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Elastic constants of $MoSi_2$ and WSi_2 single crystals

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Single crystals of $MoSi_2$ and WSi_2 with a body-centred-tetragonal C 1 1_b structure were fabricated using a floating-zone method. The elastic wave velocity was measured for samples with various orientations using a simple pulse echo method at room temperature, and six elastic stiffness constants c_{ij} were calculated. The stiffness constants were a little higher for WSi_2 than for $MoSi_2$. c_{11} and c_{33} of these compounds were approximately equal to c_{11} of tungsten and molybdenum, respectively, although c_{ij} $(i \neq j)$ was a little higher for these compounds than for molybdenum and tungsten. Young's modulus $1/s_{11}$ was the highest in the $\langle 001 \rangle$ direction, and the lowest in the $\langle 100 \rangle$ direction. The shear modulus $1/s_{66}$ was high on the $\{001\}$ plane and independent of shear direction. It was generally low on the close-packed $\{110\}$ plane and largely dependent on shear direction. The elastic constants for the polycrystalline materials were estimated from c_{ij} and s_{ij}. Poisson's ratio ν was 0.15 for $MoSi_2$ and for WSi_2, and these values were much lower than for ordinary metals and alloys. The Debye temperature θ_D was estimated using the elastic-wave velocity of the polycrystalline materials via the elastic constants such as Young's modulus and shear modulus: it was 759 K for $MoSi_2$ and 625 K for WSi_2.

1. Introduction

$MoSi_2$ and WSi_2 are intermetallic compounds with a body-centred-tetragonal C 1 1_b structure, and have melting points of 2293 and 2437 K, respectively [1]. Sintered $MoSi_2$ is known to be a heating material which is used at temperatures up to 1973 K. The compression strength of sintered $MoSi_2$ is reported to be about 400 MPa at temperatures from 1273 to 1673 K, and to decrease with temperature above 1673 K [2]. The addition of a small amount of Al_2O_3 and/or SiO_2 to sintered $MoSi_2$ gives a tensile ductility of about 0.7% at 1873 K [3].

These silicides are expected to be heat-resistant materials at high temperatures because of their high melting temperatures and their oxidation resistance at high temperatures. However, single crystals of $MoSi_2$ and WSi_2 have rarely been fabricated and their physical and mechanical properties have scarcely been investigated, although the $MoSi_2$ single crystal was prepared using the Czochralski method and its electric resistivity was measured in the temperature range from liquid helium temperature to room temperature [4].

In this work, single crystals of $MoSi_2$ and WSi_2 were prepared using a floating-zone method, the velocity of ultrasonic waves was measured at room temperature for single crystals with four orientations, and their elastic stiffness and compliance coefficients were determined.

2. Experimental procedure

$MoSi_2$ and WSi_2 rods with a diameter of about 8 mm were arc melted in an argon atmosphere using molybdenum (99.99%), tungsten (99%) and silicon (99.99%) for preparation of single crystals. Single crystals of these intermetallics were fabricated using a floating-zone method in an argon atmosphere with a optical heating furnace of halogen lamps. The moving rate of a floating zone was about 6 mm h^{-1}. The crystal orientations of the plane perpendicular to the grown direction of single crystals are shown in Fig. 1. Specimens for the measurement of ultrasonic wave velocity were cut from the crystal, and the orientations of the plane perpendicular to their axes were $\{001\}$, $\{100\}$, $\{110\}$, etc. as shown in Fig. 1. The thickness of the specimens was 3.4 to 3.8 mm.

The elastic constants were calculated from the velocity of ultrasonic waves, which was measured using a simple pulse-echo method. The transducers (diameter of $\frac{1}{4}$ in.) were supplied by Panametrics Co. Inc. Waltham, MA, USA., and the resonant frequencies of 10 MHz (model V112) and 5 MHz (model V156) were used for the longitudinal and transverse waves, respectively. The pulser/receiver was a Panametrics model 505ZPR, and the oscilloscope was a YHP model 1740A (100 MHz). The couplants between specimen and transducer were water-soluble couplants supplied by Sperry Product Div., Automatic Industries Inc., Danbury, Conn., USA with spindle oil for transverse and longitudinal waves, respectively. The determination of wave velocity was carried out by measuring the time interval between the first peaks of the first and second reflection waves on the oscilloscope, because the rising point was very difficult to detect. The average values of 7 to 25 measurements were adopted for the average sound velocity.

