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COMPOSITE MATERIALS FABRICATION, STRUCTURE, AND PROPERTIES

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I. INTRODUCTION

Composite ceramic systems may be obtained either by intentionally selecting the composition prior to thermal processing or by selective heat treatment of devitrifiable glasses. Other types of composite systems may be constituted to include either a metallic or an organic phase with a ceramic phase or phases. Irrespective of the particular system, the microstructure plays a dominant role in determining the properties. The microstructure of a processed composite may also be used in calculating extensive properties when other methods of obtaining the volume percent of phases present are not available.

Typical types of composite systems are the high-alumina two-phase ceramics, devitrified glass ceramics, filament-wound fiber glass reinforced plastics, and the metal-bonded carbides. The processing employed for the final product in each case plays an important role in the development of the microstructure. Interest in ceramic microstructures has been accelerated during the past several years because of the simpler systems used and better process control developed.

II. COMPOSITE FABRICATION

The electronics industry has led in the increased use of alumina ceramics for structural purposes. Through the industry's acceptance

of ceramic structural components, the early electrical porcelain body containing many phases and with a complex microstructure (Fig. 1) has developed into the sintered single-phase ceramic of nearly theoretical density (Fig. 2). However, the majority of high-alumina ceramics used are not subject to the exacting composition and thermal processing necessary for a dense single-phase ceramic. The general processing scheme still utilizes the formation of a glass at high temperatures to aid densification and produce vacuum tightness. Composition control determines the glass properties such as viscosity, thermal expansion coefficient, and devitrification tendencies. Phase equilibrium diagrams are useful in predicting the volume percent of glass present and its composition at the maximum temperature occurring during the firing process. However, the nonequilibrium conditions that actually exist in the fabrication process require post-processing analysis for guidance as to microstructure control.

Because of the complex nature of ceramic processing, two compositions almost identical chemically may produce microstructures of quite different character. As an example, a mullite body may appear as shown in Fig. 3 or as in Fig. 4. The microstructure as shown in Fig. 3 is probably that developed by heat treating the compacted raw materials until a glassy phase is developed which attacks the mineral constituents used for the formulation of the ceramic. It is apparent that more than one crystalline phase, a glassy phase, and porosity are present. X-ray diffraction substantiates the presence of two crystal phases by giving the diffraction patterns of both mullite and alumina. In Fig. 4 only one crystalline phase, a glassy phase, and porosity are present. Although the chemical composition of the body is close to that shown in Fig. 3,

the raw materials and processing has produced a distinctively different microstructure.

Typical alumina ceramics are produced by a number of techniques. Generally, alumina powders and fluxes or glass formers are finely ground and thoroughly mixed. The fine grinding increases the surface area and subsequent driving force for densification. The forming step which may be slip casting, dry pressing, extrusion, or hydrostatic pressing is followed by sintering at temperatures of 1400 to 1800°C.

The process is adjusted to produce a fine-grained dense ceramic with a minimum glass content. Without the added glass phase or a grain growth inhibitor, discontinuous grain growth may occur at high temperatures. These large grains will affect mechanical properties if a sufficient volume is present. In systems with a definite liquid phase present, the crystalline material will be continually dissolving and precipitating in an attempt to reduce its surface area. The actual area of crystal-crystal boundary developed and liquid-crystal interface formed will depend on the interfacial energy conditions. The shape of the crystal grains will be dependent on crystallographic surface energies. For some systems the crystal shape will be platy, while for others blocky or needle-shaped crystals will develop. Spherical crystals may be produced in some systems if continued solution of the mineral constituents in the glass occurs with no precipitation.

Hot pressing of such systems may reduce grain growth tendencies but introduce preferred orientation if plastic deformation occurs. Also, platy crystals in the presence of a glass may align under a uniaxial pressure.

The metal-bonded carbides follow essentially the same processing steps except for the necessity of atmosphere control. Wetting of the carbides by the liquid metal and solution-precipitation reactions are of equal importance in developing dense structures.

The formation of a multiphase ceramic may be made by completely melting all constituents and forming in the glassy state. Further heat treatment may then be used to devitrify the glass to a ceramic with a high proportion of crystalline material. This technique depends on a large number of nucleation sites uniformly distributed in the glass to give a dense fine-grained body. The variation of composition of the crystalline phase due to zoning and the small particle size has made microstructural and X-ray analysis difficult. The measured properties of these systems do not appear to be too different from similar multiphase ceramics produced by other fabrication techniques.

