Annual Progress Report for
Contract AEC-AT(11-1) 3153

ELASTIC AND PLASTIC DEFORMATION
OF SOLIDS

Period: February 1, 1974 - January 31, 1975

Principal Investigator
Dr. Arthur L. Ruoff, Professor
Department of Materials Science
and Engineering

Cornell University
Ithaca, New York

MASTER

October 18, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1. PLASTIC DEFORMATION AT PRESSURE.

Experiment

It has been noted in an earlier paper that the yield stress, σ_0 , of a nonporous single phase cubic material should vary with pressure according to

$$\sigma_0 = \sigma_{00} (1 + E'_0 P/E_0).$$

Here σ_{00} is the yield stress at zero pressure, E_0 is Young's modulus at zero pressure and E'_0 is the pressure derivative of Young's modulus at zero pressure.

The direct proportionality of σ_0 and E is expected from dislocation theory. We note that the proportionality between yield stress and modulus has been shown to be quite general in glassy polymer by Norman Brown. Of course these material because of their low modulus lend themselves readily to experimental study at high pressure; in fact a modest pressure of 7 kbars is adequate to increase E to $6E_0$ and σ_0 to $6\sigma_{00}$.

Earlier stress-strain plastic flow measurements on crystalline materials by Bridgman and others were made using poor experimental techniques.

More recent experiments such as that of Aladag, Gordon and Davis or of Yoshida and Oguchi utilize careful experimental techniques; however, the changes they noted were not large because the pressure range was not high for the particular materials chosen.

We have built and used a system capable of accurate measurements at

temperatures down to liquid N₂ temperatures and at pressures up to 7.0 kbars using helium gas as the pressure medium. We have also chosen to make studies on potassium metal; the reason for this choice is simple: We wanted a crystalline metal for which a significant change could be expected in our pressure range. Our available pressure equals about one-fourth the bulk modulus of potassium. (Had we worked with iron instead of potassium we estimate that we would have had to use a pressure of about 400 kbars to get the same effect.) Another reason for choosing potassium was that considerable stress-strain data was already available at liquid N₂ temperature.

To begin, we made measurements on lead because it is not a highly reactive element as is potassium. Thus we were able to perfect the apparatus prior to our work on potassium. Since lead is also fairly soft elastically, a significant increase of modulus is obtained as a result of the presence of pressure. In the case of lead, simple application and removal of the pressure modifies the stress strain curve, an added complication also observed by Aladag, Gordon and Davis on NaCl. Thus all samples were cycled between atmospheric pressure and the test pressure several times prior to measurements being made.

In the case of potassium, as already noted, a large increase of the flow stress was noted, of about 70% (the actual value depends on the final load calibrations and on the details of correction terms which are now being made).

The results agree with linear behavior.

This work has been carried out by Jamie Chua as part of his PhD research.

Theory

One of the concerns in very high pressure research (where solid, not liquid, pressure media are used) is that deviatoric stresses are present, because of the finite yield stress of the pressure medium. Thus the state of stress in an opposed anvil system is anisotropic, with the stress component σ_z in the direction of the piston motion being greater than the stress components normal to this direction (σ_r and σ_θ). While analyzing this problem³, and with Jamie Chua's work very much on his mind, the principal investigator noted that by studying the elastic strains of planes whose normal is in the z and r direction respectively (using x-rays), the yield stress could be measured. This has been described in a paper in Scripta Metallurgica.^{4, 10}

2. ULTRA FINE GRAINED SINTERED CARBIDES.

Commercial tungsten carbide is a cemented carbide made from tungsten carbide and cobalt powder. During sintering a portion of the tungsten carbide dissolves in the cobalt. Prior to cooling, the system essentially exists of carbide particles in an eutectic liquid. Upon freezing the liquid forms the "cement" of the cemented carbide structure.

