

FUNDAMENTALS OF MASSIVE GLASS
AS A NAVAL STRUCTURAL MATERIAL

REPORT OF
THE COMMITTEE ON THE FUNDAMENTALS OF
MASSIVE GLASS AS A NAVAL STRUCTURAL MATERIAL

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ABSTRACT

Future deep-sea operations by the Navy and others will necessitate the development of materials with properties superior to those currently available. One candidate for deep-submergence uses is glass because of a number of favorable properties such as potential high strength-to-weight ratio, transparency, and corrosion resistance. However, before glass can be fully utilized as a deep-sea structural material, additional information will be needed on its physical properties. This report contains fourteen recommendations for research on physical and mechanical properties that define the most important areas in which more understanding is needed. Topics covered are strength, means of strengthening, structure, dynamic processes, glass ceramics, and fundamental phenomena. The recommendations are justified in a summary of available knowledge covering: strength of glass, chemical strengthening, other methods of strengthening, transport properties, structure, vibrational properties, and glass ceramics. Many of the recommendations of this report are essential to an understanding of the vitreous state and as such have application in fields other than structural glass.

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Board Ad Hoc Committee on the
Fundamentals of Massive Glass as a
Naval Structural Material

INTRODUCTION

Exploitation of the oceans for economic and military advantages depends in part on our ability to explore the ocean depths. In recognition of this need, the Navy has played a leading role in supporting undersea technology and research. Part of this effort has been directed toward the development of deep-sea vessels and structures capable of operating on most of the ocean bottom. Vessels capable of extended operation at depths of 20,000 feet are sought because this depth encompasses 98 percent of the ocean floor. These structures and vessels are intended for eventual use in lost object location, undersea engineering tasks, oceanographic research, as back-up for academic and industrial activities in the sea, and for defense systems needs.

Vehicles capable of deep-sea exploration must be compact, maneuverable, must be able to carry a reasonable payload (say, 1,000 pounds), and must have an underseas horizontal range of several miles. Vehicles possessing some or most of these capabilities have been constructed, but the number and the effectiveness of the available vehicles drop off sharply below about 7,000 feet. This depth limitation is largely due to the lack of suitable materials of construction. The metals, presently used for deep-submergence vehicles, do not have a high strength-to-weight ratio for deeper capabilities. To attain greater depths, other materials with greater strength-to-weight ratios are being considered. Glass, the subject of this report, is one of the materials under consideration. *

* In this report the term glass typically means silicate, alumino-silicate and borosilicate glass; however, glass ceramics are also discussed and model glasses are considered for purposes of obtaining scientific information applicable to glasses of practical interest.

Glass has several advantages as a deep-submersible material. Its high compressive strength, exceeding 600,000 psi, and low density, typically 2.5 g/cm^3 , give it a very favorable strength-to-weight ratio. Absence of ductility eliminates the possibility of failure by plastic buckling or creep. Glass is also corrosion resistant and is not expected to react with the ocean environment. Furthermore, glass can be made transparent, which is of value for deep-sea exploration and lost object recovery.

One of the main disadvantages of glass for structural use is its low tensile strength. This apparent weakness is due to the extreme notch-sensitivity of glass. Small surface cracks normally present in glass concentrate stresses locally so that failure occurs at low applied loads. Glass can be strengthened by inhibiting the growth of these cracks, or by eliminating them. Commercially, crack growth is inhibited by putting the surface layer of the glass into a state of compression, by either thermal or chemical means. Surface cracks then cannot propagate until the applied loads overcome the surface compressive stress, and tensile strengths up to 100,000 psi can be obtained. Thus, practical means may be at hand for increasing the tensile strength of glass so as to permit its use as a structural material.

COMMITTEE SCOPE, OBJECTIVE, AND RATIONALE

With the above as background, the Office of Naval Research requested the National Materials Advisory Board to explore and determine the best course of future investigations to obtain the information necessary for the proper use of glass as a structural material. The Committee was requested to help identify and recommend a basic research program on glass to support the Navy's need for advanced deep-submersible materials. The strength of glass and ways to strengthen glass were to be considered from a fundamental point of view taking into account atomic, molecular, and micro-structural characteristics, and kinetic processes associated with these

characteristics. Suggestions were to be given concerning the areas of research to be supported, the kind of talent needed, and the total time likely to be needed to conduct the research.

The report is divided into two parts. The first part presents recommendations, preceded by short explanatory passages to establish their context. The recommendations of the report are divided into five sections. Section A is concerned with the strength of glass and possible failure mechanisms. Section B deals with means of strengthening glass. Section C involves structure and certain dynamic processes that have a bearing on Sections A and B. Section D is concerned with glass ceramics and problems peculiar to these materials. Finally, Section E deals with some problems of glass that are fundamental to the understanding of its properties and structure. These recommendations are meant to define the most important general areas in which more understanding is needed.

The recommendations presented in this report are classified as to priority and an estimate of the length of time required for each recommendation. Recommendations designated Priority I are aimed at providing fundamental scientific or engineering information on glass that will aid in solving problems associated with the production of structural glass. Priority II recommendations apply to problem areas that are also important, but differ from Priority I recommendations because techniques for implementation of the recommendations are not yet available. It is hoped that as good ideas are suggested, Priority II items will also be supported.

The second part of the report presents a summary of available scientific knowledge that bears on the recommendations made in the report and is divided into seven parts: strength of glass, chemical strengthening, other methods of strengthening, transport properties in glass, glass structure, vibrational properties of glass, and glass ceramics. Here will be found the

facts that justify the recommendations presented in Part I of the report. It is also intended that this part of the report provide a source of technical information for the scientist or engineer interested in glass as a subject of research or as a structural material.

Many of the recommendations of this report are essential to a better understanding of the vitreous state and as such have application in fields other than structural glass. For example, the development of better glass lasers, amorphous semiconductors, and controlled pore glasses for chromatography, will also depend on a knowledge of glass structure and the kinetic and equilibrium properties of glass. Consequently, implementation of the recommendations is expected to have an effect ranging far beyond the initial charge of this committee.

I. RECOMMENDATIONS

A. Strength of Glass

Strength measurements on glass are usually made using bending tensile, or compressive test configurations. These measurements have shown that glass always fails by tensile crack propagation. For the complex loading conditions expected in deep-submersive hulls, however, other modes of failure may occur. To investigate this possibility, it is urged that:

1. The strength and failure modes of glass and glass ceramics under complex stress fields be determined.
(Priority I, short term.)

The strength of polycrystalline materials is known to be sensitive to various aspects of the microstructure of these materials, such as grain size, composition, phase distribution, morphology, and size and type of flaws. Since glass and glass ceramics also exhibit a dependence of strength on microstructure, it is recommended that:

2. The role of microstructure in determining the strength and failure mechanisms of glass and glass ceramics be determined. The types of flaws that are critical for structural uses of glass should be determined and limits established for their dimensions and for other relevant parameters.
(Priority I, long term.)

Glass, in many deep-submersible applications, will, of necessity, be loaded in an aqueous medium and undergo cyclic loading. Because of the limited and somewhat conflicting knowledge of the effect of cyclic loading in this environment on the strength of glass, it is advised that:

3. The fatigue of glasses and glass ceramics under static and dynamic stresses should be examined as a function of environment. (Priority I, short term.)

B. Means of Strengthening Glass

Glass may be strengthened either by completely eliminating the flaws that cause failure or by stabilizing them by some sort of surface treatment. The first method has not met with any practical success, although experimental glasses with strengths of the order of 10^6 psi have been made. Immobilization of cracks has been accomplished by introducing a surface compressive layer into the glass. Methods used for surface-compression strengthening are chemical strengthening, thermal tempering, surface cladding, and surface crystallization. Of these, chemical strengthening is perhaps the most promising technique. It is capable of producing commercial glasses with abraded strengths approaching 100,000 psi. Considering the importance of surface-strengthening processes, the following recommendations are made:

4. Develop compositions and techniques to enlarge the scope and effectiveness of chemical strengthening of glasses and glass ceramics. In particular, thicker strengthening layers are desirable. Examine the limitations of the method in terms of structure, transport mechanisms, and stress-relaxation processes. (Priority I, short term.)
5. Investigate other methods of surface strengthening, such as flaw removal coupled with surface protection, use of glazes, and surface crystallization. (Priority II, long term.)

6. Study the structure as well as the physical and chemical properties of the altered surface layer. (Priority I, short term.)

C. Structure and Dynamic Processes

Chemical strengthening of glass is known to depend on the rate of stress build-up due to ion migration into the surface layer and the rate of stress relaxation due to various viscoelastic processes. By increasing the stress build-up and retarding relaxation processes, stronger glasses can be obtained. Thus, the production of strong glasses will ultimately depend on an understanding of the various kinetic processes that jointly determine the stress in the compressive surface layer. Structure of the glass is also important since the dynamic processes will depend on structure. The following research suggestions are important for an understanding of the chemical strengthening process:

7. Investigate linear and nonlinear viscoelastic properties with particular emphasis on temperature in and below the glass transformation region. (Priority I, long term.)
8. Perform fundamental studies on transport properties designed to elucidate mechanisms at the atomic level. Obtain experimental data on molecular reorientation and the flow of liquids in the high viscosity region. Develop theoretical models to describe these phenomena. (Priority I, long term.)
9. Investigate the thermodynamics, kinetics, and morphology of composition fluctuations and liquid-liquid phase separation in glasses. (Priority I, long term.)

D. Glass Ceramics

Glass ceramics are formed as molten glasses and subsequently heat-treated so that they become almost completely crystalline. Like glass, they can be strengthened by ion exchange, thermal tempering, and surface treatments. They are mentioned in this report because they possess several distinct advantages over the parent glasses. They tend to be stronger, even without special treatments, and possess higher elastic moduli. Certain compositions remain transparent after crystallization. Many of the research suggestions already presented for glass are applicable to glass ceramics. However, inasmuch as they are largely crystalline, glass ceramics have problems associated with their production, which are unique. For example, control of the final crystal size, composition, and phase distribution requires quantitative information on thermodynamic relationships and nucleation and growth processes. In addition, stress relaxation and transport processes differ from those found in glass since defect structure, recrystallization, and grain-boundary migration become important at high temperature. Relationships between strength, rates of crack propagation, and stress corrosion also differ in glass ceramics. Furthermore, previous research on these systems has been motivated by the desire to produce thermal and optical properties different from those necessary in massive structural materials. The recommendations below relate specifically to glass ceramics:

10. Study the crystallization process that controls the grain size and morphology as well as the grain and interstitial compositions in glass ceramics in terms of the relevant thermodynamic and kinetic parameters. (Priority I, long term.)

11. New compositions and heat treatments of glass ceramics should be surveyed with the goal of improving the relevant mechanical and thermal properties. Phase-equilibria and mechanical-property measurements should be made simultaneously on compositions of interest. (Priority I, long term.)

E. Structure and Fundamental Properties

Almost all the processes proposed for study above depend on a relatively small number of fundamental properties of glasses. Among these are the thermal expansion, elastic constants, specific heat, viscosity, and glass-transition parameters. These properties are not sufficiently understood because of the complexity of the atomic arrangements and our very limited knowledge of these arrangements. Recent studies suggest that significant advances in the understanding of both the atomic arrangements and the physical properties are possible within the next few years. To reach this goal the following research is suggested:

12. Determine the local atomic environments of common network formers and modifiers in oxide glasses. (Priority I, long term.)
13. Investigate the structure of glasses in the intermediate range of 8 to 30×10^{-8} cm. (Priority II, long range.)
14. Research designed to yield fundamental understanding of the vibrational properties (elastic constants, specific heat, and thermal expansion), and not merely the acquisition of new data, should be performed. (Priority II, long range.)

II. STATE-OF-THE-ART SUMMARY

A. Strength of Glass

The separation of a condensed body into two parts involves either transport processes or the tearing apart of cohesive bonds. The former case includes hydrodynamic or plastic flow, evaporation, chemical dissolution, and so forth; the latter includes cleavage and brittle fracture. As far as is known, glass does not flow at stresses less than approximately 10^6 psi at room temperature and failure is due almost entirely to brittle fracture. Theoretically, the atomic forces holding glass together should lead to cohesive strengths of the order of 10^6 psi. Yet the strength of glass is normally found to be 10^4 psi. This discrepancy between experimental and theoretical strength was explained by Griffith as being due to small cracks in the glass surface. These cracks act as stress concentrators so that the tensile stress along the crack perimeter is much higher than the imposed stress. Failure occurs when the stress at the crack tip exceeds the cohesive strength of the material. Quantitative relationships were developed by Griffith⁽¹⁾ and subsequent workers relating loads at failure to crack geometry and material properties such as elastic moduli and fracture surface energies. These developments have been reviewed adequately in a number of recent articles and will not be discussed here.⁽²⁻⁷⁾

Glass normally fails from surface flaws, as stated above. However, when the surface has been strengthened by flaw removal or by chemical strengthening, fracture may be initiated by internal stress concentrators such as bubbles or crystalline precipitates. In addition, fracture modes other than tensile failure may occur, especially when the glass is subject to complex loading. Little is known of the failure of glass from internal flaws; however, recent experiments by Errsberger⁽⁸⁾ have demonstrated both shear

fracture and densification at ellipsoidal cavities in glass, as will be discussed below. Additional experimentation should be performed to elucidate the role of internal flaws as sources of failure.

One topic that has received scant attention is the behavior of glass in bi-axial and tri-axial stress fields. There appear to be only three or four theoretical treatments of this subject and about the same number of experimental treatments. An understanding of crack propagation in multi-axial stress fields is important to the design of deep-submergence vehicles because complex stress fields are expected in vehicle hulls, especially at joints between glass and metal parts. An example of the type of stress fields expected can be obtained from a stress analysis of the spherical shell, for which the tangential stress under external pressure p_o is

$$\sigma_t = p_o b^3 (2R^3 + a^3) / [2R^3 (a^3 - b^3)]$$

and the radial stress is

$$\sigma_R = p_o b^3 (R^3 - a^3) / [R^3 (a^3 - b^3)],$$

where a is the internal radius and b is the external radius of the sphere and R is the radial distance to the point under consideration. For large spheres with relatively thin walls, the variation of the tangential stress is small from the inside to the outside of the sphere. The radial stress varies from 0 at the inside surface to p_o at the external surface. Thus, a sphere at a depth of 20,000 feet in the ocean might have a tangential stress of 200,000 psi and a radial stress that varied between 0 and approximately 7,000 psi. Hence, any crack propagation that occurred would be in an essentially biaxial stress field. Similar considerations hold for other hull geometries.

Stress distributions will be further complicated by the fact that entrance ports will have to be made in the vehicle. These ports will

probably be made from metallic parts. Thus, contact stresses will occur at joints between the metal and glass. In addition, couple stresses will arise from modulus mismatching between the metallic and glass parts of the vehicle.

