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THE CHARACTERIZATION OF THE MATRIX OF BRITTLE MATRIX COMPOSITES

J. F. Holzgraf and R. M. Fulrath

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

ABSTRACT

A soda borosilicate glass was prepared in four different ways to vary its water content. Uniaxial bend strengths of the glasses and of brittle matrix composites prepared from the glasses are reported as a function of water concentration.

Abraded and as-sawn glass and composite strengths decreased with decreasing water content. The effect of the water on the glass structure and abrasion characteristics is discussed in relation to the strength.

I. INTRODUCTION

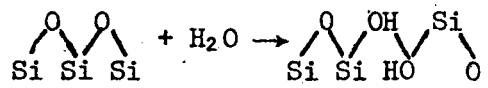
The study of the strength of brittle matrix composites has been investigated extensively by Fulrath and his co-workers.[1-5] They have chosen one general system for study in order to deal effectively with the interrelated variables. This system has been tungsten, alumina, or nickel microspheres embedded in soda borosilicate glass matrices. From this work, four variables have been shown to effect the composite strengths. They are (1) the relative size and vol. % of the dispersed phase, (2) the bonding characteristics between the dispersed phase and the matrix, (3) the difference in the thermal expansion of the matrix and the dispersed phase, and (4) the difference in the elastic properties of the matrix and dispersed phase.

The system used in this study was Al_2O_3 microspheres of the same size and vol. % dispersed in a soda borosilicate glass of the same thermal expansion as that of Al_2O_3. This insured that each of the above four variables was held essentially constant. The largest variable of a single glass composition was found to be the amount of hydroxyl ions in the glass.

Several investigators have studied the effect of chemically absorbed water on the structure and physical properties of glasses. Shölze[6] proposes that water enters the glass by the reaction

$$H_2O_{(g)} + O^{-2}_{(melt)} = 2(OH)^{-}_{(melt)} \qquad (1)$$

This breaks up the silica structure as shown in the reaction



(2)

As a natural consequence of these structural changes, the viscosity, density, and nearly all other physical properties change to some extent. These changes were discussed by Shölze,[6] and Heatherington and Jack.[7]

Infrared spectroscopy has been shown to be an effective quantitative tool in determining water contents in glass. Specifically in a soda borosilicate glass an absorption peak occurs at 2.75 microns which is attributed to the Si-OH stretching vibration (Fig. 1). Using this peak and the Beers-Lambert equation

$$\ln \frac{I}{I_o} = - \varepsilon CX \qquad (3)$$

I = transmitted intensity

I_o = initial intensity

X = optical path length (cm)

a water concentration, c, can be determined. Because the extinction coefficient, ε, is not available for all glasses, a value of 56 ℓ/mole H_2O-cm was used which was determined by Gätz[8] for a Na_2O-CaO-SiO_2 glass of nearly the same SiO_2 concentration of the glass used in this study.

II. EXPERIMENTAL PROCEDURE

A. Materials

D-glass with a composition (14% B_2O_3, 16% Na_2O, 70% SiO_2) was chosen as the matrix in this study because its thermal expansion nearly matches that of Al_2O_3. Four methods of preparation were used to vary the water content. They were:

(1) Melting and firing of boric acid, Na_2CO_3 and silica sand in a platinum crucible in air at 1350°C for 2 hr.

(2) Melting and firing of anhydrous borax, Na_2CO_3, and silica sand in a platinum crucible in air at 1350°C for 2 hr.

(3) Vacuum remelting of (2) in a vitreous carbon crucible at 1200°C for 1/2 hr.

(4) Mixing the crushed powders of (1) and (2) in a 50-50 wt % mixture.

To insure effective mixing with the alumina microspheres, the glass was then ball milled for 6 hr. which gave a glass particle size comparable to that of the Al_2O_3 spheres.

The Al_2O_3 microspheres were prepared in a R-F induction plasma unit. The raw material was Norton 38-500 abrasive grain. The spheroidized Al_2O_3 was separated with an Allen Bradley sonic sifter into a -20+10 μm size range.

