



Spherical indentation of porous ceramics: Elasticity and hardness



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ARTICLE INFO

Article history:

Received 8 December 2015

Received in revised form

28 December 2015

Accepted 30 December 2015

Available online 11 January 2016

Keywords:

Porous ceramics

Spherical indentation

Finite element modelling

Gurson model

Plastic deformation

ABSTRACT

A combined experimental and numerical approach is used to characterise the elastic and plastic deformation of a porous bulk ceramic material ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, LSCF) with porosities in the range 5–45 vol%, undergoing spherical indentation. The Gurson model was used in FEM simulations to describe the densification of the porous material in the plastic zone under the indenter. The simulated indentation response curves, extracted elastic modulus, hardness and densification in the plastic zone all showed good agreement with corresponding experimental observations. The results show that the hardness increases with maximum indentation depth over a representative depth that depends on porosity. In this particular ceramic the hardness, at sufficiently large penetration depth, is approximately 1.7 times the uniaxial yield stress of the porous material.

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1. Introduction

Porous ceramics are attractive in a wide range of applications such as filters, catalyst supports, sensors, biomedical implants and energy devices [1–6]. Load bearing capacity is generally required in these applications and additionally the porous ceramics are required to absorb mechanical energy and deform plastically at locations of concentrated loading. Therefore, the mechanical properties such as elastic modulus, hardness and yield strength, together with their mechanical deformation behaviour under contact loading, are important characteristics.

Nanoindentation, since its very first development, has drawn much attention and been extensively used to probe mechanical properties using only very small amounts of material [7]. The technique is well-established for fully dense solids, and is being increasingly applied to porous materials [8–11]. Additional complexity arises [10] with porous materials due to the granularity of the porous structure and the non-conservation of volume during plastic deformation (crushing, collapse and densification). The granularity issue can be overcome experimentally by ensuring that the scale of the indentation is much larger than the scale of the microstructure, in which case the porous material can be treated as an equivalent homogeneous solid. However, the nature of plastic

deformation in the porous material is different from that in a dense material and is the subject of the current paper.

Finite element modelling is a convenient tool for simulating the indentation process and has been extensively used in the literature to model indentation for dense materials [12–15]. FEM has also been used to simulate the elastic behaviour of bulk porous model materials containing artificially generated 2-D or 3-D pores (such as spherical pores [16] and cylindrical pores [17]) without involving an indentation process. Recently this approach has been extended to more realistic but nevertheless idealised, microstructures [18]. In our previous work [10,19,20] we have taken this approach further by FEM of elastic properties using the real 3-D numerical microstructures of the actual porous specimens reconstructed by FIB-SEM tomography. In general the elasticity (i.e. the Young's modulus) of the porous material calculated by FEM from the porous microstructure is in good agreement with the elastic modulus measured by spherical indentation using a conventional analysis of the indentation load vs. displacement curves. However, the validity of applying the conventional analysis of the indentation curve to porous ceramics is not clear, given the very different nature of the plastic deformation. In addition, it is also unclear how the indentation hardness should be interpreted in terms of material failure parameters. The Gurson model [21], originally developed to describe the deformation of porous ductile metallic systems, has been widely used to describe the mechanical behaviour of porous metals [21–24] as well as ceramic-metal composites [25–27]. The Gurson model considered isolated (closed) pores in a dense solid matrix and is generally regarded as being appropriate for

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porosities up to approximately 0.15 (15 vol%). Fleck et al. [23] analysed sharp indentation of porous partially sintered metals using two different models for the plastic deformation of the porous structure: the Gurson model and a different model for open porosities based on deformation of necks between particles (denoted FKM model). Although they did not calculate simulated load vs. depth curves for the indentation, they provide a detailed comparison of the two models for describing the densification of the porous material. Chen et al. [28] carried out a study of sharp nanoindentation (Berkovich) of polymer films on silicon substrates. One set of films was dense and the other set had a nano-scale porosity of 23 vol%. They modelled the effect of densification in the porous film using the Gurson model in FEM and showed that this could account for their experimental observations.

The aim of the current study is to include a description of densification during plastic deformation of a porous brittle ceramic in a FEM simulation of spherical indentation and thereby assess the influence of the collapsing pore structure on the interpretation of the indentation experiment. We assume that the length scale of the indentation (contact area, plastic zone and elastic field) is much greater than the characteristic length scale of the microstructure (pore size and inter-pore spacing) so that the porous material can be modelled as an effective homogeneous material. In order to facilitate this, we choose to use a spherical indenter rather than a sharp indenter, which in addition also inhibits cracking induced by the sharp edges. In the FEM in the current study, we follow the approach of Chen et al. [28] in using the Gurson model to simulate the plastic deformation of the porous material over the whole range of porosities studied (5 vol% to 45 vol%). The Gurson model only applies strictly for porosities below approximately 15 vol%, but in fact can give a good representation of the collapse of the porous structure at higher porosities even though the model parameters lose their physical meaning, as will be discussed in detail later.

In this paper we study experimentally a ceramic material ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, LSCF) which was sintered from powder at different temperatures resulting in a range of porosities. This material was used in our earlier work, and is continued here, because it is of interest as a fuel cell electrode. Indentation was carried out using a spherical indenter tip and residual plastic deformation was investigated using the FIB–SEM slice and view technique.

The results show that the conventional analysis of indentation can still give a good estimate of the elastic modulus of the bulk material and that the hardness can still be related to a yield stress even in porous brittle materials. It is also shown that the model is capable of accurately reproducing the densification in the plastic zone under the indenter.

2. Experimental and simulation procedures

2.1. Spherical indentation experiments

The instrumented indentation experiments using a spherical diamond indenter were conducted on bulk LSCF specimens prepared by die-pressing and sintering of commercial powder at 900–1200 °C to provide a range of porosities. Compared to the use of a sharp indenter, the scatter of the measurement can be hugely reduced when a spherical indenter is used. The size of the sphere (radius = 25 μm) was chosen to be much greater than the feature size of the roughness and porous microstructure (<1 μm) [10]. After indentation at loads ranging from 50 to 10000 mN, the cross-sectional microstructures under the indented areas were investigated using the focused ion beam-scanning electron microscope (FIB–SEM) slice and view technique. The cross-sectional micrographs were then processed by image analysis in order to characterise the distribution of porosity in the indented region.

Detailed information regarding the preparation of the porous bulk LSCF specimens, the indentation experiments to determine the mechanical properties (elastic modulus and hardness) and the acquisition of cross-sectional micrographs using FIB–SEM, can be found in our previous paper [10].