In the absence of the cobalt, it is not possible to obtain a fully dense solid upon sintering at atmospheric pressure. However, hot isostatic sintering can be used to obtain specimens of theoretical density. Moreover, using the latter approach sintering can be achieved without any grain growth, at least for grain sizes of 1μ . We have sintered "pure" tantalum carbide (which has the NaCl crystal structure) to fully dense solid at 40 kbars and at temperatures to 1500°C. (Higher pressures and temperatures could be achieved for modest times.)

We are now in the process of attempting to use this process for obtaining extremely fine grained carbides (maximum intercepts, eventually as small as 300A and definitely as small as 1000A). In order to achieve these structures by this procedure it is necessary to:

- 1) Begin with powders in which the largest grain is no larger than the largest grain to be allowed in the composite.
- 2) Find the (P,T) conditions under which sintering to the fully dense state occurs without grain growth or with only modest grain growth.

As mentioned, with 1 μ grain size both (1) and (2) are possible. We note that (1) must be obtained first. We spent the last year working with TaC powder from a commercial supplier. This material, has an average particle diameter determined from surface adsorption (BET) measurements of 280A. However, careful examination using electronmicroscopy techniques show that there is a small fraction of particles having significantly larger grain size with even some 1 μ particles present. If a weight average instead of a number average is used the fraction is of course much larger. There was initially a problem of agglomeration of the particles which made size measurement extremely difficult. This has been solved (a story in itself which we will not expand on at this time). We are therefore very confident of our present size characterization studies (which were incidentally carried out using the Electron Microscope facility of the Materials Science Center).

In order to obtain only fine particles, two avenues are open:

- a) Modify the powder production conditions.
- b) Separate the powder into different size fractions.

Inasmuch as we have not been involved in the production we are currently following the latter approach. We have been able using centrifuging to obtain yields of 5% with the largest particle size being 2200A and yields of 0.6% with the largest particle size being 800A. We have not attempted to produce a smaller cut-off size at present. However, for the above mentioned cut-off sizes we have shown that it is practicable to produce the required powders on the laboratory scale. (This separation was carried out in the Chemical Engineering centrifuge laboratory.) Future separation for sample separation will be carried out in our laboratory on equipment which should soon be received; the extensive use will tie up this equipment for long periods of time so that borrowing time becomes impractical.

While we ourselves have not worked on the problem of direct production of ultra fine powder it should be pointed out that there are two different research groups at Cornell who are producing and studying various physical properties of ultra fine powders including the kinetics of nucleation and growth of these powders. We currently are having discussions with these groups and are considering the possibility of getting involved in this process to produce ultra fine carbide powders.

Our present purpose of making ultra fine grained carbides has been discussed previously: We expect the fracture stress to increase as $1/d^{1/2}$. Eventually, it is possible that the fracture stress will exceed the flow stress so that extensive plastic deformations can occur. It should be noted that plastic flow of cemented tungsten carbide does occur in the presence of large superimposed hydrostatic pressure [see Chao and Ruoff Rev Sci Instr., 41, 720 (1970)]. From our studies on cemented tungsten

carbide we have shown that the expected compressive yield stress of pure tungsten carbide is very nearly $G/15$. This is what one would expect for Frenkel flow ($\tau_{\max} = G/30$ but $\sigma_0/2 = \tau_{\max}$), i.e., yielding at the theoretical strength by simultaneous slip (rather than by consecutive slip as by dislocations). A paper on the strength of these materials is now in preparation by the principal investigator. In the absence of hydrostatic pressure it is estimated that for this material to flow rather than fracture, the grain size must not exceed about 300A. This experiment on the sintered carbides is being carried out by Warren Yohe as part of his PhD program research.

The ability to produce ultra fine grain fully dense polycrystalline aggregate may have important implications in a number of other areas including the oxides reactor fuels and the potential carbide reactor fuels.

3. CAPACITANCE METHOD OF DETECTING PHASE TRANSFORMATIONS AT ULTRA PRESSURE.

When first order phase transitions occur from one dielectric phase to another, there is a discontinuity in the dielectric constant and hence as a rule in the capacitance of a given sample of material.

