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Technical Forum

Donald R. Sauder 
Conference Director

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Technical Forum

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A Message from the Technical Forum Chairman.

Near record attendance and a program of varied, highly informative presentations maintained the annual Technical Forum's well deserved reputation as a valuable, not-to-be-missed industry event. Once again the campus of The Ohio State University was the setting for the session.

This, the 46th Forum, benefitted from the unselfish contributions of many people beginning with the Technical Forum Committee itself which was responsible for the overall planning. The program participants were a vital element and all those connected with the University's role as host institution were unstinting in their assistance.

The Forum is the product of almost a year's work by the Committee starting with the selection of the subjects to be treated at the session. The next task involves actually selecting the papers to be presented and arranging for panel presentations. All this must be accomplished against the inflexible deadline of the Forum's dates.

A keynote event of this year's meeting was the annual A.I. Andrews Memorial Lecture delivered by Sherman D. Brown. Dr. Brown discussed why vitreous coatings fail and what actions can be taken to alleviate the problem.

The headings under which some three dozen presentations were grouped illustrate the range of interests being pursued by the industry: coating operations; new equipment; energy and material conservation; cost savings; color and its control and measurement; advances in metal preparation; test methods and standards; and the latest developments in no-pickle, no-nickel processing.

I am indebted to my colleagues on the Technical Forum Committee, to the PEI staff, to Dennis Readey of The Ohio State University and to Clifton Bergeron of the University of Illinois and their associates.

The 1985 Technical Forum will again be held on the Columbus campus of Ohio State, October 1 and 2. In 1986, the Forum will return to the University of Illinois in Urbana.

Donald R. Sauder, Chairman
1984 Technical Forum Committee
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The A. I. Andrews Memorial Lecture

Strength of Vitreous Enamels

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Glass-coated metal systems and the reasons for failure by fracture are discussed. Salient aspects of what is known about brittle fracture are reviewed. Factors that affect the fracture of vitreous materials are discussed. Adherence failure is treated as a fracture process. Possible means for minimizing fracture of glass-coated metal systems are suggested.

Introduction

Glasses are applied as coatings to metal substrates to perform one or more necessary or desirable functions. For instance, the coating may be intended to serve some protective, insulative, optical, and/or decorative purpose. It may be expected to bond additional layers, subsequently applied, to the coating-substrate system. Plainly, if failure due to fracture of the coating occurs, the ability of the coating to function as intended is impaired if not eliminated. Therefore, whatever reasonable measures can be taken to minimize such failure would be worthy of consideration.

Fracture is not a simple process even when it occurs in comparatively simple systems. Much more is known than understood. Certainly, the process can be complicated markedly in the case of many glass-coated metal systems by the presence of such features as bubbles, inclusions, microchemical irregularities that stem from incomplete fusion of the coating, and residual stresses. Nevertheless, some useful generalizations can be made.

The purposes of this lecture are to provide insight into the fracture process and offer suggestions that could reduce the likelihood of failure by fracture. These purposes are achieved by discussing first certain salient aspects of what is known about brittle fracture generally, when factors that affect fracture processes in glass-coated metal systems. Adherence failure is discussed as a fracture process. Finally, recommendations of a general nature are offered for minimizing failures that occur in glass-coated metal systems by fracture.

Sherman D. Brown is a professor in the Department of Ceramic Engineering, the University of Illinois at Urbana-Champaign. He has been on its faculty since 1968 and presently teaches ceramics coatings and physical chemistry for engineers and a graduate course in glass science. Dr. Brown holds a B.S. degree and doctorate in chemical engineering, both from the University of Utah. He has held faculty and research positions with that university, the California Institute of Technology, and Thiokol Chemical Corp. Before accepting his present post, he was principal scientist, ceramics, Research Division of Rocketdyne, a division of North American Rockwell. He is a member of several honorary professional organizations and author of more than 50 published works.
Strength and Fracture

When the stresses applied to a body exceed its mechanical strength, the body breaks. That is, fracture occurs, creating surfaces within some region (or regions) where previously the material had been coherent. Plainly, interatomic bonds are broken in the process, and it seems reasonable to think that the mechanical strength should be related to the strengths of the interatomic bonds.

If the theoretical strength of a silicate glass is calculated on the basis of the interatomic bond strength, a value of the order of 6.9 GPa (10^6 psi) is obtained. This is substantially higher than the 104–173 MPa (15 000–25 000 psi) strengths commonly observed for bulk glasses.