2.2. Finite element modelling

2.2.1. Axisymmetric model set up

The indentation simulations were performed using ABAQUS CAE 6.12 (Dassault Systemes, USA). Since the length scale of the indenter was much greater than the characteristic scale of the microstructure the porous materials were modelled as isotropic homogeneous solids having the possibility to collapse and densify under the compressive loading. As the problem exhibits axisymmetric geometry, the system was simulated by defining a 2-D square half-space with side length much larger than the indentation depth reached, and a rigid spherical indenter, as shown in Fig. 1. The system is axisymmetric around the central axis of the indenter (Y-axis). Here the indenter radius R_i was set to be 25 μm , which is identical to that of the real indenter used. The square side length was set to be 100 μm , which is significantly larger than the indentation depth ($h_{\text{max}} < 5 \mu\text{m}$). Similar to the process in a real indentation test, in the simulation the indenter was loaded in the Y direction to press into the specimen surface. Once a preset maximum depth was reached, the indenter was unloaded in a reverse path to its original position. In experiments, the indenter was made of diamond, which has a very high elastic modulus and thus suffers little deformation upon loading. In order to save computation time and simplify the problem, the spherical indenter was modelled as an analytical rigid surface in ABAQUS, with a reference point attached to the tip point.

A 4-node bilinear axisymmetric quadrilateral reduced integration element type with hourglass control (i.e. CAX4R in ABAQUS) was adopted to generate the meshes. The indentation region was very small with respect to the indenter size and the specimen size. For this reason, and in order to simulate the deformation of the region with sufficient accuracy, a higher density of meshes with very fine size was needed under the indenter contact. The size of elements was progressively increased towards the far field domain in the specimen model, as shown in Fig. 1.

2.2.2. Application of boundary conditions, material parameters and Gurson model

In the simulation, the nodes on the left and bottom edges of the square were constrained so that they could not move in their normal directions (i.e. $U_1 = 0$ for the left edge and $U_2 = 0$ for the bottom edge). For the indenter, a displacement constraint in the horizontal direction was also imposed at the tip point (set as a Reference Point in ABAQUS) to retain symmetry in the simulation process.

The typical loading and unloading steps of the indenter were executed by imposing designated downward and upward displacement (h) at the reference point, incrementally increased from 0 to h_{max} (negative Y direction in Fig. 1) and then returned to the initial position (i.e. $h = 0$ in positive Y direction). The friction coefficient of the contact was assumed to be zero in the simulation, as reported in other FEM literature due to the negligible effect of the precise friction coefficient on the results [12,29,30]. Our simulation also found that no noticeable change in the load vs. depth curves was observed when using a friction coefficient of 0 or 1. The indenter surface was defined as the “master” surface and the specimen surface was defined as the “slave” surface to enforce the contact. The specimen was assumed to be homogeneous and isotropic and to exhibit elastic–plastic behaviour.

In the current study, the material parameters for the simulation were chosen to be consistent with mechanical properties measured previously using nanoindentation, and the measured bulk porosi-

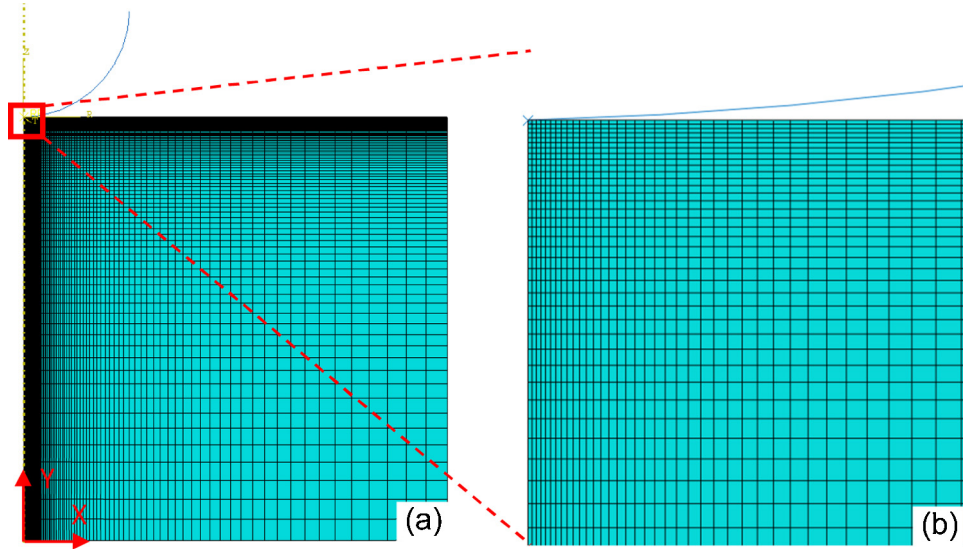


Fig. 1. (a) FEM model with adaptive meshing resulting in 11025 elements. (b) shows a magnified view of a dense mesh area close to the indenter contact. The thin solid line indicates the profile of the rigid indenter tip.

Table 1

Summary of bulk LSCF properties measured in Ref. [10].

Sintering temperature (°C)	f (vol%)	E (GPa)
900	44.9 ± 0.3	34.2 ± 2.1
1000	36.3 ± 1.1	44.5 ± 3.2
1100	28.7 ± 0.9	80.2 ± 1.9
1200	5.2 ± 0.1	174.3 ± 2.8

ties based on 3-D tomography [10,19], as listed in Table 1. The Poisson's ratio for the fully dense LSCF was assumed to be 0.3, as reported in [31].

Gurson [21] proposed a constitutive relationship with the yield condition as a function of the porosity (f) for metals containing a dilute homogeneous distribution of isolated pores. The yield condition is given by the following expression [21,32].

$$\Phi = \left(\frac{q}{\sigma_y^d} \right)^2 + 2f \cosh \left(-\frac{3p}{2\sigma_y^d} \right) - 1 - f^2 = 0 \quad (1)$$

where σ_y^d is the yield stress of the dense matrix material (dense LSCF in this case), q is the effective von Mises macroscopic stress given by $q = \sqrt{\frac{1}{2} \{ (\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2 \}}$, with σ_1, σ_2 , and σ_3 being the three principal macroscopic stresses (i.e. the stresses in the porous aggregate equivalent medium), and p is the macroscopic hydrostatic stress given by $p = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3}$. When $f=0$ (fully dense), the Gurson yield condition reduces to the von Mises yield condition, i.e. $q = \sigma_y^d$. For each volume element at a given increment in displacement of the indenter, the plastic strain due the hydrostatic stress is assumed to be fully accommodated by a local change in porosity. The updated porosity is then used in the yield condition for the next increment of indenter displacement. This assumes that plastic deformation of the dense matrix conserves volume. In this study, the Gurson model was used to account for the porosity and to simulate the densification behaviour of our specimens under the indenter. The plastic property (i.e. the yield stress) was chosen based on an inverse FE analysis using the measured hardness values. This will be discussed later in more detail.