The major problem in attempts to use this technique at ultrahigh pressure (with very small quantities of the dielectric material being studied) is that one must both obtain the very high pressure and measure only the capacitance of the sample. Several different attempts were made to achieve simultaneously these conditions.

While supported opposed anvils of cemented tungsten carbide can attain pressure of hundreds of kilobars, this configuration (with the opposed anvils as capacitor plates) unfortunately measures a capacitance which includes

the sample, the pyrophyllite washer and the pyrophyllite support material on the conical faces. In order to attempt to eliminate this difficulty, we attempted to use composite anvils. These consisted of cylinders whose diameter was equal to the dia. of the tiny anvil face placed along the axis of a ceramic piston. While in this technique, the capacitance was essentially that due to the sample only, unfortunately even moderate pressure could not then be attained. Thus, it was not possible to see transformations in AgCl and CaF₂ although the transformation in KCl could be nicely seen. While it appeared that certain configurational changes might be made which would make it possible to use this technique to see the AgCl and CaF₂ transitions, we do not currently see how it might be used to reach, e.g., the 300 kbars needed for the NaCl transformation.

This work was carried out by Robert L. Alworth as part of his M.S. thesis research program.⁸

4. EQUATION OF STATE

Theoretical

Several years ago very careful measurements of the pressure derivatives of the elastic constants of sodium were made in this laboratory. The results at 195°K were obtained at a higher pressure than those at the other temperatures and moreover because of the peculiarities of the bonding material which bonded the transducer to the sodium, the bonds were nearly ideal, at pressure at this temperature. Therefore a very good value of B_0'' (the second derivative of the bulk modulus with respect to pressure) was obtained as were also B_0 and B_0' . Although a number of theoretical papers have appeared in which $P(V)$ were calculated and even $B(V)$, the specific quantity B_0'' had not been computed. We have used the Ashcroft-Langreth pseudopotential to compute B_0' and B_0'' . The result is shown be-

low for 0°K. The analysis used here utilizes a static lattice.

	Exptl	Theory
B_0	77 kbars	77 kbars
B'_0	3.904	3.945
B''_0	-0.070 kbar ⁻¹	-0.0510 Kbar ⁻¹

This work, carried out with K. J. Dunn, was recently published in Physical Review.^{1,11}

We have also examined in some detail the relation between certain empirical equations of state [such as the Murnaghan equation of state (based on the bulk modulus relation $B = B_0 + B'_0 P$) and the Grover-Getting-Kennedy equation of state (based on $B = B_0 \exp(B'_0 (V_0 - V)/V_0)$)] and the theoretical equation of state of the material. Two model materials, sodium and sodium chloride, were studied. The Ashcroft-Langreth pseudopotential model was used to describe sodium and a Born-Mayer model to describe sodium chloride.

This work was also carried out with K. J. Dunn². In both cases the GGK equation more closely fitted the theoretical curve than the Murnaghan equation. What is of particular interest is for B vs P , B vs V/V_0 , or V/V_0 vs P , the Murnaghan equation represents an upper bound to the theoretical curves while the GGK curves represent corresponding lower bounds.

In the absence of phase transformations and in the absence of a sound theoretical model (as exists in the present two cases) a reasonable approach to the equation of state would be to use the experimentally obtained B_0 and B'_0 for the material (obtained from ultrasonic studies at

modest pressures) and to use these two equations of state to get the upper and lower bounds as mentioned previously.

Experimental

Four different sets of measurements involving elastic constants and equation of state have been completed or are underway. These include studies on a two phase glass ceramic, on cesium bromide, on lithium fluoride and on cerium.

The glass-ceramic Cervit, which is a lithium aluminum silicate consisting of a crystalline phase (75%) with small crystallites (much less than $5000\text{\AA}$) and a glass phase, was studied initially because it appeared to be an ideal working medium for the absolute pressure gauge developed in our laboratory. [see Ruoff, Lincoln and Chen, Journal of Physics D: Appl. Phys., 6, 1295(1973)].

This particular material has a zero thermal expansion coefficient at room pressure; hence Δ in the aforementioned paper is zero so the isothermal and adiabatic bulk moduli are equal, $B^T = B^S$.

