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I-Measurement of Some Elastic Properties of a Solid Material Made by Consolidated Nanosized Particles of Zinc Compounds at Different Temperatures. II- Particle Size Measurement by TEM

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Abstract. The elastic properties of a solid made by consolidated nano particles of two zinc compounds were evaluated at different temperatures (from 303 °K to 343 °K). The nano particles were prepared chemically. For studying the elastic properties of the solid and speed of sound within the material, two samples were prepared. Use of ultrasonic reverbersion technique for measuring the transit time and the wave velocity in the solid placed in oil and the effect of longitudinal and shear waves on the sample are discussed. The arrival times of individual reverbersions were compared for the estimation of compressional and shear velocities. The compressional, shear and the bulk modulus, were calculated in both the samples. In one pellet, without application of pressure on the material, some porosity was observed reducing the calculated parameters. It was concluded that the presence of cracks, twining and grain boundaries within the bulk material can alter the ultrasonic velocity as well as the elastic properties. The effect of hydrostatic pressure on the solid disk was also studied. For particle size measurements, the size distribution curve was drawn using the method of cryo-transmission electron microscopy (cryo-TEM) image analysis through dynamic light scattering (DLS) technique. A histogram has been constructed showing size distribution of particles dispersed in the medium. The sizes (weight average diameter) were recorded between 21-100 nm. The results of such particle size measurements show that the dynamic light scattering and acoustic micro imaging techniques, both are nondestructive and allow characterization of a large number of particles more rapidly. By assembling nano sized particles, the prescribed properties of the material can be altered.

Keywords: consolidated nano particles, transducer, elastic properties, cryo-transmission electron microscopy (cryo-TEM)

Introduction

The elastic properties of solids, made of consolidated nano particles, are of considerable importance in science and technology (Herman, 2005; Charles and Frank, 2003). Such properties of solids, explored by different ultrasonic techniques, are of primary importance. The present technique has now become a well established methodology. For commonly employed high frequency pulse technique, the compression and shear wave velocities within the solid are of primary concern. Measurement of elastic parameters and the density are made to determine adiabatic modulus. This can yield sufficient information regarding the interatomic spacing and binding energy in a solid (Kumar, 1995; Siegel and Hahn, 1987). Such data is highly necessary for interpreting the nature of bonds in a solid. From this point of view, the elastic properties, describing the mechanical behaviour of solids, are utmost stable for the solid designed.

There is a need to provide full elastic properties of modern engineering materials in a single test. This leads to the changes in the measurement of compression modulus and shear modulus (Love, 1934). Study of propagation behaviour of high frequency compressional waves in solids is a well established technique. This is used for examining the acoustic properties in single crystal. Highly accurate absolute velocity data can be used to determine the properties, which are related to lattice vibration or anharmonicity in a solid (Thomas and Abdulkhadar, 1995; Uvarov *et al.,* 1994). In this method of acoustic micro imaging, we used one transducer that generated a pulse of high frequency (5.0 MHz) in a sample and another transducer received the return echo signal (Kesseler and Adams, 2003). The amplitude and the phase of an echo signal relate to the acoustic reflectivity of an interface in terms of material density and modulus (Shanker *et al.,* 1980; Mason, 1972). The arrival time of the echo signal relates to the depth of sample and the velocity of sound through the material. Each echo is rich in information about the sample structure and interfaces in the interior of the sample.

Transmission electron microscope (TEM) was used for particle size measurement through image analysis. TEM is a powerful tool which allows the analysis of the microstructure

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and chemistry of a metal or a complex compound. The importance of such characteristics are realized, when the chemical and the physical nature of a material controlled by their particle size, bulk density and the reological properties of suspension etc are examined (Collins *et al.*, 1975). The average particle size and the size distribution are the essential data on which the stability and dispersion of a polymer depends (Durrieu *et al.*, 2004). Light scattering and the cryo-transmission electron microscopy have been proved to be complementary technique to characterize various natural and synthetic polymers and polymer nano composite (PNC) of nano particles dispersed in water (White and Fenton, 2003). According to Cankurfaran *et al.* (1989), the bulk modulus of any porous material is obtained by the measurement of ultrasonic velocity at atmospheric pressure which is comparably smaller than that obtained at high pressure. In the present method, oblique compression waves were passed incident on the sample, which is placed slightly tilted with the transducer; it resulted in both the compression (longitudinal) and shear wave reverbersions in the sample, which can be separately time resolved at the receiver. The arrival times of individual reverbersions were evaluated. By measuring the bulk density and the ultrasonic velocity the corresponding modulus was obtained.