Filament-wound fiber glass reinforced plastics, although processed at room temperature or slightly above, offer an excellent example of controlled microstructure by processing techniques. The winding of fiber glass strands on a mandrel with specific orientations can allow mechanical properties to vary in specific directions and be optimized for service conditions.[1]

III. COMPOSITE STRUCTURE AND PROPERTIES

Of the systems discussed, it is readily apparent that the microstructure may vary between wide limits. In attempts to analyze the properties of such systems, the general method has been to establish simple models and relate properties to the model. The models are of two general types: First, the model based on spherical inclusions in a continuous

matrix, and second, the model based on a series of slabs (Fig. 5). The attempt is then to vary the volume percent of the phases and predict composite properties from the properties of the individual phases.

It is apparent that such approaches may be successful for some systems but due to specific microstructure fail for others. Kingery[2] has studied thermal conductivity of composite systems in this manner with reasonable success. The thermal expansion of composite systems is another area that has been approached in this manner. However, agreement between predicted and measured properties has not been so successfully demonstrated.

The mechanical properties of composite systems has also been approached by the model approximation. A new variable appears when mechanical properties are discussed, namely, the effect of interfacial bonding between phases. For example, if a composite with no interfacial bonding is formed by a series of slabs as shown in Fig. 5(b), then the tensile strength parallel to the slabs (in the Z direction) would be a function of the tensile strength, elasticity, and volume percent of the two phases. However, perpendicular to the slabs (the X direction) the composite would have zero tensile strength. The introduction of interfacial bonding not only affects the mechanical properties but introduces internal stresses if the thermal expansion coefficient of the phases differ. These microstresses may develop as the composite is cooled from the high temperatures used in the processing.

The complexities of the mechanical properties of composite systems will be demonstrated by examples from studies on idealized systems of glass-crystal combinations.[3-6] These systems were formed by vacuum hot pressing crystal and glass powders at low temperatures. This low

temperature fabrication produced a continuous glass matrix and reduced the tendency for glass-crystal chemical reactions on a macro scale. The glass matrix contained controlled volume percentages of dispersed crystal particles. Further, the crystal particle size and shape in the composite was controlled by the original crystal size and shape used. All strengths reported were for specimens cut from the hot pressed composite with a diamond saw. No attempts to surface finish the specimens were made.

Composite systems made using alumina as the dispersed phase in a glass matrix have demonstrated the remarkable mechanical properties of composite systems. For a reference material glass powders were vacuum hot pressed into a compact of the same density as melted and cast material. These compacts were diamond sawed into specimens for strength measurements. The strength of glass is noted for its sensitivity to surface flaws.[7] The glass exhibited a flexural strength of approximately 6000 psi. On the addition of small (2 to 3 micron) alumina particles into a glass matrix the strength was increased as shown in Fig. 6 to a maximum value of 32,000 psi (an increase of five times). This increase in strength can be hypothesized as being due to the reduction in length of existing microcracks in the glass matrix. This technique of strengthening glass was limited because of porosity introduced when the volume percent of alumina exceeded 50%. The effect of increased porosity in this type of composite system caused the strength to decrease exponentially as the volume percent porosity increased. This is similar to the effect of porosity on crystalline ceramic bodies as discussed by Knudsen.[8]

The question of interfacial bonding and internal stresses was answered by compacting alumina dispersed in glass matrices where the

glass used had higher and lower thermal expansion coefficients than alumina. Strengths were determined in these systems and the magnitude and sign of internal stresses detected by X-ray diffraction techniques.[9] The 2 to 3 micron alumina particles which were platy in shape gave excellent internal stress patterns. The magnitude and sign of the stress determined agreed with the predicted values. Therefore, the interface between the crystal particles and the glass must have developed a bond.

When 50 volume percent alumina particles were dispersed in a glassy matrix the induced internal stress appeared to have little effect on the composite properties. Table I gives the determined flexural strengths for composites in which the matrix has a higher (Glass A), matching (Glass D), and lower (Glass C) thermal expansion coefficient than the included particles. It is apparent that the particle size of the included phase is far more important than the internal stress. This substantiates the earlier hypothesis that the crack length in the glass phase is the controlling factor regarding the strength. As the particle size is increased at constant volume percent of dispersed phase the average path length in the glass phase increases and a decrease in composite strength results.