We therefore made measurements at pressure to see if this relation remained or was very closely approximated at pressure. If this is true and the material behaves reversible under pressure (no permanent densification), it would be ideal not only for use as the medium of the pressure gauge but also as a reference length at pressure which is essentially independent of temperature. It should be noted that the pressure dependence of the volume thermal expansion coefficient, β , is given by

$$\left. \frac{\partial \beta}{\partial P} \right]_T = - \left. \frac{\partial (1/B^T)}{\partial T} \right]_P$$

Although β increases as pressure increases, it is found to be still small at 10 kbars.

Of considerably more interest is the pressure variation of the bulk modulus. Not only is B'_0 negative as is the case for many glasses, but B''_0 is also a large negative quantity. We have

$$B = 621.5 - 13.36P - 3.02P^2/2$$

where B and P are measured in kilobars. These results were obtained from elastic constant measurements to 4 kilobars. If this quadratic representation is correct (coefficients of cubic and higher order terms are zero, a result not expected in general), then at a pressure of $P = 16.3$ kbars we would find B approaching zero. Physically $B < 0$ corresponds to a macroscopic elastic instability, i.e., there would be a spontaneous change to a solid with a smaller volume. Inasmuch as permanent densification of glasses does regularly occur often in the neighborhood of 20 kbars (as first shown by R. Roy and their coworkers), it was not inconceivable that this might occur in the present material (which was partially crystalline; the crystalline material, having precipitated from the glass). To test for this possibility, specimens were placed in a pressure vessel successively at 10, 15, 20, 25 and 30 kbars. Specimen lengths were measured before and after each pressure level was attained. Pressurization was carried out at room temperature slowly; so there was little heating of the pressure media (methanol-ethanol). The pressure was held at each pressure level for one hour. The length was measured with a van Keuren (pressure sensitive) micrometer; a difference in length less than 0.01%

could readily be observed. No length difference was found at the highest pressure used. This suggests that B_0'' is positive (or at least the overall contribution from cubic and higher order terms in the expansion of $B(P)$ is sufficiently positive at 30 kbars to outweigh the negative contributions of $B_0'P$ and $B_0''P^2/2$.)

This work also suggests that it would be of interest to investigate single phase glasses to see if the permanent densification which occurs (which necessarily involves a structural change and hence is a phase transformation) is associated with a macroscopic instability of B . This work was carried out with Mr. K.Y. Kim.⁹

The second project involved work on CsBr. This work was carried out to obtain B_0'' not only at room temperature, but at a number of temperatures. It should be pointed out that an earlier measurement of B_0'' had been made in Barsch's group at Penn State U. The result obtained for $B(P)$ at 298°K is

$$B(P) = 143.7 + 6.30P - 0.044 P^2/2$$

(again the units are kilobars).

Chang and Barch obtained $B_0'' = 0.050 \text{ kbar}^{-1}$ [in Accurate Characterization of the High Pressure Environment ed. by E. C. Lloyd, Nat. Bur. Stds. Pub 326. Wash. D.C.(1971)].

In the expression for the bulk modulus in which B depends linearly on pressure, $B_0'' \equiv 0$ (the Murnaghan equation); however in the expression in which B depends exponentially on the volume change according to $B = B_0 \exp[B_0'(V_0 - V)/V_0]$ it follows that

$$B_0'' = -B_0'/B_0.$$

It is of interest to compare the B''_0 computed from the ultrasonically measured B'_0 and B_0 for crystalline materials for which we have measured B''_0 ultrasonically.

$B''_0(\text{exptl}) \text{ kbar}^{-1}$	$-B'_0/B_0 \text{ kbar}^{-1}$
(195°K) Na -0.070 ± 0.007	-0.056 ± 0.002
(298°K) CsBr -0.044 ± 0.007	-0.044 ± 0.003

The values for sodium are from reference 1. The values for CsBr will be part of Mr. Dunn's Thesis.

The essential agreement lends credence to the idea that this two parameter exponential expression is a close description of the physical situation here.