Calculations

The following equations were used to calculate these acoustic parameters (Bhatia, 1967):

Ultrasonic velocity V_c or V_s = frequency × wavelength λ ..... (1)

V_c or V_s is compression or shear velocity (Cantrell and Breazeale, 1978)

Compressional modulus, E_c = density × $(V_c)^2$ bar .....(2)
Shear modulus G = density × $(V_s)^2$ kbar .....(3)
Bulk modulus or volume elasticity, K = E - 4/3 G bar .....(4)

For compressional velocity, the time difference t (CCC) between the arrival of the first compression pulse (C) and the pulse which has made three compression transits (CCC) in the sample was calculated as follows:

$$t(CCC) = \frac{2\,\Delta x}{\cos\theta_c}\left(\frac{1}{V_c} - \frac{\sin\theta_i \sin\theta_c}{V_w}\right) \quad \text{.....(5)}$$

where:

Δx = thickness of the sample under test
θ_i = angle of incidence
θ_c = angle of refracted waves w.r.t normal to the sample surface
V_c = compression wave velocity
V_w = ultrasonic wave velocity in the surrounding medium,
$\theta_c = 20^\circ$
$\sin\theta_i = \sin 70^\circ = 0.9396$
$\cos 20^\circ = 0.939$

Particle size and dimension evaluation in dispersed media

If
D_N = the number of average diameter of particles
D_w = the weight average diameter
N_i = the number of particles at the ith class in the size distribution histogram
W_i = molecular weight
D_i = the weight for ith molecule, then

$$D_N = \Sigma D_i N_i / \Sigma N_i \quad \text{(Venessa } \textit{et al.}\text{, 2004) and .....(6)}$$

$$D_w = \frac{\Sigma W_i D_i}{\Sigma W_i} \quad \text{.....(7)}$$

From the data obtained by dynamic light scattering (DLS) for a Z average mean diameter, D_z was calculated from TEM data as follows:

$$D_z = \frac{\Sigma N_i D_i^6}{D_i^5} \quad \text{.....(8)}$$

From the size distribution histogram D_i will be determined, considering a total of about 1000 particles over a 1" x 1" film area.

Materials and Methods

Chemicals. All the chemicals were highly pure (99.99%) AR grade, obtained from BDH and were used without further purification. For making this compound, 100 ml of 1M solution of ZnS (mol. wt. 97.43) and 100 ml of 1M solution of $ZnSO_4$ (mol. wt. 161.45) were prepared and mixed with 25 ml of 0.1 M (EDTA a chelating agent) to make a colloidal solution in distilled water, with total volume of 250 ml at room temperature. The liquid was vapourized in water bath at a temperature of 60 °C with continuous stirring the homogeneous mixture.

Production of nano sized particles by chemical method. In principle, a chemical method for sample preparation was adopted for making material of nano size structure, taking advantage of low solubility of powder in water. Equi molar solution of analytical grade of ZnS+$ZnSO_4$+ water was prepared and the sample was dried for 72 h (Mason, 1972).

Solid sample preparation from powder. A circular piece of thickness (2.72 mm) and 2.5 inch dia was prepared comprising this material and plaster of paris (20% of the whole volume) applying pressure of 1M Pascal with a piston and cylinder system, using silicon oil as pressure transmitting medium;

A pre-calibrated Maganin resistance gauge was used for pressure measurement, carried out at room temperature. A pressure of 1.0 M Pascal was applied to make sample less porous. It was observed that the presence of irregular shapes, pores, grain boundaries, microscopic cracks and intergranular defects can substantially affect the elastic stiffness and other pressure-depending properties (Radhakrishna and Daud, 1991). The sample prepared from these consolidated nano particles can be treated as an isotropic material, having independent parameters in all directions, elastic stiffness, compression and shear modulus. For particle size distribution, the optical transmission pattern of this material was characterized by TEM and the morphology of the film prepared by the cryo image transmission electron microscope was studied.

Major steps taken in image processing of samples by transmission electron microscope. Samples for such measurements were prepared by using a thin layer of the above mixed liquid 1 mg/ml of nano particles in dispersion. The recorded electron diffraction pattern was observed in bright field contrast image analysis of TEM.