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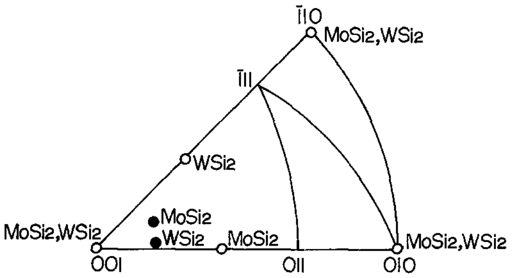

Figure 1 Orientation of the plane perpendicular to the axis of samples and as-grown crystals. Solids marks, as-grown crystals.

3. Results

The sound velocity was independent of the cross-sectional area of specimens with a cross section of more than 20 mm^2. It was also independent of the thickness of specimens more than 3.4 mm thick (Fig. 2). Specimens with a thickness of 3.4 to 3.8 mm were therefore used for measurement of the sound velocity.

MoSi$_2$ and WSi$_2$ have a body-centred-tetragonal C 1 1$_b$ structure, and the matrix of their elastic stiffness constants is given by non-zero elements of c_{11}, c_{33}, c_{44}, c_{66}, c_{12} and c_{13} because of the symmetry of their crystal structure. Their elastic compliance matrix is given by the reverse matrix of their stiffness constants.

Table I shows sound velocities and their associated elastic stiffness constants for WSi$_2$ and MoSi$_2$ single crystals which were annealed for 18 ksec at 1623 and 1573 K, respectively. These annealing temperatures are about $\frac{2}{3}$ of their melting temperatures. The standard deviations are given in Tables II and III. Here, the densities of the compounds were calculated from lattice constants [5] and atomic weights of the constituent elements. The velocity of the longitudinal wave in the ⟨0 0 1⟩ direction was about 9000 m sec^{-1} and 7500 m sec^{-1} for MoSi$_2$ and WSi$_2$, respectively. The velocity of the transverse wave was about 0.6 times as fast as that of the longitudinal one. The ratio of the elastic constant of WSi$_2$ to that of MoSi$_2$ was about 1.03 to 1.09, and WSi$_2$ had slightly higher elastic constants.

Table II shows the sound velocities and elastic stiffness constants of WSi$_2$ single crystals annealed at 1623 K. The values of c_{44} which were calculated from ⟨0 0 1⟩, ⟨1 0 0⟩ and ⟨1 1 0⟩ specimens were in good agreement. Those of c_{12} which were calculated from the velocities of longitudinal and transverse waves in ⟨1 1 0⟩ specimens also agreed. Here, the values which had a lower standard deviation were used for the calculation of c_{12} and c_{13}.

TABLE I The velocity of ultrasonic waves and the associated elastic constants for MoSi$_2$ and WSi$_2$ with various orientations. MoSi$_2$ and WSi$_2$ were annealed at 1573 and 1623 K, respectively

Orientation (plane)		Velocity (msec^{-1})		Elastic constants (10^2 GPa)	
		WSi$_2$	MoSi$_2$	WSi$_2$	MoSi$_2$
[0 0 1]	lw	7497	9054	5.523	5.145
(1 0 0)	tw	4640	5699	2.116	2.038
[1 0 0]	lw	6713	8151	4.428	4.170
(0 0 1)	tw	4705	5705	2.175	2.042
(1 0 0)	tw	4641	5554	2.116	1.936
[$\bar{1}$ 1 0]	lw	7126	8541	4.990	4.580
(1 1 0)	tw	4042	4993	1.605	1.564
(0 0 1)	tw	4618	–	2.096	–

lw = Longitudinal wave; tw = transverse wave.