2.2.3. Computation of elastic modulus and hardness using simulated load-displacement curves

The vertical (i.e. in the Y direction) reaction force and displacement at the reference point of the indenter was output at each increment of the loading and unloading steps, which was then used to generate the indentation load versus depth curves for the determination of the simulated elastic modulus and hardness using the same procedure as used for experimental data. The detailed calculation procedure is explained below.

The radius of the projected contact area (a_n) between the indenter and material when the load and depth reach their maximum values was calculated from the indentation load versus depth curve of each individual indentation simulation as described below. The elastic modulus, E , and the indentation hardness, H_n , were determined from the simulated load vs. depth curves using the conventional analysis of Oliver and Pharr [7]. The indentation hardness is given by the following equation and includes both elastic and plastic deformation.

$$H_n = \frac{P_{\max}}{\pi a_n^2} \quad (2)$$

where $P_{\max}$ is the maximum load applied and a_n is the contact area radius at maximum load and is given by the following equation,

$$a_n = \sqrt{2R_i h_c - h_c^2} \quad (3)$$

where R_i is the indenter radius, which was 25 μm in the current study; h_c is the contact depth and was deduced using Eq. (4),

$$h_c = h_{\max} - 0.75 \frac{P_{\max}}{S} \quad (4)$$

with S being the contact stiffness calculated as the slope of the initial unloading curve at maximum load. The elastic modulus, E , of the material is related to the reduced modulus E_r , by the following expression,

$$E = \frac{1 - \nu^2}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}} \quad (5)$$

$$E_r = \frac{S}{2a_n} \quad (6)$$

where ν is the Poisson's ratio of the specimen. E_i and ν_i are elastic modulus and Poisson's ratio for indenter, respectively. In the

experiments these equations were used to make the small correction for the elastic deformation of the indenter and extract the experimental value for E . In the simulations for simplicity the indenter was assumed rigid and in that case Eq. (5) becomes:

$$E = E_r(1 - \nu^2) \quad (7)$$

Most FEM approaches used for the extraction of mechanical properties from indentation measurements use inverse analysis [16,33–35]. A similar approach based on the Levenberg-Marquardt (LM) method [36–38] was used in this study to identify the most appropriate material yield stress by best matching the FEM-derived loading-unloading data to the measured data in the least squares sense. Essentially, optimisation was performed to minimise the discrepancy between the two types of data. The fitting was carried out on selected experimental indentation curves acquired at relatively large maximum indentation depths. The adjustable variables in the FEM are Young's modulus E of the porous material and the yield stress σ_y^d of the dense material in the Gurson model. The value of E was set to the measured value and therefore the assumption of a rigid indenter does not influence the fit. The initial value of σ_y^d was set equal to the experimental hardness. The value of σ_y^d was then adjusted to obtain an acceptable fit to the experimental load-displacement loading and unloading curves (examples are shown later). It should be noted that here we consider σ_y^d to be a fitted parameter which is different for each material. In principle σ_y^d should be the same for each material porosity if the Gurson model is strictly valid. However, here we use the Gurson model as a way of accounting for the collapse of the porous structure at porosities greater than the limit of its strict validity. Hence σ_y^d is applied here as a variable parameter that depends on porosity. The implications of this are discussed later.

3. Results and discussion

3.1. FEM results and comparison with experiments

3.1.1. Effect of mesh density and Poisson's ratio on the modelled indentation curves

A typical simulated indentation plot is shown in Fig. 2 using parameters appropriate for a specimen sintered at 900 °C containing 44.9 vol% porosity. The loading curve shows some oscillating perturbations which are not directly related to the discrete nature of the data, as each individual curve consists of hundreds of data points. The oscillations were also present with smaller amplitudes even at lower loads and depths. Furthermore, the perturbations were not reduced by increasing the number of load increments or refining the mesh size, as shown in Fig. 2. It is therefore likely that the oscillations are caused by the computational iteration process in the Gurson subroutine of ABAQUS. Conversely, the figure shows a high consistency and smoothness of the unloading curves. This is also consistent with the oscillations on the loading curves being caused by the Gurson subroutine, because there is no densification of the pore structure during unloading. Since the indentation response was shown to be insensitive to the number of mesh elements in the range investigated, the 6241-element mesh was selected as giving the best compromise between resolution and computation time.

The sensitivity of the simulations to the value of the Poisson's ratio was also studied. Poisson's ratios of 0.2 and 0.4 were used in simulations of indentation at each porosity level after fitting the curve using a Poisson's ratio of 0.3. The results showed that slightly larger elastic modulus and hardness were generated when higher Poisson's ratio values were assumed. For the most porous material the modulus increased by 4.8% on increasing Poisson's ratio from 0.2 to 0.4. The sensitivity was larger for the least porous

material with the modulus increasing by 13% for the Poisson's ratio increasing from 0.2 to 0.4. Therefore the simulations are relatively insensitive to the assumed Poisson's ratio and use of the experimental value of 0.3, measured for the dense material [31], is justified in the simulations.

The Gurson model in ABAQUS also contains additional parameters introduced to improve agreement with more detailed modelling of metals containing ordered arrays of voids [32]. In the present study various combinations of these additional parameters were explored, but it was found that the fits were indistinguishable from those using the simple model of Eq. (1) and therefore this was used in all simulations using the Gurson model.

3.1.2. Inverse finite element analysis

Fig. 3 gives examples of the simulated and measured indentation loading-unloading curves for specimens with different porosities. It can be seen that the oscillations in the simulated loading curves gradually diminish as the porosity decreases. In addition, it was also found in the later stage of the study that dense models without the use of the Gurson subroutine did not produce any oscillation in the simulated loading curves. This is consistent with the oscillations being related to the iteration procedure in the Gurson implementation in ABAQUS.

A noticeable discrepancy between the simulations and experimental data is that the simulations predict a larger residual indent depth than is observed experimentally. This discrepancy also increases with porosity and reflects a lower elastic recovery of the material near the indenter tip in the simulation than in reality [39]. This effect is probably partially due to the granular nature of the porous microstructure and initial surface roughness of the specimens. Towards the end of unloading, the parts of the microstructure that are locally stiffer dominate the contact with the indenter leading to a more gradual final unloading than expected for a homogeneous medium that is initially perfectly smooth and flat. These issues increase as the porosity increases and are not included in the simulation. The initial unloading is not sensitive to these effects because then the elastic field has much longer range and extends over a relatively larger volume. A second contributing factor to this discrepancy comes from the assumption in the Gurson model that the elastic modulus in the densified region is not influenced by the densification, whereas in reality it will increase. This influences the shape of the contact as the load approaches zero and the local properties become dominant. When there is densification, the higher local modulus leads to a larger radius of curvature for the fully unloaded depression (than would be the case without densification) and hence a smaller contact circle for a given unloading displacement [40]. The smaller contact circle results in a reduced stiffness (and lowers the slope of the unloading curve) despite the fact that the local modulus is higher. This is because the unloading is still mainly influenced by the lower modulus of the non-densified material outside the plastic zone. As with surface roughness and local inhomogeneity, this effect increases as the porosity increases and the densification increases in agreement with the experimental observations. As a result, when judging the best fit of the simulation to the experiments priority was given to matching the maximum load at maximum depth (which determines the indentation hardness) and the initial part of the unloading curve (which determines the derived elastic modulus) since these are the material parameters of interest.