- Low contrast was kept between the particles in cryo-TEM image analysis;
- With simultaneously increasing the contrast, background noise from the negatives image was reduced (Harris, 1997).
- Carbon substrate size area is 1" x 1". The whole area on which the nano-particles were dispersed was characterized by high resolution transmission light microscopy (HRTLM) and nearly spherical particles were found. The sphericity and the diameter measured were in the range of 21-100 nm, whereas the recognizable isolated particle sizes were about 20-40 nm, which is consistent with the formulae.

Particle size evaluation by cryo-TEM DLS (dynamic light scattering). For studying the particle size and contrast enhancement, semi-automatic image analysis was adopted. The morphology and the structure of such fine particle size distribution were studied with transmission electron microscope JEOL Japan model JS-100 operated at 100 kv, selected with different magnification factor, $\alpha = 80{,}000\text{-}100{,}000$. The specimen was observed at temperature of -150 °C. The high magnification factor α was selected in order to include a large number of particles in the field of low contrast, viewed with suitable resolution (Dennis *et al.*, 2001). A sampling rate of picture 5 nm/pixel was considered to be a good compromise. Recorded micrographs were observed (Kodak 163 films) at high magnification factor with a limit of 5-10 nm. Cryo-TEM image sizes were plotted in a histogram (Fig. 2).

Velocity measurements in bulk material by pulse reverbersion technique. The velocities of compressional waves emitted by transducer were measured by pulse reverbersion technique - a high frequency wide band ultrasonic technique. (Challis *et al.*, 1993). Two test pieces were taken one by one and placed in a medium (oil) and kept tilted at an angle θ of 20° with the transducer, emitting compression waves incident on the sample resulting in both compression and shear waves which can be separately time resolved at the receiver (Fig. 1). The arrival time of individual reverbersion at the receiving transducer in the medium is the Y-input to the oscilloscope. The temperature of the medium is controlled by accuracy of ±1°C. The arrival time of high frequency short ultrasonic pulses, and both compressional and shear reverbersions (which are time resolved) are measured in the material, separately. Longitudinal and shear velocities in the test piece are calculated by passage of short ultrasonic pulses of high frequencies resulting in reverbersion signals showing both the compression and shear waves when the sample is incident at an angle of 20° (Kesseler and Adams, 2003). Quartz crystal of the transducer was cemented to one end of the specimen having parallel end faces to emit the ultrasonic waves within solid. It was polished lightly on both sides to give flat parallel surface reflection. Echo train of pulses was chosen for the measurement of ultrasonic velocity. By this technique, the arrival time of individual reverbersions was compared for estimation of time measurement, carried out by single ended pulse echo technique at a carrier frequency of 5.0 MHz. Quartz transducer (x- cut for longitudinal, y- cut for shear) was used to excite and detect the ultrasound.

Frequency measurements. Frequency counter TRIO 754-A Japan was used for measuring frequency or repetition rate of pulse, with an accuracy of ±1 Hz.

Results and Discussion

For studying the acoustic behaviour of this solid, the ultrasound pulses in the form of echoes are propagated in the bulk of the sample (Fig. 1). Amplitude variation occurs in the resulting echo reverbersion after three transits CCC, within the sample (Fig. 2). It is reflected only at the material interfaces inside the bulk. Since this solid material is non-homogeneous, ultrasound pulses were reflected in the form of echoes (from the top or bottom of the material with angle θ_c or θ_s). The bulk material contains cracks or grain boundaries or spaces in it, creating material interfaces. A portion of ultrasound is reflected and refracted inside the material (Carbone, 1992); the amplitude of the echo signals are measured using Oscilloscope Tetronix 100 MHz (four channels), which determines transit time and consequently the component of ultrasonic velocity

within the material. The velocities are evaluated from the equations (5) and (9) for compressional mode and for shear mode, respectively. The sample was kept slightly tilted in the medium (oil) between two transducers, one emitting short ultrasound pulses after striking the sample which are reflected, refracted and propagated as reverbersions.