The weakness of glass, compared with its theoretical strength, is attributed to the presence of small, even submicroscopic, stress-magnifying surface flaws (cracks). These flaws may arise from damage incurred during processing, handling, and/or storage. Studies have indicated that while flaw size can affect the magnitude of the weakening effect provided by a crack, the crack acuity (its sharpness at the tip) is of key importance in this regard. For example, the Inglis equation, relates the maximum stress at the crack tip \( S_c \) to the applied stress \( S_a \) for a thin elliptical crack (Fig. 1).

\[
S_c = S_a [1 + 2(c/r)^{1/2}]
\]

(1)

Here, \( c \) represents crack length (i.e., the length of the major semi-axis of the elliptical crack), and \( r \), the crack tip radius. If \( c \) is, say, 1 \( \mu \text{m} \) and \( r \) is of the order of an interatomic distance, a reasonable assumption, \( S_c \) would be roughly 142 times \( S_a \). Thus, if the applied stress were increased to about 138 MPa (20 000 psi), the maximum stress at the crack tip would be roughly 19.3 GPa (2.8 \( \times \) 10^6 psi) which is close to the theoretical strength. Thus, the weakening effect of the surface crack is manifest.

Avoidance or elimination of surface cracks can increase dramatically the measured strength of a glass vis-a-vis that which it exhibits with the flaws present. For instance, pristine glass in bulk form is often found to have strengths greater than 0.7 GPa (10^6 psi). Glass fibers with strengths exceeding 3.5 GPa (5 \( \times \) 10^6 psi) are not uncommon. And, ordinary glass rod stock with strengths of 104–173 MPa (15 000–25 000 psi) can be etched with dilute hydrofluoric acid or fire-polished to remove flaws from the surface and thereby achieve strengths reaching 2.1 GPa (3 \( \times \) 10^6 psi). It is unfortunate that such high strengths are short-lived unless certain extraordinary measures are taken to protect the surface from damage (e.g., by impacting dust particles). Upon exposure of the glass surface to ordinary air atmospheres, the strength of the article degrades sharply with time to ordinary levels.

Atmospheric moisture plays a prominent role in this time-dependent weakening of glass. Moreover, the process, at least in part, is temperature-dependent. Once a crack is initiated in the surface by, say, the impact of a dust particle from the atmosphere, the water acts to facilitate the rupture of stressed silicon-oxygen bonds at the crack tip (Fig. 2). The crack propagates as a result, growing larger and more sharp, albeit slowly. This results in a weakening of the glass. If a tensile stress of sufficient magnitude is applied, a critical condition is reached at which the crack spreads catastrophically through the glass, resulting in failure. Residual stresses as well as applied stresses can drive the growth of these cracks.
The critical condition just mentioned obtains when the rate at which strain energy is released from the strained bulk regions of the material into a small region at the crack tip is more than enough to drive the crack growth processes and any associated energy dissipating processes that occur there. Thus, one way to toughen brittle materials would be to provide regions within the materials that undergo energy absorbing processes when triggered by the presence of a growing crack. Transformation toughened ceramics and the new fiber-reinforced ceramic-ceramic composites provide examples of this approach.

Static fatigue (or delayed failure) is a phenomenon that is closely related to the aforementioned time-dependent weakening process. A glass specimen is stressed statically (e.g., Figs. 3 and 4) to some subcritical level at which the cracks in its surface are driven to sharpen and grow. In time, one of the cracks achieves the critical condition at the particular applied stress, and catastrophic fracture ensues.

The data typically obtained (e.g., Fig. 5) indicate the existence of a static fatigue limit, a stress level below which delayed failure will not occur. For those glass or ceramic systems exhibiting such behavior, it may be possible to design so as to avoid delayed failure. However, not all systems seem to have a static fatigue limit, and in some cases the limit may occur at stresses that are impractically low for such an approach to be feasible.

The importance of the surface condition to the strength of the glass deserves further emphasis: Scott and Pask observed microscopic surface devitrification to occur at temperatures as low as 25°C in sodium disilicate glass. Atmospheric moisture was an important factor in the process. Brown saw a similar phenomenon take place in the surfaces of freshly drawn fused silica fibers; however, surface cracks also formed in association with the sparsely distributed crystallites, weakening the fibers. It is surmised that in this instance the crystallization resulted in localized densification in the surface (since the cristobalite formed was more dense than the glass). This, in turn, generated tensile stresses in the surface which served to open the cracks.