It is unfortunate that similar studies on composites with brittle crystalline matrices have not been made. It is predicted that similar results would be attained provided the matrix grain size was controlled by the dispersed phase and that interfacial bonding occurred.

Thorium oxide dispersed in glass matrices behaved similarly to alumina even though the particle shape was blocky instead of platy.[10] Mullite crystals dispersed in a glass matrix of matching expansion

coefficient did not increase the strength unless the vacuum hot pressing was carried out at temperatures high enough to form an interfacial bond.[6]

The lack of interfacial bonding in composites was studied by Jacobson[5] using dispersed nickel spheres in glass matrices. A typical microstructure of such a system is shown in Fig. 7. The spheres of nickel appear to be of random size because of the random cross-section of the sphere cut on sectioning. The dark holes are due to the spheres dropping out of the composite.

Nickel metal spheres dispersed in a glass of lower thermal expansion coefficient caused the strength of the composite to decrease as the nickel content was increased (Fig. 8). If the glass had a higher thermal expansion coefficient than that of nickel the nickel particles were mechanically gripped in the glass matrix by the developed radial compressive stresses and the resultant composite behaved as if interfacial bonding had occurred. This is shown in Fig. 8 where the strength of the composite increases with increased dispersed particle content.

To date, detailed analysis of the mechanical strength of composite materials is extremely difficult because of the number of variables associated with the nature of the stress distribution in the composite. However, even though the field appears complex, basic studies are contributing to a better realization of the more important parameters. For composites of brittle materials the minimizing of flaw length by microstructural control appears to be the most fruitful approach to increasing strengths. Interfacial bonding appears to be mandatory where thermal expansion coefficients and microstructure cannot be controlled.

IV. SUMMARY

The processing of composites plays a dominant role in determining the developed microstructure. The analysis of the properties of composite materials based on models, while successful for thermal conductivity and in some cases thermal expansion, is less successful for predicting mechanical strength. The interface between phases in a composite system is the most important parameter in the development of a composite of high strength. Interfaces which are chemically bonded or mechanically formed may improve the strength of composite materials.

ACKNOWLEDGMENT

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Table I. Strength of glass-alumina composites.

All compositions equal volumes of glass and alumina with the glass forming matrix.

Average dispersed particle size (microns)	Glass thermal expansion relative to that of alumina	Flexural strength of the composite system for vacuum hot pressed composites (psi x 10^3)
	Higher	36.1
2.5	Matching	33.8
	Lower	31.0
	Higher	28.7
17.0	Matching	24.8
	Lower	27.0
	Higher	17.2
60.0	Matching	19.6
	Lower	21.1

FIGURE LEGENDS

Fig. 1. Microstructure of a high Al_2O_3 body containing a crystalline phase, a glass phase, and porosity (500X). Courtesy Dr. A.G. Pincus.

Fig. 2. Microstructure of a translucent polycrystalline Al_2O_3 ceramic (500X). Courtesy Dr. A.G. Pincus.

Fig. 3. The microstructure of a mullite ceramic showing two crystalline phases, a glass phase, and porosity (1040X).

Fig. 4. The microstructure of a mullite ceramic containing one crystalline phase, a glass phase, and porosity (870X).

Fig. 5. Two examples of model microstructures.