The first treatment of failure under multiaxial stress conditions was given by Griffith for a biaxial state of stress. ⁽⁹⁾ Griffith assumed that failure began with small, pre-existing elliptical cracks and that the stress field gradient in the material was small so that the cracks could be treated as if they existed in a uniform stress field. The stress tensor representing the stress field was resolved into its principal stresses, and the distribution of stresses along the surfaces of the cracks was determined as a function of crack orientation. For a given crack size, failure was assumed to occur for the crack so oriented as to give the maximum stress at some point along the crack perimeter. Assuming a distribution of randomly oriented cracks, the condition for failure in a biaxial stress field is

$$(\sigma_1 - \sigma_2)^2 + 8 \sigma_0 (\sigma_1 + \sigma_2) = 0 \text{ for } \sigma_2 < -3 \sigma_0$$

where σ_1 and σ_2 are the principal stresses and σ_0 is the stress for uniaxial tensile failure. The condition for failure when $-3 \sigma_0 \leq \sigma_2 \leq \sigma_1$ is $\sigma_1 = \sigma_0$. These failure conditions are depicted in Figure 1. Regions within the envelope represent stress conditions for crack stability. Outside of the envelope, fracture occurs.

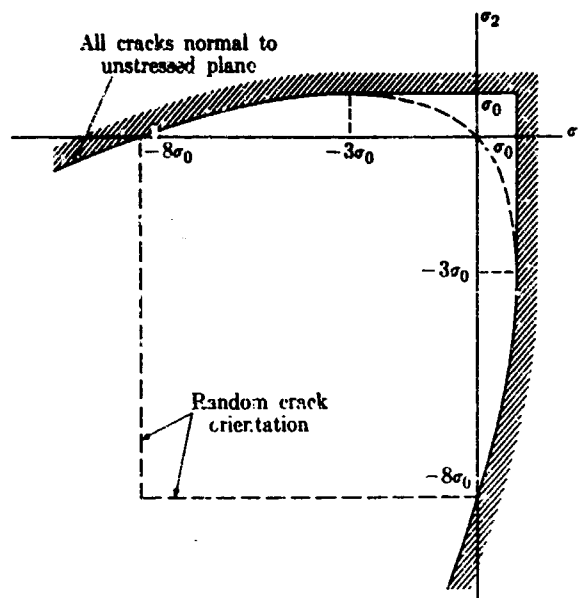


Fig. 1. Brittle Fracture Under Biaxial Stress, Griffith Criterion. ⁽⁹⁾

The above treatment of biaxial failure assumes the surfaces of the crack to be stress free. However, McClintock and Walsh ⁽¹⁰⁾ pointed out that crack surfaces experience normal and shear stresses under biaxial loading because of contact between the surfaces. They generalized Griffith's approach and obtained failure criteria that depended on the magnitude of these surface stresses (Figure 2). The various curves in Figure 2 depict failure limits for various assumed surface-stress conditions. The theory of McClintock and Walsh is supported by data obtained on the crushing strength of rocks under a confining pressure.

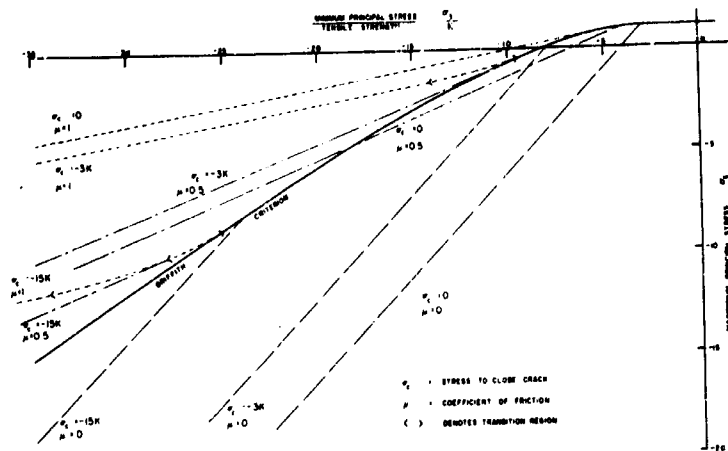


Fig. 2. Generalization of Biaxial Fracture Criterion to Include Crack Surface Loading, McClintock and Walsh. ⁽¹⁰⁾

Hoek and Bieniawski ⁽¹¹⁾ have shown that crack propagation from open cracks (ultrasonically drilled slots) in a biaxial stress field followed the predictions of Griffith. Cracks were found to be initiated at a point on the crack boundary but not at the crack tip, and followed a curved path (Figure 3). They also showed, from a compilation of rock-fracture data, that the McClintock-Walsh theory was borne out with a coefficient of friction ranging between 0.5 and 1.5. Biaxial compressive studies by Hoek and Bieniawski on closed cracks suggested a need for modification of the McClintock-Walsh theory, since fracture initiated from crack-surface irregularities rather than from the crack tip.

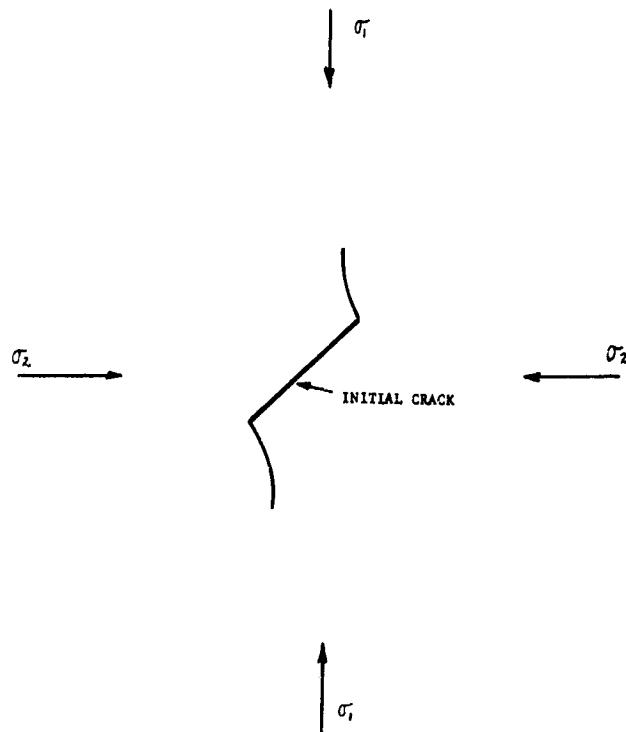


Fig. 3. Effect of Biaxial Loading on Crack Propagation direction. ⁽¹¹⁾

A different approach to biaxial failure of brittle materials was taken by Erdogan and Sih, ⁽¹²⁾ who analyzed the failure conditions for a two-dimensional slit rather than an ellipse. The stress distribution around the tip of a crack was used to calculate conditions for crack propagation, and crack extension was assumed to occur from the crack tip in a radial direction and in a plane perpendicular to the direction of greatest tension. The equations developed were checked experimentally on Plexiglas and found to agree well with the initial assumptions. An interesting conclusion was that the shearing modes of crack propagation did not occur in Plexiglas.

Cracks that are not perpendicular to one of the principal stresses are always subject to shear stresses, which, in principle, may give rise to shear modes of crack propagation. Theoretical discussions of crack propagation induced by shear stresses are available in the literature.⁽³⁾ Shear induced crack propagation occurs if the solid can resist only a finite amount of elastic shear strain and does not flow plastically. From the data available in the literature, shear failure is not probable under normal loading conditions. However, in the high biaxial stress fields expected in deep-submergence hulls, particularly at joints, the possibility cannot be dismissed.

High compressive stresses in glass are capable of causing a type of permanent deformation known as densification.⁽¹³⁻¹⁵⁾ Fused silica, for example, can be densified at temperatures of 300°C and 60 kilobars pressure.⁽¹¹⁾ Densification of glass at hardness indentations has also been observed at room temperatures.⁽¹⁶⁾ The effect of densification on fracture has not been studied.

Recent experiments by Ernsberger⁽⁸⁾ have demonstrated the occurrence of both shear fracture and densification at ellipsoidal cavities in glass. Experiments were conducted by subjecting an internal bubble in the shape of an oblate spheroid to uniaxial compressive stress. The stress at the surface of the spheroid ranged from 0.6 to 1.1×10^6 psi for failure, depending on the glass tested. Failure occurred either by densification or shear crack formation at the bubble surface. These experiments furnished fairly reliable compressive strength data and should be useful for future studies of failure at voids due to biaxial stresses.

Failure of glass is believed by most investigators to be completely brittle. Despite this predominant opinion there is some experimental evidence for plasticity, and the possibility of plastic deformation influencing crack propagation cannot be dismissed. Marsh⁽¹⁷⁾ and others attribute the permanent deformation at hardness indentations in glass to plastic flow. In addition, Marsh has been able to relate the hardness value to the fracture strength in various environments. Ernsberger⁽¹⁶⁾ has shown that densification accompanies hardness indentations and believes the deformation at indentations to be due to densification and not plastic flow.

Evidence for irreversibilities during fracture comes from fracture energy measurements, which yield surface energies that are greater than the theoretically expected value by a factor of 2-3.⁽¹⁸⁾ The difference between theoretical and experimental fracture-energy values has not really been explained, but may be due to plastic deformation or other irreversibilities at the crack tips. Additional studies will be necessary to clarify the role of plastic flow during fracture.

Environmental effects on the strength of glass will also be important to the deep-submergence program. Moisture in the environment is known to be deleterious to the tensile strength of glass. The effect exhibits itself as a time delay for failure or a loading rate dependence of strength and is so severe that, all other things being equal, the long-term strength of glass is reduced 80 percent by the presence of water or water vapor. Several excellent reviews on this subject are available in the literature^(6, 7) so only the main facts pertinent to the subject will be outlined here.

The weakening effect of water on glass has been termed static fatigue or delayed failure by glass technologists and is presently believed to be a stress-corrosion process. The effect was first reported in 1899 by Grenet,⁽¹⁹⁾ who observed that the strength of glass depended on the rate of loading and that glass could statically support a given weight for a time before failing. These experimental facts were in contradiction of the Griffith theory, which predicts a time-independent failure load and the absence of failure once a glass object has been shown to support the load.

Experimental studies on static fatigue of glass have shown that:

1. Most commonly, corrosive environments are required for the occurrence of static fatigue.
2. Static fatigue behavior depends on glass composition.
3. Static fatigue is an activated process and vanishes at cryogenic temperatures.
4. There is a threshold stress level below which static fatigue will not occur.

Experimental data on which these conclusions are based were usually obtained by three or four point bend tests and results were expressed in the form of load, time-to-failure curves. Data taken from groups of specimens of varying surface treatment are usually scattered, bearing little relationship to one another. However, Mould and Southwick⁽²⁰⁾ showed that the various static fatigue curves could be correlated provided the ratio of the strength in the test ambient to that in liquid nitrogen, σ/σ_N , was plotted against the logarithm of the reduced time to failure, $\log_{10}(t/t_{0.5})$, where $t_{0.5}$, the characteristic duration, is the time to failure of a specimen loaded at half its liquid-nitrogen strength. The universal fatigue curve is valuable

for engineering use and is also a severe test of any theoretical treatment of the problem.

The theory of static fatigue that seems to be most consistent with experimental data is the one suggested by Charles and Hillig.⁽²¹⁾ They assumed that stress corrosion is the result of a chemical reaction between water and the glass at the crack tip. The rate of the reaction is enhanced at the crack tip because of the high localized stresses there. Chemically induced crack growth occurs until the Griffith condition for spontaneous rupture is satisfied. Charles and Hillig treated the problem thermodynamically and arrived at specific expressions for the rate of crack growth and the total time of failure, which satisfy the universal fatigue curve. The crack-velocity equation derived by Charles and Hillig is

$$v = v_0 \exp - [E^* - V^*\sigma + \Gamma V_M / \rho] / RT, \quad (1)$$

where E^* is the activation energy for the process, V^* is the activation volume, σ is the crack-tip stress, Γ is interfacial surface energy of the glass-corrosion product layer, V_M is the molar volume of the glass, and ρ is the radius of curvature of the crack tip.

Equation 1 may be checked quantitatively by employing fracture-mechanics techniques that use specimens containing large, well-defined cracks, thus eliminating the crack length as an experimental uncertainty.^(22, 23) Information on the kinetics of the stress-corrosion process can be obtained by monitoring the rate of crack growth as a function of temperature, stress intensity, environment, and temperature. So far, the following conclusions have been inferred from experimental data:

1. Crack-velocity data quantitatively satisfied the Charles-Hillig theory.
2. Crack-velocity data are consistent with the universal fatigue curve.

3. Glasses of different chemical composition exhibit varying degrees of resistance to stress-corrosion cracking.
4. In gaseous nitrogen containing water vapor, it can be demonstrated that there are three distinct mechanisms of crack growth. At low stress-intensity levels, the rate of crack growth is reaction rate-limited. At intermediate levels, the rate of crack growth is limited by the rate of water transport to the crack tip. At the highest stress-intensity levels, crack growth is independent of environment.

Information on the stress-corrosion of glass is far from complete. Effects of pressure, glass composition, and electrolyte composition on stress corrosion are not known and should be investigated to provide engineering information on the behavior of glass in the deep-ocean environment. Using newer experimental techniques, stress corrosion of glass can be described in terms of thermodynamic variables and may be related to chemical processes occurring at glass surfaces. Thus, the selection of glass composition for greatest stress-corrosion resistance may be put on a rational basis.

The effect of cyclic loading on glass failure is also not understood. Some view dynamic fatigue of glass as an aspect of static fatigue, but the experimental evidence is far from complete on this point. Since deep submersibles will undergo cyclic loading, additional experimental evidence should be collected to determine the importance of dynamic fatigue to glass fracture.

B. Chemical Strengthening

1. Introduction

The word "strength" implies a great many variables: tension, compression, shear (and their combinations), in one, two, and three dimensions; cyclic and static stressing; ambient environment; failure modes. This discussion of chemical strengthening will be mainly concerned with strength as measured by uniaxial tension in the normal atmosphere, with time to fracture of the order of 10 seconds.

Tensile strength is an important engineering parameter even when the contemplated structural application nominally involves only compression. Glass is so strong in compression that fracture is usually to be ascribed to a parasitic tensile stress of some kind. From an engineering standpoint, therefore, any method for increasing the tensile strength of glass will have the effect of increasing its effective strength under compressive and shear loading.

2. Need for Increased Strength

It is customary to design very conservatively when glass is to be used in a structural application. ^(24, 25) Such conservatism is justified, because glass fails by brittle fracture rather than by yield, and brittle fracture usually means a complete loss of load-bearing capacity. In contrast, the ductile yield that is characteristic of metal failure may actually increase the effective strength of the part. The absence of yield also means that glass is "unforgiving"; that is, it may fail from some purely local stress that was not considered in design, such as an over-tightened bolt or an ill-fitting frame. The effective strength of glass may also decrease unpredictably in service, if it is exposed to mechanical damage.

