Influence of Water on Crack Growth in Glass

As early as the 1920s, the strength of glass and other brittle materials was understood to be limited by the presence of small cracks. Under stress, the small cracks would grow into larger cracks until reaching a critical size, at which point the material would fracture catastrophically. It also was well known that humid environments reduced the strength more severely than did dry environments. Furthermore, a glass loaded at a stress below its ultimate strength did not show infinite life, but rather failed without warning after some finite time. Understanding the nature of this “delayed failure” had become a vital issue for industries that wanted, and perhaps needed, to use glass as an engineering material. This was the setting in which Sheldon Wiederhorn, newly arrived at the Bureau after a short stint at DuPont, began his research into the growth of cracks in glass. In two papers, the first in 1967 [1] and the second in 1970 [2], Wiederhorn became the first to quantify crack growth rates using fracture mechanics techniques that were only just then emerging as a means of analyzing crack phenomena. In doing so, he laid the foundation for understanding the environmentally enhanced fracture of all brittle materials.

Wiederhorn’s work was the culmination of a sequence of advances that occurred over a period of approximately 120 years. In the mid-1890s, Brodmann [3] conducted experiments on the strength of glass and found that specimens whose surfaces were etched in HF solution were significantly stronger than specimens tested without etching. That result provided the first reported evidence that glass fails from surface defects. The next major advance occurred in 1920 when Griffith [4] established unequivocally that glass fails from surface flaws and that the strength of glass is determined by the density and severity of such flaws. More than two decades passed before Orowan [5] clearly asserted that the relevant surface energy of fracture should be a function of the environment in which it is measured. Gurney [6] then showed that moisture enhanced fracture could be explained in terms of thermodynamic concepts. Stuart and Anderson [7] subsequently extended those ideas to model delayed failure using chemical rate theory. In that same time frame (although unknown to Wiederhorn until after his 1967 paper), Irwin [8] and Irwin and Kies [9] were advancing the analytical concepts of fracture mechanics and their application to brittle materials. These experimental and theoretical advances formed a convergent timeline in Wiederhorn’s papers of 1967 and 1970.

The critical feature in Wiederhorn’s work was the direct observation of a growing crack. Prior to Wiederhorn’s study, all research into delayed failure had been conducted by measuring the times to failure and only inferring the extension of microscopic cracks. Although others had observed the subcritical growth of macroscopic cracks, Wiederhorn was the first to quantify their growth rates. He used a diamond stylus to scratch the surface of a glass specimen and then observed the growth of the crack through a microscope while the specimen was being stressed. Using a double cantilever beam specimen, he applied a constant load to the ends of the slide and made crack velocity measurements using a traveling microscope and a filar eyepiece.

Wiederhorn’s study established several characteristics of the effect of water vapor on crack motion in glass at room temperature (see Fig. 1). Wiederhorn observed that his results could be separated into three qualitatively different regions indicating three distinct mechanisms controlling crack growth: (I) a slow growth region in which the crack velocity depended exponentially on the load; (II) a plateau region in which crack growth was limited by the diffusion rate of water to the crack tip; and (III) a region in which crack growth was rapid and

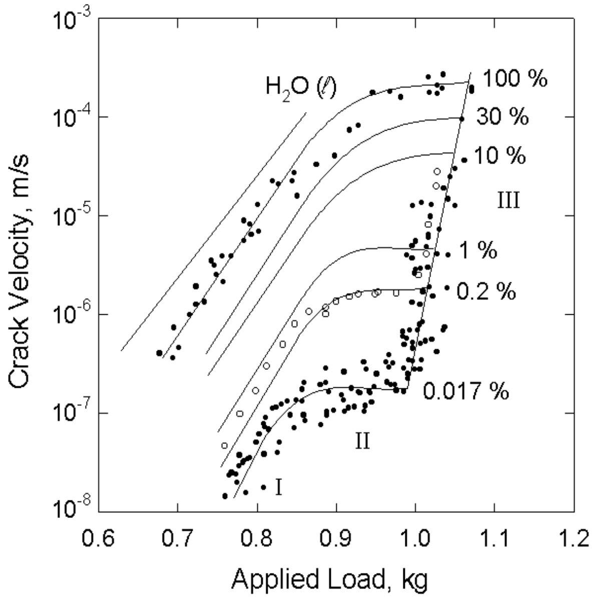

Fig. 1. The effect of water vapor on crack motion in glass at room temperature for relative humidity ranging from 0.017 % to 100 %.

independent of the amount of water in the environment. The data of region I were in complete accord with the static fatigue theory put forward previously by Charles and Hillig [10] which indicated that water vapor produced a corrosive attack on the glass at the crack tip. Wiederhorn reasoned that this corrosive attack continued into region II, but the plateau occurred because the crack extension could not proceed any faster than was allowed by the diffusion rate of water to the crack tip. In region III, the crack velocity was independent of water vapor. Later, Wiederhorn *et al.* [11-13] showed that the dielectric properties of the environment controlled crack growth in region III.

The fracture mechanics formalism he adopted in these two papers captured the dependence of the growth rate on the size of the crack and the stress. Wiederhorn also showed the crack growth rate depended on humidity in accord with an existing theory of delayed failure in glass. These two contributions demonstrated that the delayed failure did indeed result from the subcritical growth of cracks, and put the prediction of glass lifetime under load on a solid theoretical foundation.

This work influenced the scientific and engineering community in two ways. First, it illustrated the power of fracture mechanics as a tool for investigating the fracture behavior of ceramics. Shortly after the publication of Ref. [1], a host of other groups launched fracture mechanics studies of brittle failure of ceramics. Second, engineers used the method of quantifying crack growth to develop new techniques for assuring the reliability of structural ceramics. Both of these themes became important fields of research in ceramics. The recognition of the importance of the environment at the crack-tip to crack growth led to a series of studies [11,12,13] of crack growth rate in electrolytes as a function of zeta potential, ionicity, and pH. Of these, only pH was critical in establishing the relationship between crack velocity and stress intensity factor. These studies showed that ion exchange between the electrolyte and the glass at the crack tip determined the crack tip pH and consequently the relationship between crack velocity and stress intensity factor.

In those works and others, Sheldon M. Wiederhorn has researched the mechanisms of fracture in glasses and brittle ceramics for more than 35 years. He joined the Physical Properties Section of the Inorganic Solids Division at NBS in 1963. Recently, his work has led him to investigate the creep and creep rupture of structural ceramics. The Department of Commerce recognized his accomplishments in awarding him both the Silver Medal (1970) and the Gold Medal (1982), in addition to the NBS Samuel Wesley Stratton Award (1977) for his work in brittle fracture. The American Ceramic Society (ACerS) independently recognized his work, awarding him the Ross Coffin Purdy Award (1971), the Morey Award (1977), and the John Jeppson Award (1994). ACerS further elected him a Fellow (1970) and named him a Distinguished Life Member (1999). In 1985, he was chosen by ACerS to present the distinguished Sosman Lecture, on the subject of subcritical crack growth in glass, at the Annual Meeting of the American Ceramic Society. In 1991 he was elected a member of the National Academy of Engineering. He has held various positions of administrative responsibility at NIST (Section Chief, Division Chief, and Group Leader), and is now a Senior NIST Fellow in the Materials Science and Engineering Laboratory.

Fig. 2. Sheldon Wiederhorn, 1964.

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