The procedure for hot-pressing the glasses and the composites was identical. Composites were prepared from 60 vol. % glass and 40 vol. % Al_2O_3. The powders were mixed thoroughly to eliminate any powder conglomeration and then heated at 400°C for 1 hr. in air. This was to insure that there were no differences between the surface absorbed water

on the hot-pressed glasses and composites. The powder was then placed immediately in a graphite die and evacuated in the hot press. Graphite dies were all lined with .005 in. thick Grafoil* sheet to insure easy die release as well as minimum die wear.

The glasses were hot pressed from 630-680°C and the composites from 700-740°C. This depended on where the glass powders or glass and alumina powder mixtures reached a sufficiently low viscosity for hot pressing a theoretically dense compact. A pressure of 1000 psi was applied at temperature and held for 10 min. The final specimen size after hot pressing was 2 in. in diameter and 1/4 in. thick.

The surfaces of the hot-pressed discs were ground off with a 30 μm diamond wheel and mounted on graphite blocks for sawing. The saw blade used was a Di-Met model (D200-A100-MB 1/8) with an outside diameter of 4 in. and a thickness of 0.020 in. Sawing was done parallel to the hot-pressed direction. Strength bar sizes were all approximately 0.080 in. by 0.25 in. with varying lengths. Density and thermal expansion samples were also cut from the hot-pressed discs. The density of all the glasses measured by an Archimedes technique in 200 proof ethyl alcohol was 2.46 gm/cc. Within experimental error the thermal expansion coefficient of all the glasses was found to be 8×10^{-6} in/in°C.

B. Mechanical Testing and Infrared Measurements

Uniaxial strengths were measured on a four point loading device with an overall span of 3/4 in. and a supporting span of 1/4 in. Time to fracture of glass specimens was about 20 sec. and for the composites

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* Product of Union Carbide.

about 60 sec. Abraded specimens were uniformly abraded with 240 grit SiC on a glass plate lubricated with kerosene.

Infrared measurements were made with a Beckman IR-4 spectrometer using a double beam technique with air as the standard. Specimens were cut from hot-pressed discs and mechanically polished on both sides to approximately 0.030 in. thickness.

III. RESULTS AND DISCUSSION

Uniaxial glass strengths are shown in Table I and plotted against water concentration in Fig. 2. Figure 2 shows that (1) the as-sawn and abraded glass strengths increased with increasing water content, and (2) the difference between the as-sawn and abraded strengths increased with increasing water contents.

In the composites, there was a slight difference in the interparticle spacing from composite to composite which would vary the strengths as hypothesized by Hasselman.[1] Therefore, an interparticle spacing (λ) was measured by a statistical line technique described by Nivas.[3] Multiplying the observed strength by $\lambda^{1/2}$ standardizes the different composite strengths to the same interparticle spacing. Figure 3 shows that the standardized composite strengths follow the same trend as the glasses with varying water concentration.

At the start of this investigation it was thought that there would be an increase in the strength of the glasses and composites with decreasing water content, the reason being that the elastic moduli, E, and fracture surface energy, Y, in the Griffith equation

$$\sigma_c = \sqrt{\frac{4YE}{\pi d}} \qquad (4)$$

σ_c = critical stress for failure

d = flaw length

would both increase. From the data it is evident that an increase of E and Y opposes the increasing strength with increasing water contents.

Therefore, elastic modulus and fracture surface energy changes were considered to be small.

It was also postulated that the water content could affect the degree of bonding between the alumina and the glass. Figure 4 is a scanning electron micrograph of a composite fracture surface. This type of fracture was typical for all the composites and showed a good bond (i.e. no pull-outs) in all cases. Also, with the aid of the electron microprobe it was found that the dissolution of Al_2O_3 into the glass was negligible and did not vary with water content. Because a good bond existed in all the composites and the bond was uniform with varying water contents, its effect on the strength was considered negligible.

The scanning electron microscope did reveal some interesting differences in the as-sawn and abraded glass surfaces which could be related to the strength. Figures 5 and 6 show the cutting action of the fine grit saw blade on glasses with varying water contents. Figure 5 shows that the low water content glass was cut by a chipping process which develops large pits and sharp intersections in the as-sawn surfaces. Comparing Fig. 5 to Fig. 6 the sawing action has caused the high water content glass to flow and create large smooth patches on the sawn surface. This suggests that with increasing water content the low temperature viscosity decreases enough so that the heat generated by sawing causes viscous flow.

