UCRL-11775

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

PROPOSED FRACTURE THEORY OF A DISPERSION STRENGTHENED GLASS MATRIX

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-11775

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

PROPOSED FRACTURE THEORY OF A DISPERSION STRENGTHENED GLASS MATRIX

D. P. H. Hasselman and R. M. Fulrath

April 2, 1965

PROPOSED FRACTURE THEORY OF A DISPERSION STRENGTHENED GLASS MATRIX

D. P. H. Hasselman and R. M. Fulrath

Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering, University of California, Berkeley, California

ABSTRACT

A fracture theory is proposed for a composite system based on a continuous glass matrix. It is hypothesized that hard crystalline dispersions within the glass matrix will limit the size of Griffith flaws and lead to strengthening of the composite. Quantitative relations are derived for the effect of a dispersed phase on composite strength. At low volume fractions of the dispersed phase, the average flaw size is statistically reduced independent of the size of the dispersed particles. At high volume fractions of the dispersed phase, the average flaw size is governed by the average distance between particles dispersed in the matrix. The strength of a composite should, therefore, be a function of the volume fraction of the dispersed phase at low volume fractions and dependent on both the volume fraction and particle size of the dispersed phase at high volume fractions.

For the verification of the above theory, crossbending strength measurements were made on a sodium borosilicate glass containing varying volume fractions of spheroidized alumina over a range of particle sizes.

Values of the average distance between dispersed particles ranged from approximately 15 to 500μ. Good agreement with theory was found. Values of glass surface energy calculated from the experimental data agree well with literature data.

At the time this work was done the writers were, respectively, graduate student research assistant and associate professor of ceramic engineering, Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering, University of California.

I. INTRODUCTION

Calculations of the theoretical strength of brittle solids based on force-distance relationships between atoms suggest values of strength of the order of one tenth of the value of Young's modulus of elasticity.[1]

Observed values of strength of commercial materials generally are less than the theoretical values by two or three orders of magnitude. This huge discrepancy is attributed to the existance of structural flaws within the material which act as sources of weakness. Among the various approaches[2, 3] to determine quantitatively the effect of the presence of flaws on strength, Griffith[3a] calculated the elastic energy stored in the vicinity of an elliptical flaw oriented with the major axis perpendicular to the applied stress and determined the decrease of this energy with increasing flaw size. Equating this decrease of elastic energy with the energy needed to form the fracture surface resulted in the critical stress, i.e., the macroscopic strength (S_o), required for failure. For a flat plate containing an elliptical flaw the expression for (S_o) becomes:

$$S_o = \left(\frac{4\gamma E}{\pi a} \right)^{\frac{1}{2}} \qquad (1)$$

where γ = the surface energy.

E = Young's modulus of elasticity.

a = twice the major axis of the ellipse, i.e., the flaw size.*

---

* The Griffith equation for surface flaws generally is expressed in terms of the flaw depth (a/2) when the specimen is subjected to a uniform tensile stress. In this study cross-bending tests were used on relatively thin specimens. Because of the high stress gradients imposed in this type of test it is the opinion of the authors that the original Griffith equation for a flat plate with an elliptical flaw is more applicable. The flaw size is now the length of the flaw measured along the surface.

The predicted inverse square root relationship between strength and flaw size was confirmed for glasses by a number of investigators.[3a, 4] A rough estimate of the flaw size of a glass can be made by substitution of appropriate values for the physical quantities in equation (1) and solving for a. Taking $S_o = 10^4$ psi, $\gamma = 5 \times 10^3$ erg. cm^{-2} for the surface energy,[5, 6] and $E \approx 10^7$ psi, equation (1) yields a value for the flaw size of the order of 50μ. For a high strength brittle ceramic (such as alumina) the flaw size can be calculated to be of the order of a few microns. The flaw size in glasses, therefore, are considerably larger than those in high strength crystalline ceramics. Although flaw-free laboratory specimens of glass can be manufactured which exhibit near theoretical values of strength, commercial glasses will contain surface flaws due to mechanical handling, abrasion, etc.

It is the purpose of this paper to propose a fracture theory based on the criterion that hard crystalline dispersions within the glass will limit the flaw size which can be produced in the surface. The result of limiting the flaw size will give rise to an increase in strength.

II. THEORETICAL

The effect of the existence of dispersions on the size of flaws distributed statistically throughout the bulk or surface of a glass speciman can be divided into two regions. The first region (hereafter referred to as Region I) is characterized in that the average distance between particles is greater than the flaw size. This condition can be attained with proper volume fractions and particle size of the dispersed phase. However in this region, at least on a statistical basis, the size of the

average flaw will be reduced, the reduction being equal to volume fraction of dispersed phase or:

$$a = a_o (1 - \phi) \tag{2}$$

where a = the flaw size within the composite.

a_o = original flaw size within the glass.

ϕ = volume fraction of the dispersed phase.

Substitution for a in equation (1) and rearranging, the effect of dispersions on the strength (S) of the composite, can be written:

$$S = So(1 - \phi)^{-\frac{1}{2}} \tag{3}$$

At higher volume fractions or smaller particle size, the flaw size as given by equation (2) will be larger than the average distance between particles, i. e., flaw size is now governed by the "mean free path" between particles. This region will be referred to as Region II. A convenient expression for the "mean free path", (d), between spherical particles of uniform radius, (R), distributed statistically throughout a matrix, can be obtained from the expressions given by Fullman[7] and is given by:

$$d = \frac{4R(1 - \phi)}{3\phi} \tag{4}$$

Substitution of d for a in equation (1) yields for the strength (S) in the Region II:

$$S = \left(\frac{3\gamma E \phi}{\pi R (1 - \phi)} \right)^{\frac{1}{2}} \tag{5}$$

