Single crystal elastic constants of tungsten monocarbide

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The elastic constants of single crystal tungsten monocarbide were determined using high-frequency (20 to 50 mHz) ultrasonic pulse–echo measurements. The measured values from this study are a full order of magnitude lower than the previously reported values estimated from X-ray elastic constants. The elastic modulus of polycrystalline tungsten carbide was also measured to verify the accuracy of the ultrasonic method used.

1. Introduction
Tungsten forms two carbides, ditungsten carbide (W_2C) and tungsten monocarbide (WC). WC has a simple hexagonal unit cell [1] with strongly anisotropic mechanical properties [2] and is the major constituent in cobalt-bonded, cemented tungsten carbides which are used extensively in industry as cutting tools and dies and other wear resistant parts. In spite of its industrial importance and popular use, its single crystal elastic properties, other than simple hardness, have not been very well studied, primarily because of an inability to grow large single crystals. Tungsten monocarbide decomposes in a peritectic reaction at 2776° C into melt and graphite [3], and has a very narrow homogenity range up to its decomposition temperature. Therefore, growing WC crystals from a melt is not possible. An alternative approach is to grow the crystals from a liquid metal, such as cobalt, saturated with tungsten and carbon [4]. Crystals up to 10 mm size have been grown by this technique [5, 6]. The 10 mm dimension is parallel to the *a*-axis but the dimension parallel to the hexagonal axis is considerably smaller because the growth habit of WC crystals leads to formation of trigonal plates. Therefore, it has been difficult to determine a set of elastic constants from such crystals.

Hauk and Kockelmann [7] published estimated values of single crystal elastic constants of WC. Their values were based primarily on the elastic stiffness constants of WC determined in various crystallographic orientations by X-ray diffraction analysis of cemented tungsten carbide. However, their estimated elastic constants are an order of magnitude larger than the elastic modulus of the polycrystalline WC used in their analysis. The purpose of our investigation was to verify Hauk and Kockelmann's analysis by measuring the adiabatic elastic constants of small, but relatively stress-free, WC single crystals by a high-frequency, pulse–echo ultrasonic technique.

2. Experimental methods
The ultrasonic apparatus used to transmit, receive, display and analyse the ultrasonic signals is shown in Fig. 1. All measurements were made with hand-held transducers operated in the pulse–echo mode.

Both the longitudinal and shear wave transducers have high-frequency piezoelectric elements that are permanently cemented to fused quartz buffer rods. In the case of the longitudinal velocity measurements, the transducer buffer rod is acoustically coupled to the sample with a glycerin film. For shear velocity measurements, the buffer rod is coupled to the sample with a film of 276-V9 Dow resin.

The longitudinal wave transducer element is 3.175 mm in diameter, cut to a resonant frequency of 50 mHz, and critically damped to 1.5 to 2.0 wavelengths. In materials where the longitudinal velocity runs $7.0 \, mm \, \mu sec^{-1}$ this amounts to a wavelength of $\lambda = 0.14 \, mm$ and a corresponding 2λ pulse length of 0.28 mm. Since the measurement is made in the pulse–echo mode, pulse lengths of up to twice the specimen thickness can
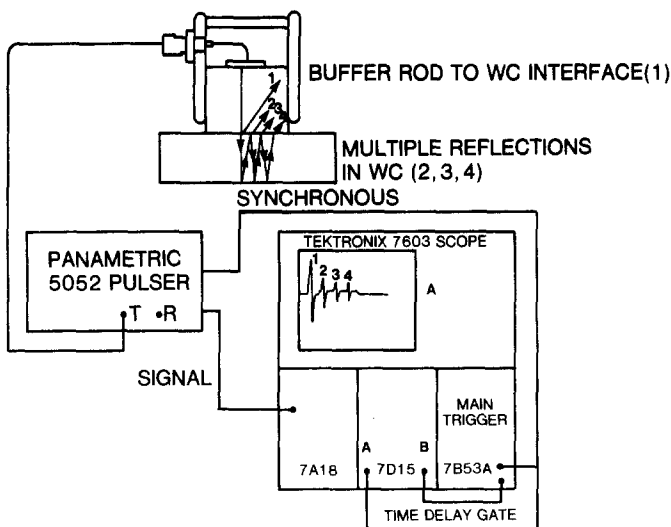
BUFFER ROD TO WC INTERFACE(1)

MULTIPLE REFLECTIONS
IN WC (2,3,4)

