helps to account for the relatively large quantities of CaO observed by Ghosh. Phase equilibria in the $CaO-SiO_2-CaSO_4$ system are further complicated by the appearance of a silicosulphate phase [6] whose stability is sensitive to traces of atmospheric moisture, even at temperatures as high as 1050° C [7].

Fluorides have long been recognized as an effective flux for the formation of Ca_3SiO_5. A comprehensive review [8] summarizes the fundamental data and practical uses of fluoride fluxes.

The widespread use of fluxes in cement making presents a challenge to the scientist to explain their action on a systematic basis. Since cement clinker closely approaches equilibrium during its firing, it is essential to consider the equilibrium phase distribution as well as the kinetics of reaction. Moreover, as the complexity of the relevant system is increased by addition of more components, it becomes essential to make use of existing information if the action of the flux is to be interpreted in a systematic physicochemical manner.

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F. P. GLASSER
Department of Chemistry,
University of Aberdeen,
Old Aberdeen,
Scotland

Internal stress dependence of the hardness of crystallized glasses

Stryjak and McMillan [1] recently reported hardness values of a partly crystallized silicate glass increasing linearly with the volume fraction and the grain size (d) of the crystallites developed, i.e. a d^{+1} dependence. An interesting aspect of their data that they did not address was that as the glass begins to crystallize, hardness values were lower than the parent glass. Only when the volume per cent of crystallization was ~15% did the linear increase in hardness with d begin to raise hardness values above that of the parent glass. The Stryjak and McMillan proposed mechanism of grain boundary deformation to justify the d^{+1} hardness dependence does not appear applicable to their specimens for two reasons. First, the d^{+1} dependence results from creep processes that are very unlikely to be operative at the rate needed for room temperature hardness indents. Second, this mechanism fails to address why (a) such a dependence occurs instead of the usual $d^{-1/2}$ dependence observed for ceramics [2], and (b) the hardness of crystallized bodies actually can be less than that of the parent glass.

The purpose of this note is to propose an alternate explanation that addresses the above initial drop in hardness and includes the normal $d^{-1/2}$ dependence expected for the crystallites. The approach is to consider two aspects of the partially crystallized bodies. First, it is suggested that the linear dependence of the hardness on the volume fraction crystallite reflects the crystallized glasses following a rule of mixture combination of the hardness of the glass matrix and the crystallites, i.e.

$$H = (1-\beta)H_c + \beta H_g \qquad (1)$$

where H is the hardness of the composite, β is the volume fraction of glass, H_c is the hardness contribution of the crystalline phase and H_g is the hardness of the glass matrix. Note that Stryjak and McMillan showed a direct relation between the volume fraction of crystals $(1-\beta)$ and d, e.g. see their Fig. 10 and Table I here. Thus, correlation of $(1-\beta)$ and d provides an explanation of their observed d^{+1} dependence of hardness.

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Second, it is suggested that the internal stresses due to the mismatch in expansion between the glass matrix and the crystallites lower the hardness. Because the thermal expansion coefficient of the cubic crystalline phase (gahnite, $ZnAl_2O_4$), α_c, is substantially higher than that, α_g, of the glass matrix ($\alpha_c \sim 7.7 \times 10^{-6}\,°C^{-1}$ versus $\alpha_g \sim 2.4 \times 10^{-6}\,°C^{-1}$) upon cooling the gahnite will be in hydrostatic tension and the surrounding glass in hoop compression and radial tension. Wherever hoop compression adds to the compressive stress from the indenter, it will aid in plastic deformation, e.g. compaction, of the glass. As such combined stresses deform or compact the glass, the radial tension in the glass and hydrostatic tension in the gahnite can relax elastically to contribute to the net permanent effective "compaction" of the system. Thus, stresses in both the gahnite and the glass matrix can contribute to the compressive deformation for indentation. With such contributions, a lower load would be required for an equivalent deformation without such stresses, giving a measured decrease in hardness. A lower hardness of the partially crystallized compared to the parent glass would persist until hardness increases from increasing volume fraction of crystallites would more than compensate for the lowering of hardness due to the stresses from the interaction of the glass matrix and the crystallites.