The time difference between arrival of the first compression pulses is calculated, according to Snell's Law, as follows:

$$\text{Time } t(CCC) = 2\Delta x/\text{Cos}\theta_s(1/V_s - \text{Sin}\theta_i \text{ Sin } \theta_s/V_w) \quad \ldots\ldots (9)$$

where:

V_w = the velocity in the medium

CCC = the pulse which has made three compressions transits in the sample medium

The shear waves were propagated at single sample temperature; the velocity decreased with the increase of temperature through built-in heater of the bath and recorded within ±1 °K by digital temperature controller (Autronic ZN_4N_4), using thermocouple as a sensor. The time of arrival of waves was measured by ultrasonic pulse echo technique through an oscilloscope. For a theoretical understanding of the physical nature of interatomic forces binding the solid, the pressure derivatives of elastic modulus for nonporous matrix is computed which is in accordance with the work of Radhakrishna and Daud (1991) who developed the mathematical expressions for composite materials.

Conclusion

The limits of experimental errors, the calculated values of compressional (longitudinal) velocity and shear velocity of the stress waves propagated in this bulk material in the temperature range of 303 °K - 343 °K are listed in Table 1 and Table 2. It was observed that the velocity in the material decreases with the increase of sample temperature. Thermal vibration of the structural particles of the perfect crystal may cause the observed changes in ultrasonic velocity and other elastic constant. In order to achieve the required time resolution, a parallel thick PZT transducer was used as a transmitter of the waves and another PZT transducer, as receiver of echoes in the bath. Since, the acoustic signals are non-destructive, this method does not alter the properties of physical sample while creating a data file. The transducer is excited by very short ultrasonic pulses. Other elastic parameters of the materials were calculated by the measured values of ultrasonic velocity and density of pellet, and was found to be lower than that of corresponding bulk crystal. Both the compressional and shear ultrasonic velocities on a pressed pellet are higher as compared to less pressed sample. Broadening of the received pulses by scattering at the grain boundaries in the material were not observed. This led to the conclusion that, material is an isotropic solid, which has only two independent elastic constants; these can be taken as E_c and G as shown above, but it is some times convenient to use other elastic constants, such as young modulus and poisson ratio. For this material, the latter two constants cannot be deter-

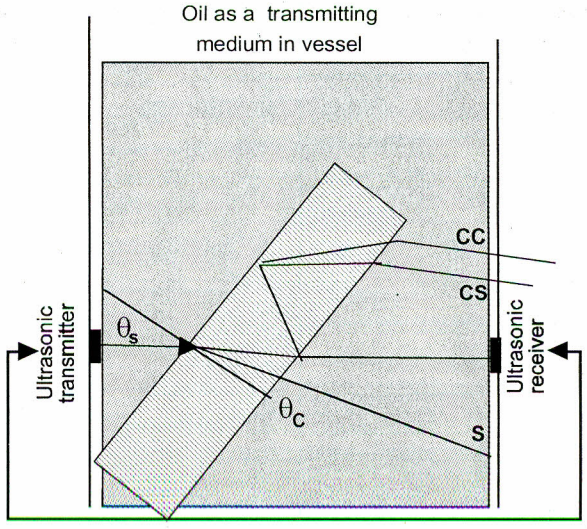

Fig. 1. Actual acoustic ray path in the bulk of the sample.

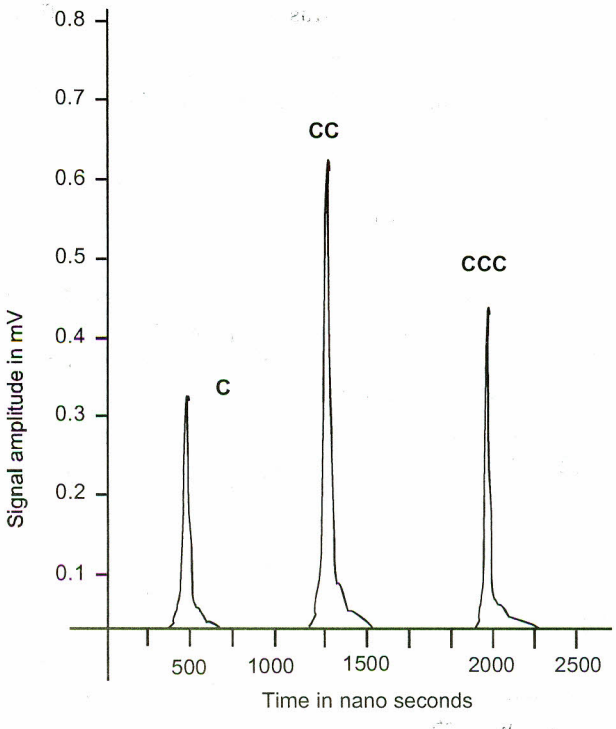

Fig. 2. Reverbersion signals in sample 2.77 mm thick observed through oscilloscope.