The results of expressions (3) and (5) for the effect of dispersion on the strength of a brittle glass matrix can be summarized as follows: In Region I strength is a function of volume fraction only, requiring relatively large volume fractions before an appreciable increase in

strength is obtained. In Region II strength is a function of volume fraction as well as particle size. A plot of strength against the reciprocal square root of the "mean free path" should at high values of "mean free path" be practically horizontal apart from minor deviation as dictated by equation (3). Where the "mean free path" equals the original flaw size, a discontinuity in slope should occur. As the "mean free path" decreases, the plot should follow a straight line passing through the origin. At this point it is of interest to point out the analogy between the theory proposed in the present paper and the theory of dispersion strengthened metals and alloys discussed by Ansell.[8]

III. EXPERIMENTAL

A. Materials

The system selected for the verification of the above theory consisted of a glass matrix containing spherical particles of alumina. The glass used was of the same composition as the D-glass (16% Na_2O, 14% B_2O_3, 70% SiO_2) employed in previous investigations.[9] The coefficient of thermal expansion of this glass is nearly identical to the coefficient of thermal expansion of alumina. Therefore, internal stresses are avoided. The alumina consisted of an alumina powder spheroidized in a D.C. plasma jet. The spheroidized powder was separated into suitable size fractions by means of an air elutriation. The spheroidized alumina particle size ranged from approximately 15 to 60 μ. Particle size was determined microscopically. During spheroidization some porosity was introduced in the alumina spheres as observed by Das and Fulrath.[10] The porosity determined by pycnometer technique was approximately 8%.

Glass-Al_2O_3 compacts were produced by intimately mixing desired proportions of the glass in powder form (average particle size 3-5μ) with the alumina followed by vacuum-hot-pressing at 725°C for 15 min. Blanks 2 in. diameter by approximately one quarter inch thick were prepared. Volume fraction of spheroidized alumina ranged from 0.055 to 0.475. Composites were made with the matrix "mean free path" ranging from about 14 to 500μ. Compacts containing more than 50 volume percent alumina could not be pressed to full density, presumably due to particle-particle contact. Similarly, fully dense compacts containing alumina spheres of particle size smaller than about 15μ could not be obtained.

After hot-pressing, the compacts were cemented to high alumina porcelain ceramic plates and cut into strength specimens approximately 0.070 in. thick with a precision diamond saw using kerosene as a coolant. The diamond blade thickness was 0.020 in. The blade speed was 2800 surface ft/min. The saw was advanced through the specimen at a rate of approximately 0.35 in. per minute. The saw cut was made through the compact as well as the underlying ceramic plate. In this manner chipping of the edges of the strength specimens was avoided. After cutting the strength specimens were removed from the plate and any remaining cement removed with ethyl alcohol. Profilometer* measurements of the cut surface gave an rms surface roughness of 20 micro-inches (approximately one half micron) independent of composition and direction along the surface. Microscopic measurements suggested a maximum surface

---

* Type Q, Physicists Research Company, Ann Arbor, Michigan.

roughness ranging from one to two microns. No further surface treatment was given. A surface roughness of 20 micro-inches corresponds to a surface obtained in a wet grinding operation and should assure an adequate number of flaws in the surface. Figure 1 shows a typical as-cut surface of a glass specimen.

Crossbending strength measurements were made using 4-point loading and a 3/4 in. span. Specimens were loaded to failure in approximately 20 sec. Specimens were loaded so that the diamond sawed surface was stressed. For most compositions 30 or more data points were obtained.

In order to render visible the Griffith flaw, the lithium ion exchange process described by Ernsberger[11] was used. Heating a glass containing sodium ions in a eutectic mixture of KNO_3-$LiNO_3$ causes an exchange between the sodium and lithium ions. Due to the smaller size of the lithium ions, this creates a tensile stress in the surface. Moistening the glass, catalyses the propagation of cracks--the resulting cracks being representative of or originating at the original Griffith flaw. In order to see the results of cracks in the present material more clearly, the aqueous-HF etch used by Ernsberger was eliminated and a gold plating was substituted to increase the reflectivity of the surface.

B. Experimental Results

Table I. lists the mean values of crossbending strength and their standard deviations for the various compositions and particle sizes. Original glass strength was 14,700 psi. Figure 2 shows the values of strength plotted against the reciprocal square root of the calculated "mean free path". These results agree with those predicted. The

division between Region I and II was obtained by drawing a horizontal line from the original glass strength to the straight line describing Region II. This results in a value of $d^{-\frac{1}{2}}$ of 0.158 or a flaw size of approximately 40μ. Values of strength of composites with "mean free path" greater than 40μ then fall in Region I, as shown in Fig. 3, which illustrates strength plotted against volume fraction.

Considerable difficulty was encountered in revealing the Griffith flaws by means of the lithium ion exchange. Generally, the cracks could not be distinguished from the general background of the surface markings due to the diamond sawing. It was found however that with partial oblique light, cracks in the surface could be made visible due to reflection of the incident light at cracks oriented more or less perpendicularly to the incident light as shown in Figs. 4a and 4b. Figure 4a shows normal illumination, while Fig. 4b shows the same area under oblique lighting. Figure 5 shows the same phenomena in a composite containing 42.3 volume percent of 42μ alumina spheres. Much better results were obtained with specimens which were first polished to eliminate all other surface markings followed by the lithium ion exchange. Figures 6a, b, and c show the Griffith cracks in glass containing 0, 10.9, and 42.3 volume percent alumina having calculated values of "mean free path" of ∞, 81, and 13.5 microns, respectively. The cracks in Fig. 6c do not appear to be as wide as those in Fig. 6a and b. This is thought to be due to the constraining effect of the alumina particles. The sample of Fig. 6b with a "mean free path" of 81μ, lies in Region I and the figure clearly illustrates the partial limiting of the flaw size. Similarly the sample of Fig. 6c lies

in Region II and illustrates the complete limiting of the flaw size by the dispersed particles.

Figure 7 shows a fracture surface. Crack propagation appears to take place preferentially through the glass matrix. The alumina spheres appear to offer considerable resistance to crack propagation.