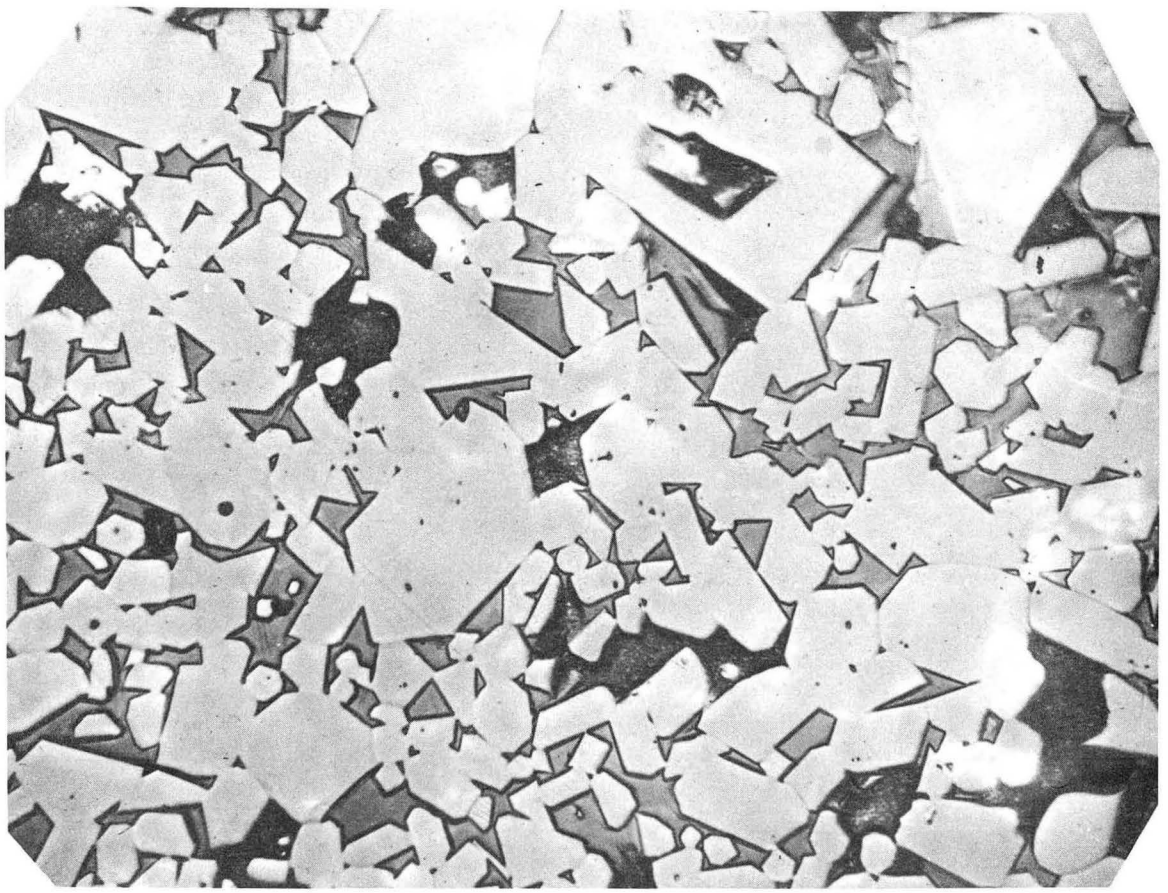
(a) A system of spherical inclusions in a matrix material.

(b) A system of parallel slabs of two different materials.

Fig. 6. The variation in composite strength as a function of dispersed phase content. Two to three micron alumina particles dispersed in a glass of matching thermal expansion coefficient. Porosity is encountered at approximately 50 volume percent alumina and increases linearly to approximately 48 percent for 100 volume percent alumina.

Fig. 7. Spherical nickel metal spheres included in a glass matrix (250X). The nickel phase is 40 volume percent of the total composite.

Fig. 8. The variation of composite strength with increased included particles. Glass matrix with spherical nickel metal inclusions. Glass 8 and glass D have a higher and lower thermal expansion coefficient, respectively, than that of nickel.



ZN-3937

Fig. 1.

