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Porosity-dependence of elastic moduli and hardness of 3Y-TZP ceramics

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Abstract

The elastic moduli and Vickers hardness of porous 3Y-TZP ceramics have been measured and related to a computed model. At the low porosity level (less than 8%), the spherical model can best represent the effect of porosity on the elastic moduli. As the porosity content increases, the oblate spheroid model needs to be used to interpret the more complex morphology of the porosity and its effect on the elastic moduli. The empirical expressions are also important in a description of the effect of porosity on the elastic moduli. The effect of porosity on hardness is very similar to that on the bulk modulus, which contributes to the body stress, and consequently to the densification taking place beneath the hardness indenter.

1. Introduction

Over the past 40 years, extensive experimental and theoretical work has been undertaken to determine the effect of porosity on the elastic moduli of engineering ceramics. A number of expressions for the relationship between elastic moduli and porosity have been proposed, and several attempts have been made to relate the complex interaction of microstructure and mechanical properties [1,3]. The following expressions are those most frequently employed to describe this behaviour:

$$M = M_0 \exp(-bP) \quad (1)$$

$$M = M_0 (1 - fP)^n \quad (2)$$

$$M = M_0 (1 - C_1 P + C_2 P_2) \quad (3)$$

$$M = M_0 (1 - P)/(l + aP) \quad (4)$$

where M_0 and M usually represent the Young's modulus of dense materials and porous materials, respectively and P is the volume fraction of porosity. b, c_1, c_2, f, n, and a are constants, and can be determined from experimental results by data fitting. The Young modulus is widely accepted as the definitive elastic modulus for a material, with the consequence that the effect of porosity on the relevant Poisson's ratio has often been ignored. This leads to the inference that the equations listed above could well have less physical significance. In contrast to the Young's modulus, the bulk modulus allows for the possibility of a volume change and the shear modulus for the possibility of a shape change in mathematical descriptions of elastic behaviour. In the present study, Eqs. (1)–(3) are also used to express the effect of porosity on the bulk and shear moduli. Recently the application of micromechanics has made it possible to calculate the relationship between the elastic moduli and porosity [4–10]. The effect of inclusions (pores) on elastic moduli of the materials can be expressed by Eq. (4). The equation was originally derived by Hasselman [11] based on Hashin's results [12] and also by Wu [13] using the self-consistent method. Luo and Stevens [4] and Zhao et al. [10] have extended to a general case independently using slightly different approaches. The parameter a in Eq. (4) is related to morphology and Poisson ratio of the matrix. A simple case is that for spherical porosity and the constant a is given by:

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$a = (13 - 15\nu)(1 - \nu)/(14 - 10\nu)$ for Young's modulus

$a = (1 + \nu)/(2 - 4\nu)$ for bulk modulus

$a = (8 - 10\nu)/(7 - 5\nu)$ for shear modulus

where ν is the Poisson ratio. The spherically shaped pores have the least effect on the elastic moduli, but a more significant effect occurs with the presence of oblate spheroidal pores. Fig. 1 shows the effect of pore shape on the constant, a [4]. The more significant effect occurs in changes to the bulk modulus, whereas the effect is less marked for the shear modulus.

When the porosity content increases to a certain level, the effect of interaction between adjacent pores can become significant, and even more so when the pores interconnect with each other to form open porosity. When this occurs, a quantitative evaluation becomes difficult. Nevertheless, Hashin's bounds of the effective elastic moduli could be still valid [14–16]. Namat-Nasser and Hoii have published a comprehensive review on the subject of such bounds [5].