The effect of maximum indentation depth on the values of Young's modulus and hardness extracted from the experimental indentation curves is shown in Figs. 4 and 5. The results in Fig. 4 shows an increase in modulus with depth for shallow depths less than approximately 100 nm and then the modulus becomes essentially independent of depth for greater depths. Fig. 5 shows that the hardness also increases with indentation depth, but the

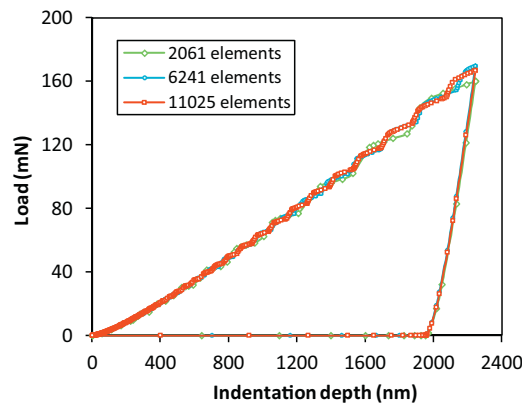


Fig. 2. Simulated indentation load versus depth curves at three different mesh densities for a specimen sintered at 900 °C having an average porosity of 44.9 vol%.

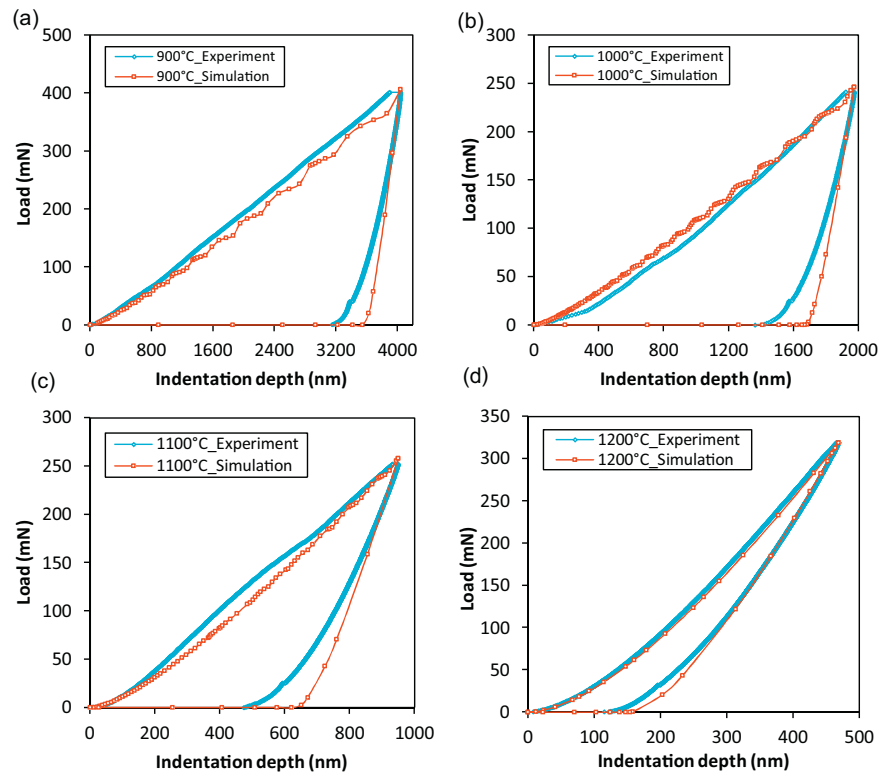


Fig. 3. Comparison of loading-unloading curves generated from experiments and best fit FEM simulations for samples with different porosities resulting from the different sintering temperatures of (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C.

increase extends to greater depth than for the elastic modulus. For the lowest porosity sample, the hardness has still not reached a plateau even at the limit of the load and depth studied. These experimental observations were compared with results of FEM simulations in the following way. First, experimental indentation curves were selected that were at sufficiently large maximum indentation depths to have given modulus values in the plateau regions of Fig. 4 and these are listed in Table 2 and shown in Fig. 3. The value of σ_y^d resulting from the best fit simulations are also listed in Table 2. Using these fitting parameters, simulations were then carried out for different indentation depths and the values of modulus and hardness were calculated using the standard analysis for each of the simulated indentation curves. The results are compared with experiment in Figs. 4 and 5 and it is clear that the simulations reproduce well the trends with indentation depth observed in the experiments. It should be noted that each experimental data point represents a different indentation on the surface of a given

Table 2

The maximum indentation depth and Gurson yield stress used in fitting the simulations and the corresponding uniaxial yield stress of the porous material.

Sintering temperature (°C)	h_{max} (nm)	σ_y^d (GPa)	σ_y^p (GPa)	H_n/σ_y^p
900	4037	0.83	0.43	1.72
1000	1973	0.9	0.55	1.65
1100	950	2.19	1.34	1.62
1200	468	4.56	4.29	1.64

specimen. The apparent increase in the elastic modulus with depth, at shallow depths, in the experimental data in Fig. 4 is caused by surface roughness and local inhomogeneity in the specimens used in the experiments. The hardness data are plotted in Fig. 5 as a function of the indentation strain, ε_n , which is expressed as the ratio of contact area radius a_n over the spherical indenter radius R_i , a_n/R_i . The indentation strain increases with indentation depth

