Swelling strains from density measurements
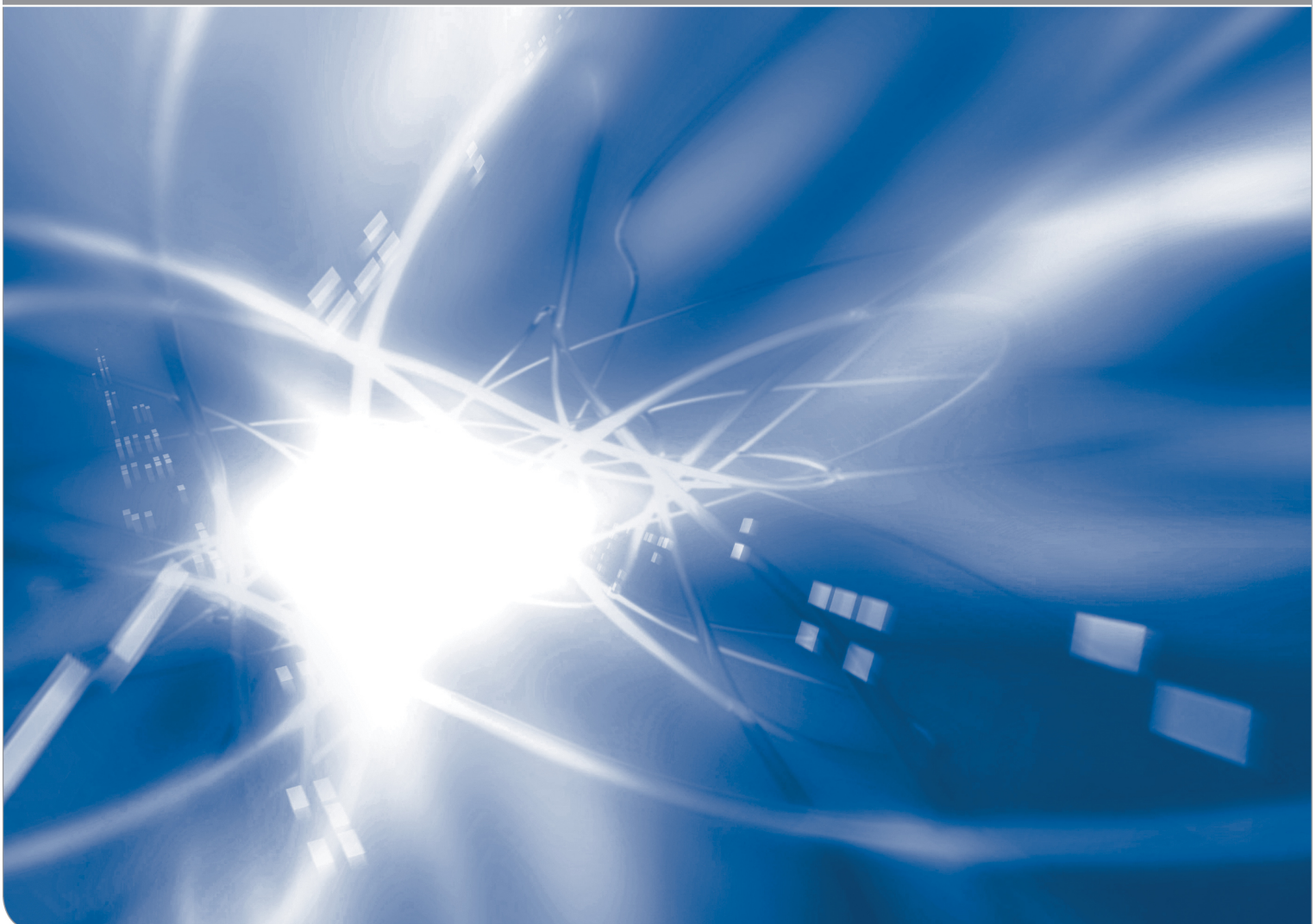
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Abstract

Water in contact with silica glass surfaces diffuses into the glass, and reacts with the silica network under hydroxyl generation. Clear evidence has been reported in the literature for a volume swelling due to the water uptake and reaction in silica. In the past, the authors showed in a couple of papers the principle effects of volume swelling by hydroxyl generation on mechanics and fracture mechanics properties.

From literature data on density as a function of water content a linear dependence of the volume swelling strain with water concentration was established. This dependency will be discussed in the present report including data scatter.

Contents

1. Introduction

In the past, the authors showed in a couple of papers the principle effects of volume swelling by hydroxyl generation in silica on mechanics and fracture mechanics properties [1,2,3].

An experimental proof of the swelling effect was given by deformation measurements on silica discs under 1-side soaking. The predicted and measured bending moments showed good agreement [4]. In this paper, we apply the effect of volume increase by swelling for an estimation of the molar volume of hydroxyls in silica.