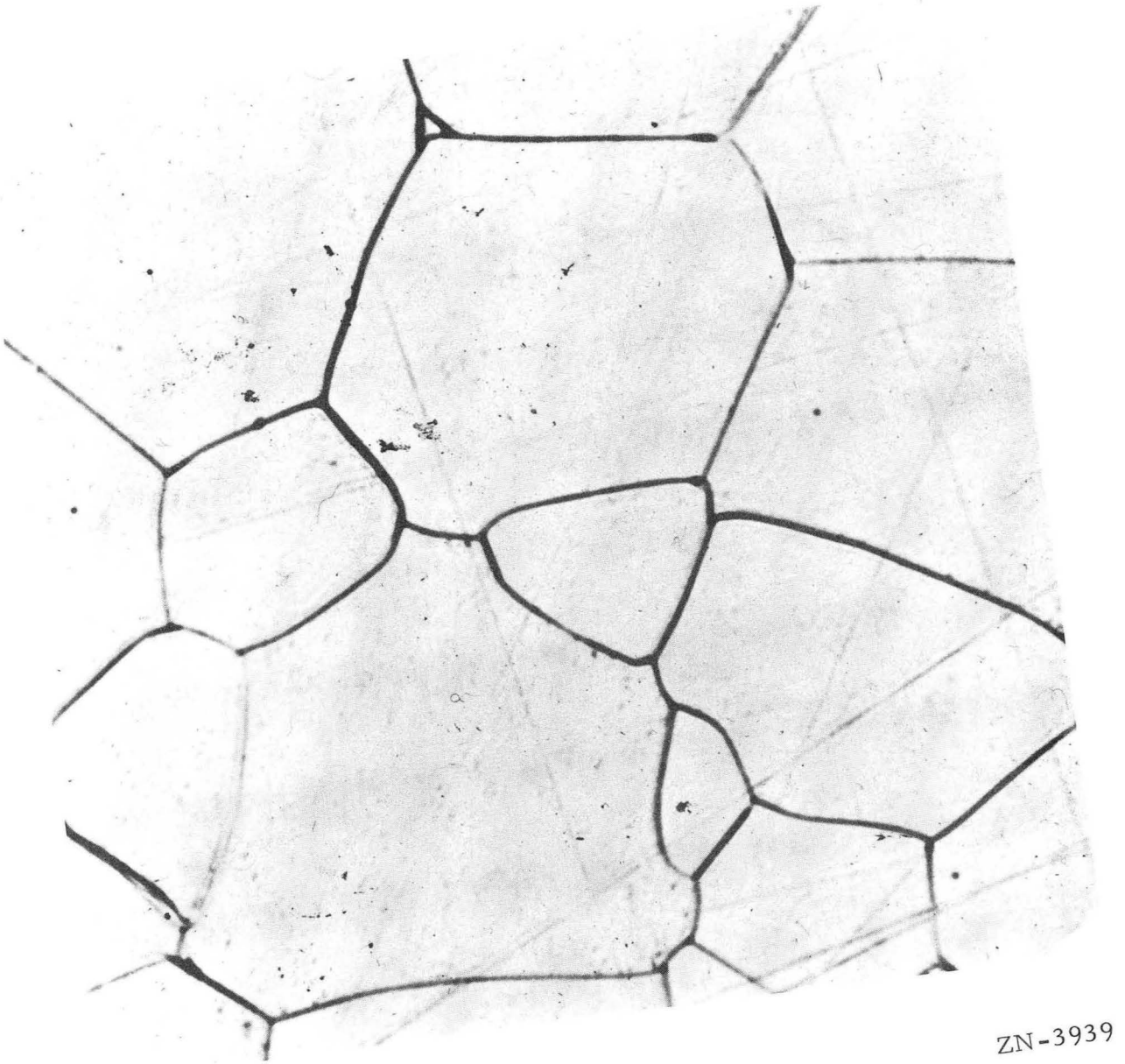
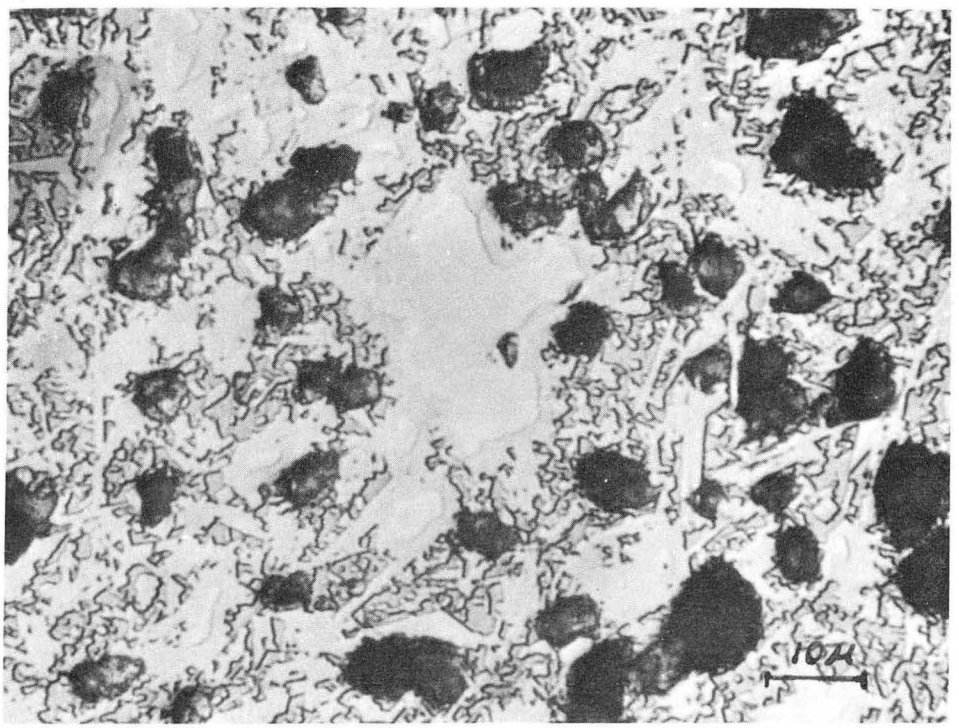
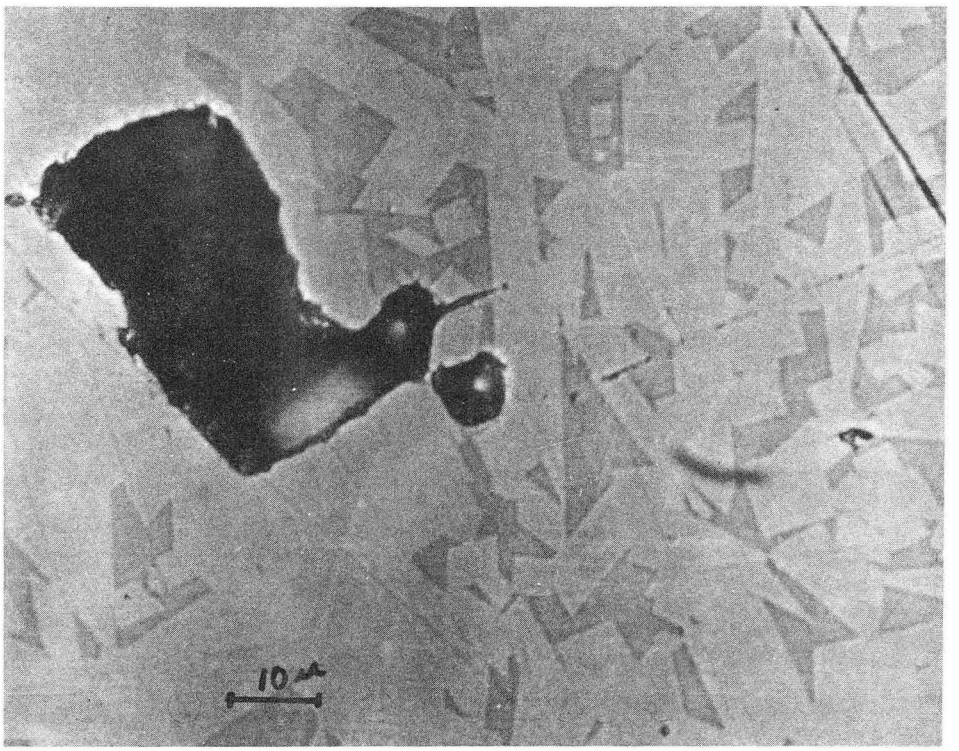