The abrasion treatment of the SiC is clearly of a different nature than sawing. Figures 7 and 8 show the abraded glass surfaces with high and low water contents. It can be seen that with decreasing water contents the surface appears to be less severely damaged by the abrasion.

This immediately suggests the reason for the increasing difference between the as-sawn and abraded glass strengths with increasing water contents. Apparently as the water content increases, the flaw severity caused by the sawing decreases. This is because the viscous flow absorbs energy of the impacting saw blade, and heat is generated which can heal cracks at the surface. When the sawn surfaces are abraded though, the existing cracks of the high water content glass are extended further than they are in the low water content glass. The simple difference in the change of the average flaw length, d, in Eq. (4) is then the reason for the strength differences.

The composite strengths follow this same line of reasoning, but it is evident that the drop of the as-sawn strength from the SiC abrasion is only 1/4 to 1/2 of that shown with the glasses. This would be reasonable because the microspheres would be expected to inhibit any crack extension past the average interparticle spacing, λ. Also, the severe SiC abrasion would be expected to cause the maximum size of flaws in the composites because the flaws are limited by the dispersed phase. Further analysis of the abraded composite standardized strengths in Fig. 3 show that even when the flaw size should be equal and a maximum there is still a decrease in the strength of the composites with decreasing water contents. This suggests another strength controlling variable.

The observed difference in the viscous behavior of the glasses in Figs. 5 and 6 is an explanation. Irwin[8] has hypothesized that there is a "plastic" (viscous) zone at the crack tip in brittle materials. This zone absorbs energy and increases the strength by decreasing stress concentrations at the crack tip over a material which shows no "plastic"

behavior. It is possible in this system that with increasing water contents the sphere of influence of this "plastic" zone increases and in turn increases the strength.

Finally, because all the samples were broken in air at relatively slow loading rates (20-60 sec), it is possible stress corrosion at the crack tip from the water vapor in the air might vary the strength. Priest and Levy[9] found that in alkali borosilicate glass the corrosion resistance against 20% HCL acid decreased with decreasing water contents of the glass. It would also seem reasonable that attack by water vapor in the air would increase with decreasing glass water contents. This would be due to a change in the thermodynamic equilibrium between the water in the atmosphere which can chemically absorb on the surface and the water content in the glass. This increasing corrosion with decreasing water contents would then account for the drop in strength with decreasing water contents.

The size of the viscous zone and/or the degree of stress corrosion are then logical explanations for the decreasing strength of the abraded glasses and composites with decreasing water content. Priest and Levy's[10] work as well as the low temperature viscosity differences seen in scanning electron micrographs of the as-sawn surfaces give credence to these explanations. More work though is necessary to clarify this point.

IV. CONCLUSIONS

This work has shown that the water concentration in the glasses has a significant effect on the as-sawn and abraded glass and brittle matrix composite strengths. The change in water content also varies the sawing and abrasion characteristics as shown by scanning electron microscope examination.

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Table I. Crossbending strength and statistical data for the composites and the glasses

Glass No.	Water Concentration (Moles H_2O/ℓ)	Glass* Hot-Pressed Temp.(°C)	σ Glass†# as-sawn ($x10^4$ psi)	σ Glass†# Abraded ($x10^4$ psi)	σ Composite†# as-sawn ($x10^4$ psi)	σ Composite†# Abraded ($x10^4$ psi)	γ $(wm)^{1/2}$
1	.0592	620	1.01 (11.7)	.80 (11.2)	-	-	-
2	.0362	640	.93 (10.3)	.78 (5.1)	1.68 (7.3)	1.55 (8.3)	3.12
3	.0013	680	.79 (8.8)	.67 (4.6)	1.53 (2.1)	1.47 (3.8)	3.01
4	.0485	630	1.00 (6.8)	.77 (5.1)	1.94 (2.9)	1.74 (4.9)	2.92

* All composites were hot-pressed 70-80°C above this temperature.

† Number in parentheses is standard deviation (percent of the mean).

\# All strengths represent average of 25 samples. (Two highest and lowest strengths were neglected.)