In order to put the above concept in more quantitative terms, it is necessary to estimate the spatial averages of the internal stresses, $\bar{\sigma}_1$. As a first approximation for the average internal stress ($\bar{\sigma}_{ic}$) in the gahnite, note that at the crystal–glass boundaries, the stress is $\sim (\Delta\epsilon)\,E_c$ where $\Delta\epsilon =$ the mismatch strain and E_c is the average Youngs modulus of gahnite, and that these show the usual $1/r^3$ decay for elastic stresses where $r =$ the distance from the grain boundary. Because the $1/r^3$ dependence goes to infinity at $r = 0$, we limit the stress there, i.e., at the boundary, to $(\Delta\epsilon)E_c$, which can be done by normalizing r by $d/2$, giving

$$\bar{\sigma}_{ic} = \frac{1}{d/2}\int_0^{d/2} (\Delta\epsilon)E_c\,\frac{(d/2)^3}{r^3}\,dr \qquad (2)$$

which results in

$$\bar{\sigma}_{ic} = (\Delta\epsilon)(E_c)\left[\frac{1}{2}-\frac{d^2}{4}\right] \sim \frac{(\Delta\epsilon)E_c}{2} \qquad (3)$$

(considering only absolute values for now). In an exactly analogous fashion, we get:

$$\bar{\sigma}_{ig} \sim \frac{(\Delta\epsilon)E_g}{2} \qquad (4)$$

Now consider that there are two hardness values, the first (H_1) being the hardness neglecting internal stresses, i.e. $H_1 \propto \text{load}/(\text{diagonal})^2$ as measured, and the second (H_2) being the hardness when internal stresses are present and accounted for. Then

$$H_2 = H_1 + B_c'(\bar{\sigma}_{ic}) + B_g'(\bar{\sigma}_{ig}) \qquad (5)$$

where B_c' and B_g' are coefficients weighting the contribution of the internal stresses to the indent formation. These B's would, for example, reflect the volume over which the internal stresses are effective, as well as the volume fractions of each phase. The volume fraction is simply accounted for by making $B_c' = (1-\beta)B_c$ and $B_g' = \beta B_g$. To consider the volume over which the stresses are effective, note that in the above simple integrated average, the stresses have been calculated basically per unit length of a slab of granite of thickness $d/2$ jointed to a slab of glass of thickness $\lambda/2$. To consider the three-dimensional character of the grains and the intervening glass we must consider the stresses in the other two directions, and each of these must reflect the other half of the grain or the glass section and the stress due to the opposite boundary. For example, if we consider a grain to be a cube, in Equations 3 and 4 we have evaluated the stress for only one of six sides. Thus, $B_c \sim B_g \sim 6$.

H_2 should be the true hardness and hence should be equated to Equation 1. Doing this, using $H_c = H_0 + kd^{-1/2}$, recognizing that $\bar{\sigma}_{ic}$ and $\bar{\sigma}_{ig}$ both aid deformation and hence are subtracted terms, and solving for H_1, the measured hardness gives:

$$H_1 \sim (1-\beta)\left[H_0 + kd^{-1/2} - B\frac{(\Delta\epsilon)E_c}{2}\right] + \beta\left[H_g - B\frac{(\Delta\epsilon)E_g}{2}\right] \qquad (6)$$

Finally, note that $\Delta\epsilon = (\Delta\alpha)(\Delta T)$ were $\Delta\alpha$ is the difference in thermal expansion between the glass and crystals, and ΔT is essentially the temperature

TABLE I Comparison of measured and calculated hardness values

Volume fraction of glass (β)	Gahnite crystal size, G (10^{-9} m)	Hardness values (10^9 Pa)			
		Measured	Calculated		
			$\alpha_g = 24 \times 10^{-7}\,^\circ C^{-1}$; $k = 0.1$ MPa $m^{-\frac{1}{2}}$	α_g = corrected from Table II for	
				$k = 0.1$ MPa $m^{-\frac{1}{2}}$	$k = 0.15$ MPa $m^{-\frac{1}{2}}$
1.00		6.56	6.56	6.56	6.56
0.88	19.5	6.42	6.51	6.40	6.44
0.86	21	6.60	6.64	6.57	6.62
0.83	22	6.90	6.84	6.76	6.82
0.82	23	6.95	6.91	6.85	6.92
0.80	24	7.04	7.04	6.98	7.05
0.79	28	7.02	7.10	7.02	7.09

below which significant stress relief does not occur, i.e., $\Delta T \sim 10^{3\circ}$ C.