On the other side of the coin, surface treatments can be used to strengthen glasses: the strengthening effects of hydrofluoric acid etching and flame polishing already have been cited. Coatings such as lacquer, polyvinyl chloride, or a silicone can be applied to surfaces thus treated to retard the aforementioned time-dependent weakening process. However, even a pinhole in the coating will admit sufficient moisture from the atmosphere to the coating-glass interface to quickly and substantially weaken the glass, even at points several centimeters from the breach.

Physical (i.e., thermal) tempering of glass in which the glass is unevenly cooled so as to put a residual compressive stress in the surface to inhibit crack formation and growth is a strengthening method of long standing. More recently it has been found that annealing soda-lime glass in an atmosphere of sulfur oxides, water, and oxygen depletes the surface of sodium ions. The resulting silica-rich layer relaxes at the annealing temperature. However, when the glass is cooled, a compressive stress is set up in the surface owing to the lower thermal contraction of the silica-rich layer vis-a-vis that of the bulk which is comparatively sodium-rich. This too strengthens the glass.

Kistler found that nonuniform ion exchange in which smaller alkali ions in the glass surface are replaced by larger ones could be used to induce permanent compressive stresses estimated to be as much as 0.9 GPa (124 000 psi).
in glass surfaces, thereby offering a strengthening effect. Other schemes for strengthening glass by ion exchange and/or surface crystallization have been proved out as well.16,17

Bubbles and solid inclusions also affect the strength markedly. Inasmuch as vitreous coatings often contain such imperfections, it is appropriate that that aspect of glass strength be reviewed. Bubbles or pores weaken materials, and reduce their stiffness. If the bubbles are spherical and uniformly distributed throughout the glass, the strength can be related rather roughly to the volume fraction of void space (i.e., the porosity, \( P \)) by the following simple, semiempirical formula:18-20

\[
\sigma = \sigma_0(1 - \frac{3}{2}P)
\]

Here, \( \sigma \) and \( \sigma_0 \) represent the strength (modulus of rupture) at porosity \( P \) and at zero porosity, respectively. Ali, Knapp, and Kurtz20 tested Eq. (2) experimentally with sintered glass specimens having spherical porosity, uniformly distributed (Fig. 6). The behavior exhibited by bubble-containing glasses made by melting (as opposed to sintering) is expected to be similar over most of the range.

However, Eq. (2) was developed from the simplifying assumption that the sole effect of bubbles or pores is to reduce the effective load-bearing cross-sectional area in the material. Stress concentration and fracture energy effects were ignored. Plainly, this places limitations on the validity of the relationship.

As demonstrated by Hasselman and Fulrath,21 introduction of the few first bubbles or pores into a body results in a drastic decrease in strength, a fact predicted by their stress-concentration approach. Thus, the strength represented by the zero porosity intercept, \( \sigma_0 \) of Eq. (2), is substantially less than that of the bubble-free glass. Another point deserves mention here: sometimes bubbles (or pores) can blunt, deflect, or pin propagating cracks to limit damage from a transient application of stress;21-23 e.g., as in thermal shock.

The effects of solid inclusions (particles) on glass strength are more complex and less well understood than those of bubbles. They may be governed by any one or more of several factors, among which are the following:24-31

1. Young's modulus of the inclusion vis-a-vis that of the matrix,
2. Concentration (volume fraction) and distribution of inclusions in the glass,
3. Inclusion-matrix adherence,
4. Particle size,
5. Particle shape,
6. Thermal expansion coefficient of the inclusion vis-a-vis that of the glass matrix, or
7. Thermal expansion anisotropy characteristics of the inclusion.

Solid inclusions can serve to either weaken or strengthen a glass. If, for instance, the thermal expansion coefficient of the inclusion phase is sufficiently greater than that of the matrix glass, and if the inclusion-matrix adherence is poor enough that separation of the inclusions from the matrix occurs upon cooling from the temperature of formation, the effect is to produce pores which weaken the glass.

On the other hand, interaction of a propagating crack front with second-phase particles can increase the fracture energy to give a strengthening effect.
The magnitudes of the various stresses will depend upon the thermal expansion coefficients, elastic moduli, and relative thicknesses of the coating and substrate. Much can be done to minimize unwanted stresses by proper design of the coating-substrate system, for example, by adjusting the glass composition so as to more nearly match the thermal expansion coefficients of the coating and substrate. However, the picture is complicated by the fact that there is a decided thermal history dependency of the magnitude and spatial distribution of the stress as well: that is, the rate at which the system is cooled Several workers\textsuperscript{24,25,29} have found that alumina particles dispersed in various glasses generally increase the strength. For example, Lange\textsuperscript{25} found a significant strength enhancement in sodium borosilicate glass as alumina particles (three different average sizes; 3.5, 11, and 44 $\mu$m) were added. The thermal expansion coefficients of the inclusions and matrix glass were about equal, and the strength was found to be primarily dependent upon the volume fraction of alumina and the particle size.