In the case of annealed glass, conservative design usually means that the average breaking stress should be reduced by a safety factor of about 10 to estimate the permissible working stress. The useful strength of annealed glass is therefore only about 1,000 psi. Obviously, glass has little potential as a structural material unless the useful strength can be increased by one or two orders of magnitude.

There is only one known approach to the strengthening of glass; namely, the provision of a state of compression in the surface.⁽²⁶⁾ The so-called thermal tempering process raises the long-term mean breaking stress of soda-lime glass to 15,000 - 20,000 psi. The nature of the strength distribution is such that a safety factor of 5 is sufficiently conservative, so the useful strength of fully-tempered soda-lime glass is about 3,000 - 4,000 psi. This strength is enough to permit the use of glass for the walls of large aquarium tanks, for doors, and so on. However, there is still a large gap between the strength of tempered glass and the strength of structural steel (yield strength, about 50,000 psi). In recent years, this gap has been essentially closed by the advent of the so-called "chemical" approach to surface-compression strengthening.^(27, 28)

3. General Characteristics of Chemical Strengthening

There are many chemical strengthening processes, but they have in common one basic principle: the treatment tends to produce an increase in the molar volume of the surface structure relative to that of the interior. Since the expansion of the surface structure is restrained in two dimensions by the underlying material, a two-dimensional state of surface compression results. Usually, the change in molar volume is brought about by a change in the chemical composition of the surface; hence the term "chemical" strengthening.

The magnitude of the surface stress associated with a given volumetric change can be shown from elementary principles of stress analysis to be

$$\sigma = k \frac{1 - 2\nu}{1 - \nu} \frac{\Delta V}{V},$$

where k is the bulk modulus and ν is Poisson's ratio. The bulk modulus is usually not known, but it is related to Young's modulus by the following equation:

$$k = \frac{E}{3(1 - 2\nu)}.$$

Combining these two relationships,

$$\sigma = \frac{E}{3(1 - \nu)} \frac{\Delta V}{V}.$$

Thus, a 1 percent volumetric change in a material having a Young's modulus of 10 million psi and a Poisson's ratio of 0.25 would be expected to provide a surface compressive stress of about 44,000 psi.

Obviously, this analysis has involved a number of assumptions: a surface layer that is much thinner than the substrate, elastic properties that are unchanged by the chemical treatment, absence of stress-relaxing processes, etc. Deviations from the simple theory will be discussed later.

According to the usual approximate rule, the useful strength of a surface-compressed glass is equal to the sum of the surface-compression stress and the annealed strength. This rule may be applied to chemically strengthened glass, but only after due consideration of the effective thickness of the compressed layer relative to the depth of the surface abrasions that may be expected in manufacture or in service. The compression depth of chemically strengthened glass is controllable, in principle, but in practice it is limited to a few hundred microns. The reasons for this limitation will

be discussed below, but the general nature of the problem can be inferred from the fact that chemical strengthening is ordinarily accomplished by the diffusive penetration of some reagent supplied at the surface, and diffusive penetration depth is proportional to the one-half power of time.

The subsurface profile of stress in a plate of chemically strengthened glass is ordinarily quite different from that of thermally tempered glass. In the latter, the profile is very near to a simple parabola and the magnitude of the surface compression maximum is approximately twice the magnitude of the tension maximum existing in the interior of the glass. In chemically strengthened glass, however, the profile in general is not parabolic. Instead, the stress tends to reproduce the error-function profile of the ion distribution. However, the profile may be considerably distorted by stress relaxation. It is not uncommon for a subsurface stress maximum to occur. The stress profile is also strongly dependent on the depth of penetration relative to the thickness of the plate. There is a nearly flat central region of tension, which changes abruptly to compression in the chemically altered region. The depth of compression is measured (optically) from the surface to the plane at which this crossover occurs. The depth of compression is related to the depth of ion exchange, but is not necessarily identical with it. The ratio of surface compression to interior tension may be as high as several hundred. If the interior tension is small enough, chemically strengthened glass can be cut and drilled. On the other hand, if the thickness of the surface-compressed layer is about 10 percent of the plate thickness, the central tension will be high enough to support spontaneous propagation and bifurcation of any crack that reaches the interior, and the material will "dice" in the manner of thermally-tempered glass. ⁽²⁹⁾

4. Ion Stuffing

The chemical-strengthening principle that is presently of

most commercial importance involves the substitution of large ions for small. (30-35) This substitution distends the surface structure and leads to surface compression, as explained in the preceding section.

There are two ways in which the substitution can be brought about: by diffusive exchange, and by electrically induced migration. These modes will be separately discussed in detail below.

From the practical standpoint, only the ions of Li, Na, K, and Ag exhibit a useful degree of mobility. In principle, the remaining alkali ions, polyvalent ions, and even anions should produce stuffing effects, but experimentally the results are unsatisfactory or inconclusive.

Composition is an important variable in the practical utilization of this principle. Thus, alkali ions are more mobile in aluminosilicates than in silicates, but less mobile in the borosilicates.

The temperature at which the foreign ions is introduced is necessarily somewhat below the annealing range of the glass. How far below is a compromise between the desirable increase in rate of diffusion that attends an increase in temperature, and the undesirable spontaneous stress relaxation that accompanies viscous flow.

a. Diffusive Exchange

Alkali-containing silicate glasses have ion-exchange properties much like those of the zeolites, except that higher temperatures are required and only anhydrous ions come into consideration. Instead of an aqueous solution, fused salts are employed. Nitrates are commonly used, but other salts are sometimes useful.

To a first approximation the diffusion process follows Fick's law, and the concentration profile of the entering ion has the typical error-function contour. (36) However, the process is unusual in that the diffusing species are charged. Electrical neutrality requires that the sum of the

concentrations of the two (or more) interdiffusing monovalent cations remain essentially constant throughout the exchange within every volume element of the glass. Consequently there is a coupling between the diffusion of the displaced and the displacing ions. Therefore, the process is characterized by an "interdiffusion coefficient,"⁽³⁷⁾ which is a function of the self-diffusion coefficients of the ions in the process.

Closer examination, of course, reveals a host of second-order considerations, including concentration-dependent diffusion rates, specific ion effects, stress-dependence of diffusion, mixed-alkali effects, fictive state, microstructure effects, etc. Most of these are poorly understood.

It is possible to chemically strengthen a thermally strengthened glass, thereby superimposing the effects. The results tend to be disappointing because of relaxation of the thermally induced stresses during the lengthy chemical treatment.

b. Electrical Migration

The fact that the diffusing species are charged affords the opportunity to influence the direction and rate of ion diffusion by the application of electrical fields. Electrically induced migration does in fact occur, and offers several potential advantages.

The profile of ion concentrations is quite different in the cases of electrical migration and diffusive exchange. Normally a larger, less-mobile ion will be used to displace a smaller ion. Under these conditions, the resistivity of the volume occupied by the incoming ion is larger than that of the original glass, and the electrical field is correspondingly more intense. This has the effect of sharpening the boundary between the leading and the following ions to an indefinite extent; that is, a shock front develops, and a square-wave ion concentration profile is maintained as long as the field is applied. A given depth of penetration will therefore produce a higher surface

stress than in the diffusive-exchange case.

The use of electrical fields offers other potential advantages. If the foreign ions can be introduced at a lower temperature than that required for unaided diffusion, stress relaxation should be minimized. Thicker compression layers may also be attainable, inasmuch as electrical penetration should tend to be linear with the first power, rather than the one-half power, of time. It would also be expected that the replacement of native ions by foreign ions should proceed more nearly to completion.

The electrical process has certain serious practical disadvantages, however. The fact that glass has a positive temperature coefficient of conductivity tends to cause channeling of current flow to any slightly overheated area of a plate-shaped conductor, and the result is perforation. This instability is, to some extent, compensated by the buildup of resistance with depth of penetration.

Depth of penetration should increase linearly with time for the electrical process, which would be a substantial advantage over the diffusion process. However, the overall resistivity of a plate increases so rapidly as penetration proceeds that the maintenance of constant current soon requires such high voltages that the I^2R power developed in the glass throws the system into the unstable current distribution already mentioned.

It is apparent that the electrical process is fundamentally one-directional, which is a disadvantage for many purposes. It has been demonstrated, however, that both sides of a flat plate can be more or less equally strengthened by electrolyzing one side to twice the required depth, followed by a reversal of polarity and the passage of half the original quantity of charge in the opposite direction.

Another fundamental difficulty with the electrical process is that some part of the surface of the object must be left untreated, to serve

as electrical insulation between the cathode and anode compartments of the treatment cell. The untreated surface, of course, remains vulnerable.

c. Temperature Limitations of Ion Stuffing

Both the process and the product tend to be limited by relaxation processes that occur at elevated temperatures.

It is characteristic of the ion-exchange process that the tensile strength of the product tends to go through a maximum as the processing time is extended. The higher the processing temperature for a given glass composition, the earlier the maximum is reached and the steeper the decline thereafter. The reason for this behavior is qualitatively understood. Even though the temperature of the treatment may be below the nominal strain point of the glass, the temperature is still high enough to permit viscous and viscoelastic relaxation processes to occur at an appreciable rate. This is particularly true of the surface layer, where stress levels are in the 100,000-psi range. It must be remembered that "annealing" and "strain" temperatures were arbitrarily defined in terms of the rate of release of the very small stresses that occur in the final stages of annealing.

In the use of an ion-exchange-strengthened product at elevated temperatures, these same viscous and viscoelastic processes can continue.⁽³⁸⁾ There is, however, an additional relaxation: in the absence of a supply of the foreign ion, the ionic concentration gradients tend to disappear. Both types of relaxation have been shown to be highly significant at temperatures that approach those of the original chemical treatment.

5. Differential Thermal Expansion

For practical reasons, the chemical modification of glass surfaces to a significant depth can be done only at elevated temperatures.

If the chemical modification is one that substantially lowers the thermal expansion coefficient of the surface layer, the operation of cooling the glass to ordinary ambient temperatures will give rise to a compressive stress in the surface.

a. Change in the Composition of the Surface

The simplest realization of the differential thermal-expansion concept is simply the coating of a low-expansion glass on one of higher thermal expansion. This concept has seldom been usefully applied to glass, but the principle is important in the specification of glazes for ceramic ware.

Glasses can be superficially dealkalized by high-temperature treatment with a variety of acidic reagents, such as gaseous SO_2 or SO_3 .⁽³⁹⁾ The resulting surface skin has a lower thermal-expansion coefficient as well as higher durability. Unfortunately, the process tends to be self-limiting; that is, the dealkalized surface tends to prevent further diffusive loss of alkali oxide.

Ion exchange affects the thermal expansion of the surface; thus, the treatment of a soda glass with a fused lithium salt above the strain point gives a strengthened product on cooling.^(40, 41)

b. Change in State at the Surface

A change in state from glass to crystal will, in general, have a large effect on the thermal-expansion coefficient. It is particularly easy to produce such an effect, because glasses that do not contain special nucleating agents are highly resistant to devitrification everywhere but at the surface. It happens that lithium aluminosilicate glasses within a not-too-restricted range of compositions devitrify to a phase (the beta eucryptite solid solution series) that not only has a very low thermal-expansion coefficient, but also has nearly the same refractive index as the parent glass. Therefore, it is possible to strengthen such glasses by controlled surface devitrification and

to do it without loss of transparency. This approach has a theoretical advantage over diffusive strengthening processes, in that the depth of devitrification should increase linearly with time.

Modifications of this basic principle are possible; for example, a sodium aluminosilicate glass can be converted superficially by ion exchange into a lithium aluminosilicate glass, which devitrifies during or after the exchange.⁽⁴²⁾ Still another approach is to design a lithium aluminosilicate composition in which nucleation can be controlled by exposure to ionizing radiation. The surface-compressed layer can then be made as thick as desired by adjusting the depth of penetration of the radiation.^(43, 44)

6. Differential Structural Change

Significant volumetric changes accompany the rearrangements of the glassy structure that can be brought about by various means. Of these, perhaps the most familiar and universal is the "compaction" that occurs spontaneously during prolonged heat treatment. Volume changes have also been reported to occur during neutron irradiation^(45, 46) and even during ultraviolet irradiation.⁽⁴⁷⁾ Volumetric changes may also accompany phase separation in some cases. Any of these is potentially the basis for a strengthening process; all that is necessary is to arrange that the surface and the interior undergo the volumetric changes differentially.

C. Other Methods of Strengthening

1. Thermal Tempering

Thermal tempering is a classical method of strengthening glass and is commonly used today to produce safety glass for windows. The technique involves quenching glass from temperatures above the glass transition. Quenching is accomplished through the use of cold jets of air or by other means. The outside of the glass is cooled at a much more rapid rate than the inside and as a result becomes rigid while the inside of the glass is still molten. As cooling continues, the interior regions of the glass contract at a greater rate than the rigid exterior region, and a stress profile is established. The stress profile is very nearly parabolic in thermally strengthened glasses, the magnitude of the compressive stress at the surface being approximately twice the magnitude of the tension maximum existing in the central plane, regardless of the glass thickness.

Descriptions of thermal tempering have been given by Bartenev⁽⁴⁸⁾ and Gardon et al.^(49, 50) The original simplified approach by Bartenev describes the process well; however, the more sophisticated approach by Gardon gives an even better description and suggests more refined approaches for the process of thermal tempering. Two of the important variables in thermal tempering are the initial temperature of the glass from which it is quenched, T_0 , and the heat-transfer coefficient, h , which defines the rate of heat transfer from the glass surface and depends on engineering variables such as air pressure, nozzle size, and nozzle configuration. For small heat-transfer coefficients, radiation plays a role in the process and must be included in the heat-transfer calculation. Figure 4 illustrates the relationship between the maximum tensile stress in the interior of the glass and the engineering variables, T_0 , and heat-transfer coefficient, h . It is seen that:

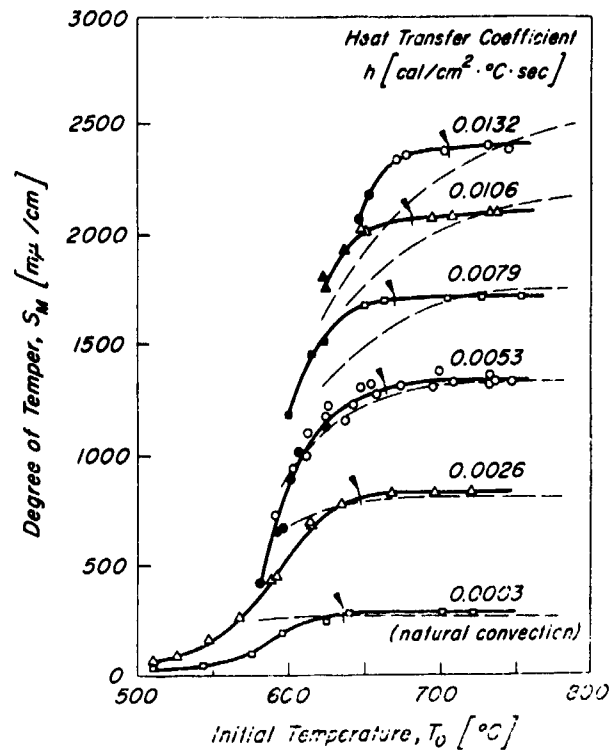


Fig. 4. Degree of Temper as a Function of Initial Temperature and quenching rate, R. Gardon. ⁽⁴⁹⁾

- (1) The degree of temper, S_M , increases with temperature, T_0 , rapidly at first and then more slowly, approaching a plateau. No significant gain in strength is obtained by increasing T_0 above a certain maximum value.
- (2) For higher heat-transfer coefficients, this plateau starts at higher temperatures.
- (3) The degree of temper increases with increases in the heat-transfer coefficient.

