Discussion of the indentation hardness of a glass-ceramic with particulate microstructure

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On the basis of a theory previously developed by the authors for the indentation hardness of glass matrix, particulate composites, an attempt was made to interpret published hardness data for a $ZnO-Al_2O_3-SiO_2$ glass-ceramic in which gahnite ($ZnAl_2O_4$) crystal particles are dispersed in a glass matrix as a major crystalline phase. The elastic moduli for gahnite were estimated using both the bulk modulus–molar volume relationship and the density–Poisson's ratio relationship, established for oxide crystals. After determining the variation of the matrix Young's modulus with heat-treatment, the variation of the overall hardness with volume fraction of crystal phase as well as the crystal-size effect were discussed. The hardness behaviour of the present glass-ceramic could be interpreted well in terms of the properties and amounts of the constituent phases and the microstructural effects.

1. Introduction

It is well-known that the indentation hardness of glass-ceramics is considerably higher than that of ordinary glasses [1]. However, little study has been made on the hardness of glass-ceramics in terms of their microstructure. Limited studies which have been presented are often complicated because of little or no microstructural characterization.

The microstructure of partially crystalline glass-ceramics containing a large proportion of glass phase generally consists of dispersed crystalline particles embedded in a continuous glass matrix [2]. The indentation hardness data for this type of glass-ceramic have been reported by Stryjak and McMillan with comprehensive microstructural characterization [3, 4]. They measured the variation of hardness with heat-treatment of a spinel transparent glass-ceramic based upon the $ZnO-Al_2O_3-SiO_2$ system. They found that the hardness increased linearly with the volume fraction and particle size of the crystallites developed. Rice [5] discussed their experimental results and proposed ideas concerning effects of internal stresses on the hardness of crystallized glasses.

Indentation behaviour of partially crystalline glass-ceramics having particulate microstructure must be different from that of fully crystalline glass-ceramics which can be regarded as polycrystalline materials almost free of glass phase. Recently, the authors [6] proposed a theory of the indentation hardness of glass matrix, particulate composites, based upon a microstructural viewpoint of flow in glass. In the present study, an attempt is made to interpret Vickers hardness data for the partially crystalline glass-ceramic published by Stryjak and McMillan [3, 4] on the basis of our theory. The variation of the overall hardness with volume fraction of crystal phase as well as the crystal size effect will be discussed.

2. Theory

Miyata and Jinno [6] analysed the indentation hardness of glass matrix, particulate composites regarding glasses as elastic–plastic materials on a microscopic scale. Based upon Marsh's theory [7]

TABLE I Microstructural parameters, Young's modulus and Vickers hardness of a ZnO−Al₂O₃−SiO₂ glass-ceramic [3, 4]

Heat-treatment time at 950° C* (h)	Vol % crystalline phase ϕ	Particle size d (nm)	Mean free path between particles λ (nm)	Young's modulus E (GPa)	Vickers hardness H (GPa)
(Base glass)	−	−	−	41 ± 2	6.56 ± 0.03
1	12.0 ± 2.0	19.5 ± 2.5	143 ± 7	56 ± 9	6.42 ± 0.05
2	14.0 ± 2.0	21.0 ± 3.0	129 ± 7	56.5 ± 8	6.60 ± 0.06
3	17.0 ± 2.5	22.0 ± 4.0	107 ± 8	55 ± 9	6.90 ± 0.05
4	18.0 ± 1.8	23.0 ± 4.0	105 ± 8	55 ± 9	6.95 ± 0.06
5	20.0 ± 1.5	24.0 ± 4.0	96 ± 8	56 ± 6	7.04 ± 0.06
6	21.0 ± 1.5	28.0 ± 4.0	105 ± 8	55 ± 8	7.02 ± 0.04

*The base glass samples were heat-treated at 800° C for 4 h before treatment at 950° C.