Water penetrated into silica reacts with the silica network according to

$$\equiv\text{Si-O-Si}\equiv + H_2O \leftrightarrow \equiv\text{SiOH} + \text{HOSi}\equiv \qquad (1)$$

with the concentration of the hydroxyl $S = [\equiv\text{SiOH}]$ and that of the molecular water $C = [H_2O]$.
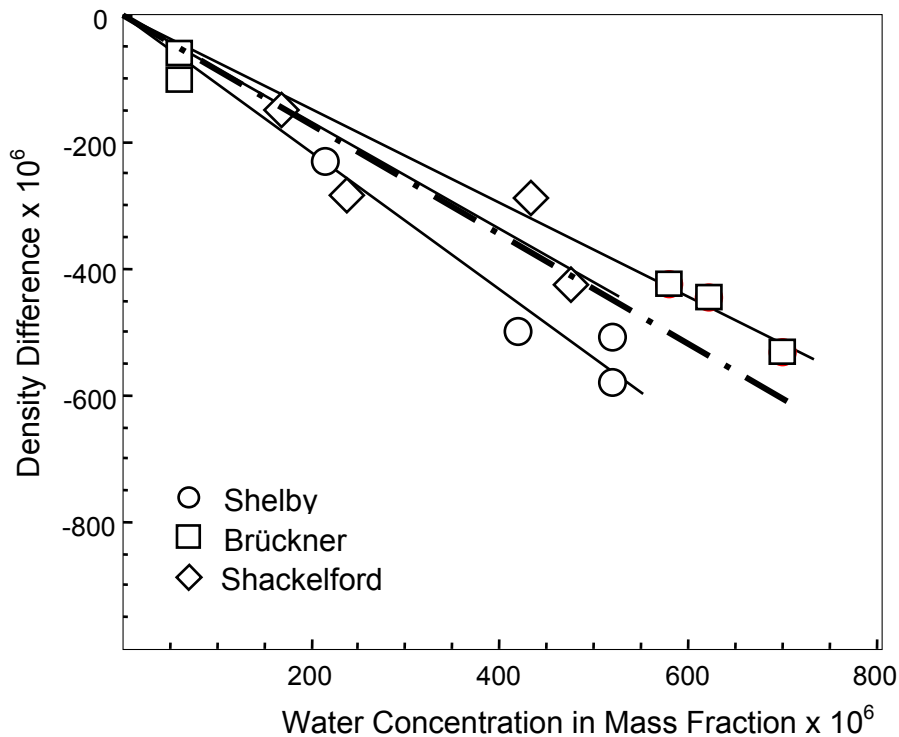

Fig. 1 Effect of water concentration on density of vitreous silica, results by Shelby [8], Brückner [5,6], and Shackelford [7]. The dash-dotted line represents the value given in (2a).

A swelling effect in water-containing silica at high temperatures was early reported by Brückner [5,6], Shackelford [7] and Shelby [8]. These authors showed that the density decreased by reaction (1) at 1100°C according to

1

$$\frac{\Delta\rho}{\rho_0} = -\chi\,C_w \quad , \quad \chi = \begin{cases} 0.96 & \text{Shelby} \\ 0.84 & \text{Shackelford} \\ 0.71 & \text{Brückner} \end{cases} \tag{2}$$

where C_w is the weight fraction of water. The literature data are shown in Fig. 1 with the coefficients χ for the individual curves as reported by Shelby [8]. By a least-squares fit over all data points, we obtain

$$\chi = 0.836\,[0.739, 0.933] \tag{2a}$$

with the 95%-Confidence Interval in brackets. The dependency given by this value is indicated in Fig. 1 as the dash-dotted line. In our former papers [1-4] we used a value of $\chi=0.84$ as was obtained simply as the average of the 3 values given in eq.(2).

2. Volume swelling strain

From the definition of the density as the quotient of mass m and volume V, $\rho=m/V$, it follows for the volume swelling strain ε_v

$$V = \frac{m}{\rho} \;\Rightarrow\; \varepsilon_v = \frac{\Delta V}{V} = \frac{\Delta m}{m} - \frac{\Delta\rho}{\rho} \tag{3}$$

Since only the water content m_w can change during water soaking, the mass change is

$$\Delta m = m_w = C_w m \tag{4}$$

and the volume swelling strain ε_v simply results from eqs.(2)-(4) as

$$\varepsilon_v = (1+\chi)\,C_w \tag{5}$$

We believe that the molecular water in the glass to be located in molecular size holes in the silica glass network [9, 10], where the water does not contribute to the volume of the glass. On the other hand, it is well known that molecular water at high temperatures of 1100°C is nearly absent. Under these circumstances, the volume swelling is due to hydroxyl generation by the reaction (1).

Shelby expressed C_W as weight fraction of water in the glass (weight water/weight of glass). C_W has to be converted to mole fraction of water, x_{H_2O}, in the glass.

$$x_{H_2O} = \frac{M_{glass}}{m_w}\,C_w = (60/18)C_w \tag{6}$$

Here we used the molar mass for water m_w =18g/mole and as an approximation of M_{glass}=60g/mole for the molecular weight of the glass. For every water molecule that reacts with the glass, two SiOH are formed, therefore:

2

$$x_{SiOH} = 2 x_{H_2O} \tag{7}$$

Combining (6) and (7) yields

$$x_{SiOH} = 2 \frac{60}{18} C_w \tag{8}$$

By assumption, the volume expansion is just due to the ≡SiOH formation.

We believe that the molecular water in the glass to be located in molecular size holes in the silica glass network [4, 11], where the water does not contribute to the volume of the glass.

The hydroxyl mass concentration S is

$$S = x_{SiOH} \frac{m_{SiOH}}{M_{glass}} = x_{SiOH} \frac{17}{60} \tag{9}$$

Consequently the volume swelling strain in terms of the water concentration C_w is

$$\varepsilon_v = (1 + \lambda) C_w = 1.836 \times C_w \ \ [1.739 \times C_w, 1.933 \times C_w] \tag{10}$$

The same relation in terms of the hydroxyl mass concentration S reads

$$\varepsilon_v = \tfrac{18}{17}(1 + \lambda) \frac{S}{2} = 0.97 \times S \ \ [0.92 \times S, 1.02 \times S] \tag{11}$$

Our equation used so far [4] was $\varepsilon_v = 0.92 S$ that is located at the lower boundary of the 95%-CI.

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