FIGURE CAPTIONS

Figure 1. Infrared transmittances of glasses 1, 2 and 3.

Figure 2. Uniaxial bend strengths of the glasses as a function of their water concentration.

Figure 3. Standardized uniaxial bend strengths of the composites as a function of their water concentration.

Figure 4. Scanning electron micrograph of a typical composite fracture surface. (~50X)

Figure 5 and 6. Scanning electron micrographs of the as-sawn glass surfaces.

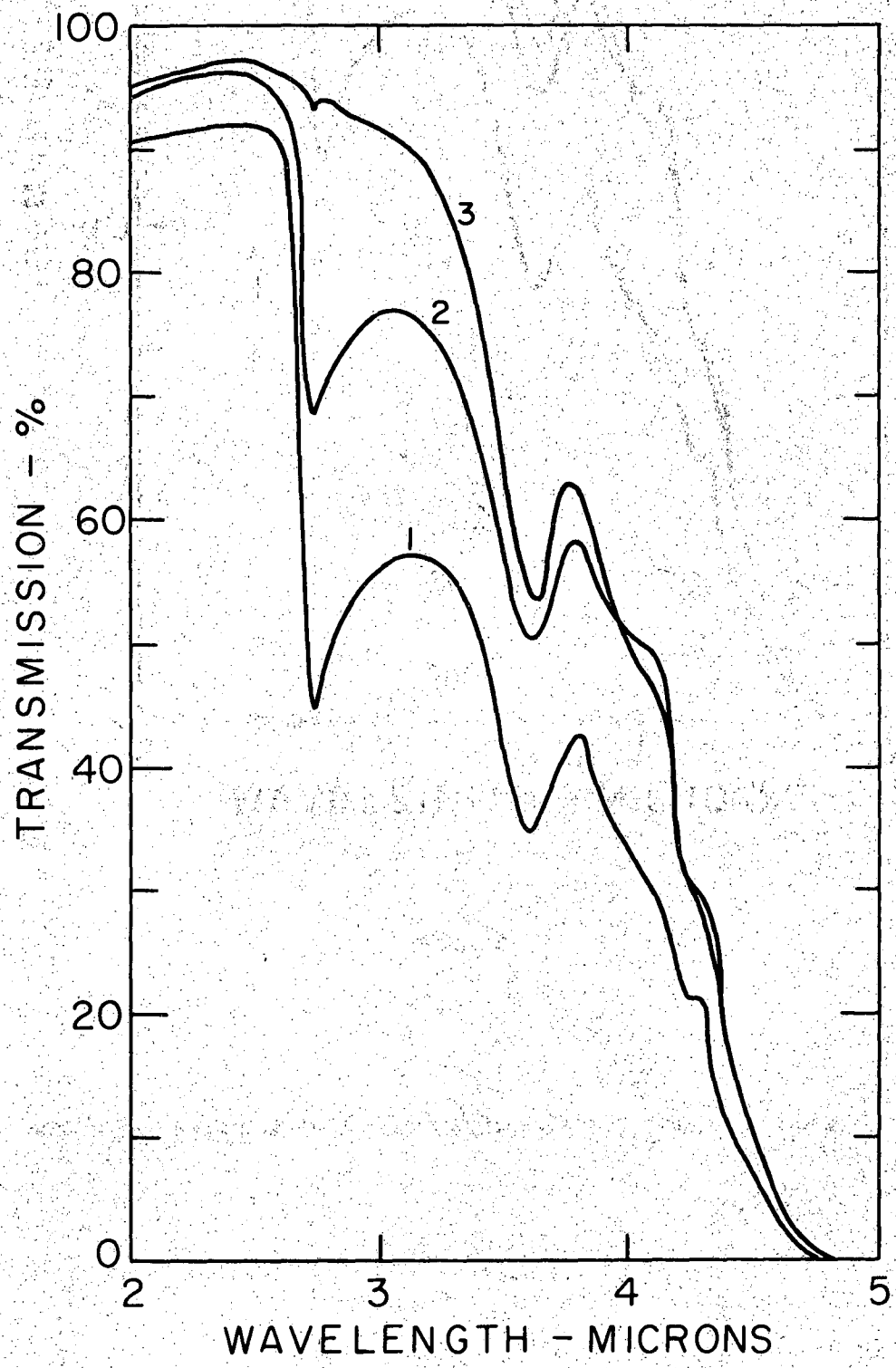
Fig. 5 - .0013 moles H_2O/ℓ (left)

Fig. 6 - .0485 moles H_2O/ℓ (right)

Figure 7 and 8. Scanning electron micrographs of the SiC abraded glass surfaces.