IV. DISCUSSION

The experimental results as illustrated in Fig. 2 appear to be in agreement with the hypothesis advanced in this paper. The experimental results in Region II seem to lie on a straight line through the origin in support of the validity of equation (5).

The experimental values for strength in Region I, as shown in Fig. 3, all are less than predicted by equation (3). Only at higher volume fractions does a smooth curve drawn through the experimental points appear to be parallel to the predicted curve. The validity of equation (3) appears in doubt. However, it is felt that this discrepancy, at least in part, can be attributed to stress concentration near the dispersed particles, which arise due to the differences in elastic properties of the two phases. This is being investigated currently and will be the subject of discussion in a future report.

It is of interest to note that for the experimental data for strength the coefficient of variation of all composites is less than the coefficient of the glass itself. With a few exceptions, the coefficient of variation generally decreases with increasing volume fraction of dispersions. This suggests that this type of composite can be employed in industrial design with a greater degree of reliability. A lower coefficient of variation (for strength) for multiphase systems was also observed by others.[12]

The presence of some porosity within the dispersed spheres does not appear to have affected the results for strength. If the pores had been responsible for failure, the addition of the dispersions would have caused a decrease in strength, in contradiction with observation.

It appears unfortunate that with the hotpressing technique used for the manufacture of the specimens, that composites with matrix "mean free path" less than about 15μ could not be produced. Smaller "mean free paths" would have allowed the investigation of strength behavior in Region II over a wider region of stress. However, other manufacturing techniques which may be suggested will have the disadvantage of less control over the final microstructure, introducing uncertainties in the values of "mean free path".

The actual value to be used for surface energy when applying the Griffith criterion to glass always presents some difficulty as to whether one should use the thermodynamic surface free energy or the surface energy found in crack propagation studies. The present study allows an estimate of the surface energy applicable to the glass used. Examination of equation (5) reveals that the surface energy (γ) can be calculated from the slope of the data in Region II as shown in Fig. 2 by means of:

$$\gamma = \frac{\pi (\text{slope})^2}{4E}$$

Substitution of the appropriate value for E[9b] yields a surface energy of approximately 4,000 ergs. cm^{-2}, in good agreement with values reported in the literature.[5, 6]

It is of interest to note that the size of the cracks produced by the lithium-ion exchange process, as shown in Fig. 6a, are approximately

equal to the flaw size calculated from equation (1). It appears, therefore, that at least for the present glass and the ion-exchange treatment, that the cracks do represent the Griffith flaws and are not necessarily flaws enlarged by the ion exchange treatment. The results shown in Figs. 6a, b, and c clearly illustrate the effect of dispersions on flaw size in support of the theory advanced in this paper.

It should be pointed out that the results obtained in the present study presumably are valid only for the range of values of "mean free path", particle size and levels of stress investigated. At higher values of stress other types of flaws may become operative, such as those which may exist within the dispersed phase. For flaws within the dispersed phase, strength would be a function of particle size only and independent of volume fraction. Because of the relatively large flaw size, the theory and results of this investigation from a practical viewpoint appear to be applicable to glasses only. Other brittle matrices, such as high strength dense alumina, have relatively small flaw size ($\approx 1\mu$), making it difficult to select a composite system which would reduce the size of these small flaws.

It is suggested here that the fracture behavior of many industrial ceramics containing appreciable fractions of a glassy phase may be governed by the theory outlined in this paper.

V. SUMMARY AND CONCLUSION

A fracture theory is presented for a glass matrix containing a dispersed phase of crystalline particles, based on the hypothesis that the presence of the dispersed phase limits the possible size of the Griffith

flaws. Expressions are derived for the strength of the composite in terms of volume fraction and particle size. The theory is supported by experimental values for strength obtained for a sodium borosilicate glass containing a dispersed phase of spherical alumina particles. Values for the fracture surface energy for the glass calculated from the experimental data agree with literature values.

ACKNOWLEDGMENT

The authors are grateful to Messrs. Parker and Rossi for many helpful discussions and Frease and Dahl for technical assistance.

This work was done under the auspices of the United States Atomic Energy Commission.

REFERENCES

1. a I. Naray-Szabo and J. Ladik, "Strength of Silica Glass," Nature, 188, 226-227 (1960).

   b W. B. Hillig, "Sources of Weakness and the Ultimate Strength of Brittle Amorphous Solids," pp. 152-194 in Modern Aspects of the Vitreous State, Vol. 2. Edited by J. D. Mackenzie. Butterworths, Washington, 1962. 260 pp.

   c J. J. Gilman, "Strength of Ceramic Crystals," pp. 79-102 in Mechanical Behavior of Crystalline Solids. NBS Monograph 59, U. S. Dept. of Commerce, 1963. 113 pp.

2. C. E. Inglis, "Stresses in a Plate Due to the Presence of Cracks and Sharp Corners," Trans. Inst. New Archit., London, 55, 219-241 (1913).

3. a A. A. Griffith, "Phenomena of Rupture and Flow in Solids," Phil. Trans. Roy. Soc., A221 [4] 163-98 (1920); abstracted in J. Am. Ceram. Soc., 4 [6] 513 (1921).

   b S. Timoshenko and J. N. Goodier, Theory of Elasticity, 2nd ed., p. 161. McGraw-Hill Book Co., New York, 1951. 506 pp.

4. a J. P. A. Tillet, "Fracture of Glass by Spherical Indenters," Phys. Soc. Lond. Proc. B., 69B, 47-54 (1965).

   b W. C. Levengood, "Effect of Origin Flaw Characteristics on Glass Strength," J. Appl. Phys., 29 [5] 820-826 (1958).

   c R. E. Mould and R. D. Southwick, "Strength and Static Fatigue of Abraded Glasses under Controlled Ambient Conditions, I., General Concepts and Apparatus," J. Am. Ceram. Soc., 42 [11] 542-47 (1959).