We note that neither equation gives a proper description for B''_0 for the glass-ceramic we mentioned earlier, for which experimentally $B''_0 = -3.0$ and the value of $-B'_0/B_0$ is 0.02, i.e., even the sign predicted for B''_0 by the GJK equation is wrong.

A theoretical analysis is underway to include thermal contributions to the Gibbs free energy in addition to the Born-Mayer contribution and to obtain expressions for B_0 , B'_0 and B''_0 as a function of temperature.

This work is being carried out by Mr. K.J. Dunn as part of his PhD research program.

The third project involves length and ultrasonic measurements on LiF with the purpose of accurately obtaining the equation of state. The length

measurements are made in our length system as described previously (see Lincoln and Ruoff, Rev. Sci. Instr., 44, 1239 (1973). The system has been modified by Dr. Chhabildas with the addition of a lock-in-amplifier which increases the accuracy of the length measurement system further. The overall system has been beset with a number of difficulties this past year through no fault of the scientists (Dr. Chhabildas and K.Y. Kim). There have been difficulties with the (very accurate) temperature control system and a fatigue fracture of the managanin gauge cell (which is located in a constant temperature bath in its own pressure vessel and separated from the specimen chamber by high pressure tubing). This failure resulted in having to recalibrate the manganin gauge which is a time consuming process. Nonetheless even with these difficulties the first set of data at these temperatures has been obtained.

It appears now that these troubles are behind us and we are now in the process of taking additional data. While we expected to have these data completed and analyzed before now, we must recognize that research progress is not always uninterrupted. This work is being carried out by Dr. Chhabildas and Mr. K.Y. Kim with the latter's work being part of his Ph D research program.

The fourth project involves elastic constant studies on high purity cerium as a function of pressure. Previous work of commercial grade material (98.5%) [Voronov, Vereschagin and Goncharova, Soviet Physics-Doklady 135, 1280(1960)] showed rough agreement with Bridgman's $P(V)$ data on similar material from length measurement comparison with iron (the value of B_0' is negative). We felt that studies on very pure material should be made. First, because B_0' is negative it would be interesting to see whether

B_0'' is negative in the pure material as it is for other crystalline materials for which it has been obtained, or whether it is positive. Second, it is not inconceivably that the impurities usually present ($\sim 1\%$) could have a major effect on B_0'' in particular because the material has a phase transformation at room temperature at modest pressures. (7 kbar). Initial attempts to make high purity polycrystalline aggregate without porosity failed. Upon contacting Prof. Gschneider at Iowa State University as concerns production techniques we found him willing to share in our effort. He would provide the material and the final samples and their complete chemical analysis and structural characterization and we would make the pressure studies. We are now in the midst of this effort, having obtained the samples and having more or less solved the known difficult problem of bonding transducers to the cerium.

This work is being carried out by Dr. Weiss.

5. STRESS CONCENTRATIONS AROUND RIGID SPHERICAL INCLUSIONS IN SOLID PRESSURE MEDIA.

In very high pressure physics, a solid pressure medium with a finite yield strength such as sodium chloride or silver chloride is used. It has been pointed out by Bobrowsky and later by Jamieson and Olinger that if a pressure P is present in an elastically soft solid medium of radius c then the pressure on a stiff elastic inclusion of radius $b < c$ is greater than P ; for the case where no plastic flow occurs in the medium, the solution is given by the above authors and in fact is easily obtainable from the work of Lamé in 1851. Of course, in the high pressure area we are interested most in the situation where plastic flow has occurred through much or all

of the pressure medium. It is then common to assume that the medium behaves as a liquid instead of a plastic solid with a finite yield stress. As we have mentioned earlier, it is also true that their yield strength increases as the pressure increases (essentially in a linear fashion). This means that the problem is a nonlinear plasticity problem. This problem has been solved for the case of a rigid inclusion. The solution is applied to the case of an iron particle embedded in a sodium chloride matrix (iron is over six times as stiff as sodium chloride) so this assumption is justifiable. It is found that the stress concentration factor may be as large as 1.11 at 100 kilobars. Because of the increases of the flow stress with pressure, the stress concentration factor does not decrease to zero as the pressure gets very large, but rather approaches a finite value greater than one.