Fig. 2.



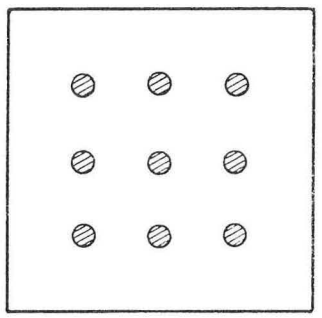
ZN-3722

Fig. 3.

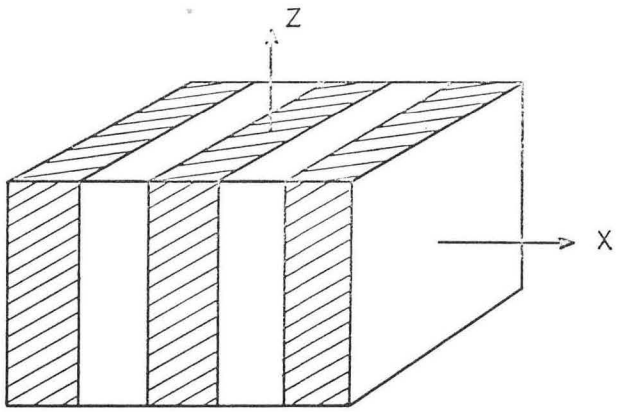


ZN-3724

Fig. 4.



