying elements (Mo, Ta) in a concentration of w = 1.5 % did not significantly influence the magnitude of this quantity in comparison with the single crystals of pure tungsten. A similar effect can also be observed when determining Debye temperature Θ of these samples, which was found to be (381.8 ± 0.45) °C.

4 CONCLUSIONS

It may be concluded on the basis of the obtained results that a non-destructive ultrasonic method can be used for quality control of the purity and structure of single crystals of tungsten and its low-alloyed alloys, with which we measure the attenuation effects of ultrasound waves in various parts of the tested samples. Using the obtained data on the velocities of longitudinal and transverse ultrasound waves it is possible to determine and assess, using suitable relations, the elastic or physical properties of tungsten low-alloyed alloys, as well as the influence of the alloying elements on the given quantities.

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