Highly localized stresses were associated with the inclusions, and the inclusions acted as precursors of small cracks. Particle size controlled the crack size; the larger the inclusion, the larger the associated crack. Evidence for pinning of crack fronts by inclusions was observed (viz., fracture steps, indicative of breakaway). Interestingly, strength decreased at first as the larger particles were added to the glass, and continued to do so until the volume fraction reached about 0.10 to 0.15; then, it increased with increasing volume fraction. Similar behavior was reported earlier by Hasselman and Fulrath.\textsuperscript{21}

If the thermal expansion coefficient of the inclusion phase is significantly larger than that of the glass matrix, propagating cracks will tend to be deflected around the inclusions.\textsuperscript{26,28,29,31} Cracks will tend to run into and through the inclusions if the thermal expansion mismatch is reversed or made insignificant. Some workers have found that this effect can be an important element affecting the toughness.\textsuperscript{28,31} However, others have reported data to indicate that the effect is minor compared with other factors; e.g., differences in elastic modulus between the inclusion and matrix phases.\textsuperscript{29}

By way of summary, then, the actual strength of glass is substantially less than what is theoretically possible owing to surface flaws and the ubiquitous influence of moisture. The surface flaws can grow and sharpen with time under the influence of stress, temperature, and moisture; and if a critical condition is reached, catastrophic fracture will ensue. The fact that glass can be loaded at some stress below that at which it immediately fails, then fail at some future time, if the load is maintained, is explained on this basis. Inclusions (bubbles and solid particles) can weaken or strengthen a glass depending upon a number of factors. Indeed, glass matrix composites can be designed and fabricated, with particulate inclusions selected for the purpose, that are tougher than the matrix glass. However, adventitious inclusions can be expected to degrade the strength of glass and should be avoided.

**Pertinent Characteristics of Glass-Coated-Metal Systems**

What factors change with regard to the mechanical failure of a glass when it is joined as a coating to a metallic substrate? And, what factors remain the same? Perhaps the most important new considerations stem from the fact that the thermal expansion coefficients of the coating and substrate almost always will be significantly different. Under most circumstances, the thermal contraction of the metallic substrate will be greater than that of the vitreous coating
This means that the vitreous coating, at ordinary temperatures, will be subject to residual, lateral compressive stresses (Figs. 8 and 9) that under some conditions can be of substantial magnitude. The substrate will be in tension. It also means that there will be stresses acting at the glass-metal interface, tending to fracture the coating from the substrate. These interfacial stresses will have shear components acting roughly parallel to the plane of the interface, and tensile components acting normal to the same plane (Fig. 10). After the coating has been fused onto the substrate, and the time the system is at elevated temperatures where viscous processes can relax strains that develop in the coating (or substrate) and reactions can proceed are both important factors. Appropriate thermal programming can thus serve to mollify the stresses generated.

If the aforementioned lateral compressive stresses in the coating are large enough, spalling will occur. Generally, the said stresses are enhanced in the exposed surface of the coating (Fig. 9). It is the exposed surface that is first to cool and become rigid. Therefore, the glass coating is tempered physically, the effect of the greater substrate contraction being mainly to amplify the compressive stresses in the coating and modify the stress distribution. Plainly, there is a trade-off here; an appropriate level of compressive stress in the glass will serve advantageously to strengthen the coating, inhibiting the formation and growth of cracks. It is a matter of coating design and process control to achieve the optimum result.

Whatever the case, the bond developed between the glass and the metal must be sufficient to withstand the aforesaid interfacial stresses, however large they may be, or adherence failure will occur: a crack will propagate at or near the interface to separate the coating from its substrate. Often, in an actual failure of this kind, the crack will run just inside the glass near the interface, leaving a very thin vitreous layer on the substrate. Thus, excessive compressive stresses in the coating and their associated interfacial stresses can be important factors causing or contributing to spalling. If the coating is too thick or its thermal contraction too low compared with that of the substrate, spalling is more likely. Of course, abusive handling or dirty metal can lead to spalling even if these other parameters are properly set and controlled.