Hardness is a further important parameter. In the elastic–plastic system, both the form and size of a sharp indentation are related to the elastic moduli and the yield stress in the guise of hardness, whereas the ratio of fracture toughness and indentation hardness is used to express brittleness in non-ductile materials. The indentation method is also widely used to evaluate the toughness of ceramics [17], and the technique can be extended to determine residual stress [18] and elastic modulus [19]. Nevertheless, whereas the effect of elastic modulus has been extensively investigated, much less attention has been paid to the effect of porosity on the hardness of materials, with the exception that an exponential relationship between hardness and porosity has been reported [20]. In the present study, the effect of porosity on the elastic moduli and Vickers hardness of 3Y-TZP ceramics has been examined. Specific established models have been used to fit the experimental results, and the relationship between hardness and elastic moduli are discussed.

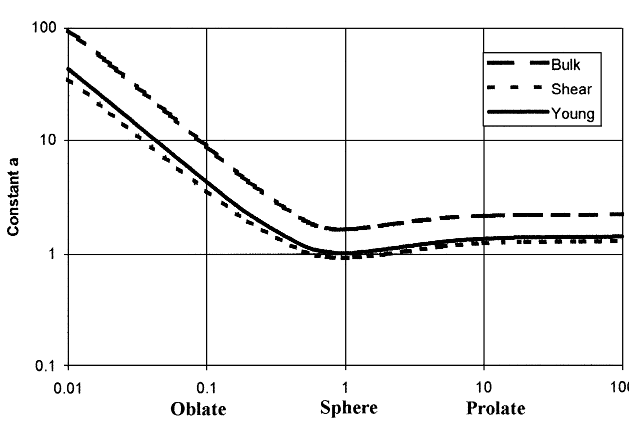

Fig. 1. The shape effect of the spheroid porosity on the constant a in Eq. (4). A value of Poisson's ratio for the porosity-free material of 0.32 was applied in the calculation.

2. Experimental

A commercial as-received 3Y-TZP nano-size powder (Tioxide Specialties, England) was used in the present study. The green bodies were prepared using single action die pressing followed by cold iso-static pressing. The pellets were fired at different temperatures in the range 1150–1450°C, in order to obtain the 3Y-TZP ceramic with various levels of porosity. The elastic moduli of the sintered pellets were measured using an ultrasonic velocity method, in which the longitude and shear velocities were measured by a pulse echo overlap technique. The Vickers hardness of the pellets were measured by indentation of a polished surface of the pellet.

The microstructure and morphology of the porosity was examined using polished and thermally etched specimens in a scanning electron microscope (SEM).

3. Results and discussion

Fig. 2 shows the values obtained for the measurements of the three elastic moduli (Young, shear and bulk) of the 3Y-TZP ceramics. The solid circles are experimental results, each calculated from the measurements of ultrasonic velocity and density. The elastic moduli were fitted to curves using Eqs. (1–3), by means of the least squares technique and the results listed in Table 1. The R-squared values determined for all three of the equations are higher than 0.95, indicating that all the equations employed to analyse the results have a very good fit with the experimental data. The values predicted for the porosity-free elastic moduli are close to the measured values, (Young 215 GPa, shear 81 GPa, and bulk 200 GPa, respectively). The most significant effect of the porosity occurs on the bulk modulus and the lowest on the shear modulus. This observation was predicted by spheroid model, (see Fig. 1). It is difficult to determine which equation is the most representative, since all three equations have been empirically derived. In addition, the curve fitting was carried out using the three elastic moduli, but only two of the moduli are mutually independent. The Young's modulus E, for example, can be expressed by bulk (K) and shear (G) moduli as:

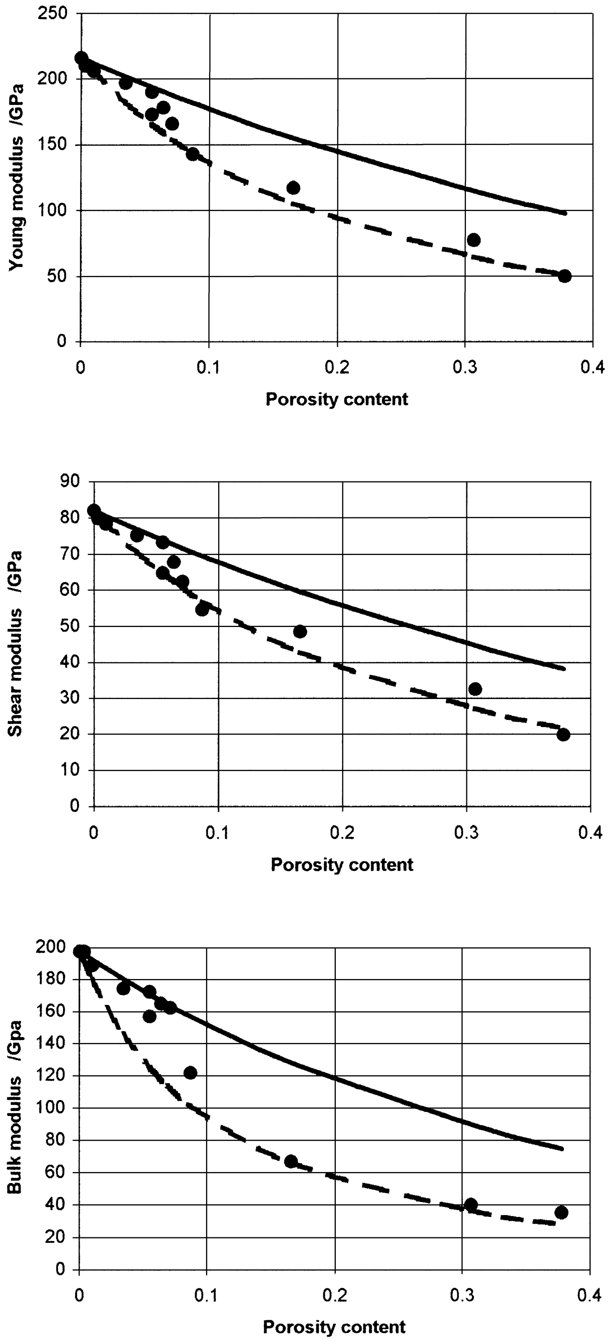

Fig. 2. The effect of porosity content on the elastic moduli. The solid circles are the experimental data, whereas solid lines are obtained by spherical porosity model. The dashed lines are obtained from the spheroid model and the ratio of the radii of the oblate spheroid used was 10.

$$E = 9KG/(3K + G)$$

Therefore, the three elastic moduli cannot independently relate to one expression at the same time, with the exception of Eq. (4). In addition none of the first three equations and their relevant constants indicate any obvious physical significance. Phani has discussed the usefulness of Eq. (2) in his series of papers [2,3,21], but it is quite difficult to find any convincing evidence to suggest that Eq. (2) is superior to the other equations in describing the effect of porosity on the elastic moduli, the reasons for which can be attributed to the complexity of morphology of porosity in real materials.

Table 1
Summary of curve fitting results for elastic moduli and hardness

Modulus	$M = M_0 \exp^{(-bP)}$	$M = M_0\ (1-P)^n$	$M = M_0(1-c_1P + c_2P^2)$
Young's	216.0exp(-3.69P)	$210.6(1\_p)^{2.96}$	$214.6(1-3.3P + 3.54P^2)$
	$R^2 = 0.985$*	$R^2 = 0.985$	$R^2 = 0.981$
Shear	$82.0\exp^{(-3,46P)}$	$79.9(1-P)^{2.79}$	$80.8(1-3P + 2.87P^2)$
	$R^2 = 0.971$	$R^2 = 0.976$	$R^2 = 0.970$
Bulk	$204.0\exp^{(-5.03P)}$	$195.5(1-P)^{4-02}$	$205.0(1-4.57P + 6.23P^2)$
	$R^2 = 0.964$	$R^2 = 0.951$	$R^2 = 0.9664$
Hardness	$11.75\exp^{(-5.04P)}$	$11.32(1-P)^{4.10}$	$11.09(1-3.63P + 3.63P^2)$
	$R^2 = 0.980$	$R^2 = 0.991$	$R^2 = 0.986$

* R^2 is R squared.

