HIDDEN DEFECTS: GRIFFITH'S FLAWS IN SILICATE GLASSES

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The perplexing nature of Griffith flaws in silicate glasses is reviewed. Progressive surface removal techniques and equivalent flaw size calculations suggest that Griffith flaws are a few microns or tens of microns in size. However Griffith flaws have have never been directly been observed on the surfaces of silicate glass. The precise nature and the origin of the Griffith flaws in silicate glasses has therefore never been determined. Recent models of the structure of alkali silicate glasses suggest that the alkali ions occupy channels between regions of pure silica. It is suggested that interaction of these channels with atmospheric water may explain the origin of Griffith flaws. Such flaws would develop with time and could therefore explain why new drawn glass fibres have very high strengths.

INTRODUCTION

The failure of silicate glasses to achieve their theoretical strength is generally attributed to small defects in the surfaces of these glasses. However in the 75 plus years since Griffith first suggested that failure in silicate glasses was controlled by such surface flaws there has been no direct observation of a Griffith flaw. The origin of these flaws is therefore not well understood. This paper is an attempt to resolve this long standing question.

FLAWS IN GLASSES

Equivalent flaw sizes can be calculated by conventional fracture mechanics arguments. For example if we treat the crack as a short through edge crack then for a typical soda-lime-silicate glass (bend strength of ≈70 MPa; toughness ≈0.75 MN $m^{-3/2}$) a flaw depth of ≈30 μm is predicted. More involved calculations yield very similar crack sizes. In attempt to make a more direct assessment of the flaw sizes Pavelchek and Doremus (1) progressively etched the surface of silicate glass until there was a noticeable increase in strength. This work indicated that flaw depths are of the order of 6 μm. Thus, whether

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theoretical or practical approaches are utilised, the calculated flaws sizes are between a few microns or a few tens of microns long. However despite many attempts including optical, scanning electron and most recently atomic force microscopy (AFM) Griffith's flaws have never been observed directly (2).

It is well known that newly drawn glass fibres, and glass fibres that have been protected from the atmosphere since they were manufactured, have strengths that are essentially equivalent to the theoretical strength of glass. These results imply that, if it is meaningful to talk of flaws in new-drawn and protected glass fibres, they have atomic dimensions. More realistically it would appear that the glass is essentially flaw free and that some type of flaw initiation process needs to be invoked to explain the origin of normal aged glass strength.

There are two possible types of aging process that could affect the mechanical strength of fibres: one involves mechanical damage via contact and the other involves chemical interactions with the atmosphere. Mechanical damage requires that the stresses associated with any mechanical interactions are sufficient to overcome the bond strength of the material in the absence of any stress concentrating mechanism. Lawn and Evans (3) suggest that the minimum intrinsic flaw size for a sharp indenter to result in flaw extension in silica is about 0.6μm. Even allowing for this value to be order of magnitude too large (Lawn and Evans indicate that the assumptions made in obtaining this minimum value are such that the value could be up to an order of magnitude out), it is still significantly larger than the atomic dimensions implied by the near theoretical strengths of new-drawn glass fibres.

Although crack initiation is not identical to crack extension based on these results it would appear unlikely that even contact with sharp objects is going to be sufficient for flaw initiation within undamaged silicate glasses. Chemical interactions with the atmosphere therefore seem to be a more probable source of the flaw initiation. In fact the development of surface pits with time has been observed on pure silica using scanning tunneling microscopy (Robinson and Yuce (4)); this tends to support the idea that flaws in the surface of silica glass fibres are the result of chemical interactions with the atmosphere.

The relationship between the strength of very fine glass fibres and bulk glass is less clear; the strength of bulk glass effectively is never observed to approach the near theoretical level displayed by glass fibres. However it is also true that Griffith flaws have never been directly observed even on bulk glass. This failure to observe Griffith flaws directly implies that, even on normal bulk glass the flaws, must be closed or have lateral dimensions on an atomic scale.

GLASS STRUCTURE

Glasses have amorphous structures. However this does not necessarily mean that the structure is fully homogeneous as suggested by the random network (RN) model of glass structure (see figure 1) proposed by Zachariesen (5) and Warren (6). Although the random network model has won wide acceptance more recent workers have suggested that there are distinct heterogenities within the structure of the alkali silicate glasses with the alkali modifier ions being found in distinct channels within the structure (Greaves at al (7)). A 2D representation of this modified random network (MRN) model for a soda-silicate glass is shown in figure 2. Greaves (8) and Greaves et al. (9) have suggested that the modifier channels in themselves constitute Griffith flaws. However the species within the channels are ionically bonded to oxygen in the silica whilst the silica itself is covalently bonded, and although ionic bonds tend to be weaker than covalent bonds they are not sufficiently weaker to explain the observed strengths of glasses. Thus these channels cannot simply constitute Griffith flaws. Furthermore if they did constitute Griffith flaws then there is no reason why new drawn glass fibres and fibres that have been protected from the environment maintain essentially theoretical strengths. However, as discussed below, these channels can help to explain the origin of Griffith flaws.

WATER AND GRIFFITH FLAWS

It is well established that the surface of silicate glasses reacts with atmospheric water to form a relatively soft gel layer (see, for example, Doremus (10)). In addition it has been established that in the alkali silicate glasses water, in the form of hydroxonium ions, interdiffuses with the alkali ions. Hand and Seddon (11) have therefore suggested that atmospheric water, in the form of the hydroxonium ion, inter-diffuses with the sodium in these channels. As a result these near surface regions of these channels are hydrogen bonded rather than ionically bonded as shown in figure 3. The significantly lower strength of the hydrogen bond compared to the ionic bond means that the interaction with atmospheric water has essentially generated flaws within the glass surface. These flaws develop with time and have atomic width and therefore one would not expect to be able to observe them directly.