5. F. C. Roesler, "Brittle Fractures near Equilibrium," Proc. Phys. Soc. (London), 69 [442B] 981-92 (1956); Ceram. Abstr., 1957, April, p. 82d.

6. E. B. Shand, "Fracture Velocity and Fracture Energy of Glass in Fatigue," J. Am. Ceram. Soc., 44 [1] 21-26 (1961).

7. R. L. Fullman, "Measurement of Particle Size in Opaque Bodies," Trans. AIME, 197, 447-52 (1953).

8. C. S. Ansell, "Mechanical Properties of Two-Phase Crystalline Materials," pp. 325-50 from: High Temperature Technology, Proc. of an International Symposium on High Temperature Technology. Butterworths, Washington, 1964. 598 pp.

9. a P. L. Studt and R. M. Fulrath, "Mechanical Properties and Chemical Reactivity in Mullite-Glass Systems," J. Am. Ceram. Soc., 45 [4] 182-88 (1962).

b D. P. H. Hasselman and R. M. Fulrath, "Effect of Small Fraction of Spherical Porosity on Elastic Moduli of Glass," J. Am. Ceram. Soc., 47 [1] 52-53 (1964).

c D. P. H. Hasselman and R. M. Fulrath, "Effect of Alumina Dispersions on Young's Modulus of a Glass," scheduled for April issue of J. Am. Ceram. Soc.

10. A. R. Das and R. M. Fulrath, "Liquid Solid Transformation Kinetics in Al_2O_3," in Proc. of 5th International Symposium on the Reactivity of Solids. Elsevier Publishing Co., Amsterdam, in press.

11. a F. M. Ernsberger, "Andrade-Tsien Cracks and the Detection of Griffith Cracks in Glass," Physics and Chemistry of Glasses, 1, [1] 37-38 (1960).

b F. M. Ernsberger, "A Study of the Origin and Frequency of Occurrence of Griffith Microcracks on Glass Surfaces," pp. 511-24 in Advances in Glass Technology-Technical Papers of the Sixth International Congress on Glass, July 1962. Plenum Press, Inc., New York. 639 pp.

c F. M. Ernsberger, "Current Status of the Griffith Crack Theory of Glass Strength," pp. 57-75 in Progress in Ceramic Science, Vol. 3. Edited by J. E. Burke. Perfoman Press, 1963.

12 a W. B. Crandall, D. H. Chung, and T. F. Gray, "The Mechanical Properties of Ultra-Fine Hot-Pressed Alumina," pp. 349-79 in Mechanical Properties of Engineering Ceramics. Edited by W. W. Kriegel and H. Palmour III. Interscience Publishers, New York, 1961. 646 pp.

b D. P. H. Hasselman and P. T. B. Shaffer, "Factors Affecting Thermal Shock Resistance of Polyphase Ceramic Bodies," WADD-TR-60-749, Part II, April 1962.

Table I. Crossbending Strength of Sodium Borosilicate Glass Matrices Containing Dispersed Spherical Alumina Particles (psi x 10^{-4}) (Glass Strength = 14,700* psi)

Alumina particle size (microns)	Volume fraction Al_2O_3 (ϕ) 0.055	0.109	0.216	0.320	0.423	0.475
60+	--	1.32 (10.2)	1.32 (5.6)	1.41 (5.9)	1.60 (5.3)	1.69 (5.4)
51+	1.44 (8.1)	--	1.31 (6.3)	1.38 (5.6)	1.60 (6.4)	1.68 (5.1)
42+	--	1.32 (8.4)	1.28 (9.0)	1.39 (6.8)	1.60 (6.9)	1.72 (4.4)
32+	--	1.38 (9.4)	1.35 (8.2)	1.56 (10.8)	1.89 (4.9)	2.10 (10.6)
25++	--	1.36 (10.0)	1.33 (6.8)	1.58 (7.8)	1.92 (4.9)	2.12 (9.3)
21++	--	1.54 (11.6)	1.56 (9.1)	1.82 (7.6)	2.16 (6.1)	2.36** (3.7)
15++	--	1.46 (5.3)	1.67 (5.3)	2.06 (5.2)	2.53 (6.5)	--

Numbers in parenthesis represent coefficient of variation (percent).

* Coefficient of variation 12.7%.

\+ Particle size range, approximately ± 10%.

++ Particle size range, approximately ± 15%.

** Average of six specimens. All other strength values average of approximately thirty specimens.

FIGURE CAPTIONS

Fig. 1 Typical as-cut surface of a glass specimen.

Fig. 2 Experimental data for strength plotted against reciprocal square root of "mean free path".