Unlike the first three equations, Eq. (4) has a limited theoretical basis and is physically acceptable; the three moduli (bulk, shear and Young's) can be expressed by the same equation with the exception that the constant employed differs in each case.

The constant a in Eq. (4) reflects the shape effect of porosity on the elastic moduli. Earlier investigation of the effect of porosity on Young's modulus of a limited selection of engineering ceramics showed that the porosity can be considered as an oblate spheroid [4,22], the ratio of long radius and short radius being as large as 10 [4]. At low porosity levels, below 8 %, the isolated pores are close to a spherical shape, which is in accord with observations on ceramics in the final stages of sintering, whereas a value for the ratio of long and short radii of the ellipsoid of 5 is in good agreement with the experimental results at porosity levels below 20%, since at such a porosity level, the pores exist in the sintering materials in various shapes, even as open porosity. At high porosity contents, greater than 25%, percolation starts and increasingly open pores are formed. For this range of porosity, any predictions made by the model could result in large errors, since the model has been developed on the assumption that inclusions (i.e. pores) are present in the material as a minor constituent.

Recently, Martin et al. [23] employed a similar model [9,10] and examined the effect of porosity on the elastic moduli in zinc oxide. Their results also showed the effectiveness of oblate shape in the description of pore morphology and their effect on the elastic moduli. Similar to our observation [4], the aspect ratio for a wide range of porosity is 5 in zinc oxide and the aspect ratio increases with the porosity level [23], although the difference occurs at low porosity level.

The spheroid porosity model has also been used in the present study to evaluate the relationship between porosity and the elastic moduli, as illustrated in Fig. 2, which shows a comparison with the experimental results. The predictions made are quite similar to the earlier results [4], in which the experimental data fits within the range defined by the two cases of spherical and oblate (the ratio of the radii $=10$) voids. In low porosity material, isolated pores are best represented by the spherical model. At a higher porosity content, the pores could well be present in various shapes, including extended pores in the form of open porosity. In this case, oblate porosity best represents the overall effect on the elastic moduli, and the ratio of the radii will tend to increase with porosity content. Since the porosity content used in the experiments is within a range up to 38%, i.e. to a relatively high level, many of the pores are in the form of open porosity and predictions based on the spheroidal porosity model can result in large deviations from the experimental data. In this case the empirical equations, as listed, need to be used to give good fit to the data, otherwise it is only possible to evaluate the upper and lower bounds. Consequently, the use of empirical equations can be seen to be of importance in any discussions involving the effect of porosity on the elastic moduli at high porosity contents.

In order to confirm the presence of the oblate porosity, the morphology of the pores present in the 3Y-TZP was characterised using SEM. Fig. 3 shows a series of micrographs illustrating the shape and distribution of the pores at different densities. At low porosity levels ($<6\%$), the pores are isolated and located randomly throughout the structure. They tend to be spherical, a consequence of the minimisation of the surface energy of the pores which tend towards the minimum energy state as equilibrium is approached. As the porosity content increases the pores become increasingly irregular and in this situation the spherical model would underestimate the effect of porosity on the elastic moduli. However, the oblate model will still give a good representation of the elastic properties and acceptable values of the moduli.

Vickers hardness was measured on the polished surface of the porous zirconia materials. Fig. 4 shows the experimental relationship between porosity and Vickers hardness. In order to compare the effect of porosity on the hardness with its effect on elastic moduli, a similar process of curve fitting was carried out and the results can be seen listed in Table 1. It is apparent that the three empirical equations employed for elastic properties, Eqs. (1)–(3), can also fit the experimental results of hardness quite well. It is evident, as would be expected, that the effect of porosity on the hardness is similar to its effect on the elastic moduli.

