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Elastic constants of body-centered-cubic titanium monocrystals

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We report estimates of body-centered-cubic titanium's monocrystal elastic constants C_{11} , C_{12} , and C_{44} . Two constants resulted from measuring a pure-titanium polycrystal at high temperatures using resonant-ultrasound spectroscopy. The third constant resulted from assuming a Zener elastic anisotropy and using inversely Kröner's monocrystal–polycrystal elastic-constant relationship. Our values are $C_{11}=97.7$, $C_{12}=82.7$, and $C_{44}=37.5$ GPa at 1000 °C. © 2004 American Institute of Physics. [DOI: 10.1063/1.1688445]

I. INTRODUCTION

Before melting at 1670 °C, titanium transforms from the familiar close-packed-hexagonal (cph) form to a body-centered-cubic (bcc) phase at 882 °C with a notably smaller atomic volume. Titanium's isoelectronic companion elements, zirconium and hafnium, show similar behavior. Often, the transformation is described in terms of a Burgers mechanism,¹ which relates the cph close-packed plane to the bcc (110) plane, which shows a small distortion from close packing. It also relates two close-packed directions: $[\bar{2}110]$ in cph to $[111]$ in bcc. Zener² ascribed high-temperature bcc phases to their possibility for higher vibrational entropy, related to high elastic anisotropy, often to a low value of the elastic-shear constant $C'=(C_{11}-C_{12})/2$. Friedel³ took another view: the excess bcc vibrational entropy arises from a lower Einstein frequency expected from the smaller nearest-neighbor number. As emphasized by Dehlinger,⁴ elements tend more to be cph when they contain one, two, or three valence electrons. With four valence electrons, titanium is borderline cph.

Special interest in bcc titanium arises because it may provide a good example of phonon softening. Local-density-approximation calculations⁵ for zirconium showed that the cph phase shows lower energy, but that the bcc phase N -point transverse phonon shows *negative* frequencies. This phonon plays a key role in the above-mentioned cph–bcc phase transformation. Neutron-scattering studies^{6,7} show temperature-dependent phonon softening. Elastic constants represent the long-wavelength limit of the phonon spectrum. Because elastic constants can be measured accurately, they

provide valuable information about long-wavelength (low-energy) phonon frequencies, about mechanical instability, and about the Debye characteristic temperature. Their temperature dependence relates simply to the quintessential anharmonic parameter: the Grüneisen parameter.⁸ Titanium's bcc elastic constants figure prominently in several recent *ab initio* studies.^{9–11}

Previous estimates of titanium's three bcc elastic constants C_{ij} came either from large extrapolations of titanium–alloy monocrystal measurements¹² or from force constants from neutron-scattering monocrystal measurements.⁶ Usual direct sound–velocity measurements¹³ remain to be made because large bcc monocrystals remain to be prepared.

Measurements of titanium's bcc elastic constants reported here were obtained more directly by measuring sound velocities at high temperatures in pure titanium. A disadvantage of our approach is that our specimen was polycrystalline; thus we measured directly only two elastic constants, say the quasiisotropic bulk and shear moduli. We overcame this disadvantage by using some relationships from continuum mechanics. Our results for the three C_{ij} — C_{11} , C_{12} , and C_{44} —differ considerably from the two previous neutron-scattering results, but they agree surprisingly closely with extrapolated alloy results.

II. METHODS

The specimen was commercially available polycrystalline titanium with 10 μm average grain size. With 99.96% purity, it showed a mass density of 4581 kg/m³ and negligible texture. To determine the elastic constants, we used resonant-ultrasound spectroscopy.^{14–16} Briefly, this method excites and detects the macroscopic resonance frequencies of a simple-shape specimen. In the present study, we used

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TABLE I. Elastic constants (GPa) of bcc monocrystal titanium at 1000 °C (present), 1000 °C,^a and 1020 °C.^b In the present study, the three independent elastic constants are derived assuming five elastic anisotropies A with the measured bcc polycrystal bulk modulus $B = 87.7$ GPa and shear modulus $G = 20.7$ GPa. Θ_D denotes the Debye characteristic temperature.

	A	C_{11}	C_{12}	C_{44}	C'	B	Θ_D (K)
Present	1	115.3	73.9	20.7	20.7	87.7	278.2
	2	105.8	78.66	27.11	13.6	87.7	275.5
	3	101.7	80.71	31.47	10.5	87.7	271.5
	4	99.3	81.9	34.8	8.7	87.7	267.7
	5	97.7	82.7	37.5	7.5	87.7	264.2
Fisher and Dever ^a	4.8	99	85	33.6	7	89.7	—
Petry <i>et al.</i> ^b	3	134	110	36	12	118	272

^aSee Ref. 12

^bSee Ref. 6.

electromagnetic–acoustic resonance for noncontacting excitation and detection.^{17–19} The specimen was inserted in a solenoid coil located within a cylindrical vacuum vessel made of austenitic stainless steel. A heater located by the solenoid coil increased the specimen's temperature up to 1030 °C. The pressure inside the vessel was kept less than 10^{-4} Torr. A pair of Nd–Fe–B permanent magnets applied biasing magnetic field to the specimen from outside the vessel to excite and detect free vibrations of the specimen via the Lorentz-force mechanism. The permanent-magnet assembly can be rotated about the cylindrical-vessel axis to a selection of detectable vibration modes. The C_{ij} result from an inverse calculation, the input being specimen mass, shape, and size, and the resonance frequencies.