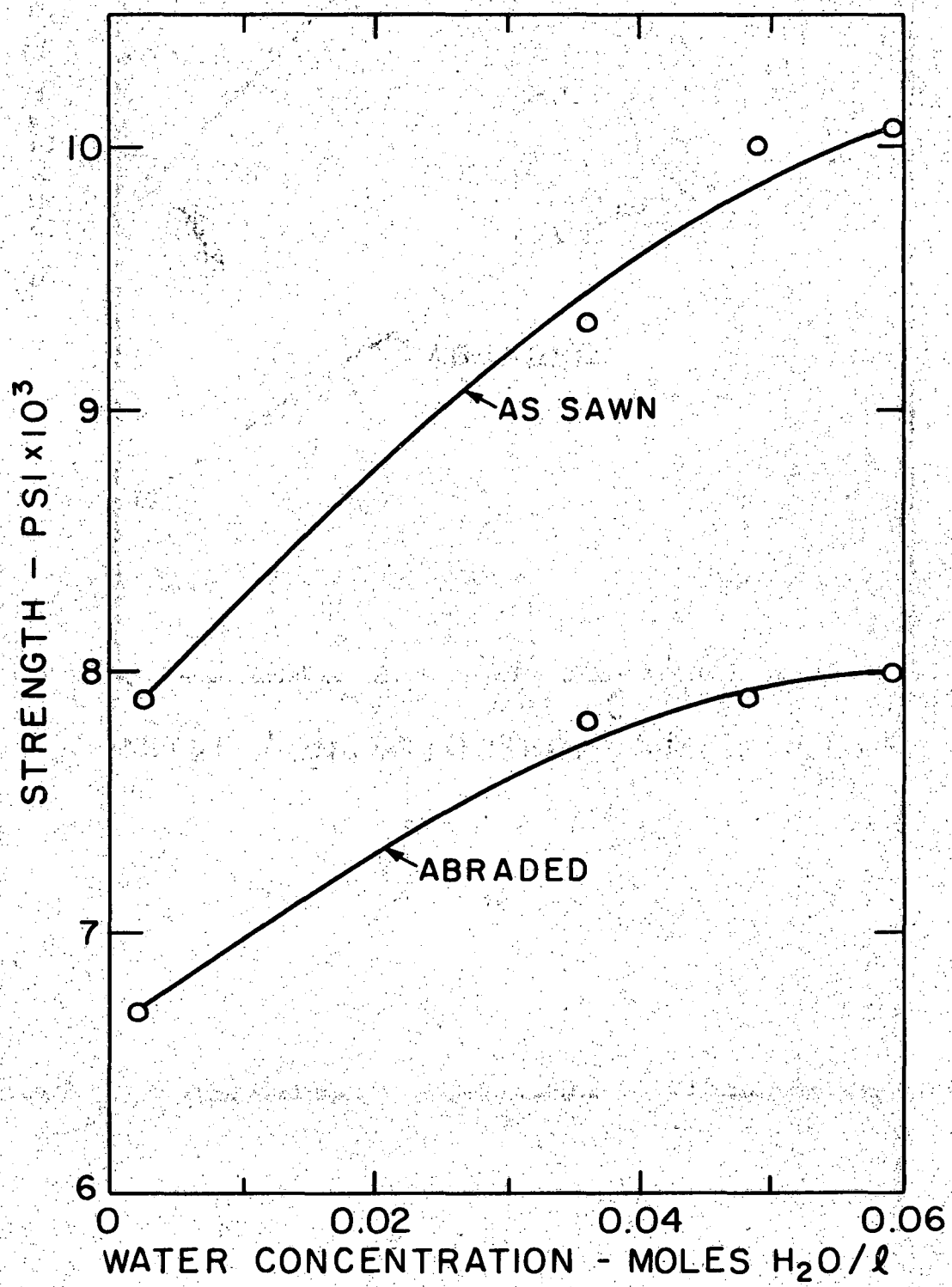
Fig. 7 - .0013 moles H_2O/ℓ (left)