The elastic moduli of dense brittle materials have been measured and observed to be related to the Vickers hardness [24], Knoop hardness [19,25] and Hertzian indentation [26], as a consequence of elastic recovery

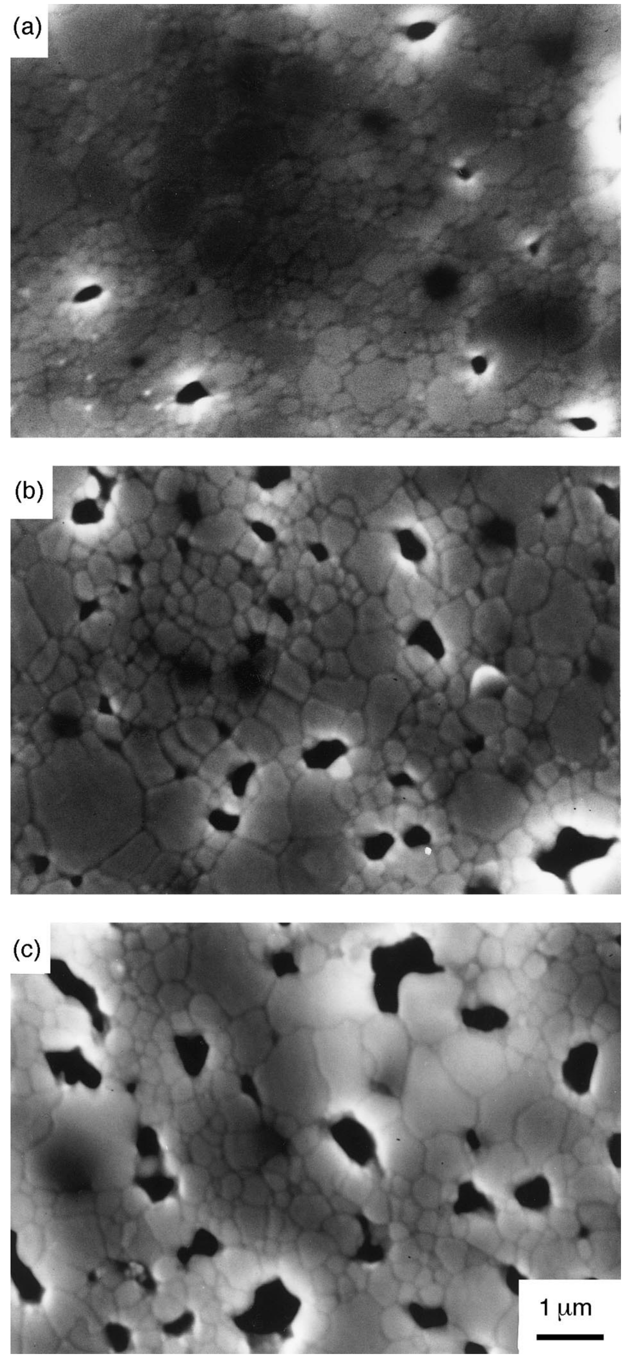

Fig. 3. SEM micrographs of 3Y-TZP with different porosity level. (a) 2 % pores, (b) 5 % pores, (c) 11 % pores.

phenomenon. The relationship between hardness and elastic moduli can be simplified as:

$$H/K = \text{constant} \quad (5)$$

The value of the constant depends on the structure of tile material [24,25]. In previous studies the effect of Poisson's ratio has often been ignored, and H/E rather than H/K has appeared more frequently in literature.