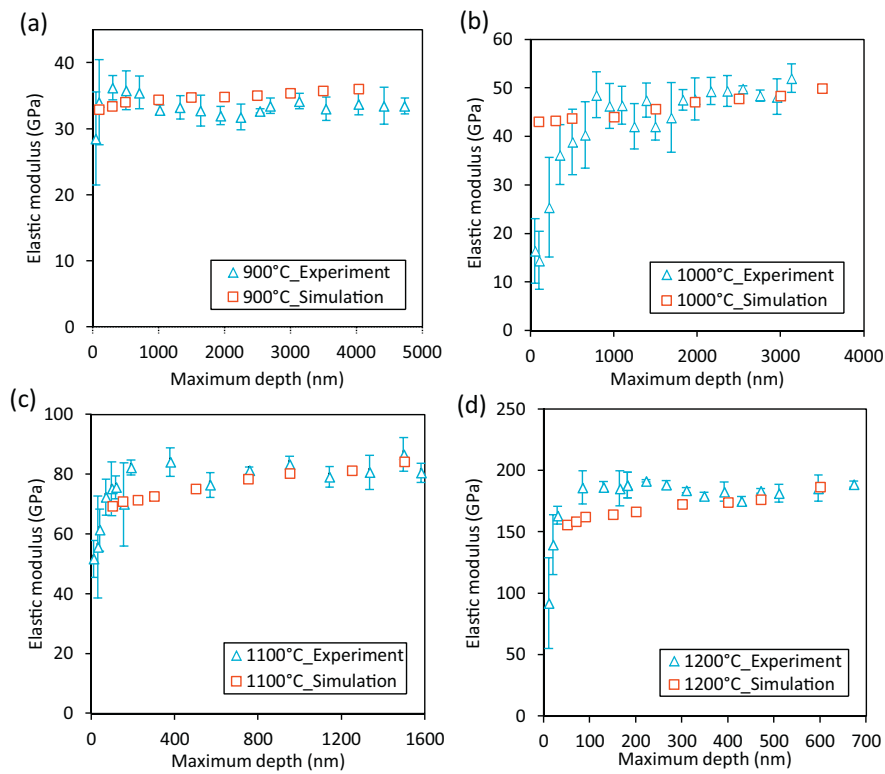


Fig. 4. Comparison of elastic moduli determined by experiments and simulations for samples sintered at (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C. Note the different depth scales in each case.

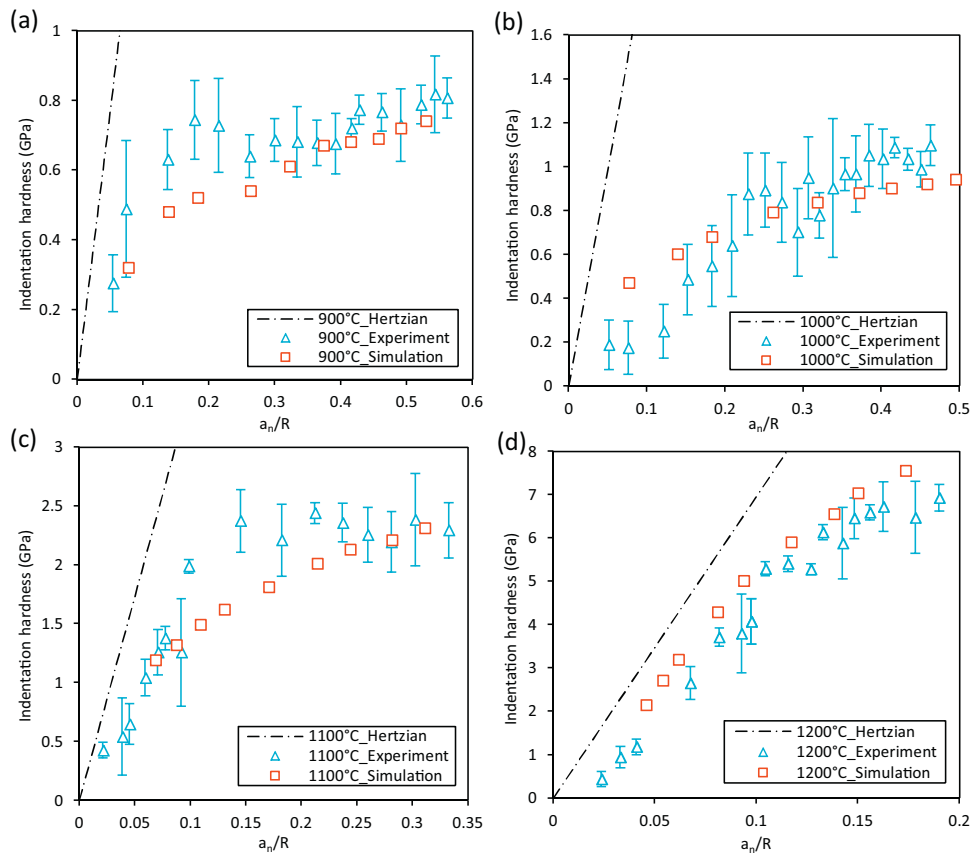


Fig. 5. Comparison of indentation hardness determined by experiments and simulations for samples sintered at (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C. Note the different depth scales in each case.

according to Eqs. (3) and (4). The increase in hardness with indentation strain (or depth) is seen in both experiments and simulations. This is caused by the transition from the elastic/plastic region to the fully plastic region in which the plastic zone extends to, or beyond, the contact circle at the specimen surface and is a well-known feature of spherical indentation [29].

Theoretically, according to the classical Hertzian elastic contact theory [41], which was further extended by Swain and Lawn [42], a linear relationship exists between the indentation stress (σ_n , which is equivalent to the indentation hardness H_n and is also known as the indentation pressure) and the indentation strain (ε_n , which is equivalent to the ratio of contact area radius a_n over the spherical indenter radius R_i , a_n/R_i) for purely elastic contacts. The relationship is,

$$\sigma_n = \frac{3E}{4\pi k} \varepsilon_n \quad (8)$$

where E is the elastic modulus of the material and k is an indenter/specimen-dependent constant, which is given by,

$$k = \frac{9}{16}((1 - \nu^2) + \frac{(1 - \nu_i^2)E}{E_i}) \quad (9)$$

The subscript i denotes the indenter material. The linear Hertzian elastic responses expected for these specimens are plotted in Fig. 5 and compared with the experimental data. It is clear that there is no well-defined elastic region in the experimental or simulated responses and correspondingly no clear yield point. However, the interpretation of such plots in terms of true stress and true strain is not straightforward [43].

3.2. Characterisation of plastic deformation

The indented specimens were FIB-milled to gain insight into the changes in microstructure in the plastic zone under the indenter. Fig. 6 shows the cross-sectional microstructure after a 2.5 μm indentation depth for a specimen sintered at 900 °C (with an initial porosity of 44.9 vol%) and Fig. 7 a similar case for a specimen sintered at 1000 °C (with an initial porosity of 36.3 vol%). The contour plots of porosities, shown as void volume fraction (VVF), for the corresponding FEM simulations for the same indentation conditions as the experiments are also displayed in the figures.