An additional factor that must be considered in thermal tempering is that a too-low quenching temperature can cause fracture of the glass. The temperature threshold for fracture increases with increases in the heat-transfer coefficient.

Additional refinements of the thermal-strengthening process have been given by Lee et al⁽⁵¹⁾ and Lee and Rogers,⁽⁵²⁾ who presented calculations to account for relaxation at every position in the glass as the temperature gradient evolves. Discrepancies between their results and experimental data were discussed by Narayanaswamy and Gardon⁽⁵³⁾ and attributed to features in the integration procedures used by Lee and Rogers. As a result of these refinements in analyses, it may now be possible to correlate engineering data with the relaxation processes occurring during tempering.

Complex stress distributions may be introduced into glasses by thermal tempering through the use of variations in time and temperature treatments.⁽⁵⁴⁾ In addition, combination effects of tempering and chemical strengthening have been claimed.⁽⁵⁵⁾ A comprehensive review of these and other developments was published very recently by Zijlstra and Burggraf.⁽⁵⁶⁾ Today it appears that the physics and engineering of tempering is well enough understood to make government support for additional research and studies unnecessary.

2. Cladding, etc.

The oldest method of strengthening glass is that of sandwiching glass of different expansivity to obtain compressive layers.⁽⁵⁷⁾ More sophisticated methods of cladding have been developed recently; however, the procedure is essentially the same. One clads a glass body at high temperatures with a second glass having a lower coefficient of thermal expansion. As the composite glass structure cools, the outer coating is put into a state of compression and thus strengthens the glass by preventing surface cracks from propagating. This technique of surface strengthening is being used

today to produce "nonbreakable" tableware.

Compressive surface layers of glasses may also be obtained by crystallization procedures that involve alteration of the glass surface layer. Strengthening occurs provided the molar volume of the surface layer of the glass increases upon crystallization. Surface crystallization can be accomplished either by heat treatment or by ion exchange with the surface. These processes were first controlled and described by Olcott and Stookey⁽⁵⁸⁾ and their full utilization remains to be explored.

A new and interesting experimental technique of surface strengthening was recently developed by Teeg et al.⁽⁵⁹⁾ The technique does not take advantage of surface compression for strengthening but instead depends on the complete removal of surface flaws and protection of the surface from further damage. Protection is afforded by cladding the glass with a second glass that is soft at room temperature. The cladding glass binds to the underlying glass very strongly and seems to protect it by absorbing abrasion and shock that might normally cause scratches or cracks in the glass surface. High strengths have been obtained using this technique. For example, ordinary soda-lime glass canes can be made as strong as 750,000 psi and aluminosilicate can be made as strong as 900,000 psi. After a certain amount of time, however, the protective nature of the coat seems to be lost. The reason for this loss in strength is not understood. Considering the enormous strengths that have been obtained in these experimental glasses, it would be worthwhile to conduct additional research on this type of strengthening process.

To sum up this discussion, there are a number of cladding techniques that increase the strength of glass. Some experimental techniques offer the possibility of strengths on the order of 10^6 psi and more research is needed to fully develop the potentials of these techniques.

D. Transport Properties in Glass

1. Introduction

Transport processes conventionally are divided into energy, momentum, and mass transport. Mass transport and momentum transport are important in the chemical strengthening process and will be discussed in this section. In these processes, the glass moves toward a state of local equilibrium by reduction of the driving forces for transport. Thus, matter is transported to reduce compositional, electrical, or stress gradients and momentum is transported to reduce stress gradients.

For purposes of this report, there are two molecular mechanisms for which the transport properties should be understood. One causes the glass transition and is characterized by silicon-oxygen covalent bond breakage and rearrangement under the influence of thermal fluctuations and applied potential gradients. This relaxation mechanism is important to the chemical strengthening process that is carried out at temperatures near the glass transition. The second molecular mechanism is associated with the transport of monovalent ions through a fixed silicon-oxygen network. This type of transport is important because it permits chemical strengthening of glass, because of its effect on the elastic moduli of the glass at low temperatures (delayed elastic effect), and because of the possibility of low-temperature stress release in the surface layers of chemically strengthened glasses.

2. Phenomenological Transport Theory

Transport processes may be described in terms of a flux and a driving force for the flux, which are related to each other through constants that characterize the material for the particular process. Thus, the diffusivity relates the flux of matter to the gradient of the chemical potential, and the viscosity and bulk modulus relate momentum flux to velocity and

stress gradients. The fluxes must satisfy a conservation condition known as the continuity equation, which states that the flux into a small region must equal the flux-out plus any accumulation in the region. Partial differential equations describing the transport processes can be obtained by combining the flux equation with the equation for continuity. In this manner one obtains Fick's second law of diffusion, Ohm's law for electrical conductivity, and the Navier-Stokes equation for momentum transport. Standard techniques for measuring the material constants associated with transport are based on the solution of these equations for simple boundary conditions that are usually static or quasi-static. Description of these techniques may be found in the literature. ^(60, 61)

The transport coefficients determined by the classical methods represent average properties of the material, which means that matter, momentum, or charge is transported over relatively great distances with respect to the structural dimensions of the glass and that the microscopic details of the transport processes are lost. Transport processes may be studied in greater detail by using dynamic methods of measurement, ⁽⁶²⁻⁶⁴⁾ which employ cyclic field potentials as driving forces for the transport processes. Thus, alternating electric fields may be used to measure transport of mass and momentum, and time-dependent stress fields may be used for momentum transport. The static methods of measuring transport properties are, of course, equivalent to the dynamic methods in the low-frequency range.

To use dynamic methods to study transport processes, one must consider the effect of disturbing a thermodynamic first order property (volume, stress, entropy, temperature, etc.) from its initial equilibrium value. The property will change, of course, so as to assume a new equilibrium value. The change will not be instantaneous but will take time, depending

on the dynamic processes that must occur to bring about the change. Assume that the time rate of change of the property from its initial value is linearly proportional to the size of the disturbance as expressed in the following equation:

$$dP(t)/dt = \tau^{-1}(P - P_0), \quad (2)$$

where P is the property at any time, t , and P_0 is the final equilibrium value. The proportionality constant, τ^{-1} , is related to the speed with which the process can occur and τ is known as the relaxation time. Solving the above equation for initial and final conditions, the following equations are obtained:

$$A(t) = (P(t) - P_0) / (P_i - P_0) \quad (3)$$

$$= \exp(-t/\tau), \quad (4)$$

where P_i is the initial value of the physical property. Equation 3 serves to define the function $A(t)$.⁽⁶⁵⁾ If a single relaxation process is occurring as described by Equation 2, then Equation 4 follows. In general, relaxation processes are not governed by single relaxation times (Equation 2) and the dynamics of the process described by the function $A(t)$ cannot be expressed in terms of a single exponential.⁽⁶²⁾ $A(t)$ may be described as a sum of orthogonal functions. It is convenient to write $A(t)$ as a weighted sum of exponentials:⁽⁶⁶⁾

$$A(t) = \int_0^\infty g(\Gamma) d\Gamma \exp(-t/\Gamma), \quad (5)$$

where $g(\Gamma)$ is a distribution of relaxation times. If $A(t)$ corresponds to a single relaxation process, then obviously $g(\Gamma)$ is a delta function. It should

be emphasized that the spectrum of relaxation times represented by $g(\Gamma)$ is a mathematical convenience in handling relaxation processes and can only be given physical significance within the framework of a molecular theory. For example, if the macroscopic relaxation process is assumed to be a sum of independent microscopic processes, then $g(\Gamma)$ is the density-distribution function for these processes. In any case, $g(\Gamma)$ is a valuable experimental parameter for evaluating molecular theories of transport processes.

The function $A(t)$ may be obtained directly from experimentally measured time-dependent properties and Equation (4) or more indirectly from frequency-dependent properties and Equation (5). By Fourier transforming Equation (5), for example, one can relate the complex elastic moduli to the relaxation times by the following formula:

$$m' + im'' = \int_0^\infty \left[\frac{(\omega\tau)^2}{1 + (\omega\tau)^2} + i \frac{\omega\tau}{1 + (\omega\tau)^2} \right] g(\tau) d\tau, \quad (6)$$

where m' and m'' are the real and imaginary parts of the reduced elastic moduli and ω is the frequency of applied stress. The distribution function $g(\tau)$ can be determined by measuring the complex elastic moduli by sonic techniques⁽⁶²⁾ as a function of frequency and by fitting the measured values to Equation (6). Similar equations can be obtained for dielectric relaxation and the frequency dependence of the diffusion constant.⁽⁶⁵⁾

Average transport coefficients may be obtained quite easily from the distribution function $g(\tau)$, as can be demonstrated for the shear viscosity. Considering the complex shear moduli, for which $m' = G'/G_\infty$ and $m'' = G''/G_\infty$, where G_∞ is the unrelaxed shear modulus obtained at high frequencies and G' and G'' are the real and complex parts of the shear modulus at any frequency. The shear viscosity is defined by the following equation:

$$\eta_s = \lim_{\omega \rightarrow 0} \left(\frac{G''}{\omega} \right), \quad (7)$$

which in the limits specified reduces to:

$$\eta_s = G_\infty \int_0^\infty \tau g(\tau) d\tau = G_\infty \bar{\tau}, \quad (8)$$

where $\bar{\tau}$ is the average relaxation time. In a similar fashion, the electrical conductivity is given by the following equation:⁽⁶⁷⁾

$$\sigma_0 = \epsilon_\infty \left(\int_0^\infty \tau s(\tau) d\tau \right)^{-1} = \epsilon_\infty / \bar{\tau}, \quad (9)$$

where ϵ_∞ is the infinite-frequency dielectric constant associated with the process and $s(\tau)$ is the distribution of relaxation times for the dielectric measurements.

The dynamic and static methods of measuring transport properties give information on the rates at which transport phenomena occur and may be used to obtain information on the microscopic processes occurring during transport. Unfortunately, the quantity of data already obtained by these techniques is not sufficient to characterize the transport phenomena occurring in the chemical strengthening of glass, and there is a great need for collecting such data. The data that do exist indicate that the present molecular theories of transport are inadequate for description of the transport processes in the regions of interest. This can be demonstrated by discussing the viscoelastic properties of glass.

3. Molecular Theory of Viscosity

An adequate molecular theory of the viscosity of glass should accurately predict $g(\tau)$ or $A(\tau)$ over a range of temperatures, and particularly in the glass-transition range of interest for chemical strengthening.

Unfortunately, the theories that do exist fail to predict the known behavior of glass in this region. For example, the two most popular current theories of viscosity, the Adam and Gibbs⁽⁶⁸⁾ theory and the free-volume theory⁽⁶⁹⁾ predict a low-temperature dependence of the relaxation time of the form:

$$\ln \Gamma = A + \frac{B}{T - T_0}, \quad (10)$$

where A , B , and T_0 are empirical parameters. Equation 10 is usually referred to as the Fulcher equation. Unfortunately, extrapolations of high-temperature data into the glass- transformation region by means of this equation deviate sharply from actual experimental values in cases in which sufficient data are available for a test. This is illustrated by the work of Macedo and Napolitano,⁽⁷⁰⁾ which shows that for viscosity values above 10^{12} poise the Fulcher equation considerably overestimates the viscosity data for B_2O_3 and borosilicate crown glass.

$A(\tau)$ in fact is not exponential for practically all glasses, and therefore cannot be characterized by a single parameter such as viscosity. A two-parameter description of the spectrum of relaxation times usually suffices to describe $A(\tau)$.^(71, 72) One parameter is the average relaxation time, $\bar{\Gamma}$, while the other parameter, b , measures the width of the spectrum. A common assumption is that for small temperature changes b is not temperature-dependent. Unfortunately, this assumption is not borne out experimentally for oxide glasses such as B_2O_3 ,⁽⁷¹⁾ GeO_2 ,⁽⁷²⁾ or $Na_2O - B_2O_3 - SiO_2$.⁽⁷³⁾ Therefore, there is a pressing need for means of either theoretically or empirically extrapolating the function $A(\tau)$ to non-

equilibrium states at temperatures below the glass transition.

Glass in and below the transition is usually in a non-equilibrium configuration, which can be described in terms of one- or two-fictive temperature parameters. Thus, new theories have to provide a framework in which transport parameters can be obtained for non-equilibrium states. Concurrent with the development of new viscosity theories, data should be collected to check these theories experimentally. This implies the collection of relaxation data well into the glass-transition region and the development of means of extrapolating the data to non-equilibrium states at temperatures below the glass transition. In addition, viscoelastic theories should predict the microscopic behavior of glass as characterized by the distribution function $g(\Gamma)$.

4. Viscoelasticity of Surface Layers

Of particular importance to the chemical strengthening of glass is a description of the viscoelastic properties of the chemically exchanged surface layer. An understanding of such properties may lead to the solution of many outstanding problems in chemically exchanged glasses. Some examples of these problems are:

(a) When glass is made from the melt having exactly the same composition as the exchanged layer, it is found to have lower chemical durability and hardness than that produced by exchange. One possible explanation for this may lie in the high surface stresses.

(b) Because of the difference in hardness, one might expect that the elastic moduli of the surface layers would be different from those of the bulk glass. If this is the case, one must take this difference into account in order to properly calculate the stresses at glass-to-metal joints.

(c) Different strengths are obtained for borosilicate and aluminosilicate glasses having the same amount of alkali exchanged. There

are at least two possible reasons. First, the surface layers may have different rates of viscoelastic relaxation. Second, the glass structure may have different levels of accommodation of foreign ions, giving different stress levels.

(d) There is an apparent limit to the amount of surface ions that can be exchanged. If this "stuffing" limitation could be overcome, much higher stress levels could be obtained.

Thus, it is suggested that measurements of mechanical properties of the surface be made and studies of molecular mechanisms peculiar to the surface be conducted to elucidate these unexplained effects in the exchange reactions.