This brings up another factor not associated with the glass alone; namely, the role of the metallic substrate in causing fishscale, a defect that involves fracturing of the vitreous coating. As pointed out by Andrews, fishscaling is caused by hydrogen gas, generally from the metal (iron), that accumulates at the coating-substrate interface, in areas of poor glass-metal contact and other interfacial pockets (Fig. 11). Hydrogen is less soluble in cold iron than in hot; so, when the system is cooled from the elevated processing temperatures, some of any hydrogen that may be in the metal escapes to fill these interfacial voids. Inasmuch as hydrogen diffuses more readily through iron than it does through glass, localized pressure builds up to place stress on the coating. Fishscale results when the coating fractures on this account. The hydrogen may derive from several sources; e.g., the steel-making process, acid etching of the iron, water in the unfired coating constituents, and the atmosphere of the furnace used to fuse the coating onto the substrate.

Treatments have been developed to reduce the amount of hydrogen in the steel; for instance, cold-working the substrate metal prior to the coating operation often reduces fishscaling markedly. Apparently, dislocations and other defects are generated in the metal that can act as channels to facilitate
the escape of hydrogen before it is trapped at the glass-metal interface. Interestingly, one remedy for the fishscaling problem involves the deliberate incorporation of bubbles in the ground coat, within about 25.4 μm (0.001 in.) of the glass-metal interface. The bubbles serve to accommodate much of the hydrogen generated, reducing the buildup of pressure. Of course, the presence of bubbles will tend to weaken the glass.

If the substrate metal has a tendency to form pits, say during pickling, a defect called pop-off may occur later on in the coating. A small, tapered piece of the vitreous coating breaks loose leaving a crater that often exposes a portion of the metal surface (Fig. 12). Sometimes pop-off is associated with a speck of some impurity at the glass-metal interface or within the coating. The residual interfacial stresses and lateral compressive stresses mentioned earlier provide the strain energy to drive the fracture process involved in generating pop-off defects.

Therefore, any applied stresses (e.g., thermal stresses) or shape factors that tend to amplify these residual stresses and/or their effects can be counted on to aggravate the pop-off problem. Careful selection of the metal substrate to avoid pits, cleanliness and/or better melting of the coating to eliminate adventitious inclusions (impurity specks) that act as precursors of cracks, and efforts to better match the thermal expansion coefficients of the coating and substrate are the indicated remedial measures.

When a glass-coated-metal system is cooled unevenly or subjected to nonuniform thermal cycling, or when the coefficient of thermal expansion of the coating is too large vis-a-vis that of the substrate, crazing can occur. A network of fine cracks appears in the surface of the coating. Plainly, the coating has been placed in sufficient lateral tension to cause these cracks to initiate and grow. Sometimes crazing is introduced deliberately to give a decorative effect; however, it is almost always considered a defect to be avoided.

The problem is usually a consequence of improper design and/or thermal programming. For example, if the substrate is more massive in one location than another nearby, providing an uneven thermal ballast effect, a temperature gradient and consequent thermal stresses will be set up that can lead to crazing if they are of sufficient magnitude. Sometimes, correction of the problem is a matter of adjusting the composition of the coating to reduce its thermal contraction compared with that of the substrate. Excessive temperature gradients due to uneven heating or cooling also need to be avoided. Hairlining is a related defect; however, the cracks have partially healed during subsequent heating. Apparently, hairlining can also be caused by underfiring and certain mechanical strains introduced during handling.

Tearing, crawling, and star marks are examples of defects that appear during firing because fracture has occurred in the dried but unfired coating. Tearing is basically a cover enamel defect. The coating cracks during drying, owing to shrinkage, and then separates along irregular tears. The cause is generally improperly prepared slip. As pointed out by Andrews, coatings which dry to a hard, firm surface are more susceptible to tearing than those which form softer ones. The softer coatings can dissipate the strain due to shrinkage without cracking.

Crawling is tearing that has rolled back during firing, owing to the action of surface tension on the molten glass, to expose substantial areas of the ground coat. Slip that is applied too wet, or drying that is too rapid are fre-
quent causes of tearing and crawling. Sodium nitrite added to a slip will often mollify its tendency to crack on drying. Star marks generally occur if there is damage done to the dried coating by impact from the underside, or by large, highly localized thermal stresses that are imposed upon the substrate while the coating is as yet unfired.