Some general observations can be made from Figs. 6 and 7. At the loads used in the current experiments, no cracking was observed in the indented samples. In addition no evidence for pileup at the perimeter of the indentation mark was found. The densification regions are approximately hemi-spherical with a radius equivalent to the contact radius a_n in agreement with the simulations. The deformed zones display compaction of the initial pores with evidence of both interparticle and intraparticle collapse, as arrowed in the figures. These zones are located underneath the indentation contact area with no evidence of lateral expansion, as indicated by the dashed curves in the figures. The cross-sectional images reveal that densification resulted in a reduction of approximately half the initial porosity immediately underneath the contact surface centre for both these samples.

In order to compare the porosity change due to indentation in the experiments with that generated by FEM simulation, the spatial distribution of experimental porosity after unloading was determined using image analysis of the cross-sectional micrographs obtained. The images were cropped into crescent-shaped areas similar to the simulated contours at evenly distributed depth increments starting from the bottom of the contact circle. The porosities were then calculated for each crescent area and the values are compared in Fig. 8 with the porosity from the simulations along the axis of symmetry.

Fig. 8 shows that the porosity distribution from the simulations is in good agreement with the experimental observations and that the Gurson model gives an accurate representation of the densification behaviour in these materials.

4. Discussion

4.1. Effect of densification on the measurement of E and H

In principle, densification under the indentation influences the apparent elastic modulus and hardness of the porous materials measured by a conventional analysis of indentation curves, as the crushed and compacted particle networks have reduced porosity and thus cause overestimation of the modulus and hardness. In order to explore this, we have fitted the same indentation curves shown in Fig. 3 using a conventional FEM simulation with elastic-perfectly plastic behaviour (i.e. no Gurson model to describe densification) and a yield stress for the porous composite, σ_y^d as a fitting parameter. The fits are similar to the ones using the Gurson model and therefore it is not possible to detect any effect of densification from the shape of the indentation curves. The values extracted for Young's modulus are presented in Fig. 9 and are the same for the two models, showing that densification has a negligible effect on the measurement of this parameter. This is consistent with our experimental results [10] where we found that Young's modulus obtained from indentation was equal to that measured using sonic resonance of a macroscopic bar. The reason for the lack of influence of densification is due to the densified zone being small when compared to the longer range of elastic deformation around the indentation. Chen et al. [28] also concluded that densification has no significant effect on the measurement of indentation modulus (for Berkovich indentation of nano-porous polymer films) because the densified region is significantly smaller than the surrounding elastic deformation region. They also considered the possible effect of the assumption in the Gurson model that there is no local increase in the elastic modulus within the plastic zone as a result of the densification. They concluded that the effect of densification on the measured value of modulus only becomes significant when the ratio of the dense modulus to the porous modulus is greater than 3. The results in Table 2 shows that in the present study this ratio is over 5 for the most porous specimen. In this regard, Jauffres et al. [16], claimed that for brittle microstructures the influence of the densified region would be greater at higher porosities. Nevertheless we observe in the present study that the densification has no noticeable effect on the measurement of Young's modulus. This is probably because any effect also depends on the relative ratio of modulus to hardness E/H . In the polymer materials studied by Chen et al. [28], E/H was typically 14 whereas in the current materials it increases from 26 for the lowest porosity sample to 47 for the highest porosity material.

The measurement of indentation hardness is not influenced by whether the Gurson model is used or not because the model is matched to experiment at the point P_{max} and h_{max} . In principle there is a difference between the indentation hardness, H_n , based on the load divided by the projected contact area under load, and the conventional hardness, H , based on the maximum load divided by the area of the residual indentation mark. This is because H_n also includes elastic deformation under load. It should be noted here that for the materials in the current study the indentation hardness was found to be very close to the conventional hardness and therefore we do not distinguish between them.

4.2. Hardness and yield stress

In general for dense materials the conventional hardness, H , can be directly related to the yield stress of the material following a