TABLE II The velocity of ultrasonic waves and elastic stiffness constants for annealed WSi$_2$

Orientation (plane)		Velocity (msec^{-1})			Elastic constant (10^2 GPa)	
		Average	S.D.	c_{ij}	Average	S.D.
[0 0 1]	lw	7497	7.7	c_{33}	5.523	0.011
(1 0 0)	tw	4640	5.9	c_{44}	2.116	0.005
[1 0 0]	lw	6713	33.5	c_{11}	4.428	0.044
(0 0 1)	tw	4705	10.4	c_{66}	2.175	0.009
(1 0 0)	tw	4641	12.5	c_{44}	2.116	0.012
[1 1 0]	lw	7126	31.6	c_{12}	1.203	0.088
(1 1 0)	tw	4042	7.9	c_{12}	1.217	0.013
(0 0 1)	tw	4618	36.3	c_{44}	2.096	0.033
Other	lw	7240	25.5	c_{13}	0.810	0.073

Table III also shows the elastic stiffness constants of MoSi$_2$ as-grown and annealed single crystals. The values of c_{44} which were obtained from ⟨0 0 1⟩ and ⟨1 0 0⟩ specimens were in good agreement, and those of c_{12} which were obtained from the longitudinal and transverse waves in ⟨1 1 0⟩ specimens almost agreed. The elastic constants of MoSi$_2$ scarcely showed any difference in as-grown and annealed specimens.

The elastic compliance constants s_{ij} were calculated from the stiffness constants c_{ij}. Table IV shows the elastic stiffness with the least standard deviation and the associated compliance of MoSi$_2$ and WSi$_2$ single crystals which were annealed at 1573 and 1623 K, respectively.

4. Discussion

Although the crystal structure of MoSi$_2$ and WSi$_2$ is different from molybdenum, tungsten and silicon, the c_{11}s of MoSi$_2$ and WSi$_2$ are a little lower and their c_{33}s are a little higher than the c_{11} of molybdenum and tungsten, respectively, and both their c_{11} and c_{33} are much higher than the c_{11} of silicon [6] (see Appendix). Their elastic constants are a little lower than those of Al$_3$O$_2$, a typical ceramic. The ratios of c_{33} to c_{11} for MoSi$_2$ and WSi$_2$ are 1.234 and 1.247, respectively, and the ratios of the distance between atoms in the ⟨1 0 0⟩ direction to an average distance between atoms in

TABLE III The elastic stiffness constants for as-grown and annealed MoSi$_2$

Orientation		c_{ij}	As-grown (10^2GPa)		Annealed (10^2GPa)	
			Average	S.D.	Average	S.D.
[0 0 1]	lw	c_{33}	5.202	0.018	5.145	0.008
	tw	c_{44}	2.030	0.011	2.038	0.014
[1 0 0]	lw	c_{11}	4.103	0.031	4.170	0.009
	tw	c_{66}	1.925	0.007	1.936	0.008
	tw	c_{44}	2.004	0.029	2.042	0.010
[$\bar{1}$ 1 0]	lw	c_{12}	1.258	0.081	1.109	0.056
	tw	c_{12}	–	–	1.042	0.048
Other	lw	c_{13}	–	–	0.838	0.127

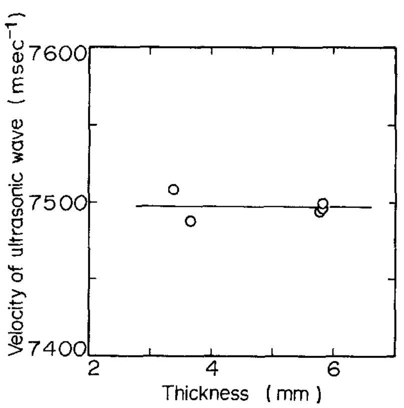

Figure 2 Dependence of the ultrasonic wave velocity on the thickness of a WSi_2 single crystal with [0 0 1] direction annealed at 1623 K for the longitudinal wave.