Because of their generally comprehensive characterization, most of the necessary values for Equation 5 are available from Stryjak and McMillan's studies, $H_g = 6.56 \times 10^9$, $E_g = 4.1 \times 10^{10}$ Pa) and $\Delta\alpha \sim 5.3 \times 10^{-6\circ} C^{-1}$). Since the hardness data being evaluated is for heat treatment at 950° C, $\Delta\epsilon \sim 5.3 \times 10^{-3}$. They give a value of 12.7×10^9 Pa for the hardness of gahnite, which is probably for a polycrystalline body and hence somewhat higher than H_0. However, this is a reasonable value for the present purposes; its use introducing limited error, e.g. depressing some of the values of k implied. This leaves E_c and k to be determined. E_c can be estimated from E_g and E for the partially crystallized glasses ($\sim 5.5 \times 10^{10}$ Pa) using a rule of mixtures. k cannot be estimated exactly, but its possible range can be estimated. Thus, H versus $d^{-1/2}$ data for MgF_2 (which is in the same hardness range) gives $k \sim 2$ MPa $m^{-1/2}$. Other ceramics of similar hardness show similar values, while harder ceramics (gahnite has about twice the hardness of MgF_2) show similar or lower ks [2]. Also Tashiro and Saka's partially ($\sim 45\%$) crystallized glasses give a k of ~ 5 MPa $m^{-1/2}$ with $Li_2O{\cdot}2SiO_2$ crystals and 0.07 MPa $m^{-1/2}$ with $Li_2O{\cdot}SiO_2$ crystals [3]. Thus k would appear to be in the range 10^{-3} to 10 MPa $m^{-1/2}$, and more commonly in the range 0.1 to 1 MPa $m^{-1/2}$.

With the above values, Equation 5 was applied to see how close a fit could be made to Stryjak and McMillan's data within the bounds estimated for k. As shown in Table I, a rather good fit is found for $k = 0.1$ MPa $m^{-1/2}$, i.e. near the lower end of, but definitely in, the expected range.

The above model does not address possible changes in the glass composition with progressive crystallization. The original glass was 63.6% SiO_2, 17.3% Al_2O_3, 5.5% ZnO, 4.5% CaO, 9.1% ZrO_2 (by weight), so precipitation of $ZnAl_2O_4$ would move from an alumina-silicate glass closer to a silicate glass. This would tend to lower both E_g and H_g. As seen in Equation 5, these would have partially cancelling effects, but for equivalent changes in H_g and E_g, a decrease in the former would give a limited net lowering of H_1. This leaves the effect of composition change on $\Delta\alpha$ and hence $\Delta\epsilon$. One might suspect that α_g would decrease because the glass is becoming more SiO_2-rich. Again, analysis is possible because of the generally comprehensive characterization of Stryjak and McMillan. Using their thermal expansion data in a rule of mixtures predicts an α that becomes progressively higher than measured with increasing crystallization. (Note that Budiansky's [4] more sophisticated theory reduces to the rule of mixtures, and hence gives the same results for ν, Poisson's ratio, $\sim \frac{1}{4}$.) Since α_c should be a constant this indicates that indeed α_g probably decreases, e.g. on the average by $\sim 6 \times 10^{-7\circ} C^{-1}$ (Table II). Such a decrease in α_g increases $\Delta\epsilon$ and thus would increase the effect of internal stresses. Using the corrected α_g values shown in Table II and fitting Stryjak and McMillan's hardness data gives less scatter, but somewhat lower results for the same previous value of k (0.1 MPa $m^{-1/2}$). Increasing k to 0.15 MPa $m^{-1/2}$ results in very close agreement (Table I). Also, as noted earlier, the value of H_0 is probably high.

Lowering H_0 to 10×10^9 Pa and using the corrected α_g would raise k to over 0.5 MPa m$^{-1/2}$ for good agreement.

Finally, it is worthwhile to consider the applicability of the above analysis to other systems and other available data. If crystals having a lower expansion than the glass are formed, the crystals will be in hydrostatic compression and glass in radial compression and hoop tension. The hydrostatic compression of the crystals is unlikely to increase significantly the plastic deformation in hardness testing, but the hoop compression of the glass should. Thus, an effect would also be expected for this opposite difference in expansion than for Stryjak and McMillan's glass. However, the effect of the mismatch in expansion on hardness would be less (e.g. $\frac{1}{2}$ for the same difference in α) due to the suggested lack of effect in the crystalline phase. Greater effect on hardness for systems having $\alpha_c > \alpha_g$ than with $\alpha_c > \alpha_g$ are also expected since the expansion of some crystal phases can often exceed the expansion of the glass by more than the expansion of the glass can exceed that of low expanding crystal phases, e.g. $\Delta\alpha$ for a crystalline phase with $\alpha_c = 0$ is α_g, but (as in the present case) $\Delta\alpha \sim 2\alpha_g$ due to $\alpha_c \sim 3\alpha_g$.