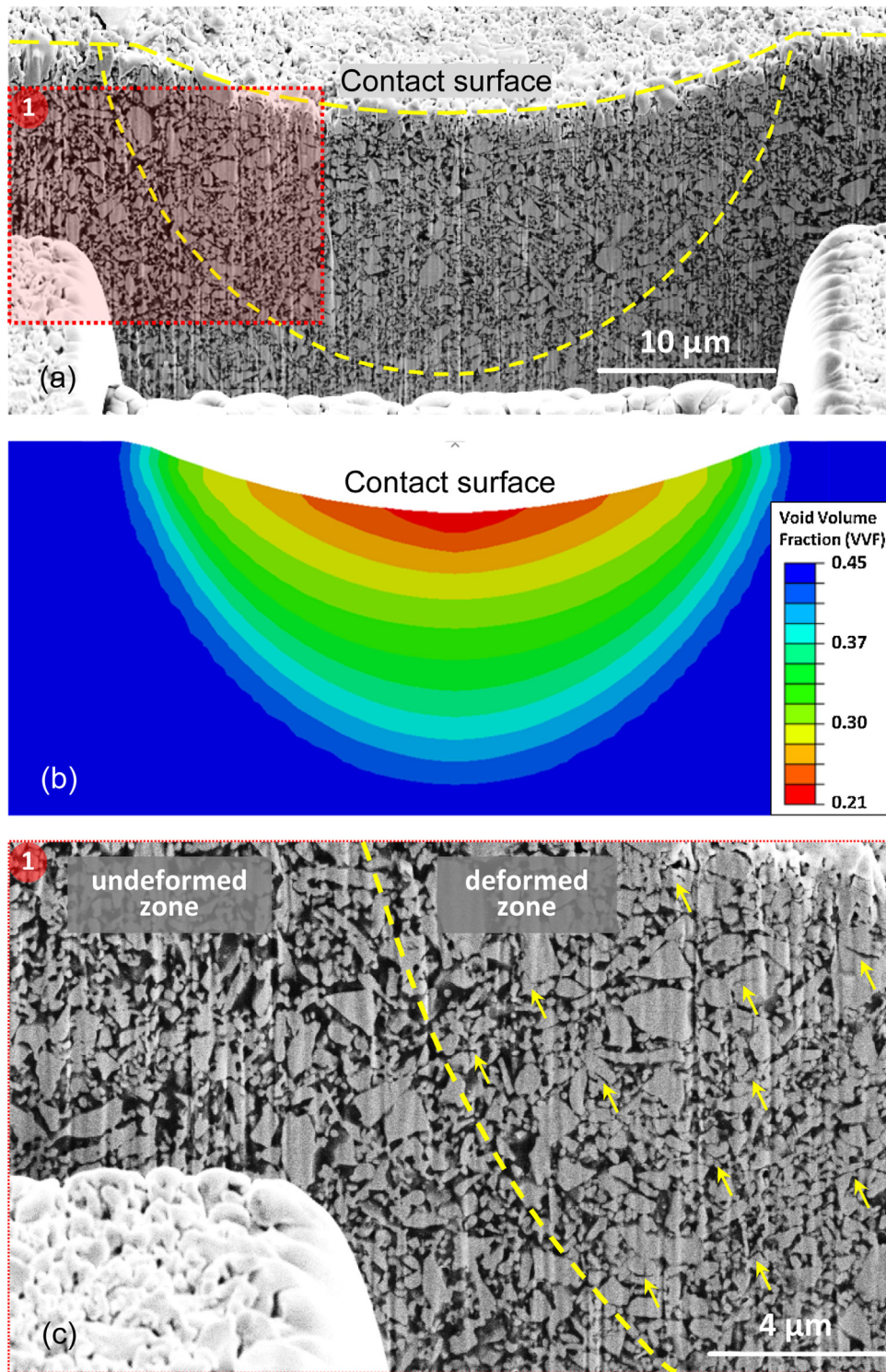


Fig. 6. (a) FIB-milled cross-sectional view of the indented region after unloading of the specimen sintered at 900 °C with an initial porosity of 44.9 vol%. The dashed curve indicates the boundary of the densification zone (i.e. the plastically deformed zone). (b) Contour plot of the porosity distribution from the corresponding FE simulation. (c) High magnification view of the marked zone ① in (a), showing the difference between deformed and un-deformed zones, with arrows marking possible collapse of pores between particles.

proportional relationship $H = c\sigma_y$. c is a constant which is normally taken as 3 for ideal plastic materials (i.e. those without work hardening behaviour) undergoing sharp indentation [44,45]. When the material has work hardening behaviour, the yield stress is taken at a representative strain [44]. Shaw and Sata [46] compared the plastic behaviour of polystyrene foam with that of fully dense polystyrene. They reported that in such cellular solids the constant c is

approximately equal to 1, rather than the value of 3 seen in conventional dense solids such as metals. This is because porous materials are compressible, and under indentation the compressed zone does not influence the surrounding material as much as when plastic deformation conserves volume - i.e. there is reduced long range deformation due to a smaller lateral expansion of the densified material [46,47]. Wilsea et al. [47], in studying the indentation hard-

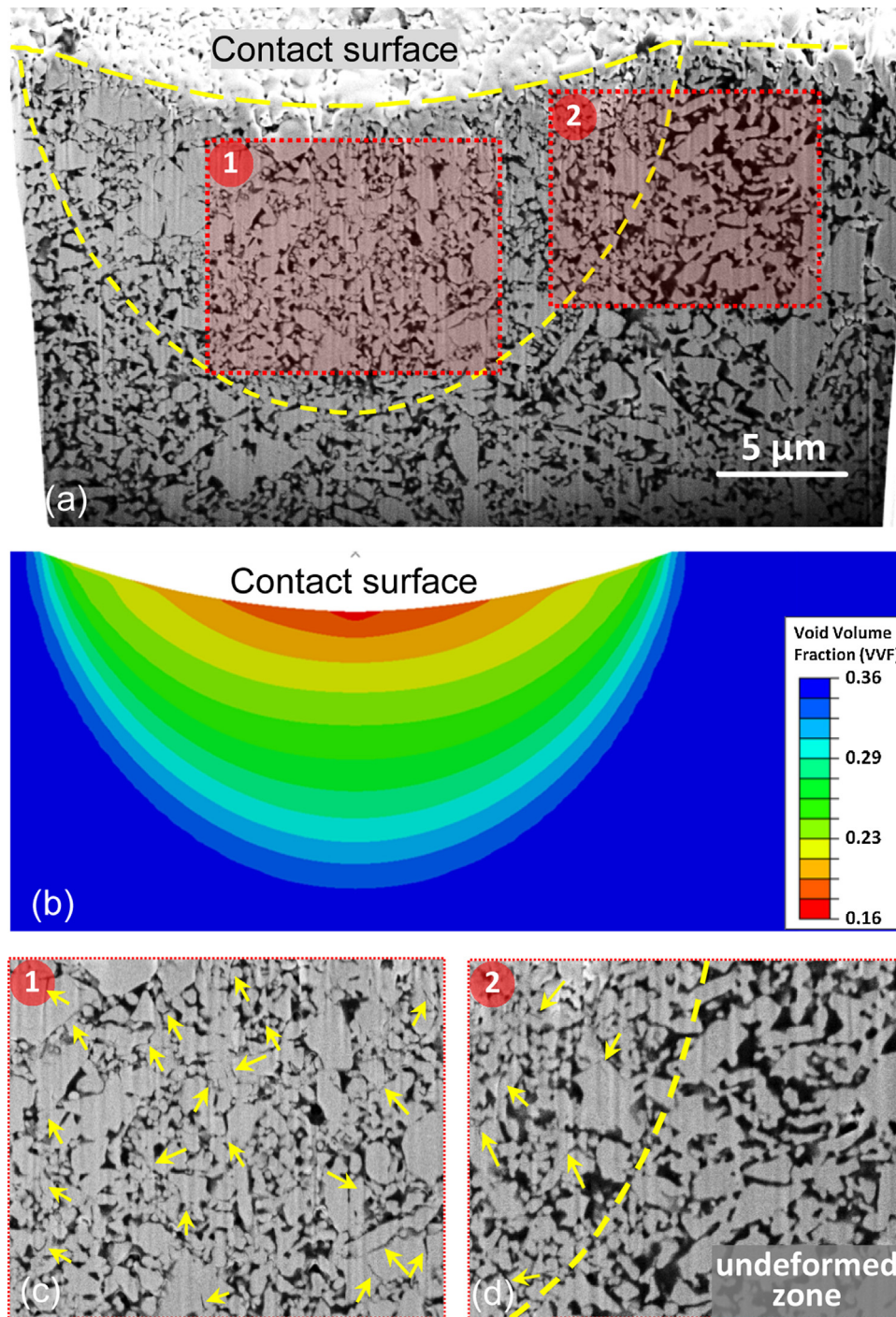


Fig. 7. (a) FIB-milled cross-sectional view of the indented region after unloading of a specimen sintered at 1000 °C with an initial porosity of 36.3 vol%. The dashed curve indicates the boundary of the densification zone. (b) Contour plot of the porosity distribution from the corresponding FE simulation. (c) High magnification views of the marked zones ① and ② from (a), showing the difference between deformed and un-deformed zones, with arrows marking possible collapse of pores between particles.

ness of polymeric foams, also found that for a low density foam under indentation, the indentation pressure (i.e. the hardness) was approximately the same as the yield stress of the foam in uniaxial compression. Gibson and Ashby [48], also concluded that the hardness is approximately equal to the yield strength for cellular foams, rather than $H = 3\sigma_y$ which characterises a fully dense material.