III. RESULTS AND DISCUSSION

Table I shows our results together with previous results by Fisher and Dever¹² who extrapolated from various Ti–Cr alloys measured ultrasonically at temperatures up to 1100 °C and by Petry and colleagues⁶ who measured phonon dispersion on an *in situ* grown monocrystal at 1020 °C.

In Table I, our directly measured results (at 1000 °C) are the bulk modulus B and the shear modulus G . For cubic crystal symmetry, the bulk modulus relates simply to the C_{ij}

$$B = (C_{11} + 2C_{12})/3. \quad (1)$$

The C_{ij} relate to the shear modulus by Kröner's relationship from continuum mechanics

$$G^3 + aG^2 - bG - c = 0. \quad (2)$$

Coefficients a , b , and c contain the three C_{ij} and were given by Kröner²⁰ and by Ledbetter,²¹ who showed that, among many proposed G – C_{ij} relationships, Kröner's method agrees best with observation. Table I shows our estimated C_{ij} calculated by assuming various Zener elastic anisotropies²

$$A = 2C_{44}/(C_{11} - C_{12}). \quad (3)$$

Our results differ strongly from those of Petry and colleagues: our bulk modulus is lower by a factor of 0.64, and our shear modulus is higher by a factor of 1.30. (Here, we converted the Petry *et al.* C_{ij} to a shear modulus using the Voigt–Reuss–Hill method.²¹) Previous bulk-modulus mea-

TABLE II. Titanium's ambient-temperature alpha-phase polycrystal elastic constants at 20 °C. Units GPa except dimensionless ν . C_l denotes longitudinal modulus, B bulk modulus, E Young modulus, G shear modulus, and ν Poisson ratio.

	C_l	B	E	G	ν
Measured	165.1	106.43	115.98	43.99	0.318
Calculated	166.4	107.6	116.39	44.1	0.320

surements on hexagonal titanium gave 99.7 GPa at 873 °C²² and 96.4 GPa at 870 °C.²³ Thus, the Petry *et al.* results give a cubic/hexagonal bulk-modulus ratio of about 1.2, a 20% increase upon transforming to the cubic phase. Although numerous phase transformations occur in metals and alloys, the authors know only one report of careful elastic–constant measurements through a hexagonal–cubic transformation. Weston and Granato²⁴ measured the complete elastic–constant tensors for both phases of the hexagonal–cubic transformation in a cobalt–nickel alloy. They found a cubic/hexagonal bulk-modulus ratio of 0.90. A simple Einstein-oscillator model^{25,26} also predicts a lower bulk modulus in the high-temperature phase.

Like Petry *et al.*, we found a lower shear modulus in the cubic phase, but lower by a smaller amount, about 5% versus 15%. From thermodynamics, it follows that the high-temperature shear modulus should be lower. Ledbetter²⁷ showed that the Debye characteristic temperature Θ goes as the square root of the shear modulus. Zener and Bilinsky²⁸ showed for crystalline allotropic transformations that Θ_2/Θ_1 is less than unity, where 1 and 2 denote the low-temperature and high-temperature phases. For the cases they considered, they found an average ratio of 0.84, the extreme (tin) being 0.81.

A check on our measurements appears in Table II, where we compare the polycrystal alpha-phase elastic constants with those obtained from the monocrystal elastic constants by Voigt–Reuss–Hill averaging. For all the elastic constants, we see agreement within a few percent.

Our results relate to three first-principles studies. In considering compression effects, Ahuja *et al.*⁹ calculated the bcc C_{44} shear modulus, obtaining 35.8 GPa, close to our result, although calculated for zero temperature. For the bulk modulus, Nishitani *et al.*¹⁰ obtained 107, or about 94 GPa when corrected to a high temperature, about 5% higher than our result. For the zero-temperature bulk modulus, Sanati *et al.*¹¹ obtained 118 GPa. Nishitani *et al.* reached a conclusion that supports our high elastic anisotropy ($A = 5$). From potential-energy-surface curvatures, they concluded that bcc titanium possesses strong anisotropic chemical bonding and marginal mechanical stability (proximity of a phase transformation).

Finally, we consider the Zener elastic anisotropy, which determines the preferred C_{ij} set in Table I. Both structural and thermodynamic factors predict that the cubic phase will show higher elastic anisotropy.^{2,3} (A bcc near-neighbor-only model allows the anisotropy to be infinite.) From high-temperature measurements on monocrystal Ti–Cr alloys, Fisher and Dever^{12,29} argued the anisotropy is near 5. We adopt this value. Thus, the lowest row in Table I shows our

best estimate of bcc titanium's monocrystal elastic constants. We estimate a slightly lower (264 K) Debye temperature than estimated by Petry *et al.*⁶ (272 K).

IV. CONCLUSIONS

Using the electromagnetic-acoustic-resonance method, we measured free-vibration resonance frequencies of polycrystalline titanium up to 1030 °C and determined the two polycrystalline elastic constants of the bcc phase. We then deduced the three elastic constants of bcc monocrystal titanium at 1000 °C using the polycrystalline values and assuming the anisotropy factor $A=5$. Our values are $C_{11}=97.7$, $C_{12}=82.7$, and $C_{44}=37.5$ GPa at 1000 °C.

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