$\langle 0\,0\,1\rangle$ direction are 1.225 and 1.224. The latter ratios are considered to be closely related to the former, because the elastic constants are closely related to potential energies between atoms. The Cauchy's relations for elastic stiffness constants, $c_{13} = c_{44}$ and $c_{12} = c_{66}$ [7], do not hold true in $MoSi_2$ and WSi_2 with a tetragonal structure, and this fact means that all of the forces between atoms are not central ones.

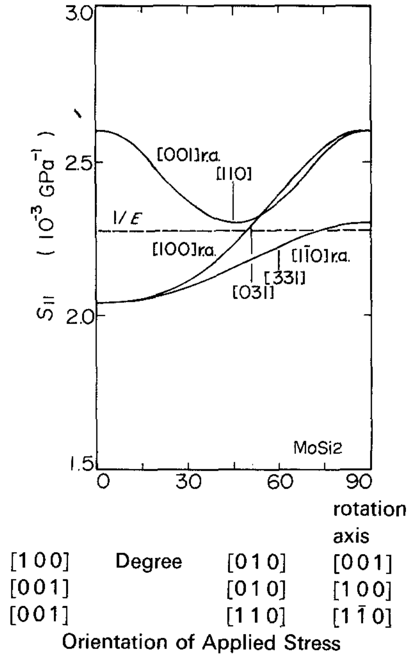

Figure 3 Orientation dependence of compliance s_{11} which is estimated from the elastic constants. The direction of applied stress is rotated round the rotation axis [0 0 1], [1 0 0], or [1 $\bar{1}$ 0].

The Young's modulus and shear modulus of a single crystal can be estimated from the elastic constants for any crystal direction and any crystal plane. They are represented by the reciprocals of compliance constants, and then the dependence of compliance s_{ij} on the crystal orientation was calculated. Fig. 3 shows the relationships between compliance s_{11} and the crystal orientation in $MoSi_2$. Here, the crystal is turned round a crystal direction. s_{11} is lowest in the $\langle 0\,0\,1\rangle$ direction, and highest in the $\langle 1\,0\,0\rangle$ direction. It is approximately equal to the $\langle 1\,1\,0\rangle$ and $\langle 0\,3\,1\rangle$ directions, although it is just a little higher in the former than in the latter. It is lower in the $\langle 3\,3\,1\rangle$ direction than in the $\langle 0\,3\,1\rangle$ direction. The reciprocal of E in Fig. 3 represents the compliance of polycrystalline (isotropic) material estimated from the elastic constants of the $MoSi_2$ single crystal in this experiment; the elastic constants of polycrystalline materials will be described later. Fig. 4 shows the relationship between shear compliance s_{66} and the shear direction on typical crystal planes. s_{66} is independent of the shear direction on the $\{0\,0\,1\}$ plane and is dependent largely on the shear direction on the close-packed $\{1\,1\,0\}$ plane. It depends a little on the shear direction on the $\{1\,0\,0\}$ and close-packed $\{1\,0\,3\}$ planes. On the close-packed $\{1\,1\,0\}$ plane, the material is generally weak elastically for shear stress, but on the close packed $\{1\,0\,3\}$ plane, it is not so weak elastically except for the $\langle 0\,1\,0\rangle$ direction. The reciprocal of G represents the shear compliance which was estimated from the elastic constants of the single crystal for the polycrystalline (isotropic) material.

TABLE IV The elastic stiffness and compliance constants for annealed $MoSi_2$ and WSi_2

c_{ij}	$MoSi_2$ (10^2 GPa)	WSi_2	s_{ij}	$MoSi_2$ (10^{-3} GPa)	WSi_2
c_{11}	4.170	4.428	s_{11}	2.611	2.482
c_{33}	5.145	5.523	s_{33}	2.051	1.890
c_{44}	2.042	2.116	s_{44}	4.897	4.726
c_{66}	1.936	2.175	s_{66}	5.165	4.598
c_{12}	1.042	1.217	s_{12}	−0.586	−0.632
c_{13}	0.838	0.810	s_{13}	−0.330	−0.271

The elastic constants like bulk modulus, Young's modulus, etc. of a polycrystalline material can be approximately estimated from the elastic constants of the single crystal. The rule of mixture for stress and strain is used to calculate the maximum and the minimum values, respectively. The former method is called Voigt's approximation, and the latter Reuss's approximation. The method in which the average value of the