SYNCHRONOUS

PANAMETRIC
5052 PULSER

T R

TEKTRONIX 7603 SCOPE

1 2 3 4

A

SIGNAL

MAIN
TRIGGER

A B

7A18 7D15 7B53A

TIME DELAY GATE

be time resolved one from another. Therefore, for a pulse length of 2λ, the minimum thickness at which the ultrasonic pulses will be separated on an oscilloscope display is approximately λ or 0.14 mm. Because the transverse velocities are slower, $(4.0\,\text{mm}\,\mu\text{sec}^{-1})$ a lower frequency may be used to determine the velocities and elastic constants. The shear or transverse wave transducer used for these measurements was 6.25 mm in diameter, with a cut frequency of 20 mHz and a pulse length of about 5 wavelengths. Although of much poorer resolution, accurate transverse velocity measurements can still be made on 0.14 mm thick specimens by phase recognition. The thickness required to resolve the transverse wave pulses is 2.5 transverse wavelengths or approximately 0.5 mm.

Measurement of the time interval between successive multiple reflections from the sample with respect to a common reference pulse (in this case the synchronous pulse) permits the time interval between the two pulses to be determined by subtraction. Measuring the time intervals between the first and several successive pulses and then taking an average value to calculate the velocity permits better precision and accuracy to be obtained.

The greatest source of error in these ultrasonic velocity determinations is the measurement of length. This is a micrometer measurement and it is to ± 0.003 mm at best.

Several triangular-prism-shaped tungsten monocarbide crystals 3 to 5 mm in width and 2 to 3 mm in thickness were obtained from the Philip McKenna Laboratory of Kennametal Inc. Note that the minimum dimensions permitted greater than 5 shear wave pulses to be easily time-resolved. The crystallographic orientations of each crystal were determined by Laue back reflection X-ray analysis. The Laue photographs showed an absence of asterism, or splitting of the diffraction spots, indicating that the crystals were relatively strain free. The density of these crystals were all somewhat lower (15.35 to $15.45\,\text{g cm}^{-3}$) than the theoretical value of $15.77\,\text{g cm}^{-3}$, but were close to other reported experimental values which range from 15.5 to $15.7\,\text{g cm}^{-3}$ [1]. Intragranular residual solvent metals in the crystals left over from the growing process are probably the cause of these small differences in density. Since images produced by ultrasonic scanning of each crystal showed no flaws, both the residual metal phase and any intragranular porosity are probably uniformly dispersed throughout each specimen. As a reference, fine-grain WC particles with a small amount of residual cobalt (< 0.4 wt%) was hot-pressed to 99% plus density, and the elastic moduli of a sample of this material approximately the same size as the single crystals was also measured. The crystals were cut and finish-ground to the desired shapes for the ultrasonic velocity measurements.

The method of calculating adiabatic elastic constants of hexagonal crystals from ultrasonic wave velocities are discussed in considerable detail by Truell *et al.* [8]. Designating the hexagonal axis as X_3 of the co-ordinate system (Fig. 2), one can use the following set of equations for the determination of the adiabatic elastic constants. For a compressional wave propagating along the hexagonal axis (X_3)
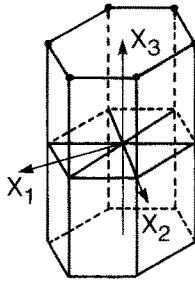
Figure 2 Cartesian co-ordinate system for hexagonal crystal.

$$\rho V_{33}^2 = C_{33} \quad \text{and} \quad V_{33} = (C_{33}/\rho)^{1/2}. \quad (1)$$

For a transverse wave along the X_3 direction polarized in any direction perpendicular to X_3,

$$\rho V_{32}^2 = \rho V_{31}^2 = C_{44} \quad \text{and} \quad V_{31} = V_{32}$$
$$= (C_{44}/\rho)^{1/2}. \quad (2)$$

For the preceding equations ρ is the density of WC and V_{33}, V_{31}, V_{33} are compressional velocity and transverse wave velocities with the respective polarizations.

A compressional wave along the X_1 direction gives,

$$\rho V_{11}^2 = C_{11} \quad \text{and} \quad V_{11} = (C_{11}/\rho)^{1/2} \quad (3)$$

while a transverse wave along the X_1 direction polarized parallel to the X_3 direction gives,

$$\rho V_{13}^2 = C_{44} \quad \text{and} \quad V_{13} = (C_{44}/\rho)^{1/2}. \quad (4)$$

A transverse wave along the X_1 direction polarized parallel to the X_2 direction gives

$$\rho V_{12}^2 = \tfrac{1}{2}(C_{11} - C_{12}) \quad \text{and}$$
$$V_{12} = \left(\frac{C_{11} - C_{12}}{2}\rho\right)^{1/2}. \quad (5)$$

Here V_{11}, V_{13} and V_{12} are the compressional velocity and the transverse velocities with the respective polarizations.