Other data in the literature suggests possible effects of internal stresses. Thus, for example, data of Tashiro and Sakka [3] for crystallization (~ 45%) of a glass (81 wt% SiO_2, 12.5 wt% Li_2O, 4 wt%, Al_2O_3, 2.5 wt% K_2O with traces of CeO_2 and Au) shows hardness extrapolating: (1) to ~ 810 kg mm^{-2} at $d = \infty$ versus the glass hardness of ~ 560 kg mm^{-2} with predominantly Li_2SiO_3 crystallites present and (2) to ~ 400 kg mm^{-2} with predominantly $Li_2Si_2O_5$ crystals present. While internal stresses are probably involved in both cases, the $Li_2Si_2O_5$ extrapolation particularly suggests this. Sakka [5] reports that α for the parent glass is ~ $85 \times 10^{-7°}$ C^{-1} and that of the matrix glass is ~ $21 \times 10^{-7°}$ C^{-1}. Since the expansion of $Li_2Si_2O_5$ is ~ 110×10^{-7} [6], this system also has a crystalline phase with a substantially higher expansion than the glass matrix.

Similarly, the hardness data of Donald and McCurrie [7] for various degrees of crystallization of 69.5 wt% SiO_2, 17.8 wt% Al_2O_3, 2.8 wt% MgO, 2.3 wt% Li_2O, 4.75 wt% TiO_2, 0.25 wt% ZrO_2, 1 wt% ZnO, 0.4 wt% Na_2O, and 1 wt% As_2O_4 exhibits significant maxima and minima, with some of the latter approaching the parent glass. The greatest relative variations and the closest approach of a body with a fair amount of crystallization to the hardness of the parent glass is for the 900° C heat treatment in which β spodumene is the major part of the crystalline phase in comparison to the 1000° C heat treatment which gave β eucryptite as the major crystalline phase in the same regime. Although specific expansion data is again not available, such glasses typically have low expansions so the greater expansion of β spodumene as opposed to β eucryptite (actually with a negative expansion), as well as probably the parent glass, is consistent with the ideas discussed earlier.

TABLE II Comparison of measured and calculated thermal expansion coefficients of Stryjak and McMillan's glass 3 as a function of crystallization

Volume fraction glass, β	Thermal expansion coefficient ($10^{-7°}$ C^{-1}, 20–800° C)		Indicated corrected α of residual glass ($10^{-7°}$ C^{-1})
	Measured	Calculated from rule of mixtures*	
1.0	24.4	24.4	24.4
0.88	24.5	30.7	17.3
0.86	27.9	31.8	19.9
0.83	28.8	33.3	18.9
0.82	31.0	33.9	20.9
0.80	31.7	34.9	20.4
0.79	31.5	35.4	19.4

*Calculated using $\alpha = \beta\alpha_g + (1 - \beta)\alpha_c$

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R. W. RICE
Naval Research Laboratory,
Washington, DC 20375, USA

Reply to "Internal stress dependence of the hardness of crystallized glasses"

While the comment by Rice puts forward some interesting ideas we believe that several of these are speculative and may be unsoundly based.

For example, Rice contends that the mechanism we proposed for a d^{+1} dependence of hardness could not be operable. The main objection to this mechanism would be that plastic deformation of the glass matrix would be needed to provide an overall deformation of the system. Indentation hardness studies on glasses certainly provide evidence of plastic flow at room temperature. Also, in discussing the possible effects of internal stresses, Rice invokes plastic deformation of the glass.

In our paper we explain the initial reduction of hardness that occurs when the glass crystallizes, in terms of the reduction of hardness of the residual glass matrix owing to changes of the composition of this phase. In all of Rice's calculations he has ignored this possibility and the effects of the initial precipitation of tetragonal zirconia. In our glass-ceramics zirconia was present as a substantial secondary phase (~9 vol%).

For the hardness of the glass matrix Rice uses the value for our base glass. This is clearly incorrect since the hardness of the residual glass phase will change progressively as the volume fraction of crystals increases. Also for the elastic modulus of the glass phase in the glass-ceramic, E_g, Rice uses the value for our base glass. Obviously this parameter will change as the composition of the glass changes. Furthermore, Rice estimates the value of E_c, the elastic modulus of gahnite, from the rule of mixtures. In this he uses an incorrect value for the elastic modulus of the glass phase and again neglects the presence of the zirconia phase.

We consider that the ideas concerning effects of internal stresses on the hardness of glasses are speculative and that some supporting evidence should have been quoted.

The apparently good agreement between the calculated and measured values of hardness (Table I) clearly depends upon the values selected for the various parameters. In particular, the choice of a value of $0.1\,\mathrm{MPa\,m^{-1/2}}$ for k is arbitrary since apparently this parameter can vary by four orders of magnitude depending on the system.

Finally, while we accept that internal stresses may have an effect upon the hardness we do not feel that the analysis proposed by Rice is meaningful because it neglects several other important aspects such as the changes in the properties of the residual glass phase and the presence of crystalline zirconia as a substantial secondary phase.

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P. W. McMILLAN
A. J. STRYJAK
Department of Physics,
University of Warwick,
Coventry, UK

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