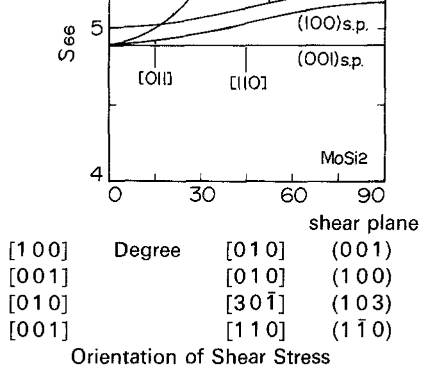

Figure 4 Orientation dependence of compliance s_{66} which is estimated from the elastic constants. The direction of shear stress is rotated on the shear planes (0 0 1), (1 0 0), (1 $\bar{1}$ 0), or (1 0 3).

TABLE V The elastic constants estimated from Tables II, III and IV for the polycrystalline compounds

Elastic constant		$MoSi_2$ (10^2 GPa)	WSi_2 (10^2 GPa)
Bulk modulus K,	K_V (max)	2.102	2.228
	K_R (min)	2.092	2.219
	K_H (average)	2.097	2.224
Young's modulus E,	E_V	4.419	4.708
	E_R	4.375	4.649
	E_H	4.397	4.679
Shear modulus G,	G_V	1.922	2.051
	G_R	1.900	2.020
	G_H	1.911	2.036
Poisson's ratio ν,	ν_V	0.150	0.148
	ν_R	0.151	0.151
	ν_H	0.151	0.149

maximum and minimum values is adopted is called Hill's approximation, and the estimated value of Young's modulus is known to be in good agreement with the measured value [8].

For the tetragonal structure, the bulk modulus K of a polycrystalline material is estimated from the following equations [8]. For Voigt's approximation:

$$K_V = (1/9)(2c_{11} + c_{33}) + (2/9)(c_{12} + 2c_{13}) \qquad (1)$$

for Reuss's approximation:

$$1/K_R = (2s_{11} + s_{33}) + 2(s_{12} + 2s_{13}) \qquad (2)$$

and for the Hill's approximation:

$$K_H = (1/2)(K_V + K_R) \qquad (3)$$

The shear modulus G is also estimated from the following equations. For Voigt's approximation:

$$G_V = (1/15)(2c_{11} + c_{33}) - (1/15)(c_{12} + 2c_{13}) + (1/5)(2c_{44} + c_{66}) \qquad (4)$$

for Reuss's approximation:

$$15/G_R = 4(2s_{11} + s_{33}) - 4(s_{12} + 2s_{13}) + 3(2s_{44} + s_{66}) \qquad (5)$$

and for Hill's approximation:

$$G_H = (1/2)(G_V + G_H) \qquad (6)$$

Then, Young's modulus E and Poisson's ratio ν are given by

$$E = 9KG/(3K + G) \qquad (7)$$

and

$$\nu = (1/2)(3K - 2G)/(3K + G) \qquad (8)$$

TABLE VI The elastic wave velocity and Debye temperature for the polycrystalline compounds

	$MoSi_2$	WSi_2
Wave velocity, v_l (msec^{-1}) (longitudinal)	8603	7090
v_t (msec^{-1}) (transverse)	5518	4552
v_m (msec^{-1}) (average)	6061	4999
Debye temperature, θ_D/K	759	625

Table V shows the elastic constants of the polycrystalline materials estimated from the values in Table IV. Both $MoSi_2$ and WSi_2 have higher Young's and shear moduli than polycrystalline molybdenum and tungsten [6] (see Appendix). The former has a much smaller Poisson's ratio than the latter. Poisson's ratio is much smaller for these compounds than for ordinary metals and alloys for which it is about 0.25 to 0.44 [6].