For the five independent hexagonal elastic constants, the above relations yield four, specifically: C_{11}, C_{12}, C_{44} and C_{33}.

As discussed by Truell *et al.* [8] a direction mutually 45 degrees to the X_1 and X_3 axes is chosen to determine C_{13} with a transverse wave polarized in the X_2 direction. This results in three arrivals, a longitudinal wave

$$\rho V^2 = \tfrac{1}{4}(C_{11} - C_{12} + 2C_{44}), \quad (6)$$

and transverse and longitudinal waves,

$$\rho V^3 = \tfrac{1}{4}(C_{11} + C_{33} + 2C_{44}) \pm \tfrac{1}{2}\left[\tfrac{1}{2}(C_{11} - C_{33})^2 \right.$$
$$\left. + (C_{13} + C_{44})^2\right]^{1/2} \quad (7)$$

The constant C_{13} is determined from the Equation 7 solved for the transverse wave.

For a homogeneous isotropic polycrystalline medium with density ρ, the longitudinal, V_1, and transverse, V_2, wave velocities give expressions for the bulk modulus, K_s, and the shear modulus, G, as

$$K_s = \rho(V_1^2 - \tfrac{4}{3}V_s^2) \quad (8)$$

and

$$G = \rho V_s^2. \quad (9)$$

The expression for Young's modulus is,

$$E = \rho V_s^2 \frac{3V_1^2 - 4V_s^2}{V_1^2 - V_s^2}. \quad (10)$$

These equations were used to calculate the respective elastic moduli for the polycrystalline specimens.

3. Results and discussion

Table I summarizes the five elastic constants determined from our study along with the published values of Hauk and Kockelmann [7]. As these data show, the measured values from our study are fully an order of magnitude lower than those of Hauk and Kockelmann. However, our data are within the same order of magnitude as the elastic modulus of the polycrystalline WC specimens tabulated in Table II. The modulus of our hot-pressed polycrystalline 99.6% WC, 0.4% cobalt sample is shown in Table II to be similar to that published by Kreimer [9], and the value is surprisingly close to the value cited by Hauk and Kockelmann [7].

The averaging method of Voigt [10] was used to estimate the elastic modulus of isotropic polycrystalline WC from the set of single crystal elastic

TABLE I The single crystal elastic constants of tungsten monocarbide crystal

Elastic constants	Current measurement (10^5 N mm^{-2})	Hauk and Kockelmann [7] (10^5 N mm^{-2})
C_{11}	7.20	102
C_{33}	9.72	121
C_{44}	3.28	46
C_{12}	2.54	44
C_{13}	2.67	24

TABLE II Elastic modulus of polycrystalline tungsten monocarbide

Modulus of elasticity (10^5 N mm^{-2})	Source of data
7.17 ~ 7.22	Current measurement of hot-pressed WC
7.07	Voigt's average of single crystal constants of this study
7.24	Hauk and Kockelmann [7]
7.17	Kreimer [9]

constants measured in our study. As shown in Table II, the averaged values are also close to the experimentally measured values.

We do not understand why the elastic constants estimated by Hauk and Kockelmann are so much larger than our measured values. However, comparison of the elastic modulus values of polycrystalline WC of our investigation with that of other published data shows that the errors due to ultrasonic measurements are at most only a few per cent.

Another discrepancy between the current data and those of Hauk and Kockelmann is the relative difference in the magnitude of C_{12} and C_{13}. Hauk and Kockelmann estimated C_{12} to be much larger than C_{13}, while our measurements showed that the values of C_{12} and C_{13} are very close with C_{13} actually slightly larger than C_{12}.

Because of the small crystal size and the special cuts required, the C_{13} value was measured using a separate crystal. However C_{12} can be estimated either from the longitudinal velocity in the 45 degree direction to X_1 and X_3 using the same crystal as the one used for C_{13} measurement or from the transverse wave along the X_1 direction polarized parallel to X_2 using other crystals. The difference in the magnitude of C_{12} values determined using the two different wave velocities were less than 0.1×10^5 (3.9%) indicating that any possible variations from crystal to crystal could not have caused the discrepancy between our data and the values reported by Hauk and Kockelmann.

4. Conclusions

The elastic constants of single crystal tungsten monocarbide were determined using high frequency (20 to 50 mHz) ultrasonic pulse—echo measurements. The elastic modulus of a hot-pressed polycrystalline WC reference sample indicates that the technique is reasonably accurate. In addition, the polycrystalline elastic modulus calculated from the single crystal constants determined in this investigation is reasonably close to the experimentally measured elastic modulus for polycrystalline WC. The agreement suggests that the values for single crystal constants are at most in error by only a few per cent.

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