Vitreous coatings are usually fraught with inhomogeneities. Inclusions are common. These features stem from the very nature of the coating process. While the frit is comparatively well fused, it is mixed with other constituents for milling and application. The final firing is limited to times that preclude the complete homogenization of the glass. In general, these adventitious particles and bubbles can be expected to act as stress raisers and crack precursors, to weaken the glass and give rise to various defects. There are exceptions: as pointed out above, introduction of a bubble structure in a ground coat is sometimes used to alleviate fishscaling.

Summary

Materials are weaker than their theoretical strengths because they contain flaws. Glasses are brittle and particularly sensitive to surface flaws (cracks). The stress at the tip of a sharp crack is magnified by orders of magnitude above the applied stress. If the rate of strain energy release into a small zone around a crack tip exceeds the rate at which energy can be dissipated by crack forming processes and associated parasitic mechanisms, the crack will grow. The rate at which the crack will grow is dependent upon the stress applied, the microstructure of the vitreous material, and the presence of moisture, among other factors.

If the surfaces of glasses can be put into compression, or if the cracks can be blunted, the glass is strengthened, sometimes substantially. Methods for strengthening glasses often rely upon these facts. Inclusions can weaken or strengthen glasses depending upon a number of factors (e.g., differences in properties such as elastic moduli and thermal expansion coefficients between the inclusion and glass matrix, inclusion size and shape, the volume fraction of inclusions, and the adherence between the inclusion and matrix). Bubbles almost always weaken glass. Inclusions generally act as crack precursors; however, they can act to pin moving crack fronts and sometimes can be used to strengthen glass.

A number of defects commonly observed in vitreous-coated-metal systems involve fracture. Examples are chipping, fishscale, shiners, pop-off, tearing, crawling, crazing, hairlining, and star marks. There are many similarities in the fracture that occurs in these composite systems and that which happens in glasses alone, and some notable differences. Like the fracture that occurs in glass alone, the cracking in vitreous coatings almost always begins at surfaces: the glass-metal interface is a surface, surfaces exist between inclusions and the matrix, bubbles provide surfaces, and there is always the glass surface that is exposed to the atmosphere. The factors which weaken and strengthen glasses also weaken and strengthen glass-coated-metal systems. However, the metal substrate is tougher (less brittle) than the glass, and this often benefits the vitreous coating.

The thermal contractions of the vitreous coating and metal substrate are generally significantly different. Usually, the metal strains more upon heating or cooling than the glass; therefore, the coating is generally subjected to residual, lateral compressive stresses. Sometimes the said stresses are substan-
tial. If the compressive stresses are not excessive, they will serve to strengthen the glass coating. However, if they are too large, fracturing will occur. The differential thermal contraction between the coating and substrate also leads to interfacial stresses that tend to separate the coating from the substrate. Thus matching of the thermal expansion coefficients of the coating and substrate is an important matter.

Sometimes, gaseous hydrogen is expelled from the metal substrate when it is cooled, and this fills flaws at the glass-metal interface and applies a pressure that leads to cracking (fishscale and shiners). If drying of the biscuit is too rapid so that the exposed surface hardens before the interior of the coating, if the slip is too wet, if the slip constituents are such that excessive shrinkage occurs during drying, and/or if the unfired ware is handled carelessly, cracks can occur in the unfired coating. These then appear in firing as defects (tearing, crawling, and star marks).

Often the circumstances associated with the processing of vitreous-coated-metal systems precludes much homogenization of the coating. As a consequence, inclusions are common. Such adventitious inclusions can be expected to weaken the glass. However, there is the possibility that the system could be designed so as to incorporate second phases that would toughen and improve the mechanical properties of the coating.

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References


*The assumption of an elliptical crack is an oversimplification. Recent work indicates that the atomically sharp crack is a more realistic supposition.*
Fig. 1. Elliptical crack proposed by Inglis\textsuperscript{4} in connection with Eq. (1).

Fig. 2. Hypothetical reaction of a water molecule with a strained Si-O-Si linkage at a crack tip (After Refs. 5 and 9). (A), (B), and (C) represent the steps that make up the reaction from the initial adsorption (A) through separation (C).
Fig. 3. Bar specimen loaded in four-point flexure in a controlled test medium. Water from a constant temperature bath is circulated through the copper coils to maintain the test at constant temperature.

Fig. 4. A simple loading apparatus used for static fatigue experiments. When the specimen breaks, the lever bar closes a normally open microswitch to stop a clock (inset).