5. Ionic Transport

At temperatures well below the glass transition, electrical conductivity, diffusion, and mechanical relaxation are caused by the migration of cations through the "frozen" structure of glass.⁽⁷⁴⁾ Since the higher the valence the slower the ion will migrate, it is the singly charged ion that is responsible for most of the transport properties observed. In fact, it is the monovalent ion migration that permits chemical strengthening of glass at high temperatures. Yet there are undesirable effects at lower temperatures. During supersonic flight the surface temperature of the chemically strengthened airplane windshield can easily exceed 200°C. At such temperature the diffusion coefficients of the cations are large enough so that ions from the surface will exchange with those in the interior, resulting in loss of strength. Another example of undesired ion migration is observed when one investigates mechanical properties at room temperature. Depending upon composition, up to a 20-percent change in the apparent Young's modulus of glass occurs due to the delayed elastic effect. This complicates the stress analysis involved in

the design of glass to metal joints. As another example, glass companies, following ASTM-certified techniques, report moduli measured by sonic-resonance methods that are at least ten percent higher than the moduli measured after one hour of static loading. In selecting glasses, it is the long-term modulus that must be used.

Qualitatively, there are two relaxation mechanisms associated with ion migration. The shortest relaxation appears in both electrical and mechanical measurements and is attributed to migration of single ions. The longer relaxation-time process can be observed only in mechanical measurements and has been attributed to exchange of positions between small and large alkali ions.⁽⁷⁵⁾ This second process is the one responsible for delayed elastic effects, which relate to a time dependence of the elastic constants at room temperature.

When only one ion is involved in transport, the Nernst-Einstein equation relates the tracer-diffusion coefficient of the ion and the electrical conductivity of the material. In single-phase glasses, such as fused silica and commercial soda-lime glass, this equation is obeyed within experimental error. However, when the glass is separated into two phases, such as in Pyrex borosilicate glass or many laboratory glasses, the Nernst-Einstein equation is not fulfilled, the tracer-diffusion coefficient being at least 50 percent lower than expected. The discrepancy has been attributed to various mechanisms of transport, but none of these take into account the effect of phase separation.

Ionic mobilities in fused silicas decrease in the order sodium, lithium, silver, and potassium,⁽⁶¹⁾ although the mobility ratios are somewhat different for the different silicas. The activation energy for conduction at low temperatures is constant and about the same for sodium, lithium, and potassium ions in fused silica. At higher temperatures the activation

energy for conduction decreases with increasing temperature.

Various defect mechanisms have been proposed for ionic transport in glass, but there is no direct support for them. Furthermore, there is no general explanation for the various results described above. It is possible to relate some ionic-transport properties in silicate glasses to the affinity or selectivity of the glass for the ion, but other results cannot be explained this way. Some transport properties seem to be related to ionic size, but others, such as the activation energies for conduction in fused silica mentioned above, are not dependent upon ionic size.

Despite the importance of ionic transport to strengthening, there is little basic information on the mechanisms of transport or on the relationship between mass transport, electrical transport, and mechanical relaxation. Furthermore, transport through microheterogeneous glasses is even less understood. Thus, more ideas and work are needed to understand the mechanisms of ionic transport in glasses. This work should include investigations by dynamic methods of measurement, which give details of molecular processes, as well as investigations by more conventional techniques, which determine average transport properties.

E. Glass Structure

The structure of glasses is generally described on three levels: (1) local atomic arrangements (scale smaller than $8\text{\AA}$); (2) submicrostructure (scale of $30\text{\AA}$ to $1\ \mu$); and (3) microstructure (scale above $1\ \mu$). On all these levels, the structure is expected to affect the properties of glasses and, in particular, their mechanical and transport properties. Similarly, most problems in our understanding of the properties of glasses are ultimately associated with the poor state of our understanding of glass structure.

In the following discussion, we shall direct our attention to the structure of glasses on these various scales, with particular emphasis on silicate glasses, since the bulk of commercial glasses as well as the glass materials considered for deep-submergence vehicles are of this type.

1. Local Atomic Arrangements

While we know a good deal qualitatively about the local atomic structure of silicate glasses, relatively little is known in satisfactory detail. It has been established^(76, 77) that silicate glasses high in SiO_2 are composed of networks of SiO_4 tetrahedra.

In glasses other than SiO_2 itself, some of the oxygens in these tetrahedra are bonded in two silicons (called bridging oxygens), while some are bonded to only a single silicon (called singly bonded or nonbridging oxygens). Near the singly bonded oxygens are believed to lie the common modifying cations, such as the alkali or alkaline earth ions.

It is generally believed, and in the case of SiO_2 it has been demonstrated,⁽⁷⁸⁾ that the SiO_4 tetrahedral units are quite regular in form (with a regularity comparable to that of crystalline silicates); and the

essential randomness of the glass arises from the distribution of Si-O-Si bond angles. In the case of fused silica, this distribution covers a broad range extending from about 120° to 180° .

In the case of boron, ⁽⁷⁹⁾ another important glass-former, the surrounding configuration of oxygens may be triangular or tetrahedral in form; in the case of aluminum it may be tetrahedral or octahedral, but is believed to be largely tetrahedral in glasses containing both aluminum and silicon in significant amounts.

In the case of certain ions of high field strength, such as the transition metal and rare earth ions, it has been possible to deduce information about the immediate local environments from the combination of various spectroscopic techniques. ⁽⁸⁰⁻⁸²⁾ In a number of such cases, the predominant coordination of oxygen around these ions has been identified, generally by comparing the observed spectra with those found for crystalline materials. More recently, studies have been undertaken to obtain information about the site-to-site variation in the local environments of such ions.

At the present time, relatively little is known about the structural state of the common modifying cations, such as the alkali or alkaline earth ions; and little or nothing is known about the structural changes introduced by combinations of network-forming cations, such as might be formed by the addition of boron, aluminum, or titanium to silicate melts.

The principal experimental methods for obtaining information about local atomic arrangements have been X-ray and neutron diffraction and various spectroscopic techniques. One of the chief limitations in obtaining precise structural information from X-ray diffraction studies is associated with the fact that many of the atoms in the important glass-forming systems are relatively low in atomic number -- for example, silicon, boron, lithium, and sodium. Because of this, the Compton modified scattering at large

values of $\frac{\sin\theta}{\lambda}$ (where θ is the diffraction angle and λ is the wavelength of the radiation) can represent a significant fraction of the total measured intensity. This modified scattering contains no useful information about atomic arrangements and must be eliminated either theoretically or experimentally. Difficulties have also been associated with various approximations used in analyzing the diffraction data for glasses containing more than one type of atom.

Recent advances in experimental techniques for eliminating the modified scattering and in analytical procedures for treating the data⁽⁸³⁾ seem to have opened a new era of glass-structure studies. It is hoped that the combination of these advances, which have thus far been applied only to SiO_2 and B_2O_3 , will yield detailed information about the important features of glass structure.

It should be recognized that such X-ray diffraction studies will be most fruitful when combined with other techniques for providing structural information. Notable in this regard is the technique of neutron diffraction, which provides information complementary to that obtained from X-ray diffraction. The utility of neutron diffraction lies primarily in the fact that the scattering amplitude is not dependent on the scattering angle. The scattering cross section for a given atom can be quite different for neutrons and for X-rays. The widespread use of neutron diffraction in structural studies has been limited by the low-flux levels available from most reactors. The recent availability of high-flux research reactors seems to offer appreciable opportunity in this regard.

Other techniques that can provide important structural information, and that should be utilized in particular applications, include the following: electron diffraction; electron microscopy; electron spin resonance; nuclear magnetic resonance; optical, infrared, and Raman

spectroscopy; and small-angle X-ray scattering.

Finally, it should be noted that at the present time the discussion of most properties of glasses represents little more than a qualitative description of the phenomena. The limitations on the development of more satisfactory physical models are most frequently associated with a lack of structural knowledge; and the structural information anticipated from the studies suggested above should contribute significantly to an improved understanding and eventual control of the properties of glasses.

2. Submicrostructure

The phenomenon of phase separation (liquid-liquid immiscibility) is widespread in glass-forming systems.⁽⁸⁴⁻⁹⁰⁾ Among two-component systems, for example, immiscibility has been demonstrated in all the alkaline-earth silicates, in the lithium and sodium silicates, in the SiO_2 - B_2O_3 systems, as well as in all alkali and alkaline earth borates. Among more complex glasses, phase separation has been observed in a large number of systems.

The occurrence of phase separation gives rise to glass structures (submicrostructures) that are heterogeneous on a scale of $30\text{\AA}$ to a few thousand $\text{\AA}$. Morphologically, the second-phase structure may consist of isolated particles of one phase in a continuous matrix of another phase, or both phases may be three-dimensionally interconnected.

The origin of these interconnected submicrostructures is the subject of considerable discussion at the present time. The suggestion that they result from a spinodal decomposition process has been supported by theoretical calculations⁽⁹¹⁾ that show significant connectivity in cross sections calculated from the initial-stage (linearized) theory of spinodal decomposition. More recently, it has been shown that this analysis would

be appropriate for compositions near the center of miscibility gaps, but that, as the composition approaches the spinodal (even within the spinodal), the bulk of the separation process resembles a nucleation-and-growth process.⁽⁹²⁾

The effect of departures from the initial-stage theory would be to sharpen the interfaces between the phases and break up the connectivity; but under what conditions such effects would result in discrete-particle submicrostructures remains to be elucidated.

An alternative explanation⁽⁹³⁾ considers the interconnected structures to arise from the formation, growth, and coalescence of discrete second-phase particles; in one study such coalescence was directly observed in the electron microscope.⁽⁹⁴⁾ Unfortunately, studies of the sequence of submicrostructural development are few in number. Most studies have directed attention to the final-phase morphologies rather than to the course of their development; the inadequacy of merely observing the final morphologies is emphasized by observations of interconnected submicrostructures forming from discrete particle structures, and under other circumstances breaking up into discrete particle structures.⁽⁹⁴⁾

In attempting to provide relevant kinetic data, several studies have been carried out on the small-angle scattering from phase-separating systems.^(95, 96) In all cases reported to date, the system investigated left much to be desired because the kinetics of separation were relatively rapid; and at the present time little can be said with confidence concerning the kinetics of phase separation within the spinodal region in any glass system.

It seems clear, then, that future studies should be directed to the chronology of submicrostructure development and not merely to observations of final morphologies. Such studies should include observations of the morphology and kinetics of separation, in both the unstable and metastable regions, as well as in the supercritical stable region.

Concerning the prediction of the location of miscibility gaps, effectively nothing is known. There are several empirical correlations based on cation field strength and other parameters; but at the present writing if an investigator is concerned with the possibility of immiscibility in a system, he makes up the glasses and examines them, rather than trying to predict the location, or in many cases even the existence, of a gap. The dependence of immiscibility on the composition, the particular types of atoms, the temperature, and other factors are still largely unknown; detailed knowledge of immiscibility behavior in ternary and more complex systems is practically nonexistent.

The last situation is complicated by the possibility, in complex systems, of separation into more than two phases. This, in turn, is often difficult to distinguish experimentally from secondary phase separation, which can occur even in binary systems.⁽⁸⁶⁾ Such secondary separation occurs after the initial separation into two phases, when either or both of the phases in turn separates on a smaller scale as the equilibrium conditions change with changes in temperature.

The morphology, scale, and extent of the second-phase submicrostructure can be expected to affect nearly all properties of glasses, from molar volume and elastic modulus⁽⁹⁷⁾ to the conductive properties, chemical durability, and mechanical-strength⁽⁹⁸⁾ effects that are most significant in the case of transport properties and durability. Relatively little has been done, however, in the way of a systematic investigation of the effects of the submicrostructure on properties. Indeed, the discussions of most properties of glasses as they appear in the literature are based upon the concept of glass as a homogeneous material, and do not consider the actual structure, which often is composed of more than one phase.

In addition to affecting the physical properties and flow characteristics of glasses, phase separation can play an important role in their

crystallization behavior. For example, as discussed in Section G, some of the standard processes for making glass-ceramic materials depend upon phase separation as a precursor to the initial nucleation of crystals. Some preliminary studies of the relation between phase separation and subsequent crystallization have been carried out, ^(99,100) but little of a systematic nature has been done.

In brief, then, in nearly any composition to be considered as a naval structural material, the existence of immiscibility is a factor which must be considered in some detail. Problems associated with immiscibility should be particularly acute when massive glass is considered, since its fabrication will necessitate long heat-treatment times.

3. Macrostructure

It has been said with some cogency that a truly homogeneous glass has seldom, if ever, been made. On the scale visible in the light microscope or with the naked eye, a variety of structural features are observed. These include chemical (compositional) heterogeneities, inhomogeneities in density and refractive index, devitrified inclusions, and the like.

In many cases, structural imperfections on this scale are reasonably well understood and controlled, and the means of eliminating or controlling them are generally well in hand. Even in these cases, however, one would like more efficacious control of such imperfections in large-scale, high through-put applications.

One of the most interesting subjects for fundamental study in this area is devitrified inclusions. Such crystalline regions seem likely to originate on condensed second-phase impurities; but the important sources of such impurities and their role in the nucleation process remain to be elucidated satisfactorily. Like immiscibility, such crystallization problems

should be most severe in the case of massive bodies, in which long heat-treatment times are involved.

4. Intermediate-Scale Structure

As noted above, information is now available, or can be obtained in the near future, about the structural characteristics of glasses on a scale smaller than about $8\text{\AA}$ and larger than about $30\text{\AA}$. Nothing is presently known about structure in the intermediate range from about $8\text{\AA}$, and no presently available technique seems promising for the elucidation of structural details on this scale.

F. Fundamental Studies of Glass Properties Related to Vibrational Spectra

Almost all the processes proposed for study in this report depend on a relatively small number of fundamental properties of glasses. Among these are the thermal expansion, elastic constants, specific heat, viscosity, and glass-transition parameters. The transport-related phenomena, viscosity, and glass transition are discussed elsewhere in this report. The first three, which are strongly related to the vibrational spectra of glasses, are the subject of this section.

An extremely large number of measurements of these parameters for various glasses exist in the literature. These are partially summarized in the reviews of Davies and Jones,⁽¹⁰¹⁾ Stevels,⁽¹⁰²⁾ Morey,⁽¹⁰³⁾ and Phillips.⁽¹⁰⁴⁾ In addition, a number of attempts have been made to correlate the variations of these parameters with structural and chemical features of the glasses. These correlations are discussed extensively by Stevels,⁽¹⁰²⁾ Lowenstein,⁽¹⁰⁵⁾ and, to a lesser extent, by Stanworth.⁽⁷⁷⁾ Because of the rather complete characterization of the glass systems likely to be important and because of the extensive past and present efforts to obtain glasses with high Young's moduli, no recommendation for surveys concerning these properties is contained herein. Similarly, no striking need for further correlative work is apparent. The most obvious limitations to our understanding are in relating atomic arrangements and interactions to those physical properties that are associated with the vibrational spectra.