of indentation, expressions were formulated for indentation hardness of glass-matrix composites containing spherical crystalline or glass particles. When dispersed particles have higher elastic limit than a matrix (hard particles−soft glass matrix), the overall indentation hardness H can be expressed, for a dilute concentration of dispersed phase, as [6]

$$\frac{H}{H_m} = \left(1 + \frac{Q-1}{1-Q\phi}\phi\right)$$
$$\times \left(1 + \kappa \ln \frac{1-Q\phi}{(1-\alpha\phi)(1-\phi)}\right) \quad (1)$$

with

$$\kappa = B\sigma_{ym}/H_m \quad (2)$$

$$Q = \frac{15(1-\nu_m)\mu_p}{(7-5\nu_m)\mu_m + (8-10\nu_m)\mu_p} \quad (3)$$

$$\alpha = \frac{15(1-\nu_m)}{7-5\nu_m}(Q-1), \quad (4)$$

where H_m is the hardness of the matrix without a dispersion, μ is the shear modulus, ν is the Poisson's ratio, σ_{ym} is the flow stress of the matrix, ϕ is the volume fraction of dispersed particles and B is an empirical constant involved in Marsh's expression for hardness [7] and equal to 0.6. The subscripts m and p refer to the matrix and particle, respectively. The constant κ which depends upon H_m and σ_{ym} can be estimated at 0.3 to 0.4 for most glass matrices [6]. Equation 1 predicts that the hardness of this type of composite increases with increasing second-phase particles when $Q > 1$ (i.e. $\mu_p > \mu_m$).

Oxide glasses generally have lower elastic modulus and lower indentation hardness than ordinary crystalline oxides. This suggests that partially crystalline glass-ceramics can be generally regarded as glass matrix composites containing

hard crystalline particles and their hardness behaviour is expected to follow Equation 1.

3. Published hardness data
Stryjak and McMillan [3, 4] measured the Vickers hardness, Young's modulus and other physical properties of a ZnO−Al₂O₃−SiO₂ glass-ceramic, derived from the glass of composition 63.6 wt% SiO₂, 17.3 wt% Al₂O₃, 5.5 wt% ZnO, 4.5 wt% CaO and 9.1 wt% ZrO₂. The base glass specimens were subjected to heat-treatment at 800° C for 4 h and successively at 950° C for 1 to 6 h. The microstructure was characterized using X-ray diffraction and transmission electron microscopy, and the variation of microstructural parameters with heat-treatment are given. This glass-ceramic contains a large proportion of glass phase and is composed of fine crystalline particles dispersed in a glass matrix. The major crystalline phase was identified as gahnite (ZnAl₂O₄) crystal by X-ray diffraction. Electron microscopy indicated that the gahnite crystals initially took the form of spherical particles but structural changes caused the particles to take on a rod-shaped formation after a 1 h crystallization treatment at 950° C. In Table I, the original data of the Vickers hardness, Young's modulus in bending, and microstructural parameters for this glass-ceramic are summarized [3, 4]. Note that the value of particle size d was taken to be the average particle length and that the mean free path between particles was calculated by Stryjak and McMillan using $\lambda = d(1-\phi)/\phi$.

4. Interpretation
4.1. Preliminary considerations
Stryjak and McMillan [3] observed that a small number of tetragonal zirconia crystals were present as a secondary crystalline phase in the glass-ceramic. But to simplify the problem, it is

assumed here that the present glass-ceramic can be regarded as a two-phase composite consisting of gahnite crystals dispersed in a glass matrix. This means that the glass matrix containing small amounts of zirconia phase is assumed as homogeneous glass phase.