The elastic wave velocity in a polycrystalline material is given by the following equations [8]. For the longitudinal wave:

$$v_l = \sqrt{\{(K + 4G/3)/\rho_0\}} \qquad (9)$$

and for the transverse wave

$$v_s = \sqrt{(G/\rho_0)} \qquad (10)$$

here ρ_0 is the density of a material. Then, an average wave velocity is given by the following equation [8]

$$v_m = \{(1/3)(2/v_s^3 + 1/v_l^3)\}^{-1/3} \qquad (11)$$

Thus the Debye temperature θ_D of a material can be calculated by the following equation [8]

$$\theta_D = (h/k)\{(3/4)(q/\pi)(N\rho_0/M)\}^{1/3} v_m, \qquad (12)$$

where h is Plank's constant; k, Boltzman's constant; N, Avogadro's number; ρ_0, the density of a material; M, molecular weight; and q, the number of atoms in a molecule. Table VI shows the wave velocity v_l, v_s, v_m and Debye temperature θ_D for $MoSi_2$ and WSi_2. The Debye temperatures are 450, 400 and 645 K for molybdenum, tungsten and silicon, respectively [9]. $MoSi_2$ has higher Debye temperature than WSi_2. Although these compounds have much higher θ_D than molybdenum and tungsten, θ_D is higher for $MoSi_2$ than for silicon and lower for WSi_2 than for silicon.

5. Conclusion

Single crystals of $MoSi_2$ and WSi_2 with a tetragonal $C1l_b$ structure were fabricated from arc-melted materials using a floating-zone method. Four samples with different orientations were cut from a single crystal for each compound, the elastic wave velocity was measured for each sample using a simple pulse-echo method at room temperature, and six elastic stiffness constants c_{ij} were calculated for these compounds. The results obtained were as follows.

(i) The stiffness constants were a little higher for WSi_2 than for $MoSi_2$. c_{11} and c_{33} of these compounds were approximately equal to c_{11} of tungsten and molybdenum, although c_{ij} $(i \neq j)$ were a little higher for these compounds than for molybdenum and tungsten. The stiffness constants of as-grown $MoSi_2$ were nearly equal to those of the annealed one.

(ii) Young's modulus $1/s_{11}$ was highest in the $\langle 0\,0\,1\rangle$ direction, lowest in the $\langle 1\,0\,0\rangle$ direction and intermediate in the $\langle 1\,1\,0\rangle$ and $\langle 0\,1\,3\rangle$ directions.

(iii) The shear modulus $1/s_{66}$ was high on the $\{0\,0\,1\}$ plane and independent of shear direction. It was generally low on the close-packed $\{1\,1\,0\}$ plane and largely dependent on shear direction. The shear modulus on the other close-packed plane, the $\{1\,0\,3\}$ plane, was close to that on the $\{1\,0\,0\}$ plane and a little higher than that on the $\{0\,0\,1\}$ plane.

TABLE AI Elastic constants of silicon, molybdenum and tungsten [6]

Material	c_{11} (10^2 GPa)	c_{44} (10^2 GPa)	c_{12} (10^2 GPa)
Si	1.68	0.840	0.660
Mo	4.550	1.100	1.760
W	5.010	1.510	1.980

(iv) The elastic constants for the polycrystalline materials were estimated from c_{ij}. Poisson's ratio v was 0.15 for both $MoSi_2$ and WSi_2 and was much lower than that for ordinary metals and alloys.

(v) The Debye temperature was estimated using the elastic wave velocity of the polycrystalline materials via the elastic constants such as Young's modulus and shear modulus: it was 759 K for $MoSi_2$ and 625 K for WSi_2. These values were relatively close to that of silicon, although they were much higher than molybdenum or tungsten.

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TABLE AII Elastic constants of polycrystalline materials [6]

Material	Poisson's ratio	E (10^2 GPa)	G (10^2 GPa)	K (10^2 GPa)
Mo	0.293	3.248	1.256	2.612
W	0.280	4.110	1.600	3.110
Si*	0.215	0.941	0.387	0.550

*Estimated from the data in ref [6].

Appendix

Table AI shows the elastic stiffness coefficients of molybdenum, tungsten and silicon single crystals with a cubic structure [6]. Table AII shows the elastic constants of polycrystalline molybdenum, tungsten and silicon [6].

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