Fig. 8 - .0485 moles H_2O/ℓ (right)



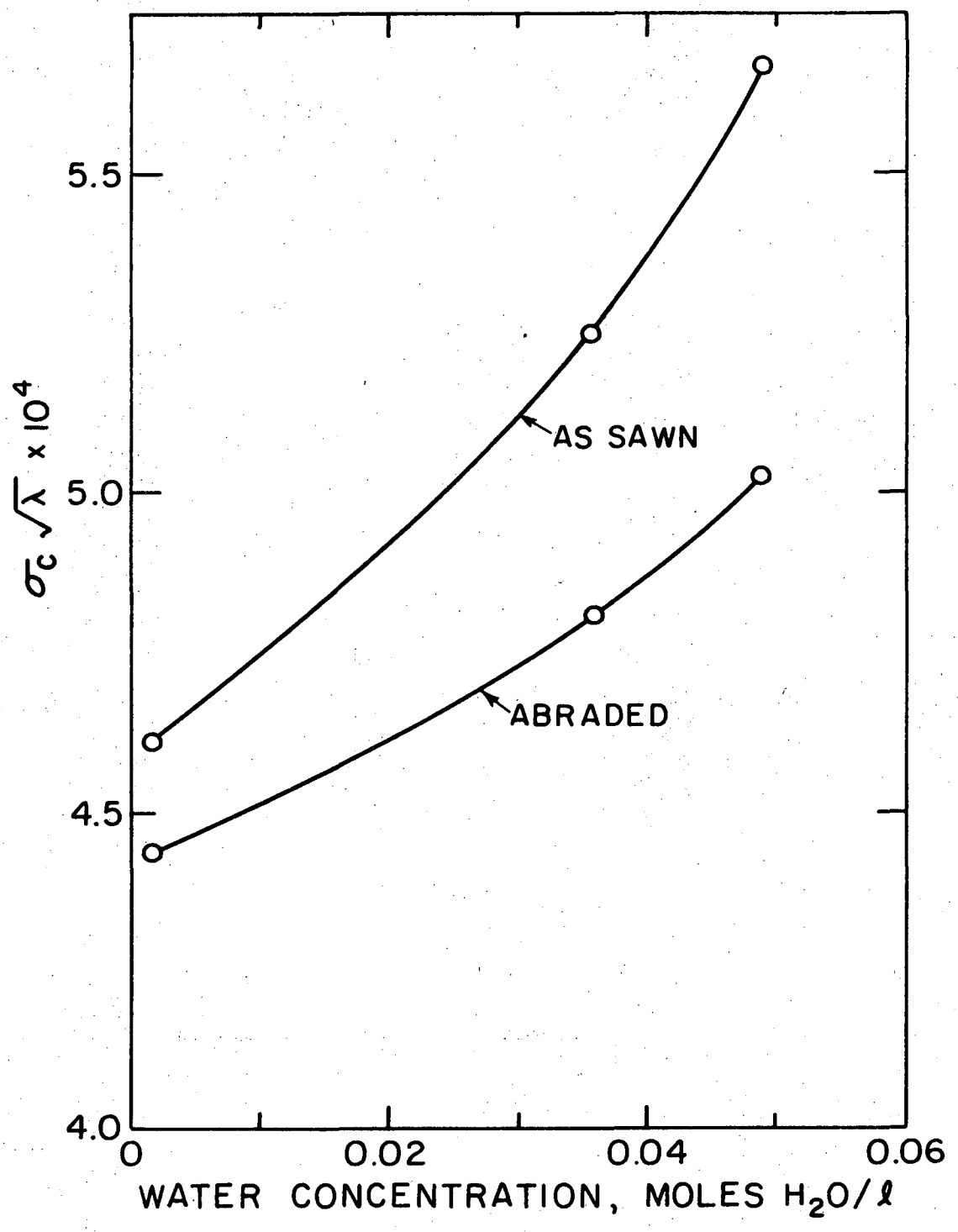
XBL 7010-6705

Fig. 1



XBL 7010-6704

Fig. 2



XBL 7010-6706

Fig. 3

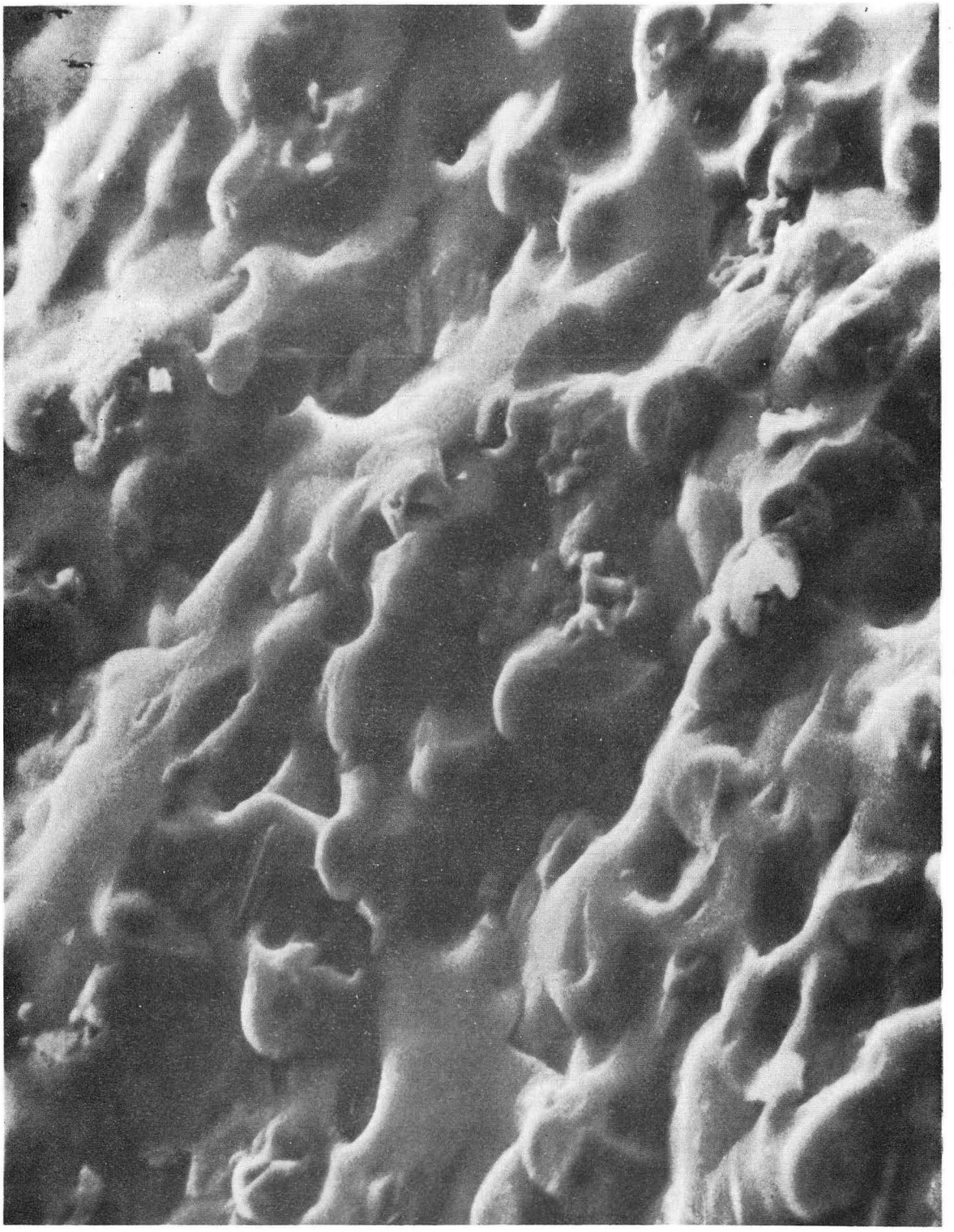