Until recently, however, there seemed little hope of explaining these parameters at an atomic level in the detail achievable with crystals. (In order to point out the problem in dealing with amorphous solids, let us review the treatment for crystals.) In that case, normal modes of vibration are describable simply in terms of a propagation vector $\underline{k}$. That is, the

displacement, $\underline{u}(\underline{r})$, of an atom at the position $\underline{r}$ in one unit cell is related to that of an identical atom at a position $\underline{r} + \underline{R}$, where $\underline{R}$ is a repeat vector of the lattice, through the equation:

$$\underline{u}(\underline{r}+\underline{R}) = \exp(i\underline{k} \cdot \underline{R}) \underline{u}(\underline{r}). \quad (11)$$

As a result, the dynamic equations that couple together all the atoms in the crystal can be factored into $3p$ coupled equations for each $\underline{k}$. Here, p is the number of atoms per primitive unit cell. These can be solved numerically, yielding $3p$ solutions for the angular frequencies, $\omega_j(\underline{k})$, in terms of the interatomic forces. In the limit of small $\underline{k}$, three modes for each $\underline{k}$ describe the acoustic spectrum, so that the frequencies are determined by the elastic constants. Thus, the elastic constants can be determined and understood in terms of the interatomic forces and the geometry of the structure. The specific heat, c_v , is a simple function of the frequencies, $\omega_j(\underline{k})$, while the volume-thermal-expansion coefficient, α , depends on both the frequencies and their volume dependences.

These relations can be expressed for all quasiharmonic solids as:

$$c_v = \sum_j c_e(\omega_j) \quad (12)$$

and

$$\alpha = (\chi_T/V) \sum_j \gamma_j c_e(\omega_j). \quad (13)$$

The sums are over the normal modes and the Einstein specific heat associated with a mode of frequency ω is:

$$c_e(\omega) = k(\hbar \omega/kT)^2 \exp(\hbar \omega/kT) [\exp(\hbar \omega/kT) - 1]^{-2}. \quad (14)$$

Here, $\hbar$ and k are Planck's and Boltzmann's constants, while χ_T and V are

the isothermal compressibility and specific volume, respectively. The γ_j are expressed in terms of the volume dependences of the ω_j by the relation:

$$\gamma_j = - \delta \ln \omega_j / \delta \ln V. \quad (15)$$

At low temperatures, only the acoustic modes are excited, so that the low temperature limits of the vibrational contributions to c_v and α are simply related to the elastic constants and their volume dependences. These relationships are almost always verified by experiment.

Even in disordered homogeneous crystalline alloys where Equation (11) is, in principle, invalid, many normal modes and, in particular, the low-frequency modes, seem to be well described by Equation (11), so that the equations relating the low temperature limits of c_v and α to the elastic constants appear to describe nature satisfactorily in most situations. The variation of the elastic constants with composition are fairly well described by averages of force constants. Room temperature c_v 's and α 's vary smoothly and simply with composition. These smooth variations may be attributed to the fact that the integrity of the lattice is maintained, except for local strains.

In amorphous materials, however, Equation (11) is completely invalid and experimental results appear to show this. The problems are most evident at low temperatures where, as discussed by Leadbetter,⁽¹⁰⁶⁾ for instance, c_v and α of vitreous silica are not at all determined by the elastic constants. The most striking example is the extremely negative low-temperature Grüneisen constant, γ ($= \alpha V / \chi_T c_v$). This constant expresses, primarily, the ratio of α to c_v at low temperatures, where χ_T and V are essentially constant. γ attains a value of -8 at 3°K compared to the value of -2 predicted by the elastic constants and volume dependences. Even the value

of -2 is significantly more negative than those observed in the zincblende compounds, which also show negative thermal expansion.

As Leadbetter⁽¹⁰⁶⁾ has shown, the low-temperature γ and c_v anomalies indicate that there are a very small number of modes of very low frequency which are not simply related to the elastic waves. A definitive description of these modes has not yet been put forth, so that they remain a challenging scientific problem. Because of their small number, however, they are not expected to influence appreciably the room-temperature properties of interest here.

On the other hand, the large negative γ , over extended ranges of low temperatures, is important because its cause is also the cause of the extremely small magnitude of the positive thermal expansion at room and higher temperatures that is so important in many aspects of silicate-glass usage. On the basis of an Einstein-like model calculation, Smyth⁽¹⁰⁷⁾ has attributed this to transverse vibrations dominated by oxygen motion. Such a picture is consistent with recent explanations⁽¹⁰⁸⁻¹¹⁰⁾ of the negative α in zincblende structure compounds. Although the Einstein model cannot be trusted, there is considerable evidence for the existence of an appreciable number of normal modes in which the predominant motion is oxygen moving perpendicular to the plane formed by the vectors from it to its two silicon nearest neighbors. The most conclusive evidence for such modes results from the numerical calculations of the normal mode spectrum of a model vitreous silica performed by Bell, Bird, and Dean.⁽¹¹¹⁾ These authors associate them with the infrared peaks near 400 cm^{-1} in vitreous silica discussed by Simon.⁽¹¹²⁾

Two features of the vibrational spectrum of silica indicate, however, that these modes may not be sufficient in themselves to explain the negative and small positive α region. The first is that γ is much more

negative for vitreous silica than for the zincblende structure compounds. The second is that the velocity of longitudinal sound waves increases with increasing volume. Both facts suggest that other modes may be important.

It would be quite valuable to have measurements of the pressure dependences of infrared peaks of silica. By combining these results with the densities of modes calculated by Bell *et al.*,⁽¹¹¹⁾ the validity of the Smyth⁽¹⁰⁷⁾ picture could be ascertained and the role of different portions of the vibrational spectrum in determining the thermal expansion could be elucidated.

At the same time, an understanding of the lattice dynamics of cristobalite, the closest crystalline analogue of vitreous silica, might be most rewarding. This compound shows⁽¹⁰⁶⁾ an anomalously large specific heat at low temperatures. Its low-temperature thermal expansion has not yet been measured. It is possible that a number of features that make vitreous silica so unusual are imaged in the lattice dynamics of the crystalline compound.

The calculation and detailed understanding of the elastic modes and constants themselves appear to be beyond our present capabilities. The above-mentioned calculations of Bell *et al.*,⁽¹¹¹⁾ are based on a random network model constructed by Bell and Dean⁽¹¹³⁾ from balls and wires. About 600 "atoms" are contained in the model, so that long-wavelength modes cannot be represented. It seems likely, however, that computer calculations of the response of their model and other models to static applied stresses would yield considerable insight.

The alloying of vitreous silica with the various components that lead to commercial glasses leads to marked changes in physical properties. As an illustration, the systems $\text{SiO}_2\text{-M}_2\text{O}$, where M is an alkali metal, are discussed here. The changes of elastic moduli with M_2O concentration are not well understood. These factors appear to be important. In apparently

homogeneous systems, it is generally believed that the introduction of M_2O destroys the continuity of the relatively still silicate network, with some oxygens bonded to one, rather than two, silicons. That is, nonbridging oxygens are introduced. This leads to decreases in the moduli. On the other hand, the alkalis fill the interstices in the silicate network, presumably leading to increases of the moduli. The role of phase separation is even less understood.

Most success relating to fundamentals may be anticipated from studies of homogeneous glasses. In these, data on shear moduli are quite incomplete and should be obtained. Of the parameters considered in this section, the most prominent changes are associated with the thermal expansion. The room temperature α 's of all the M_2O-SiO_2 glasses increase markedly with increasing M_2O concentration.⁽¹¹⁴⁾ The room temperature α of a 12-mole percent K_2O silicate glass is approximately four times that of pure vitreous silica. This suggests that the number or nature of the modes contributing negatively to the thermal expansion is changing markedly. These changes may be consistent with the concept of nonbridging oxygens because those modes, as discussed above, are pictured as consisting of oxygen motion perpendicular to the Si-O-Si planes. In addition, the alkalis add a restoring force, associated with motion of oxygens parallel to the line that joins them to the alkalis, which contributes positively to the thermal expansion and which should increase the frequencies of these modes. Support for this picture could be obtained through measurements of changes of the previously mentioned infrared peaks near 400 cm^{-1} with composition, but such measurements are quite incomplete.

In closing this description of the phenomenology of the vibrational characteristics of M_2O-SiO_2 glasses, it should be pointed out that a similar discussion of qualitatively different but quite marked changes

in $M_2O-B_2O_3$ glasses could have been presented. Here, again, there are striking changes of the thermal-expansion coefficients with composition. In this case, moreover, there is a change of boron coordination from three- to four-fold. Similar qualitative explanations for the changes of physical properties with composition have been presented in the literature. The role of phase separation in those systems in which it is present remains to be explained.

However, qualitative pictures presented above must leave us unsatisfied. Because they are qualitative, there are no means of checking their validity. The recent calculations of Bell et al.⁽¹¹¹⁾ of the vibrational spectra of vitreous SiO_2 , GeO_2 , and BeF_2 indicate, however, that a more complete, almost quantitative, understanding is not beyond reach. These authors constructed models⁽¹¹³⁾ of the structures using rules derived from radial-distribution studies and the random-network model. With simple nearest-neighbor force constants, they were able to obtain densities of modes that are consistent with infrared and Raman studies of the glasses. Finally, their analyses⁽¹¹¹⁾ of the eigenvectors have produced considerable insight into the types of atomic motions that make up the different peaks in the spectra. It seems likely that such calculations, combined with carefully chosen experiments and more detailed structural information, can lead to an understanding of the parameters of interest here, as well as optical properties, with composition. It seems reasonable to anticipate that considerably larger models of this type will be constructed on the computer. With such models, the effects of longer-range interactions could be determined and the role of appreciable concentrations of metal oxides could be studied using the numerical techniques of Bell et al.⁽¹¹¹⁾ With the rapid growth of computer memories, such studies seem possible, valuable, and, of course, exciting.

G. Glass Ceramics

Glass ceramic is the generic name for a material that is melted and formed as a glass and then almost completely crystallized with a subsequent heat treatment. Composition and heat treatment must be selected to allow controlled nucleation and crystallization.^(115, 116) The final properties of the glass ceramic are the result of the composition, morphology, and size of the crystalline phases and, to a lesser degree, the amount and composition of the residual glass.

In general, a glass ceramic as compared with its parent glass is crystalline, opaque, harder, stronger, and may have different chemical, thermal, and electrical behavior. Special compositions and heat treatments can produce transparent or translucent glass ceramics.

Commercial glasses have long been carefully compounded to avoid crystallization because, when this occasionally happens in isolated areas, the material is no longer usable. In glass ceramics, however, copious nucleation is induced so that a great many extremely small crystals are formed. Further heat treatment will allow the crystals to grow, and, in some cases, crystalline phase changes can occur.

Several factors affect the character of this controlled nucleation and crystallization; the most important is chemical composition. Many compositions will crystallize spontaneously on cooling from a melt. These tend to be variable in crystal size and orientation and generally cannot be formed by normal glass-working processes. For controlled nucleation and crystallization, nucleating agents are usually added to the batch. The constituents readily precipitate in cooling and form the nuclei upon which the crystals grow. Common nucleating agents include: the metallic colloids, titanium dioxide, and the titanates, chromic oxide, phosphorous pentoxide,

zirconium dioxide, as well as zinc sulphides and certain fluorides.

Many glass compositions, with proper heat treatment, will phase-separate into two immiscible liquids. By this process, constituents may be concentrated into one of the phases that will promote nucleation and crystal growth. A great number of glass-forming silicate compositions are stable above their liquidus temperatures as two phases.

Figure 5 is a schematic representation of a simple binary system in which two liquids may separate metastably. In Figure 5a, a dotted extension of the stable two-liquid region of the phase diagram encloses the metastable immiscibility gap, where separation can occur upon controlled cooling from the melt or upon reheating a single-phase quenched glass. Figure 5b shows the metastable region under an anomalous s-shaped liquidus curve.

Heat treatment is the second most important factor in the production of glass-ceramic materials. Since large numbers of small crystals are desired, many nuclei must be formed. This controlled nucleation is an essential step in the process. Within a temperature interval immediately below the equilibrium melting temperature of many glass-forming substances, there exists a metastable zone in which nuclei do not form at a detectable rate, but in which crystals, once nucleated, can grow. Below this metastable temperature zone, nuclei may form spontaneously and homogeneously. But as the glass cools further, a high-viscosity zone is reached in which the formation of nuclei is again inhibited. Figure 6 schematically represents the rate of homogeneous nucleation and crystal growth in a viscous liquid as a function of temperature. The kinetics controlling nucleation and crystal growth, particularly of nonhomogeneous nucleation, are not fully understood.

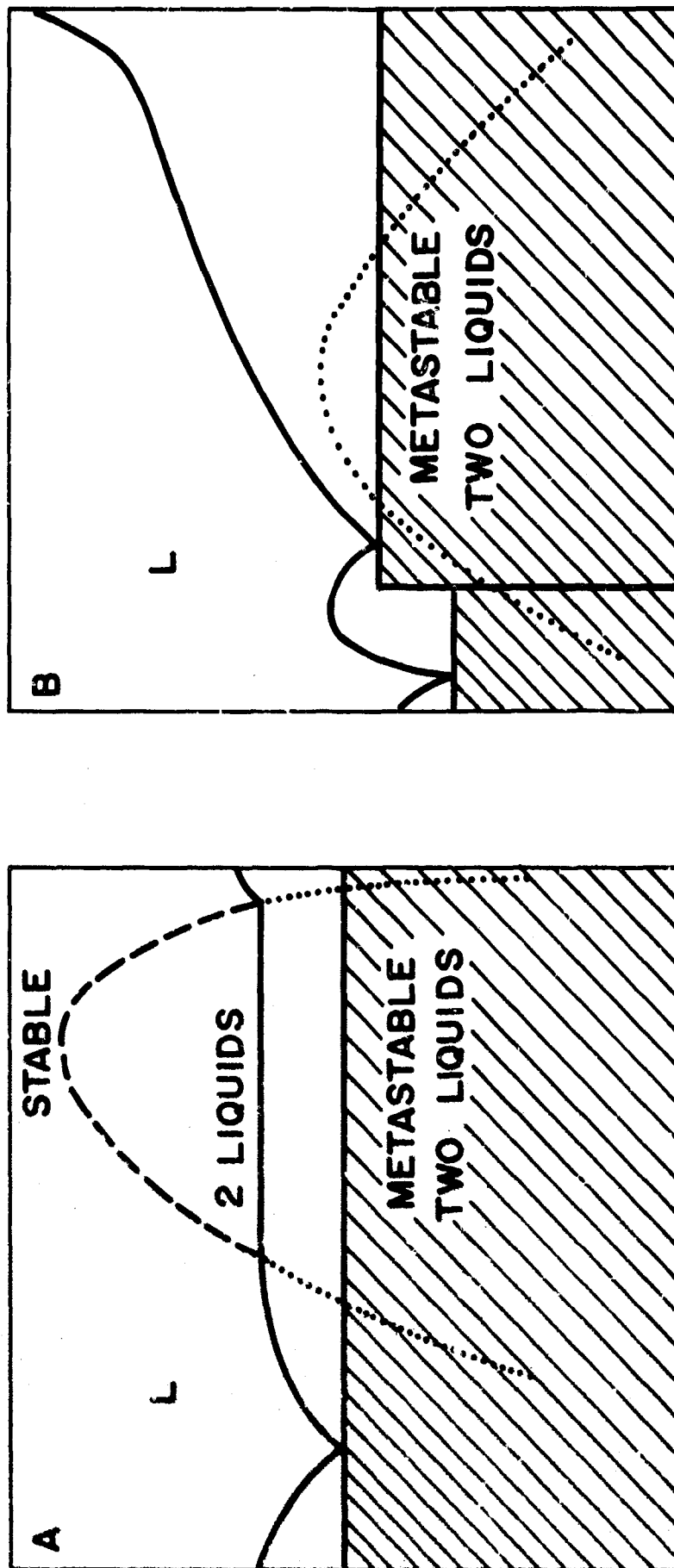


Figure 5. Schematic representation of simple binary phase diagrams showing extent of metastable immiscibility gap (a) as extension of stable two-liquid region, and (b) under anomalous s-shaped liquidus curve.