Table. 1. Calculated values of ultrasonic velocities (compressional and shear) and the elastic modulus. Density of unpressed (original) pellet, d_1 = 2065.3 kg/m^3 at atmospheric pressure; thickness of the sample = 2.77 mm

Temp °K	Compressional velocity (V_c) m/sec	Shear velocity (V_s) m/sec	Comp. modulus E_c (x 10^9) kbar	Shear modulus (x 10^9) G
303	2230	1805	10.22	6.721
308	2225	1803	10.21	6.714
313	2222	1800	10.20	6.691
318	2210	1799	10.10	6.683
323	2207	1796	10.05	6.660
328	2205	1785	10.00	6.581
333	2203	1774	10.05	6.505
338	2201	1754	10.00	6.352
343	2200	1743	9.99	6.271

Table 2. Calculated values of ultrasonic velocities and elastic modulus (compressional and shear modulus) at hydrostatic pressure of 1M Pascal. Density of pressed pellet, d_2 = 2140. 165 kg/m^3; thickness of round sample = 2.37 mm = Δx

Temp °K	Compressional velocity V_c m/sec	Shear velocity V_s m/sec	Comp. modulus E_c (x 10^9) kbar	Shear modulus (x 10^9) G
303	2380	2155	11.90	9.938
308	2365	2152	11.91	9.895
313	2360	2145	11.70	9.881
323	2349	2133	11.65	9.735
328	2345	2127	11.55	9.685
333	2339	2121	11.52	9.622
338	2335	2106	11.45	9.591

mined. It was found that porosity of the solid pellet effectively reduced the ultrasonic velocity, of the waves passing through this isotropic material. For particle size measurements, the dynamic light scattering (DLS) technique was used, which is a non-destructive technique adopted for image analysis and particle size measurements for rapid characterization of the particles of bulky samples. However, it showed some limitations in the case of polydispersed material, having particles smaller than 20 nm. On application of pressure on such material, the longitudinal modulus decreased with rise of temperature (Peterson and Rosen, 1967). The same temperature dependent trend was observed in shear modulus. In case of pellet of consolidated nano particles of ZnS + $ZnSO_4$, the change in ultrasonic velocity of waves, scattering from these particles and the elastic modulus has to be attributed both to the porosity of the sample and the physical properties of the individual particles. Thus the internal structure of the nanoparticle material can exhibit a pronounced deviation from the perfect crystal structure.

Limitations were also observed with particle sizes smaller than 21 nm. Fig. 3 shows histogram for size distribution; in a cluster of 1000 nano particles, sizes 21-25 nm are about 4.7% of the total population and 71-80 nm, 14.2%. The values of velocity calculated from equation (5) and equation (9) can be verified by equation (1).

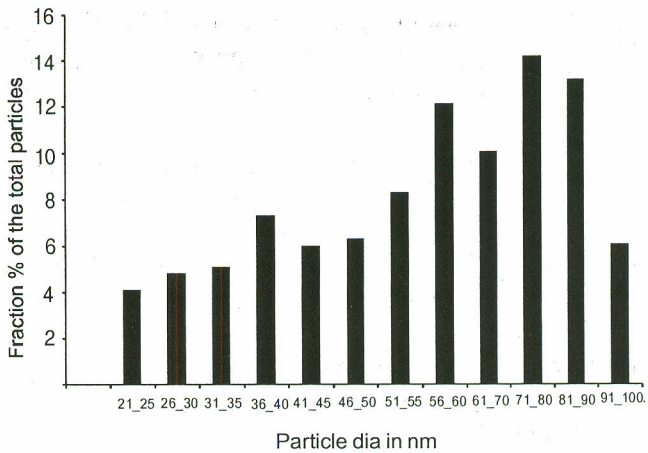

Fig. 3. Particle size distribution for 1000 particles of the sample.

The comparison between the elastic moduli as measured on a porous compound and non porous matrix showing that the porosity reduces both the ultrasonic velocity and modulus i.e. in a matrix to reduce (dB/dP) (Mason, 1965).

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