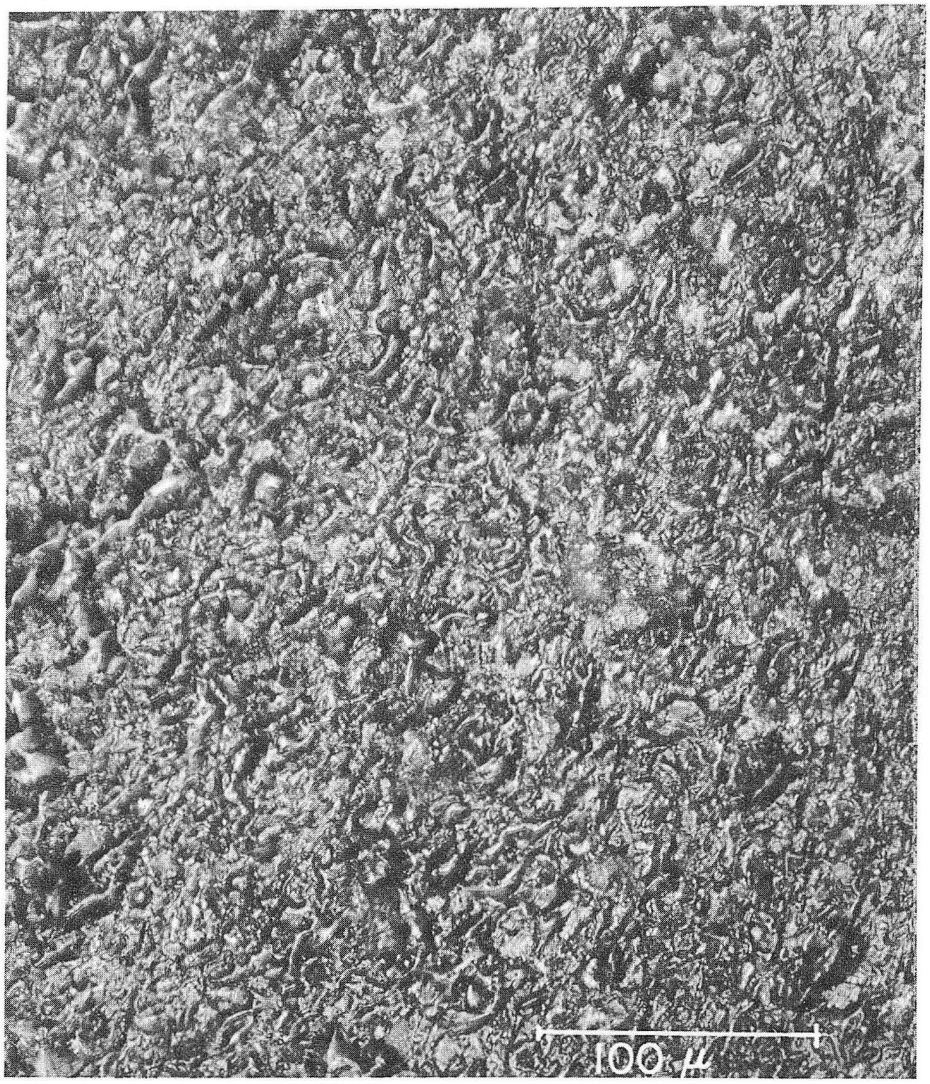
Fig. 3 Experimental data for strength in Region I as a function of volume fraction dispersions.

Fig. 4 Griffith cracks in relatively smooth surface of an as-cut glass specimen under conditions of: a. normal illumination, b. partially oblique illumination (x 260).

Fig. 5 Griffith cracks in specimens composed of glass matrix containing 42.3 volume percent of 42μ diameter alumina spheres. Partially oblique illumination (x 260).

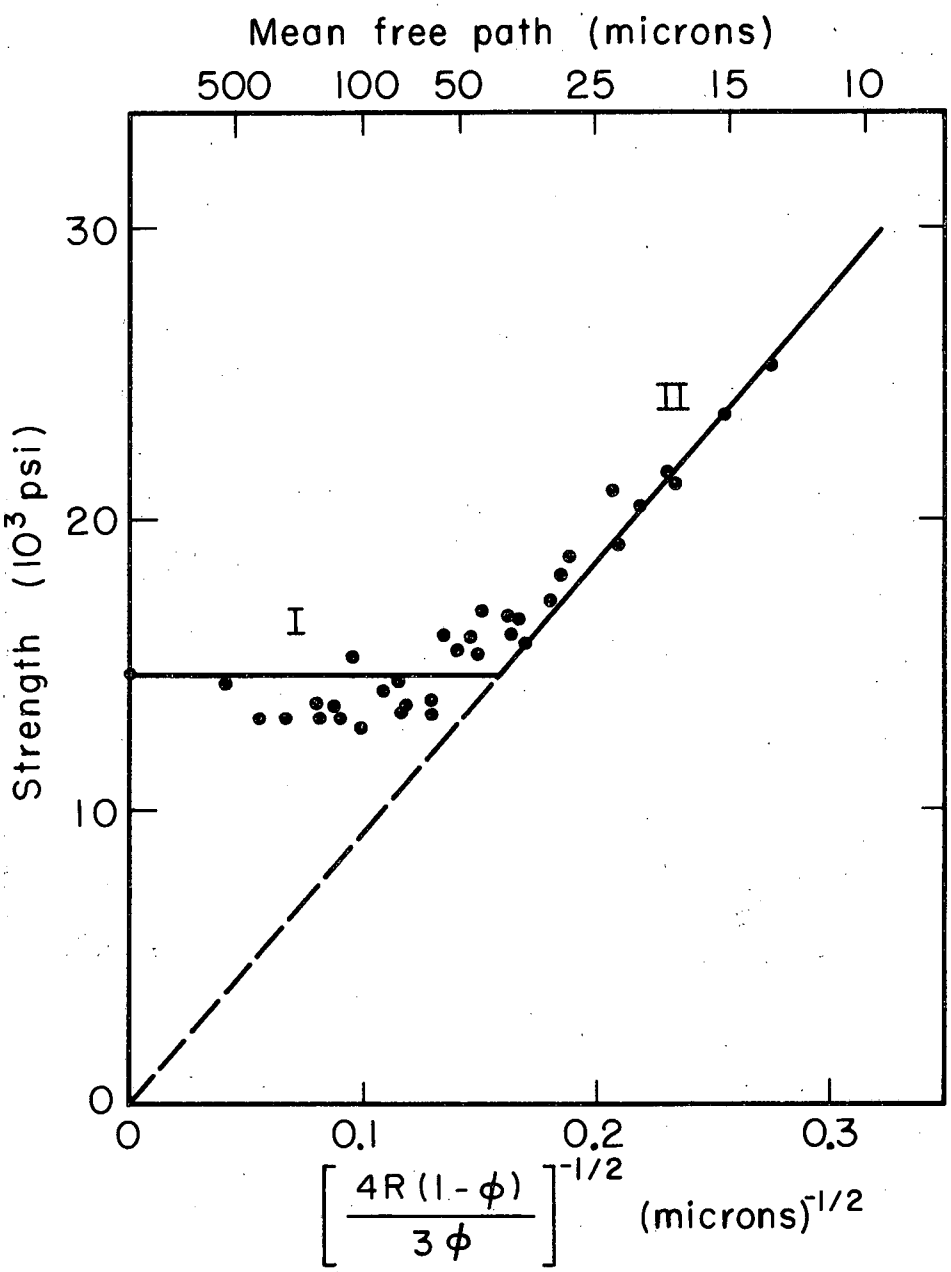
Fig. 6 Griffith cracks in polished surface of glass matrix containing a: 0, b: 10.9, and c: 42.3 volume percent 15μ diameter spherical alumina.