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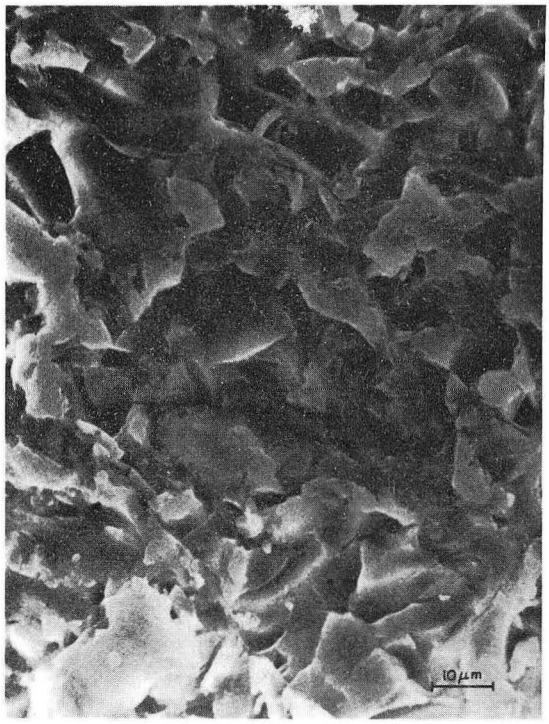
Fig. 4.



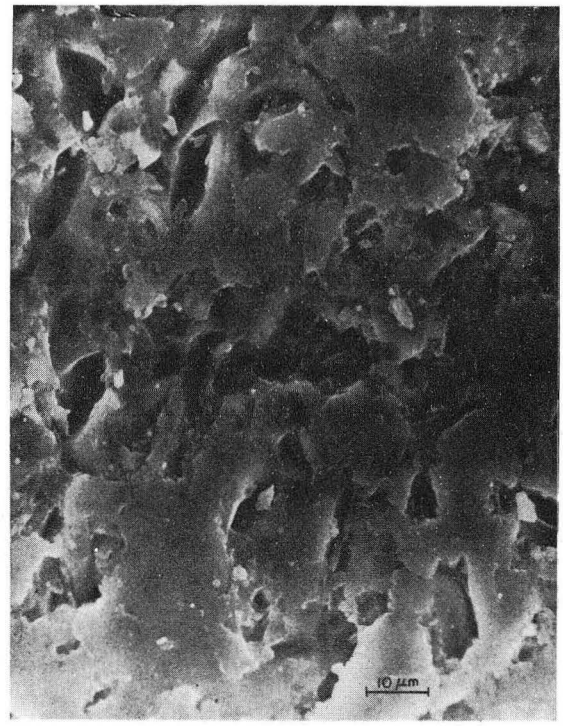


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Fig. 5.