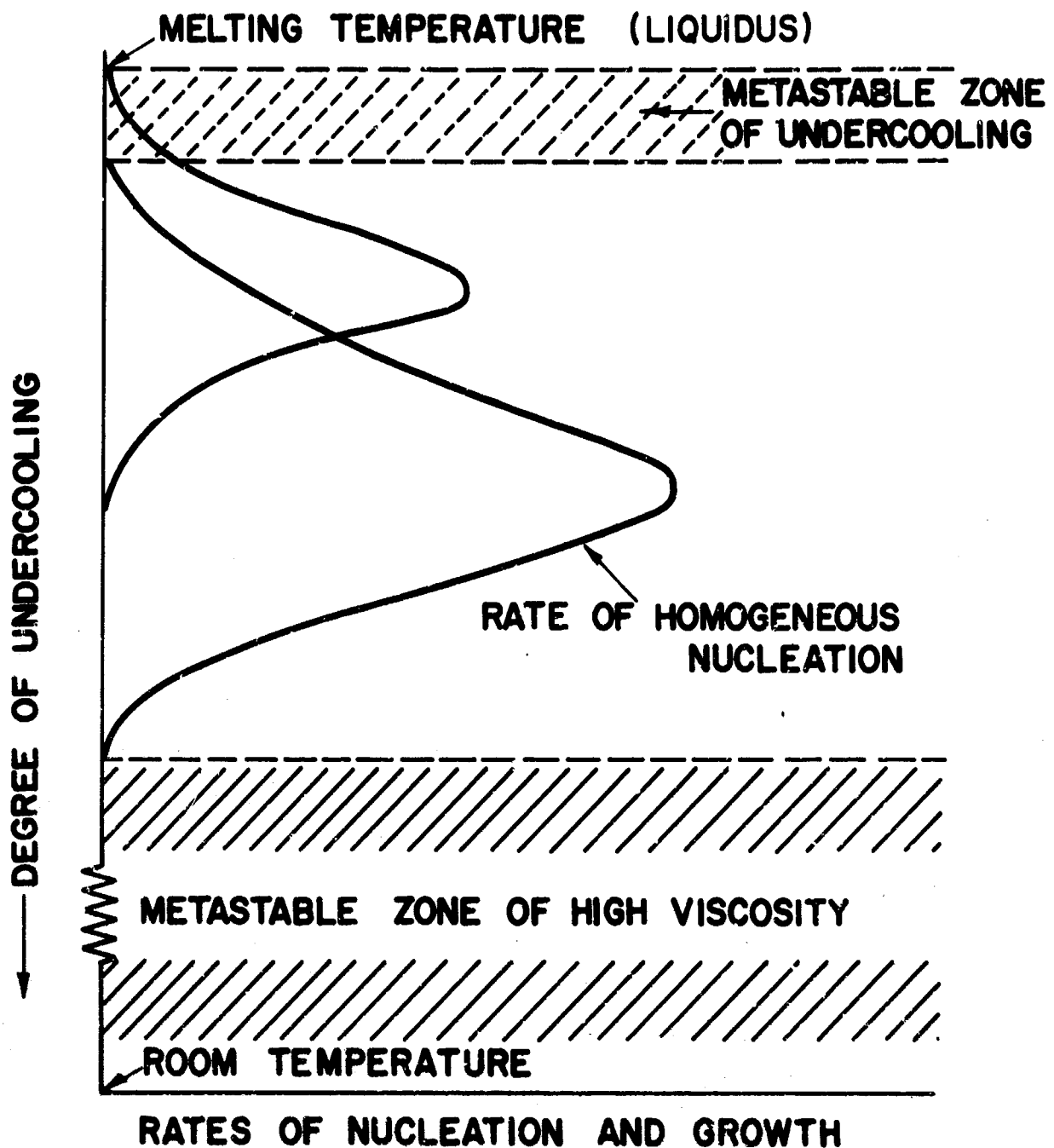


Figure 6. Rates of homogeneous nucleation and crystal growth as functions of the degree of undercooling in a viscous liquid. Note the two metastable temperature zones in which homogeneous nucleation is infinitely slow.

Most products made of glass ceramics are formed and annealed as glass prior to a crystallizing heat treatment. A heat treatment is then given the ware to nucleate and crystallize it. A typical heat-treating cycle is shown in Figure 7. In some cases, the product may be cooled just to the nucleating temperature after forming and then heat-treated directly to obtain proper crystallization. (See dotted line in Figure 7.) The time and temperature curve will depend upon the composition, size, and shape of the ware, and the character of the crystals desired.

The effect of time and temperature⁽¹¹⁷⁾ on the crystalline character of a low-expansion experimental glass ceramic is shown in Figure 8. (Composition of this glass ceramic is: 65% SiO_2 , 23% Al_2O_3 , 1.8% MgO , 3.8% Li_2O , 1.5% ZnO , 2.0% ZrO_2 , 2.0% TiO_2 , and 0.9% As_2O_3 .) It is seen from the Figure that the lowest temperature at which complete crystallization can occur is about 770°C with a longer than 15-hour hold. The crystalline phase with this thermal treatment is entirely β -quartz solid solution and the crystals are so small and so well matched in refractive index that the material is transparent. At a higher temperature, β -spodumene solid solution will appear and, after a two-hour hold at 950°C , the material will be fully crystalline and only β -spodumene will be present. This higher-temperature material will have larger crystals (about $1\ \mu\text{m}$ in diameter) and will be opaque.

The difference in expansion of β -quartz and β -spodumene is not great but considerable difference in expansion does exist between the parent glass and the crystalline phases. In a massive piece of ware made of this composition, considerable stress can develop on cooling, should different degrees of crystallization exist in any part of the piece.

In an experimental magnesium-aluminosilicate glass ceramic⁽¹¹⁸⁾

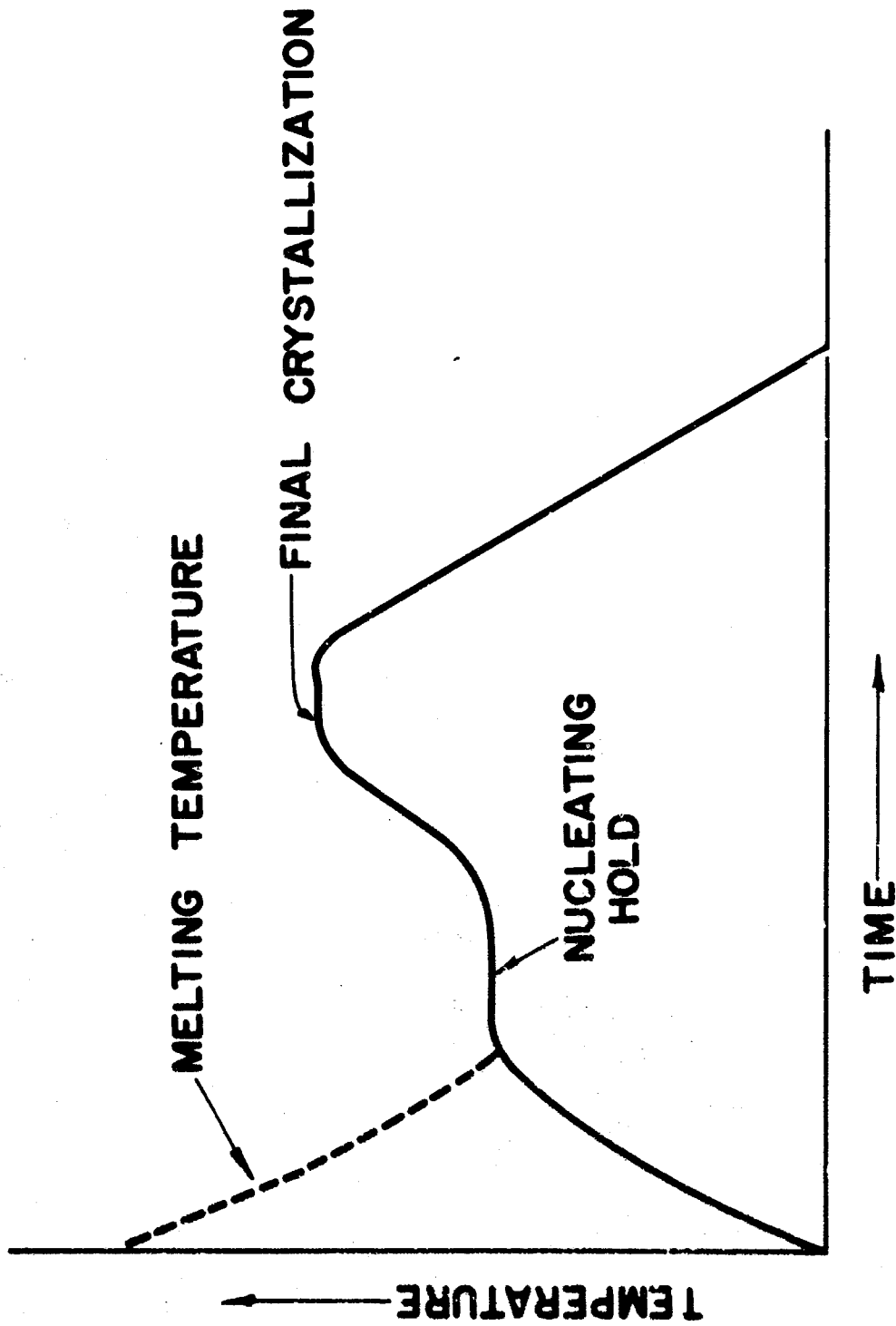


Figure 7. Typical Firing Curve for Glass Ceramic

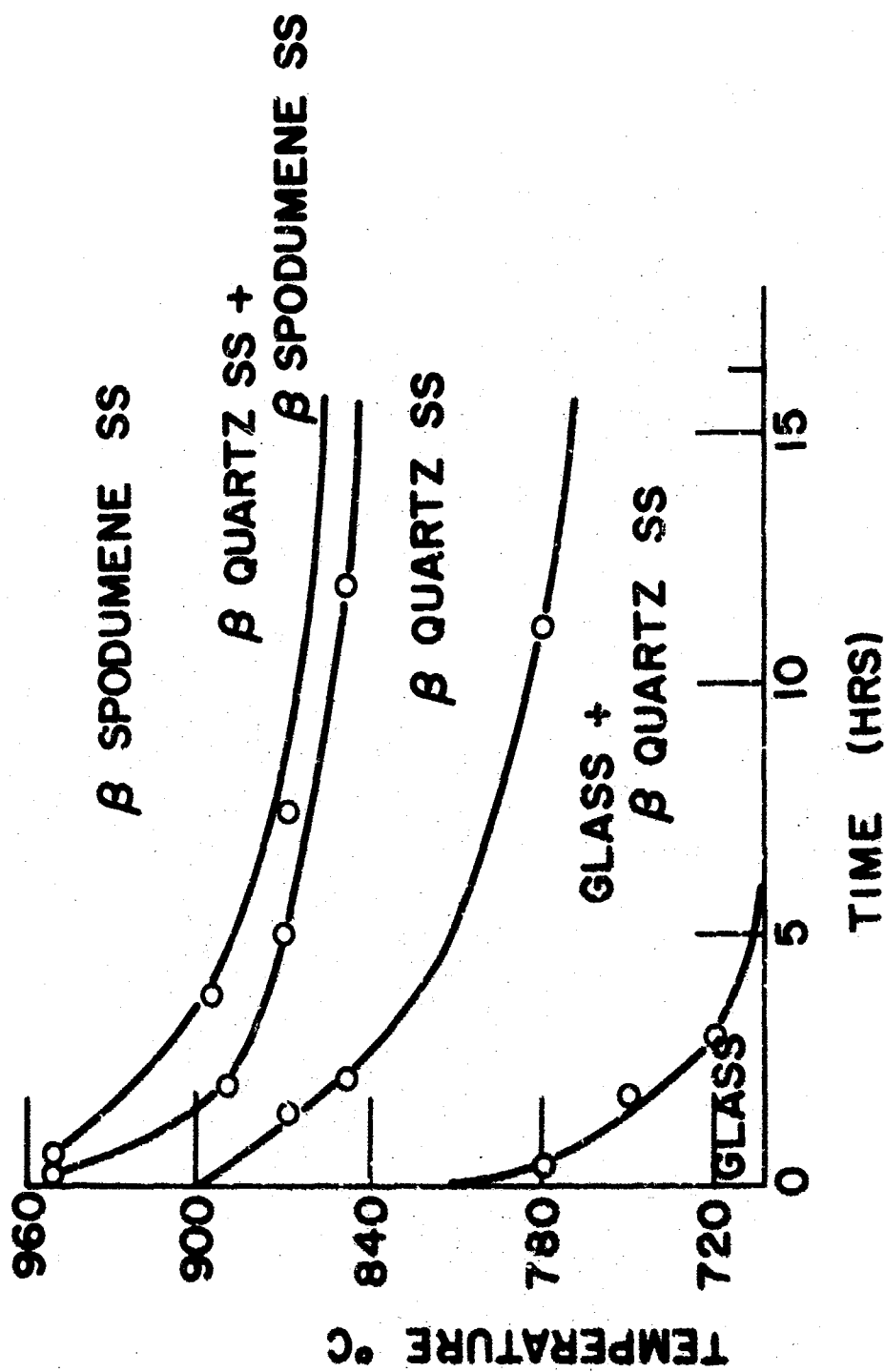


Figure 8. Time-temperature metastable phase diagram for glass ceramic composition 1

(65% SiO_2 , 25% Al_2O_3 , 10% MgO and 10% ZrO_2) when heat-treated at 880°C for four hours followed by a four-hour hold at 960°C , a transparent colorless material totally crystallized as β -quartz solid solution and tetragonal zirconia was obtained. This material has a coefficient of thermal expansion of $30 \times 10^{-7}/^\circ\text{C}$. If, however, it is heat-treated at 800°C for four hours, followed by a six-hour hold at 1100°C , the material will be totally crystallized as α -quartz, spinel, and tetragonal zirconia, and it will have an expansion of $120 \times 10^{-7}/^\circ\text{C}$. In this case, should differences in temperature exist in a massive piece during heat treatment so that these different phases would crystallize, high zonal stresses will develop.