Fig. 7 Fracture surface of glass matrix containing 32.0 volume percent of 32μ diameter alumina spheres (x 260).



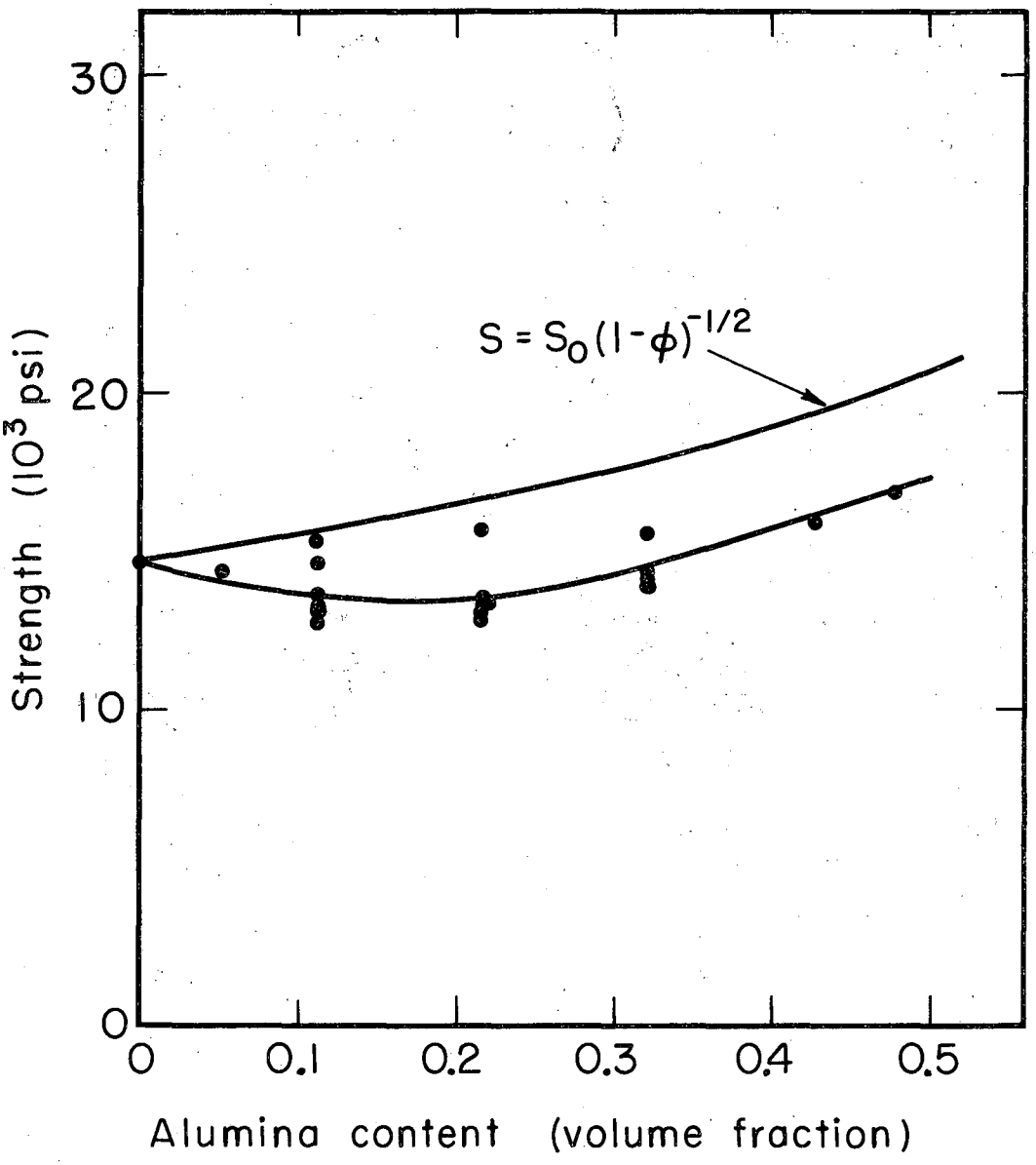
ZN-4855