Data given by Doremus (10) suggests that beneath the gel-layer there is significant diffusional exchange of the water and the alkali ions up to a depth of ~ 0.5 μm. Treating such a defect as a shallow through edge crack this implies that the strength of the glass at the end of this process is around 0.5 GPa. Whilst this value is still significantly higher than normal glass strength it represents a substantial reduction in strength from the theoretical strength. In addition it is noticeable that this type of value is similar to that suggested as the limit of size of flaws that can be extended by sharp contact (Lawn and Evans (3)). It is therefore conceivable that if flaws have been generated by the inter-diffusion of alkali ions and hydroxonium ions that they could be extended to the sizes inferred by other measurements by subsequent contact damage.

If the origin of Griffith flaws is related to the inter-diffusion of water and alkali ions then, as the mobility of ions within the glass is affected by glass composition, it is to be expected that glass strength could vary systematically with glass composition. Despite the fact that consistent measurements of glass strength are notoriously difficult to make there is some evidence for such variations within the literature (see, for example, Mazurin et al. (12)). However the trends reported in different data sets are often contradictory (again see Mazurin et al. (12)), making it impossible to draw any firm conclusions at this stage about the variation of strength with composition. This area requires further study and work is in progress in this area.

Although the strength of glass fibres drops off with age this effect is more marked with thicker fibres. It seems likely that there is some alignment of the modifier channels within the glass structure along the drawing direction. This would be more marked with smaller fibre diameters. Such an effect would mean that there is a reduced likelihood of the channels intercepting the fibre surfaces.

PURE SILICA GLASS

Pure silica does not contain modifier channels as there are no modifiers present. In this case the structure only contains SiO_4 tetrahedra connected into rings of different sizes. The smaller rings tend to have strained bonds and these will be susceptible to attack by water. Water will diffuse into the surface via sites containing strained bonds by preferentially attacking the stressed bonds within the structure. As mentioned above some evidence for surface attack with the development of pits in the surfaces of pure silica aged in water (4). Thus aged pure silica will contain hydrogen bonded near surface channels that are less strongly bonded than the rest of the structure. For thinner fibres, whose strength is less reduced with aging, it is suggested that there are less strained bonds at the fibre surface.

CONCLUSIONS

It is suggested that Griffith flaws in silicate based glasses arise from the interaction of the glass with water in the environment. The inward diffusion of water leads to hydrogen bonded regions within the glass. These regions are relatively low strength sites and can therefore act as Griffith flaws. The flaws that are generated by this model are smaller than those calculated by from failure strengths or inferred by progressive surface removal. However they do conform to the requirements for Griffith flaws in that they are atomically wide and do develop with time. Small flaws that develop in this fashion might grow subsequently under contact loading to give flaw sizes closer to those inferred for bulk glasses. This model implies that there may be some dependence of strength on composition and this is currently being studied in more detail.

It is therefore proposed that chemical interactions play an important role in the initiation of Griffith flaws in silicate glasses and that Griffith flaws are related to underlying inhomogenities within the glass structure. The flaws themselves have therefore remained hidden from direct view because they are related to inhomogenities on the atomic scale.

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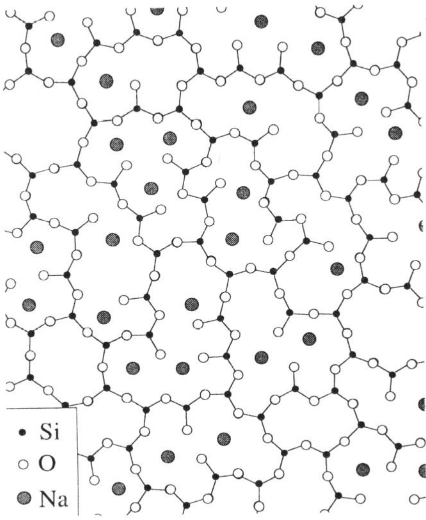

Figure 1 2D representation of the RN model of glass structure

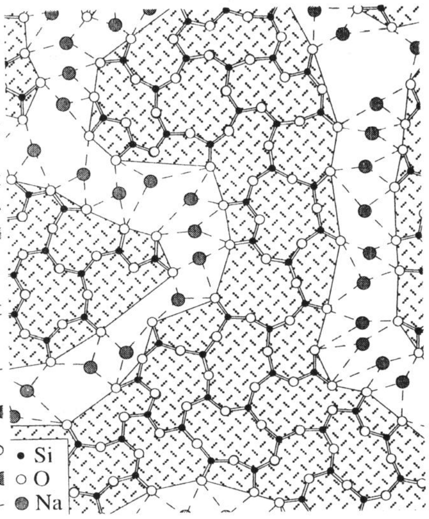

Figure 2 2D representation of the MRN model of glass structure

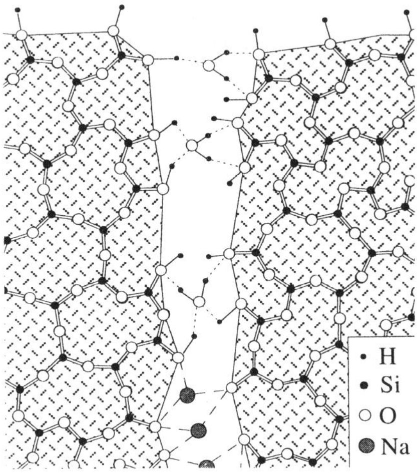

Figure 3 2D representation of a Griffith flaw in an MRN