(a)



(b)

MU-31857

Fig. 5.

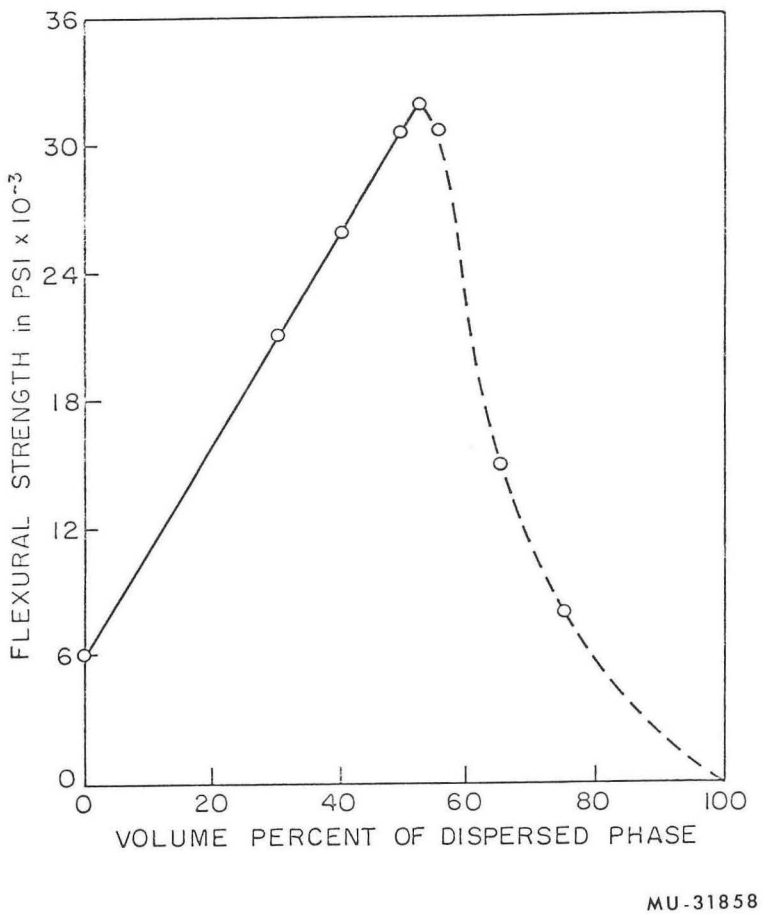
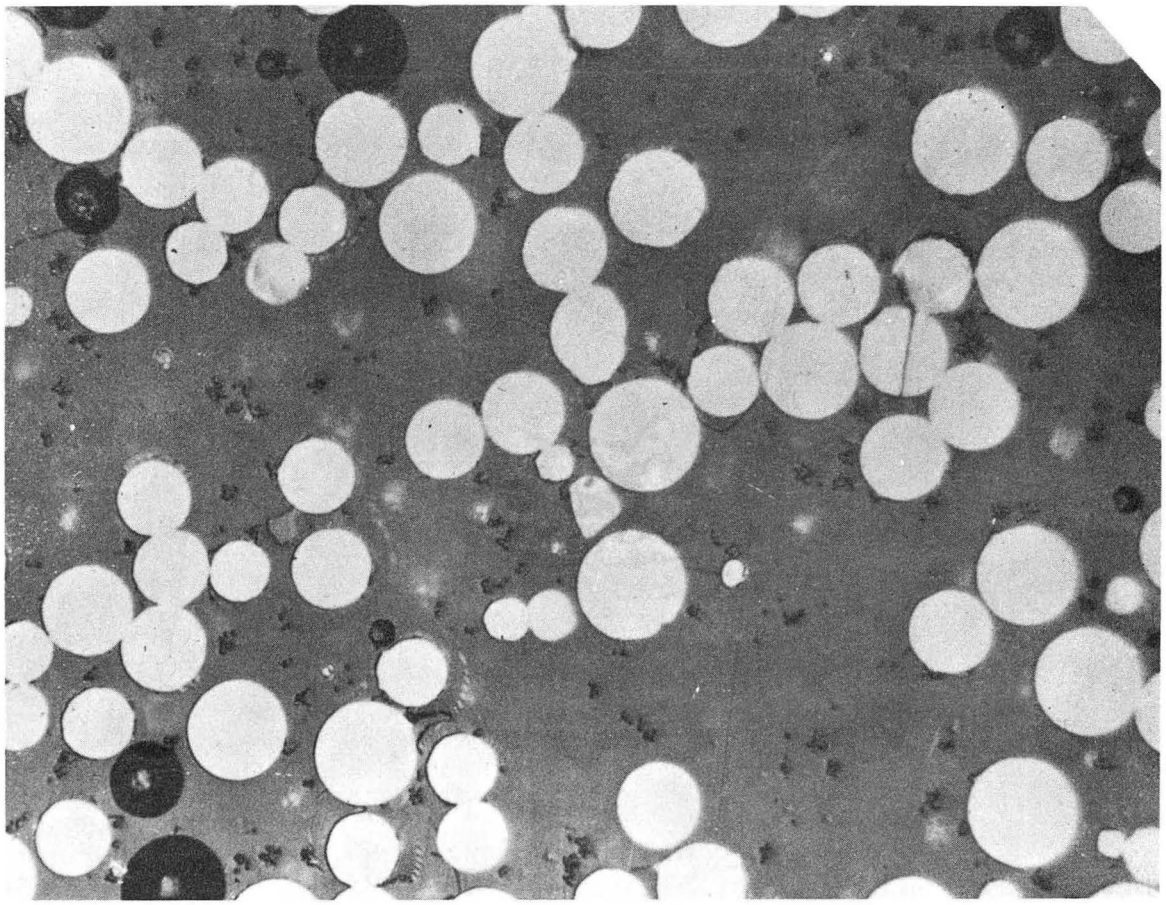