In the present glass-ceramic, gahnite crystals are present in the form of rod-shaped particles after 1 h of heat-treatment at 950° C [3]. Our theory is based upon a model consisting of spherical particles dispersed in a glass matrix. In the derivation of Equation 1, expressions for the effective elastic moduli of a two-phase composite containing spherical particles are used [6]. Strictly speaking, in the present application, Equation 1 should be modified for a composite containing prolate spheroidal particles. However, as indicated below, Equation 1 can approximate satisfactorily the indentation hardness of glass-matrix composites containing prolate particles unless they are extremely long, under the condition that E_p/E_m is less than about 10. It has been shown that the overall elastic modulus of a two-phase composite containing randomly dispersed prolate spheroids is not appreciably different from that of a composite containing randomly dispersed spherical particles as long as $E_p/E_m \lesssim 10$ [8, 9]. For example, in the extreme case where $E_p/E_m = 10$, the dispersion of prolate spheroidal particles having axial ratio $c/a = 100$ (where c is the length of unique semi-axis of spheroid and a is the spheroidal radius) results in only about 8% higher value for the overall Young's modulus than the dispersion of spherical particles [9]. This indicates that, as a first approximation, the expressions for the elastic moduli for a body containing spherical particle dispersion [10, 11] can be used for the case of relatively long prolate particle dispersion under the condition $E_p/E_m \lesssim 10$. The same argument can be made for Equation 1 which was derived using the elasticity equations of the composites with a dilute dispersion of spherical particles [6].

Table I indicates that the Young's modulus of the glass-ceramic remains almost unchanged during the course of heat-treatment from 1 to 6 h, in spite of an increase in volume fraction of crystalline phase from 0.12 to 0.21. This suggests that the chemical composition of the glass matrix will change progressively as the volume fraction of gahnite phase increases, and that the Young's modulus of the matrix decreases as the compo-

sition of the matrix changes. That is, the Young's modulus of the glass phase in each of the heat-treated samples is no more equal to that of the base glass.

Equations 1 to 4 indicate that the information on the elastic moduli of the constituent phases of a composite is required to interpret quantitatively the hardness variation with the volume fraction of dispersed phase. Unfortunately, the elastic constants of both phases are experimentally unknown in the present case. In addition, elastic modulus values for gahnite are not available in the literature. However, it is possible to estimate reasonably the elastic moduli of gahnite crystal, using both the bulk modulus—molar volume relationship [12] and the density—Poisson's ratio relationship [13] established for oxide crystals. Once the elastic moduli of gahnite crystal have been determined, those of the glass matrix may readily be calculated from measured Young's modulus of each glass-ceramic sample (Table I) using the expressions for the elastic moduli of a two-phase composite [10, 11].

4.2. Estimation of elastic modulus for constituent phases
4.2.1. Elastic moduli of gahnite crystals
Anderson and his co-workers [12] have shown that the bulk modulus K is very nearly inversely proportional to the specific molar volume v_0 at ambient conditions for oxides as well as alkali halides. That is,

$$Kv_0 = C \qquad (5)$$

where C is a constant which depends upon the crystal structure, valence product and a repulsive parameter. Equation 5 enables the bulk modulus K of oxides to be estimated if their molar volume and crystal structure are known.

For spinel structure, C is estimated at about 7.98×10^{-3} GPa m^3 mol^{-1} [12]. The density of gahnite is reported as 4.62×10^3 kg m^{-3} [14]. If this density value is used, v_0 for gahnite is evaluated at 3.97×10^{-5} m^3 mol^{-1}. On the other hand, the cell size a_0 of gahnite is 0.8086 nm [15]. The molar volume v_0 calculated from the cell size a_0 is 3.98×10^{-5} m^3 mol^{-1}. Using the latter value for v_0, the bulk modulus of gahnite is calculated at 200 GPa from Equation 5. The Poisson's ratio ν of gahnite can be estimated at 0.28 from the density—Poisson's ratio relationship [13]. Using this value for ν, the Young's modulus E and shear

TABLE II Data calculations

Heat-treatment time at 950° C (h)	Calculated E_m, H/H_m and H_m values		
	$E_m{}^*$ (GPa)	$H/H_m{}^\dagger$	$H_m{}^\ddagger$ (GPa)
1	47.5 ± 8	1.14 ± 0.01	5.63 ± 0.09
2	46.5 ± 7	1.17 ± 0.01	5.64 ± 0.10
3	43 ± 8	1.23 ± 0.02	5.61 ± 0.13
4	42.5 ± 7.5	1.25 ± 0.02	5.56 ± 0.14
5	42 ± 5	1.29 ± 0.02	5.46 ± 0.13
6	40 ± 7	1.32 ± 0.02	5.32 ± 0.11

*Calculated from Equations 6 to 8 using measured Young's modulus (Table I) and assuming $K_p = 200\,\text{GPa}$, $\nu_p = 0.28$ and $\nu_m = 0.25$.
†Calculated from Equation 1.
‡Estimated from calculated values for H/H_m and measured hardness values (Table I).

modulus μ of gahnite can be calculated at 264 and 103 GPa, respectively.