Fig. 6.

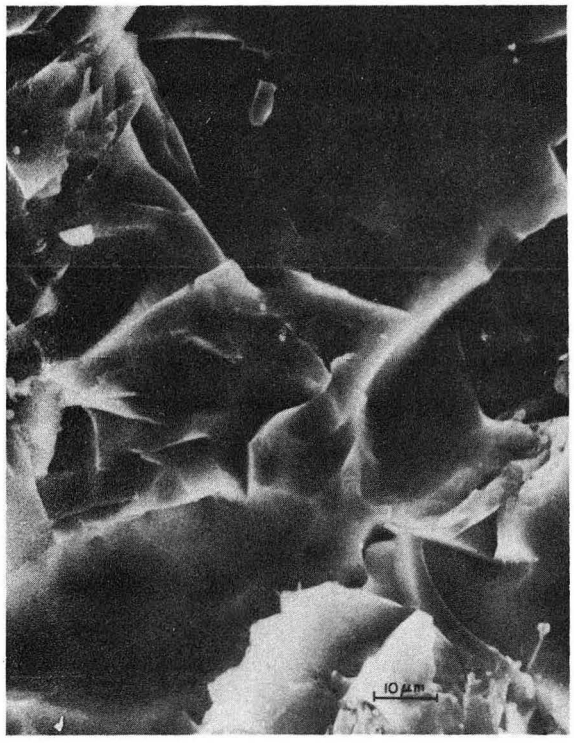

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Fig. 7.

Fig. 8.

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