36
30
24
18
12
6
0
FLEXURAL STRENGTH in PSI x 10^-3
0
20
40
60
80
100
VOLUME PERCENT OF DISPERSED PHASE
MU-31858

Fig. 6



ZN-3938

Fig. 7

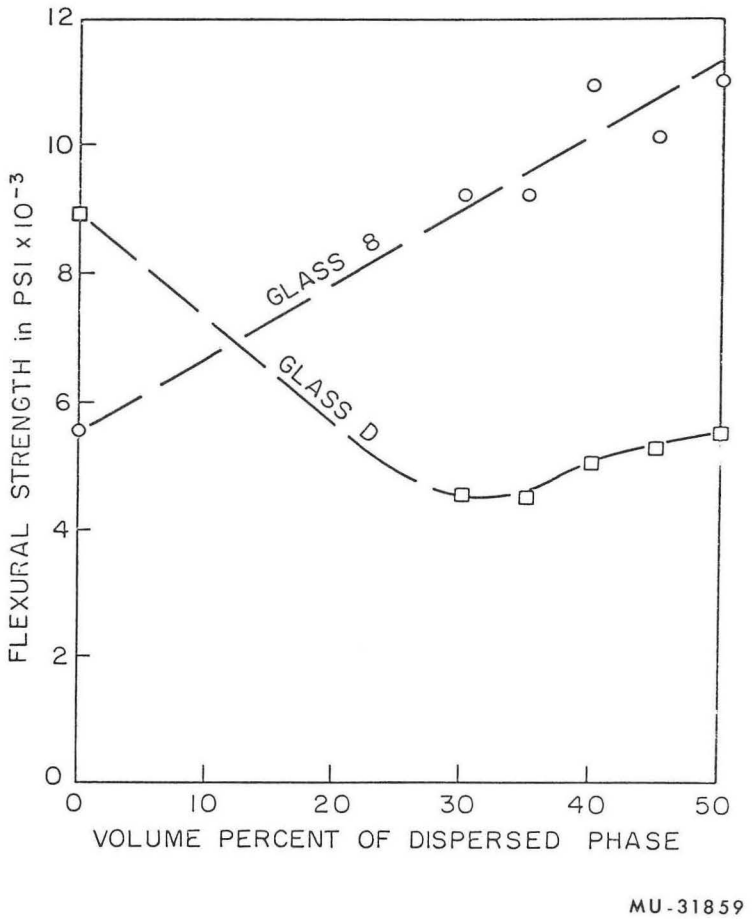

12
10
8
6
4
2
0
FLEXURAL STRENGTH in PSI x 10⁻³
GLASS 8
GLASS D
0
10
20
30
40
50
VOLUME PERCENT OF DISPERSED PHASE
MU-31859

Fig. 8

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