4.2.2. Elastic moduli of matrix glass

As indicated earlier, the expressions for the elastic moduli of a body containing spherical particles [10, 11] hold approximately for the case of prolate spheroidal particles as far as they are not extremely long, under the condition that $E_p/E_m \lesssim 10$. The calculated Young's modulus for gahnite is 264 GPa, which is within 10 times the Young's modulus of ordinary silicate glasses.

Taking the values for K_p, μ_p and E_p as 200, 103 and 264 GPa, respectively, and assuming that the Poisson's ratio of the glass matrix, ν_m is 0.25, the elastic moduli of the glass matrix, K_m, μ_m and E_m were calculated from the elasticity equations for spherical particle dispersion [10, 11]:

$$K = K_m + \phi \left/ \left[\frac{1}{K_p - K_m} + \frac{3(1-\phi)}{3K_m + 4\mu_m} \right] \right. \qquad (6)$$

$$\mu = \mu_m + \phi \left/ \left[\frac{1}{\mu_p - \mu_m} + \frac{6(K_m + 2\mu_m)(1-\phi)}{5\mu_m(3K_m + 4\mu_m)} \right] \right.$$

$$\qquad (7)$$

$$E = \frac{9K\mu}{3K + \mu} . \qquad (8)$$

The Young's modulus of the matrix, E_m, calculated for each of heat-treated samples is listed in the first column of Table II.

4.3. Interpretaton of the Vickers hardness behaviour

4.3.1. Variation of the relative hardness

Using the values for elastic moduli of the constituent phases, estimated in the preceding section,

the relative hardness H/H_m was calculated from Equation 1 as a function of heat-treatment time at 950° C. The results are summarized in Table II. In this calculation, the value for κ in Equation 1 was taken as 0.35, the representative κ value for ordinary glass matrices [6]. It is found that E_m decreases with increasing heat-treatment time but H/H_m increases during the course of heat-treatment. This calculated H/H_m behaviour is in accord with the measured Vickers hardness behaviour showing an increase with increasing heat-treatment time (Table I). The rate of increase in calculated H/H_m with increasing volume fraction of crystal phase is slightly larger than that observed for measured hardness. This suggests that H_m itself decreases during the heat-treatment process similarly to E_m. Unfortunately, independent estimation of H_m cannot be made, but H_m can be estimated if we use both the calculated values for H/H_m and the measured values for Vickers hardness. Results of such estimation are summarized in the last column in Table II. It is seen that H_m decreases with increasing heat-treatment time, but the rate of decrease in H_m is small as compared with that in E_m.

4.3.2. Interpretation of the crystal-size effect

In their discussion of the hardness data of the present glass-ceramic, Stryjak and McMillan [4] proposed an experimental relationship, $H \propto d$ (where d is the particle size). Let us now examine the way in which the overall hardness depends upon the particle size on the basis of our theory. Equation 1 indicates that the hardness of a composite has no basic dependence on the particle size and particle spacing. However, the hardness can be indirectly correlated with such microstructural parameters through a stereological relationship. For randomly distributed particles, the mean free distance between particles, λ is given by [16]