Fig. 1



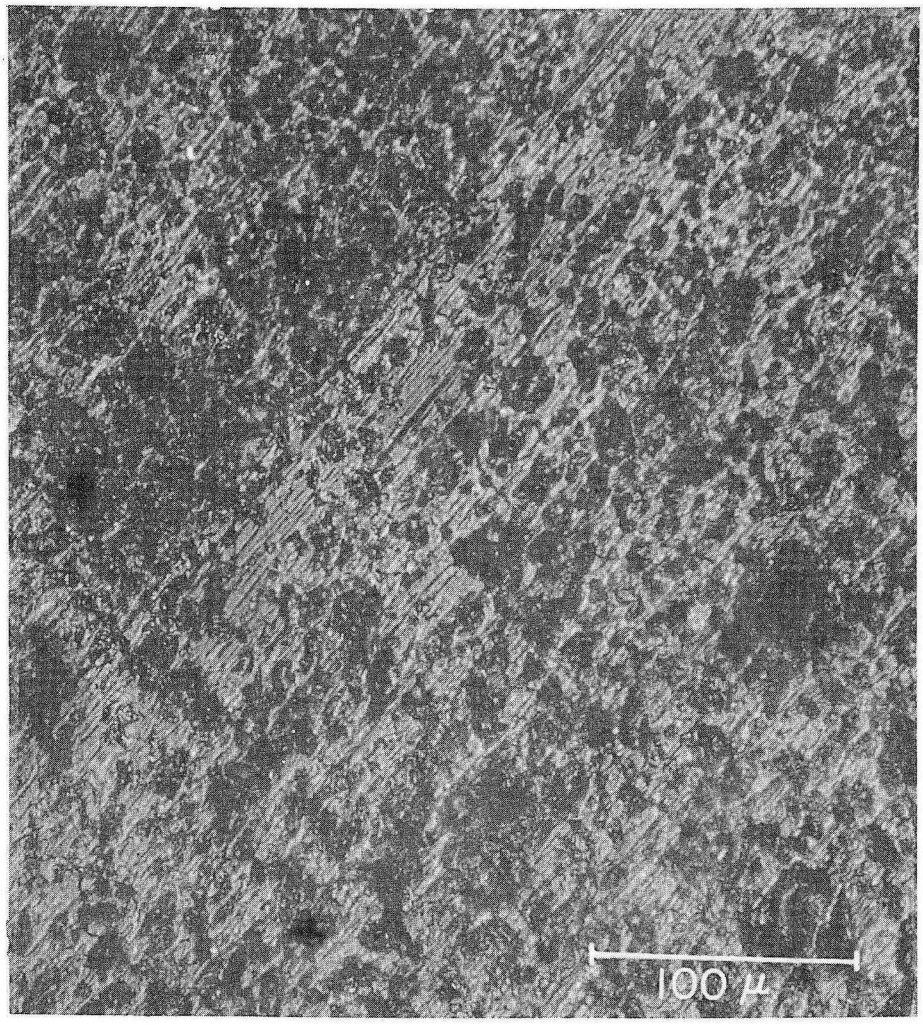
MUB-4611

Fig. 2



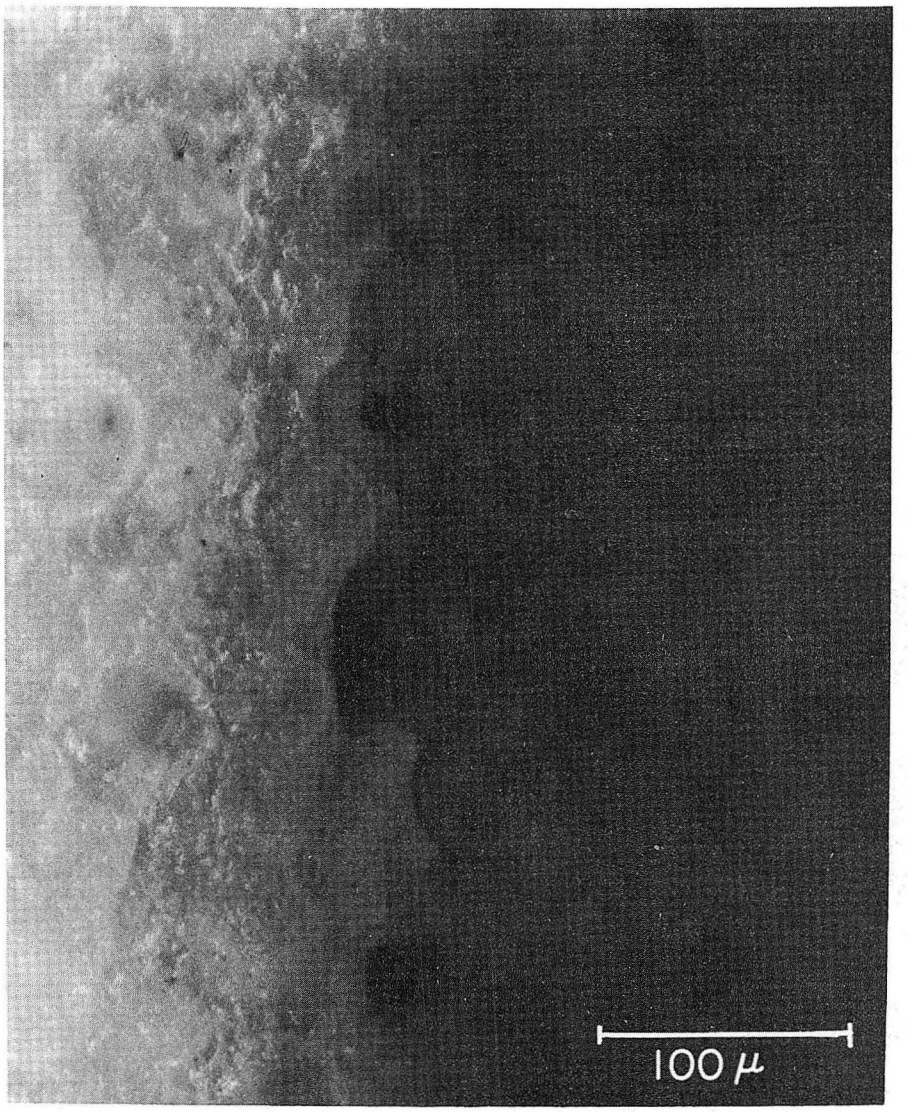
MUB-4609

Fig. 3



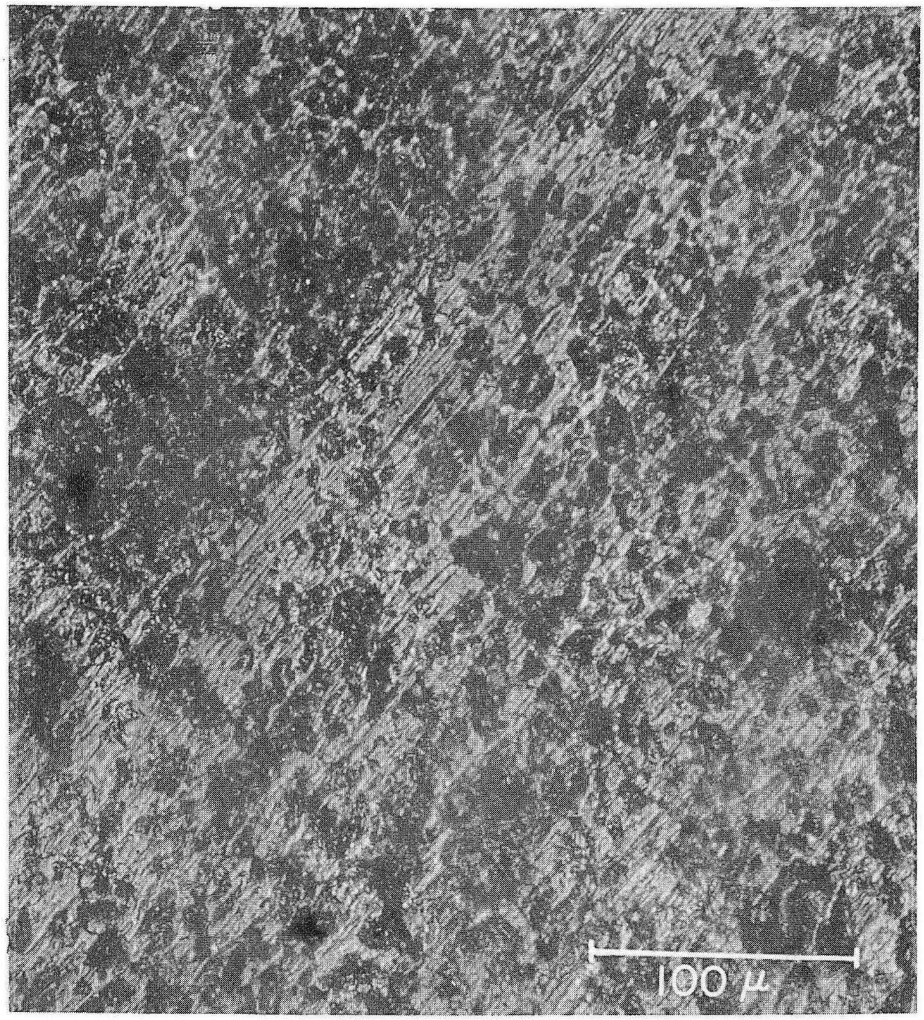