This work has been carried out with David Nelson as part of his M.S. research program.⁶

6. EFFECT ON CREEP RATE OF DOPING LiF with Mg^{++}

A model has been proposed for the effect described earlier in Hari Rao's thesis (supported under this contract). In summary, we originally showed that activation energy for high temperature creep of intrinsic LiF was equal to the activation energy for the diffusion of the slowest moving fluoride ion, i.e., equal to $E_f/2 + E_m^-$ where E_f is the Frenkel energy and E_m^- is the motion energy for the fluorine vacancy. These results were published earlier. Then we doped the LiF with Mg^{++} and studied the creep. According to the law of mass action (assuming only single vacancies are present), since the concentration of lithium ion vacancies in the heavily doped samples now essentially equals the Mg^{++} concentration, the concen-

tration of fluorine ion vacancies should be $\frac{A}{[Mg^{++}]} e^{-E_f/kT}$. The expected activation energy for creep was therefore $E_f + E_m$. We therefore expected a larger activation energy and an inverse dependence on $[Mg^{++}]$, the impurity concentration. Overall, doping was expected to slow down the creep rate which it did. However, the effect (although as large as a factor of 15) was less than expected. The effective concentration of fluorine ion vacancies was greater than expected by this single vacancy model. In our model, we attribute this difference to a decrease in actual concentration of Mg^{++} in solution. Our model assumes that the remainder of the Mg^{++} is bound at charged dislocation jogs. The binding energy for this process is an experimental parameter which is deduced by fitting the data. The general fit of the data with this model is quite good. This work was carried out with Dr. Rao (who is now at Texas Instruments) and has been recently submitted for publication.⁷

REPORTS AND PUBLICATIONS SINCE LAST ANNUAL REPORT

1. C00-3153-115 C.Y. Dunn and Arthur L. Ruoff "First and Second Pressure Derivatives of the Bulk Modulus of Sodium"
Since published in Physical Review B.
2. C00-3153-116 K.J. Dunn and Arthur L. Ruoff "A Comparison of Some Empirical Equations of State of Solids With Theoretical Equations."
Submitted for publication.
3. C00-3153-117 Arthur L. Ruoff "Stress Anisotropy in Opposed Anvil High Pressure Cells"
Submitted for publication.
4. C00-3153-118 Arthur L. Ruoff "Yield Stress Determination as a Function of Pressure at Very High Pressures"
Published in Scripta Metallurgica.
5. C00-3153-119 J. Paul Day and Arthur L. Ruoff "The Variation of the Elastic Constants of Lithium with Temperature and Pressure:
Recently published in Phys. Stat. Solidi. Reprints not yet received.
6. C00-3153-120 D. Nelson and Arthur L. Ruoff "Nonlinear Theory of Plastic Flow and Stress Concentration Around Rigid Spherical Inclusions"
Submitted for publication.
7. C00-3153-121 C.V.S. Narayan Rao and Arthur L. Ruoff "Impurity Effect on the High Temperature Creep of Lithium Fluoride"
Submitted for publication.
8. C00-3153-122 Robert L. Alworth "Investigation of Techniques With Which to Perform Capacitance Measurements at Ultra-High Pressures." M.S. Thesis Cornell University, Ithaca, N.Y. (1974).
9. C00-3153-123 K.Y. Kim and Arthur L. Ruoff "Pressure and Temperature Dependence of the Elastic Moduli of CER-VIT Glass-Ceramic"
Submitted for publication.
10. C00-3153-124 A.L. Ruoff "Yield Stress Determination as a Function of Pressures at Very High Pressures"
Scripta Metallurgica, 8, 1161 (1974).
11. C00-3153-125 K.J. Dunn and A.L. Ruoff "First and Second Pressure Derivatives of the Bulk Modulus of Sodium"
Phys. Rev. B., 10 2271 (1974).