$$\lambda = \bar{L}_3(1-\phi)/\phi \qquad (9)$$

where $\bar{L}_3$ is the mean intercept length of randomly distributed particles. Strictly speaking, $\bar{L}_3$ for the case of a dispersion of rod-shaped particles cannot be theoretically computed, unless the length to radius ratio of a particle is given. However, if we assume that the length of rod-shaped particle is within about several times larger than its radius, $\bar{L}_3$ can be taken to be approximately equal to the length of the rod-shaped particle [16]. Judging
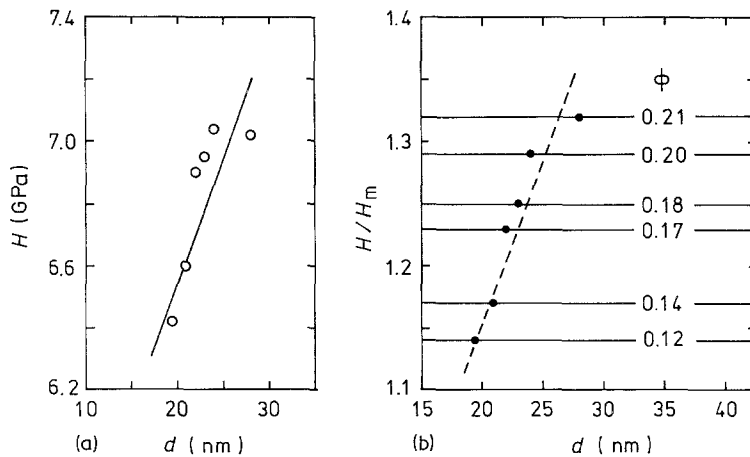
Figure 1 Interpretation of particle-size dependence of Vickers hardness of a $ZnO–Al_2O_3–SiO_2$ glass-ceramic [3, 4]. (a) Experimental hardness data plotted against the particle size d. (b) Plots of theoretical H/H_m against d curves drawn for various volume fractions of dispersed crystalline phase.

from the electron micrographs taken by Stryjak and McMillan for the present glass-ceramic [3], this assumption seems to be valid, and hence their calculation of λ, using $\lambda = d(1 - \phi)/\phi$ (Table I), may be justified. Putting $\bar{L}_3 \approx d$, we obtain from Equation 9

$$\phi = \frac{d/\lambda}{1 + d/\lambda}. \qquad (10)$$

Substitution of Equation 10 into Equation 1 enables the hardness to be expressed in terms of d/λ.

Fig. 1 shows an interpretation of particle size dependence of Vickers hardness of the present glass-ceramic on the basis of our theory. In Fig. 1a, experimental hardness data are plotted against the particle size d; the solid curve indicates the line drawn by Stryjak and McMillan [4] who suggested a d^{+1} dependence of hardness. Equation 1 predicts, on the other hand, that H/H_m is independent of the particle size and interparticle spacing if the volume fraction of the dispersed particles is kept constant. In Fig. 1b, the theoretical H/H_m curve is drawn, with particle size d as abscissa, for various volume fractions of crystalline phase listed in Table I; a solid circle represents the particle size observed for each volume fraction. Note that the variation of d is accompanied by the variation of ϕ (and also by the variation of λ) in the present glass-ceramic. Fig. 1b suggests that H/H_m increases following the broken line, as the particle size increases. Taking into account the fact that H_m varies only slightly with heat-treatment (Table II), it can be said that this theoretical H/H_m behaviour explains quite well the experimental hardness

variation with d shown in Fig. 1a. Thus it may be concluded that the particle size dependence of the hardness is not a basic character but it appears indirectly through the stereological relationship expressed in Equation 9 or 10.

4.4. Comments on the interpretation by Rice

Rice [5] tried to interpret the hardness data for the present glass-ceramic, analysing the effects of internal stresses on the hardness of crystallized glasses. However, it seems that his analysis includes several ideas whose validity should be examined.

First of all, Rice assumed *a priori* that the hardness of a two-phase composite is additive, that is:

$$H = (1 - \phi)H_m + \phi H_p. \qquad (11)$$

This linear equation may certainly hold for the hardness of two-phase composites with layered structure. However, the application of Equation 11 to the hardness of particulate composites seems to be too rough for quantitative calculations. In general, such a simple additive rule is only applicable to structure-sensitive properties of particulate systems in which either the volume fraction of dispersed phase and/or the difference in specific properties under consideration between phases are very small. A similar argument may also be made for Rice's assumption that internal stresses due to thermal expansion mismatch are linearly superimposed on to the overall hardness. However, the way in which the internal stresses influence the overall hardness seems to be a subject which must be further examined.