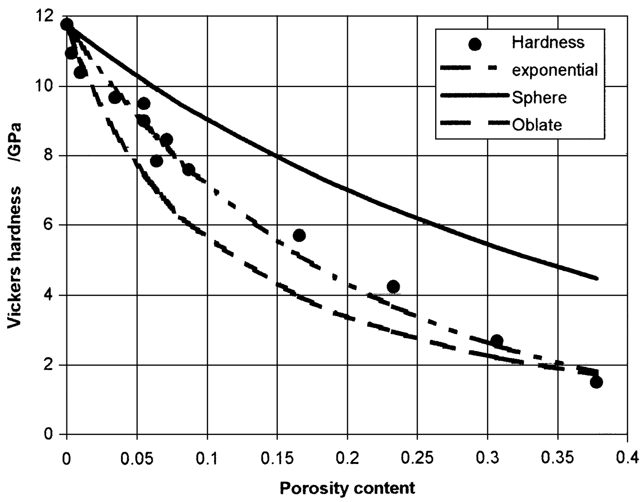

Fig. 4. The effect of porosity on the Vickers hardness of 3Y-TZP. Two of the curves are evaluated by means of Eq. (6): the solid line from the spherical model, the dashed line from the oblate spheroid model, the third curve, the dashed and dotted line from Eq. (7).

However, the value of Poisson's ratio is known to differ between materials and hence, for accuracy, needs to be incorporated into the various appropriate relationships.

The Vickers indentation is generated by elastic-plastic deformation in dense materials. In porous materials, an additional contribution to the indentation is the porosity filling generated by the high indentation stress beneath indenter [27]. The hardness decrease in increasingly porous materials is dominated by the porosity filling [27]. The degree of porosity filling is related to the stress level induced in the body, or body stress. In an elastic field, the body strain, e ($\equiv \varepsilon_{11}+\varepsilon_{22}+\varepsilon_{33}$), is related to the body stress, $\Theta(\equiv\sigma_{11}+\sigma_{22}+\sigma_{33})$, by the bulk modulus in a form such as:

$$\varepsilon = \Theta/3K \quad (6)$$

Hence, the indentation increment generated by porosity filling in the porous materials is expected to be related to a decrease in the bulk modulus. Therefore it is reasonable to assume that the decrease in hardness is linearly related to the decrease in bulk modulus in porous materials, or:

$$H/H_0 = \alpha K/K_0 \quad (7)$$

where α is a constant. In any comparison of the relationship between elastic moduli and porosity and that of hardness and porosity, as shown in Table 1, one can also readily observe that the effect of porosity on the bulk modulus is close to, even mirrors that of hardness, or $\alpha = 1$.

Thus using a known relationship between bulk modulus and porosity, one can predict the relationship between hardness and porosity. For an exponentially based relationship, for instance, the hardness can be represented by the following equation:

$$H = 11.76\exp(-5.03P) \quad (8)$$

Fig. 4 shows that the predicted values give a very good fit with the experimental data.

4. Conclusions

Porosity has a significant influence on the bulk modulus of materials and a lower effect on the shear modulus. Well established equations can accurately describe the relationships. The spheroid model can be readily fitted to the experimental results. The effect of porosity on the hardness can also be expressed by the equations which are used to relate the effect of the porosity on the elastic moduli. The relationships between the hardness and porosity are similar to those for bulk modulus and porosity, which can be attributed to the porosity filling processing taking place beneath the loaded indenter.

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References

[1] J.B. Wachtman Jr., Elastic deformation of ceramics and other refractory materials, in. Mechanical and Thermal Properties of Ceramics, National Bureau of Standards Spec. Pubi. No 303, 1968, pp.139–68.
[2] K.K. Phani, S.K. Niyogi, Elastic modulus–porosity relationship for Si_3N_4, J. Mater. Sci. Let. 6 (1987) 511–515.
[3] K.K. Phani, S.K. Niyogi, Elastic modulus–porosity relationships in polycrystalline rare-earth oxides, J. Am. Ceram. Soc. 70 (1987) 362–366.
[4] J. Luo, R. Stevens, Micromechanics of randomly oriented ellipsoidal inclusion composites, Part II: Elastic moduli, J. Appl. Phys. 79 (1996) 9057–9063.
[5] S. Nemat-Nasser, M. Hori (Eds.), Micromechanics: Overall Properties of Heterogeneous Materials, Elsevier, Amsterdam, 1993.
[6] J.W. Ju, T.M. Chen, Effective elastic moduli of two-phase composites containing randomly dispersed spherical inhomogeneities, Acta Mech. 103 (1994) 123–144.
[7] G.J. Weng, Some elastic properties of reinforced solids, with special reference to isotropic solids containing spherical inclusions, Int. J. Eng. Sci. 22 (1984) 845–856.
[8] N. Ramakrishnan, V.S. Arunachalam, Effective elastic moduli of porous ceramic materials, J. Am. Ceram. Soc. 76 (1993) 2745–2752.