1. Commercial Glass-Ceramic Materials

Several glass-ceramic materials are now available in commercial products. Some of these are listed in Table I.

Various physical properties of selected glass-ceramic compositions are given in Table II.

These materials have been developed for specific applications and not for massive structural uses. Some of the properties listed may not be attainable in thick sections without adjustment of composition and process. Research and development are needed to determine the character of the material desired and to develop the compositions and processes for massive structures for naval applications.

2. Ion-Exchange Strengthening of Glass Ceramics

Because glass ceramics are essentially free from open flaws, and are nonporous and polycrystalline, they are uniquely suitable for strengthening by surface-strengthening methods. (119) These methods can be divided into two general categories, with two subdivisions each, as follows:

Table 1 - Some Commercial Glass Ceramics

COMMERCIAL DESIGNATION	CRYSTAL PHASES	PROPERTIES	APPLICATIONS
Corning 8603	$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ SiO_2	Photochemically machineable	Printed circuit boards
Corning 9606	$2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ SiO_2 TiO_2	Low expansion, transparent to RF waves	Radomes for missiles
Corning 9608	β -spodumene solid solution TiO_2	Low expansion, good chemical durability	Cooking utensils
Neoceram (Japan)	β -spodumene solid solution	Low expansion	Cooking ware
Owens-Illinois Cer-Vit (C-101)	β -quartz solid solution	Very low expansion, transparent	Telescope mirrors
Corning 0303	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	High strength	Tableware Dinnerware
Corning 0330	β -spodumene solid solution TiO_2	High strength, low expansion, translucent, gray	Building cladding Bench tops
Corning 0333	β -spodumene solid solution	High strength, low expansion, opaque white	Building cladding Bench tops
English Electric Co.	Lithium disilicate zinc orthosilicate α -cristobalite P_2O_5	High expansion, metal seal compatible	Metal seals Insulators
Corning 9611	<u>Body</u> α -quartz solid solution $\text{MgO} \cdot \text{Al}_2\text{O}_3$ $\text{MgO} \cdot \text{SiO}_2$ <u>Surface</u> β -spodumene s. s. β -quartz s. s.	High strength, high expansion, surface compression	
PG Herculit	β -spodumene s. s.	Very low expansion, white	Cooking surfaces

Table II - Physical Properties of Some Glass Ceramics*
(* From Published Data)

	UNITS	9606 CORNING PYROCERAM® Glass Ceramic	9608 CORNING PYROCERAM® Glass Ceramic	9611 CORNING PYROCERAM® Chem. Str. Glass Ceramic	106 PPG Hercuvit Glass Ceramic	101 O-I Cer-Vit Glass Ceramic
Trade Mark Description		White Opaque	White Opaque	Blue Opaque	White Translucent	Transparent
Density	gm/cc	2.60	2.50	2.93	2.50	2.50
THERMAL PROPERTIES						
Avg. Coeff. of Exp. (10-300° C)	$10^{-7}/^{\circ}\text{C}$	57	4-20	100	-3	0
Conductivity (25° C)	cal/cm/sec °C	.0095	.0048	.0078	.004	.004
Specific Heat (25° C)	cal/gm °C	.19	.20	.18	.20	.20
Therm. Diff. (25° C)	cm ² /sec.	.018	.011	.008	.008	.008
MECHANICAL PROPERTIES						
MOR (abraded)	10^3 psi	20	12	90-140	19	13
Compressive Strength	10^3 psi	340	-	350	-	-
Young's Modulus	10^6 psi	17.2	12.5	16-18.5	12.1	13.4
Poisson's Ratio		.24	.25	.18	.26	.25
Shear Modulus	10^6 psi	6.9	5.0	6.8-7.8	-	-
Bulk Modulus	10^6 psi	11.2	8.3	8.3-9.6	8.5	9.0
Hardness (Knoop)	kg/mm ²	630 (100)*	635 (100)*	630 (100)*	540 (200)*	540 (200)*
ELECTRICAL PROPERTIES						
Dielectric Constant	(1MH _z , 25° C)	5.5	6.8	-	6.9	9.1
Loss Tangent	(1MH _z , 25° C)	.0031	.0030	-	.006	.023
Vol. Resistivity (250° C)	Log ₁₀ ohm-cm	10.0	8.1	12.6	7.0	8.0

* Indicates load in grams

1. Strengthening by Expansion Differences
 - a. Solid Solutions
 - b. Phase Transformation
2. Strengthening by "Crowding" or "Stuffing"
 - a. Solid Solutions
 - b. Phase Transformation

It is well known that the presence of a low-expansion surface on a higher-expansion body results in strengthening. This type of surface prestressing can be developed in glass ceramics by the formation of solid solutions or by phase transformations. The wide variety of metastable and stable phases that can be crystallized from a glass and the considerable compositional variation possible due to solid solution form the basis for these strengthening techniques.

The "crowding" mechanism involves the development of surface-compressive stresses by the exchange of large ions for small in a process analogous to that which takes place in the ion-exchange strengthening of glasses. ^(27, 28) Replacement of a small ion by a large ion is believed to elastically deform the cation-oxygen bonds in the crystal lattice. This atomic-level distortion produces a surface-compressive stress that is proportional to the difference in size between the two ions exchanged. The ion-for-ion replacement may also result in a surface transformation to a phase with a larger unit volume. This also results in the "crowding" and produces surface compression.

Numerous glasses are capable of controlled internal crystallization when properly nucleated. A few representative compositions are listed in Table III ⁽¹¹⁹⁾ along with the crystal phases present and the thermal-expansion coefficients of the resulting materials. These glass ceramics were chemically strengthened by either the expansion difference or the "crowding"

Table III - Compositions of Representative Glass Ceramics (Wt. %)

Composition	1	2	3	4	5	6	7	8	9	10
SiO ₂	56	51	60	69	50	71	40	44	43	41
Al ₂ O ₃	20	26	-	21	29	18	31	32	32	32
Li ₂ O	-	-	-	5	-	2	-	-	-	-
Na ₂ O	-	-	5	-	-	-	4	17	14	11
K ₂ O	-	-	-	-	-	-	18	-	4	9
MgO	15	5	-	-	12	5	-	-	-	-
ZnO	-	8	-	-	-	-	-	-	-	-
BaO	-	-	35	-	-	-	-	-	-	-
TiO ₂	9	3	-	5	9	-	7	7	7	7
ZrO ₂	-	7	-	-	-	4	-	-	-	-
Crystal Phases	γ-quartz spinel enstatite	γ-cristobalite spinel ZrO ₂	barium silic-ite	β-spodumene rutile	β-quartz MgTi ₂ O ₅	β-quartz ZrO ₂	synthetic Kaliophilite	nepheline anatase	nepheline anatase	nepheline anatase
Expansion Coefficient (25-300°C)	100	166	195	15	40	16	140	115	120	125

mechanism.

Table IV⁽¹¹⁹⁾ lists those glass ceramics in the above study that were strengthened by expansion differences, and Table V⁽¹¹⁹⁾ lists those strengthened by the "crowding" mechanism.

Compositions 1 and 5 in Table III are interesting in that they are both magnesium-aluminosilicate glasses, and both can be strengthened by ion exchange, producing a β -quartz solid-solution skin having a lower expansion coefficient than the body. In Composition 1, the body contains α -quartz, spinel and enstatite, with a linear coefficient expansion of $100 \times 10^{-7}/^{\circ}\text{C}$, and Composition 5 contains β -quartz and MgTi_2O_5 with an expansion coefficient of $40 \times 10^{-7}/^{\circ}\text{C}$. In both of these compositions, a lithium-for magnesium ion exchange will occur, and they result in strong materials with 142,000 and 160,000 psi modulus of rupture, respectively.

Other investigations have been made on the ion-exchange strengthening of β -quartz glass ceramics⁽¹¹⁸⁾ with linear coefficients of thermal expansion measured in the 0° to 300°C range from $+50 \times 10^{-7}/^{\circ}\text{C}$ to $20 \times 10^{-7}/^{\circ}\text{C}$. These materials can be made transparent or opaque. Most of the transparent and opaque stuffed- β -quartz glass ceramics can be strengthened by ion exchange, either through a potassium-for-lithium ion reaction in a potassium salt bath or a lithium-for-magnesium reaction in a lithium salt bath. Modulus-of-rupture values for abraded specimens range from 50,000 to 160,000 psi.

The high-expansion sodium-aluminosilicate and the sodium-barium-aluminosilicate systems of glass ceramics have been studied for ion-exchange strengthening.⁽¹²⁰⁾ These compositions result in nepheline crystallization and an expansion-coefficient range between 100 and $130 \times 10^{-7}/^{\circ}\text{C}$, depending upon the relative amounts of sodium, potassium, and other ions present. When they are ion-exchanged with potassium for sodium, the

Table IV - Glass Ceramics Strengthened by Expansion Difference

Composition.	Bath	Temp. °C	Time, Hours	Exchange	Surface Phase	MOR 10 ³ psi
1	Li ₂ SO ₄	950	24	2 Li ⁺ → Mg ⁺⁺	β-quartz ss	142
2	Li ₂ SO ₄	950	24	2 Li ⁺ → Mg ⁺⁺	β-quartz ss	spalled
3	52% KCl 48% K ₂ SO ₄	850	2	2 K ⁺ → Ba ⁺⁺	glass	40
3	Li ₂ SO ₄	850	8	2 Li ⁺ → Mg ⁺⁺	β-quartz ss	160

Table V - Glass Ceramics Strengthened by "Crowding" Mechanism

Composition	Bath	Temp °C	Time, Hours	Exchange	Surface Phase	MOR 10^3 psi
4	85% NaNO_3 15% Na_2SO_4	580	1/6	$\text{Na}^+ \rightarrow \text{Li}^+$	β -spodumene ss	90
5	Li_2SO_4	850	8	$2 \text{Li}^+ \rightarrow \text{Mg}^{++}$	β -quartz ss	160
6	52% KCl 48% K_2SO_4	750	8	$\text{K}^+ \rightarrow \text{Li}^+$	β -quartz ss	45
7	52% KCl 48% K_2SO_4	730	8	$\text{K}^+ \rightarrow \text{Na}^+$	Kaliophilite	100
8	32% KCl 48% K_2SO_4	730	8	$\text{K}^+ \rightarrow \text{Na}^+$	Kalsilite	90
9	52% KCl 48% K_2SO_4	730	8	$\text{K}^+ \rightarrow \text{Na}^+$	Kalsilite	178
10	52% KCl 48% K_2SO_4	730	8	$\text{K}^+ \rightarrow \text{Na}^+$	Kalsilite	200

crystals are altered from hepheline to kalsilite. The alteration exists on the surface of the nepheline crystals and the amount is time- and temperature-dependent. This conversion involves about 10 percent volume increase and produces a high-compression surface layer due to "crowding."

Glass ceramics have higher relaxation temperatures than their parent glasses and can therefore be ion-exchanged at higher temperatures. The double advantage of increased diffusion rates and less strain relaxation results in higher surface compression and thicker diffusion layers.

3. Other Methods of Strengthening Glass Ceramics

Three other methods of strengthening glass-ceramics have been developed:

1. Surface crystallization
2. Low-expansion applied coatings
3. Thermal tempering

Surface Crystallization

Certain compositions of glass ceramics tend to nucleate from the surface.⁽⁴²⁾ Other compositions may be made to crystallize from the surface by means of surface additions or a salt-bath treatment. The interior glass may or may not be crystallized. A very strong material results when the surface crystal is a low-expansion species. On cooling, large compressive stresses are developed on the surface.

Coatings

The art of glazing ceramic bodies to provide a decorative effect and to render them impermeable to liquids has been practiced for thousands of years. Recently, glazing has become a science, and the structure and properties of glazes and their reactions with the body have been investigated. Except for some hard-fired porcelain insulators, care has always

been taken to match fairly well the expansions of the glaze and the body to minimize spontaneous chipping and breaking.

Since the discovery of glass ceramics, the study of glaze reaction to these new materials has been initiated.⁽¹²¹⁾ Because of the inherent homogeneity and strength of glass ceramics, they will safely support a high-compression surface layer. With the proper pairing of glaze composition and glass-ceramic body, a good interaction is obtained between body and glaze to produce a diffused intermediate zone. These investigations have resulted in the commercial production of strong tableware. Strength of two to four times that of the body material resulted from this system of compressive glazing.

Thermal Tempering

Glass-ceramic materials can be physically tempered. Since glass-ceramic materials generally have a small amount of residual glass, they are capable of adjusting themselves to zonal strains created by thermal gradients at elevated temperatures. Should this adjustment take place and the temperature differences be maintained on cooling, reverse stresses will occur as gradients are equalized at room temperature. These tempering treatments can be superimposed upon ion-exchanged compressive layers by treatment either before or after tempering. The amount of superimposed tempering stress will depend upon the thermal expansion of the material, the shape and size of the ware, and the severity of quench.

4. Problem of Scale-Up and Control

In the case of glass ceramics, the problems of scale-up and control are not just engineering problems. The composition must be designed to allow massive fabrication. The forming, cooling, and heating of massive pieces cannot be accomplished with the speeds used for a skillet or a radome.

Therefore, it will probably be necessary to slow down the rate of nucleation and crystal growth so that the necessary control can be maintained. There is a substantial evolution of heat during the crystallization process, and the dissipation of this heat will evidently become a part of the scale-up problem. If a transparent glass ceramic is required, the heat treatment must be terminated before excessive crystal growth occurs.

This problem of the need for a proper heat treatment for controlled nucleation and proper crystal growth may limit the composition ranges available and, hence, the character of the glass ceramics suitable for this use.

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13. ABSTRACT Future deep-sea operations by the Navy and others will necessitate the development of materials with properties superior to those currently available. One candidate for deep-submergence uses is glass because of a number of favorable properties such as potential high strength-to-weight ratio, transparency, and corrosion resistance. However, before glass can be fully utilized as a deep-sea structural material, additional information will be needed on its physical properties. This report contains fourteen recommendations for research on physical and mechanical properties that define the most important areas in which more understanding is needed. Topics covered are strength, means of strengthening, structure, dynamic processes, glass ceramics, and fundamental phenomena. The recommendations are justified in a summary of available knowledge covering: strength of glass, chemical strengthening, other methods of strengthening, transport properties, structure, vibrational properties, and glass ceramics. Many of the recommendations of this report are essential to an understanding of the vitreous state and as such have application in fields other than structural glass.		

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