2697

Secondly, the present authors feel that the magnitude of internal stresses is overestimated by Rice. He roughly estimated the internal stresses based upon a slab model and extended it to a three-dimensional case. Rice gave the following equations for average internal stresses in particle and matrix:

$$\bar{\sigma}_p \simeq \frac{\Delta\alpha\Delta T}{2} E_p \qquad (12)$$

$$\bar{\sigma}_m \simeq \frac{\Delta\alpha\Delta T}{2} E_m. \qquad (13)$$

The theory of the internal stress system around and within particles in particulate composites is well established. For the case of a single, spherical particle of radius R in an infinite isotropic matrix, a uniform stress σ arises within the particle and radial and tangential stresses of $-\sigma R^3/r^3$ and $\sigma R^3/2r^3$, respectively, arise around the surrounding matrix, where r is the distance from the centre of the particle to a point in the matrix [17–19]. These equations represent a satisfactory approximation for the internal stresses set up during cooling of the composite containing low concentrations of particles. The stress σ is given by

$$\sigma = \Delta\alpha\Delta T \Big/ \left(\frac{1 + \nu_m}{2E_m} + \frac{1 - 2\nu_p}{E_p} \right), \quad (14)$$

where $\Delta\alpha = \alpha_p - \alpha_m$ and ΔT is the temperature cooling range over which the matrix plasticity is negligible. Let us now roughly estimate the internal stress within the particle, σ_p, using Equation 14 and compare it with Rice's estimation (Equation 12). If we assume that the Poisson's ratios of the matrix and particle are equal and take the value of 0.25, we obtain from Equation 14

$$\sigma_p = \sigma$$

$$\simeq \frac{2E_m E_p}{1.25E_p + E_m} \Delta\alpha\Delta T$$

$$= \left(\frac{4}{1 + 1.25 E_p/E_m} \right) \left(\frac{\Delta\alpha\Delta T}{2} E_p \right). \quad (15)$$

For the case where $E_p/E_m > 2.4$, it can be shown that

$$\frac{4}{1 + 1.25 E_p/E_m} < 1.$$

Thus, when E_p/E_m is larger than 2.4, Equation 15 gives smaller values for the internal stress within the particle than Equation 12. For example, when $E_p/E_m = 6$ (representative E_p/E_m ratio for the present glass-ceramic),

$$\sigma_p = 0.47 \left(\frac{\Delta\alpha\Delta T}{2} E_p \right)$$

which is less than one-half the estimation by Rice. Further, his estimation for ΔT ($10^3\,^\circ$C) may also contribute to an overestimation of the internal stresses. ΔT should be taken, not from the crystallization temperature, but from the nucleation temperature (800° C) which is considered to lie within the temperature range corresponding with viscosities of $10^{11} \sim 10^{12}$ P [20].

Finally, it should be noted that, for the values of H_m and E_m, Rice took the values for the base glass composition. However, these estimations seem to be incorrect for the present case. As discussed earlier, the hardness and elastic modulus of the glass-ceramic samples subjected to various heat-treatment times are no longer equal to those of the base glass, since the chemical composition of the glass matrix must vary progressively as the volume fraction of gahnite phase increases. This was already pointed out by McMillan and Stryjak [21] in their reply to the comment by Rice.

Thus, although we suppose that internal stresses may have a possible effect on the hardness of particulate composites, it is unlikely that the hardness of the present glass-ceramic is effectively influenced by the internal stresses in the manner suggested by Rice.

5. Concluding remarks
On the basis of our theory for the indentation hardness of particulate composites, the published hardness data of a glass-ceramic with particulate microstructure could be interpreted well in terms of the properties and amounts of the constituent phases and the microstructural effects. However, it is probable that internal stresses might have some effect on the indentation hardness. This possible effect should be then further analysed to examine the degree and manner in which the internal stresses contribute to the overall hardness of particulate composites.

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