In the FEM simulation of the current study the yield behaviour is characterised by the parameter σ_y^d which is in principle the yield stress of the dense matrix and should be independent of porosity in the strict application of the Gurson model. This parameter

is tabulated in Table 2 and is seen to vary strongly with porosity in order to fit the experimental results. This is partly because the microstructure of the partially sintered granular ceramics is very different from the idealised microstructure of dilute isolated pores required for strict application of the model. In particular, narrow necks between relatively larger partially sintered particles leads to local amplification of the macroscopic stress as analysed by Fleck et al. [23]. Comparison of the yield surfaces of their model with that of the Gurson model indicates that, for the same porosity, the yield of the particulate structure occurs at approximately half the

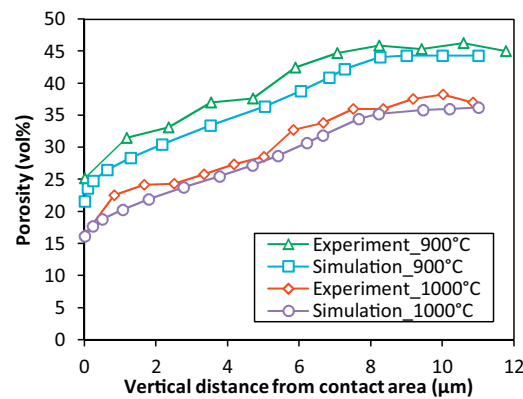


Fig. 8. Indentation-induced porosity changes under the indent for the experiments and simulations. Initial porosity was 44.9 vol% for the sample sintered at 900 °C and 36.3 vol% for the sample sintered at 1000 °C. The indentation depth in both experiments and simulations was 2.5 μm.

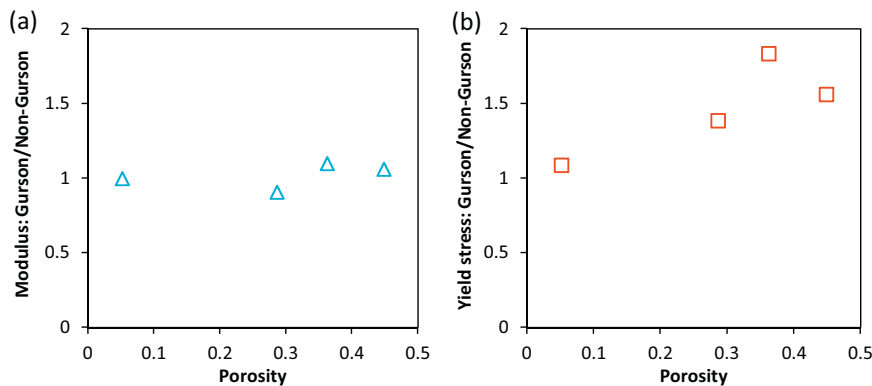


Fig. 9. The effect of using the Gurson model in the FEM on the extraction of (a) Young's modulus and (b) uniaxial yield stress. The results are normalised with respect to the corresponding values extracted using a conventional material model with no densification.

hydrostatic yield stress of the Gurson model structure. However, even this factor of two is insufficient to account for the five-fold change in σ_y^d seen in Table 2. It is suggested that this is because that in these brittle materials the plastic deformation mechanism has a greater contribution from fracture at particle necks as the porosity increases. Although the Gurson model is not strictly valid under these conditions, the effective uniaxial yield stress of the porous aggregate, σ_y^d , can be extracted by solving Eq. (1) using the fitted value for σ_y^d . The results are also shown in Table 2 together with the proportionality parameter c for the ratio of hardness to yield stress which is seen to be equal to approximately 1.7 across the whole range of porosity. This appears to indicate that this value of c is not a consequence of densification in the plastic zone, but is perhaps due to the spherical indentation geometry. However, this is not the case because if the standard (non-Gurson) model is used to fit the indentation curves then the value of c is found to take the values 1.42, 2.26, 3.00 and 3.00 for the samples sintered at 1200, 1100, 1000 and 900 °C. This behaviour is a feature of spherical indentation of an elastic-perfectly plastic material and the change in c is caused by the development of the plastic zone [40]. The same development is responsible for the increase in hardness with indentation depth seen in Fig. 5 and is reported in the literature for spherical indentation of dense materials [49–51]. Therefore the constancy of c when using the Gurson model is fortuitous and is the result of two opposing trends: namely the development of the plastic zone and densification within the plastic zone.

The effect of using the Gurson model to extract the uniaxial yield stress is shown compared to the model in which densification is ignored in Fig. 9. This shows that neglecting the densification would

lead to underestimating the uniaxial yield stress by almost a factor of two for the material with the highest porosity.

5. Conclusions

In this study, a combined experimental-numerical approach to characterise the elastic and plastic mechanical behaviour of porous bulk ceramics undergoing spherical indentation is presented. Indentation tests were performed on porous bulk LSCF ceramic specimens after sintering at temperatures from 900–1200 °C, with resulting porosities ranging from 5 vol% to 45 vol%. The Gurson model, originally developed to describe plastic deformation in porous metals, has been used in finite element simulations of the indentation process to account for collapse and densification of the porous structure in the plastic deformation zone under the indenter.

The FE simulation results were compared with the results from indentation experiments, and good agreement was found for both the indentation response curves and the dependence on the extracted values of elastic modulus and indentation hardness on maximum indentation depth. The porosity distribution in the densified regions underneath the indentation contact surface was investigated experimentally using the FIB–SEM slice and view technique. Both qualitative observations and quantitative calculations of the porosity gradient were in excellent agreement with the FEM simulations. The Gurson model provides a good representation of the densification and its effects on indentation of these materials despite not being strictly valid at the higher levels of porosity in these ceramics and the likely contribution of local fracture to the densification process. This is reflected in the fitting

parameters used in the Gurson model depending on porosity. Nevertheless the approach allows a value for the uniaxial yield stress of the porous material to be extracted from the indentation hardness and in this particular ceramic the relationship is that the hardness is approximately 1.7 times the yield stress.

Future studies will apply this combined numerical-experimental approach to fracture of porous bulk ceramics induced by spherical indentation and to porous thin layer/substrate systems incorporating porous ceramic materials (e.g. porous layer/dense substrate, porous layer/porous substrate or dense layer/porous substrate) and multilayer systems, taking into account the effect of layer thickness, and layer to layer interactions.

Acknowledgement

This research was carried out as part of the Hydrogen and Fuel Cell SUPERGEN Hub supported by EPSRC grant EP/J016454/1, part of the RCUK energy programme. The Energy Programme is an RCUK cross-council initiative led by EPSRC and contributed to by ESRC, NERC, BBSRC and STFC.

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