[9] G.P. Tandon, G.J. Weng, Average stress in the matrix and effective moduli of randomly oriented composites, Compos. Sci. Technol 27 (1986) 111–132.
[10] Y.H. Zhao, G.P. Tandon, G.J. Weng, Elastic moduli for a class of porous materials, Acta Mech. 76 (1989) 105–130.
[11] D.P. Hasselman, On the porosity dependence of mechanical strength of brittle polycrystalline refractory materials, J. Am. Ceram. Soc. 45 (1982) 452–453.
[12] Z. Hashin, The elastic moduli of heterogeneous materials, J. Appl. Mech. 29 (1962) 143–150.
[13] T.T. Wu, The effect of inclusion shape on elastic moduli of a two-phase materials, Int. J. Solids Struct. 2 (1966) 1–8.
[14] Z. Hashin, S. Shtrikman, On some variational principles in anisotropic and nonhomogeneous elasticity, J. Mech. Phys. Solids 10 (1962) 335–342.
[15] Z. Hashin, S. Shtrikman, A variational approach to the theory of the elastic behaviour of polycrystals, J. Mech. Phys. Solids, 10 (1962) 343-352.
[16] Z. Hashin, S. Shtrikman, A variational approach to the theory of the elastic behaviour of multi-phase materials, J. Mech. Phys. Solids 11 (1963) 124–140.
[17] B. Lawn (Ed.), Fracture of Brittle Solids, 2nd ed., Cambridge University Press, 1993.
[18] K. Zeng, D. Rowcliffe, Experimental measurement of residual stress field around a sharp indentation in glass, J. Am. Ceram. Soc. 77 (1994) 524–530.
[19] D.B. Marshall, T. Noma, A.G. Evans, A simple method for determining elastic modulus to hardness ratio using Knoop indentation measurements, J. Am Ceram. Soc. 65 (1982) C175–176.
[20] I.J. McColm (Ed.), Ceramic Hardness, Plenum Press, New York, 1990.
[21] K.K. Phani, S.K. Niyogi, Porosity dependence of ultrasonic velocity andelastic modulus in sintered uranium dioxide—a discussion, J. Mater. Sci. Lett. 5 (1986) 427–430.
[22] E.A. Dean, Elastic moduli of porous sintered materials as modeled by a variableaspect ratio self consistent oblate spheroidal inclusion theory, J. Am. Ceram. Soc. 66 (1983) 847–854.
[23] L.P. Martin, D. Dadon, M. Rosen, Evaluation of ultrasonically determined elastic-porosity relations in zinc oxide, J. Am. Ceram. Soc. 79 (1996) 1281–1289.
[24] B.R. Lawn, V.R. Howes, Elastic recovery at hardness indentations, J.Mater. Sci. 16 (1981) 2745–2752.
[25] J.C. Conway Jr, Determination of hardness to elastic modulus ratios using Knoop indentation measurements and a model based on loading and reloading halfcycles, J. Mater. Sci. 21 (1986) 2525–2527.
[26] K. Zeng, K. Breder, D.J. Rowcliffe, C. Herrstrom, Elastic modulus determined by Hertzian indentation, J. Mater. Sci. 27 (1992) 3789–3792.
[27] W. Lo, A.M. Campbell, J. Luo, R. Stevens, Indentation-induced deformation and microcracking of highly textured superconducting $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$, ceramic, J. Mater. Res. 10 (1995) 568–577.