ZN-4856

Fig. 4



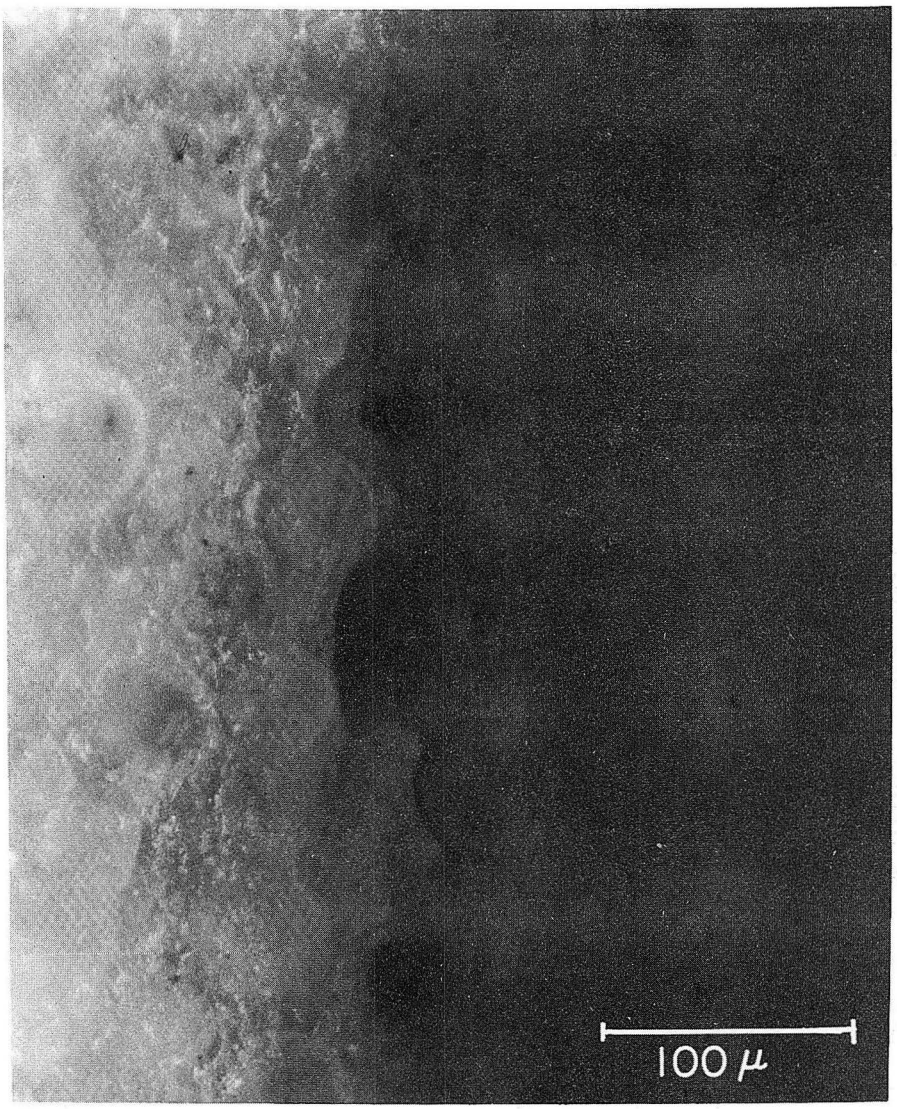
ZN-4857

Fig. 5



ZN-4856

Fig. 4



ZN-4857

Fig. 5

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.